An optimal transport approach to density-functional theory

Rodrigue Lelotte

Abstract

In this short note, we present the readers a glimpse at *multi-marginal optimal transport* theory by looking at a concrete problem arising in the field of *density-functional theory*, a successful computational modelling method used in quantum chemistry. More precisely, we introduce to readers that might only be acquainted with the theory & numerics of the traditional (two-marginal) optimal transport theory, a numerical scheme introduced in [4] by Benamou *et al*. We present both the numerics and the underlying theoretical guarantees, before experimenting on toy examples, which allows us to access the overall limitations of their approach.

1. Introduction

Density-functional theory (DFT) is one of the most widely used methods to conduct computations in condensed matter physics and quantum chemistry, for instance to give reasonably accurate quantitative and qualitative descriptions of the electronic structure of atoms, molecules, crystals and surfaces. Being able to carry out those computations in a realistic time-frame stands out as a key issue in a wide range of scientific industries, advocating for the overall importance of the field.

In the recent years, it has been noticed [7, 12] that some problems arising in DFT could be reframed through the scope of *optimal transport* (OT) theory. As such, the toolbox of algorithms developed in the well-established context on mass transportation might provide novel numerical methods in DFT and vice-versa. In this short note, we present such an approach, drawing on the work of Benamou *et al* [4].

The plan of the note is as follows: in section 2, after providing a self-contained introduction on DFT, we show that a particular approach to this theory can be rephrased as an OT problem. In section 3, we briefly review some theoretical results concerning multi-marginal OT theory. In section 4, we introduce two numerical schemes to solve multi-marginal OT problems. In section 5, we present some numerical results, and finally, in section 6, we conclude by assessing the current limitations of the application of OT to DFT from a numerical point-of-view.

2. Theoretical background on DFT

In section 2.1, we very briefly recall the formalism of the many-electron problem in quantum mechanics. In section 2.2, we review the vary basic aspects of density-functional theory, emphasizing the *Kohn-Sham* approach (KS-DFT) and its counterpart the *Strictly Correlated Electrons* approach (SCE-DFT). Finally, in section 2.3, we show how the latter can be reformulated as a mass transportation problem.

2.1. The quantum many-electron problem

Recall that, given N electrons together with some time-independent external potential V, the resulting quantum system is completely described by the operator H (*i.e.* the *Hamiltonian*) defined as

$$\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2}\Delta_{x_i}\right)+\sum_{i=1}^{N}V(x_i)+\sum_{1\leq i<j\leq N}\frac{1}{|x_i-x_j|},$$

where Δ_{x_i} denotes the Laplacian w.r.t. x_i and $\hbar$ the famous *Planck's constant*, which encodes the quantization of the classical energy.

Remark 2.1. *Under the mild assumption that V be a real-valued potential belonging to the space $L^{3/2}(\mathbb{R}^3)+$*

$L^\infty(\mathbb{R}^3)$*, accounting for a rather large class of physical potentials, the operator* H *is well-defined as a self-adjoint semi-bounded operator over some dense subspace* $\mathcal{D}(H) \subset L^2(\mathbb{R}^{3N}, \mathbb{C})$.

Example 2.1. *In the case of a molecular systems under* Born-Oppenheimer approximation*, that is where we regard nuclei as classical point-like particles at fixed loci* R_j*'s with nuclear charges* z_j*'s, the external potential is given by*

$$V(x) = \sum_{j=1}^{M} \frac{z_j}{|x - R_j|},$$

and the domain of self-adjointness of H *is* $\mathcal{D}(H) = H^2(\mathbb{R}^{3N}, \mathbb{C})$*. Note that one must further require that* Ψ *be antisymmetric, for electrons are* fermions*, as they obey* Pauli exclusion principle*.*

Given any quantum state $\Psi \in \mathcal{D}(H)$, its corresponding energy reads $\mathcal{E}(\Psi) := \langle \Psi, H\Psi \rangle$, which we will decompose as

$$\mathcal{E}(\Psi) = T_\hbar(\Psi) + V_{ee}(\Psi) + \int_{\mathbb{R}^3} V(x)\rho_\Psi(x)\mathrm{d}x,$$

where

$$T_\hbar(\Psi) := \left\langle \Psi, \left(\sum_{i=1}^{N} -\frac{\hbar^2}{2}\Delta_{x_i} \right) \Psi \right\rangle,$$

$$V_{ee}(\Psi) := \left\langle \Psi, \left(\sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} \right) \Psi \right\rangle,$$

are respectively the *kinetic energy* and the *electron-electron interaction energy*, and ρ_Ψ is the *electronic density* of the state Ψ, which we remind to be defined as

$$\rho_\Psi(x) := N \int_{\mathbb{R}^{3(N-1)}} |\Psi(x, \widetilde{x})|^2 \mathrm{d}\widetilde{x}.$$

Given a quantum system, of paramount interest is the problem of identifying (if any) the *ground-state* Ψ_0 and its corresponding energy E_0, that is the state of lowest possible energy, *i.e.*

$$E_0 = \mathcal{E}(\Psi_0) = \inf_{\substack{\Psi \in \mathcal{D}(H), \\ \|\Psi\|_{L_2} = 1}} \mathcal{E}(\Psi). \qquad \text{(Min1)}$$

Solving this problem analytically is infeasible, at the exception of very peculiar systems (*e.g.* Hydrogen atom, harmonic oscillator etc.). Furthermore, traditional numerical approximations are usually impractical, for the number of degrees of freedom grows exponentially with the number of particles when using straightforward numerical discretizations, so that only very small systems can be considered in practice.

2.2. A primer in density-functional theory

The *density-functional theory* (DFT) dates back to the seminal work of Hohenberg and Kohn [16], and was latter rigorously formalized by Levy [21] and Lieb [23]. It entirely relies on the fundamental property that the ground-state energy E_0 and density ρ_0 of a many-electron system can be obtained by minimizing some functional of the electronic density ρ, *i.e.*

$$E_0 = \inf_{\rho \in \mathcal{R}_N} \left\{ F_{LL}(\rho) + \int_{\mathbb{R}^3} V(x)\rho(x)\mathrm{d}x \right\}, \qquad \text{(Min2)}$$

where F_{LL} is the famous *Levy-Lieb* functional, defined as

$$F_{LL}(\rho) = \inf_{\Psi \in \mathcal{D}(H), \rho_\Psi = \rho} \{T_\hbar(\Psi) + V_{ee}(\Psi)\}$$

and where $\mathcal{R}_N$ is the set of N*-representable* functions, that is those functions ρ that arise as densities of admissible quantum states (which reduces [23] to positive functions ρ of total mass N such that $\sqrt{\rho} \in H^1(\mathbb{R}^3)$).

The minimization problem (Min2), while equivalent to (Min1), seems to be much more accessible. Indeed, the minimization runs over a subset of real-valued functions on $\mathbb{R}^3$, so that in particular the number of particles N no longer (explicitly) appears. Nevertheless, very little is known about the functional F_{LL}, so that in practice one needs to use approximations : the very core of DFT lies within the ability to provide approximations as accurate as possible.

One famous route is the one proposed by Kohn and Sham [18] (KS-DFT), based on the assumption that there exists a reference non-interacting system of fermions which has exactly the same ground state density as the one from the initial, physical system. This roughly amounts to purporting that the kinetic energy largely dominates electron-electron interactions. As such, we write

$$F_{LL}(\rho) = \min_{\Psi \in \mathcal{D}(H), \rho_\Psi = \rho} T_h(\Psi) + E_{Hxc}(\rho), \qquad (2.1)$$

where $E_{Hxc}(\rho)$ is the so-called *Hartree* and *exchange-correlation* energy, which is *defined* by (2.1) and accounts for the remaining internal energy.

In the case where the system displays strong correlation, another route to follow is the so-called *Strictly Correlated Electrons* approach (SCE-DFT), first proposed by Seidl *et al.* [28], which stands as the exact counterpart of KS-DFT: the reference system is purported to have infinite electronic correlation and zero kinetic energy. The roughly amounts to first minimizing the electron-electron interaction and then correct with the remaining energy, *i.e.*

$$F_{LL}(\rho) = \min_{\Psi\in\mathcal{D}(H),\rho_\Psi=\rho} V_{ee}(\Psi) + E_{kd}(\rho),$$

where E_{kd} is the so-called *kinetic-decorrelation* energy. In this context, let us define

$$V_{ee}^{SCE}(\rho) := \min_{\Psi\in\mathcal{D}(H),\rho_\Psi=\rho} V_{ee}(\Psi).$$

The rest of this short note is dedicated to better understand this functional and to deploy numerical methods to compute its values. Before that, let us mention that SCE-DFT is an exact theory at the *semi-classical* limit (*i.e.* when $\hbar \to 0$):

Theorem 2.1. *For any $\rho \in \mathcal{R}_N$, we have the following semi-classical limit*

$$\lim_{\hbar\to 0} F_{LL}(\rho) = V_{ee}^{SCE}(\rho).$$

This theorem was first proved by Cotar *et al* [12] in the two-particle case $N = 2$, by Bindini and De Pascale [5] for the case $N = 3$ and was eventually generalized by Lewin [22] to the cases $N \geq 4$.

2.3. SCE-DFT as an optimal transport problem

We're now interested in the functional V_{ee}^{SCE}. If we define π_i the projection of $\mathbb{R}^{3N}$ onto the i-th electron space (*i.e.* $\pi_i(x_1,\dots,x_N) = x_i$), we see that $V_{ee}^{SCE}(\rho)$ is exactly equal to

$$\inf_{\substack{\gamma \text{ symmetric} \\ \text{probability on } \mathbb{R}^{3N} \\ (\pi_i)_\sharp\gamma=\rho/N, i=1,\dots,N.}} \int_{\mathbb{R}^{3N}} \sum_{1\leq i<j\leq N} \frac{1}{|x_i-x_j|}\mathrm{d}\gamma, \quad (\heartsuit)$$

where we recall that the *push-foward* measure $(\pi_i)_\sharp\gamma$ is defined as $(\pi_i)_\sharp\gamma(S) = \gamma(\pi_i^{-1}(S))$ for every Borel $S \subset \mathbb{R}^3$.

Remark 2.2. *We can naturally extend the problem* ($\heartsuit$) *to the case where the electrons live in the d-dimensional space $\mathbb{R}^d$.*

As it turns out, the problem ($\heartsuit$) is an instance of the broader class of problems of the form

$$\inf_{\gamma\in\Pi(\mu_1,\dots,\mu_N)} \int_{\mathcal{X}_1\times\cdots\times\mathcal{X}_N} c(x_1,\dots,x_N)\mathrm{d}\gamma, \quad (\mathrm{K})$$

where the $(\mathcal{X}_i,\mu_i)$'s are (Polish) probability spaces, $\Pi(\mu_1,\dots,\mu_N)$ denotes the set of couplings of the μ_i's and c is some abstract cost function. We therefore see that the problem (K) corresponds to nothing but the Kantorovitch formulation of OT in a multi-marginal setting.

Thus, finding the minimum possible electron-electron interaction energy for a given electronic density ρ actually amounts to find the optimal way of transporting $N-1$ times the density ρ into itself, where the cost function is given by the *Coulomb repulsion*, *i.e.*

$$c(x_1,\dots,x_N) = \sum_{1\leq i<j\leq N} \frac{1}{|x_i-x_j|}. \quad (2.2)$$

In particular, we can also look at the associated Monge problem, which in the general setting of (K) reads

$$\inf_{\substack{T_i:\mathcal{X}_1\to\mathcal{X}_i \\ (T_i)_\sharp\mu_1=\mu_i \\ i=2,\dots,N}} \int_{\mathcal{X}_1} c(x,T_2(x),\dots,T_N(x))\mathrm{d}\mu_1. \quad (\mathrm{M})$$

Remark 2.3. *The physical intuition behind this Monge problem is as follows: reminiscent of theorem 2.1, in the SCE approach, the electrons are so tightly bounded by each others that they no longer display quantum behaviors. Indeed, the position of the i-th electron is classically determined by the position of the first electron, via the so-called* co-motion *maps T_i.*

3. Multi-marginal optimal transport theory

The problem ($\heartsuit$) is challenging for two reasons : *(i)* OT problems are traditionally formulated in a two-marginal setting, and the current literature on the multi-marginal setting is rather restricted in comparison, and *(ii)* the cost function considered here is of a repulsive kind, and can even take infinite values.

Nonetheless, bits of theory addressing those two issues are available. In the case where c is the usual

quadratic cost, one can prove [13] the existence of optimal solutions to both (K) and (M). The case of the *determinant cost*, *i.e.* $c(x_1, \dots, x_n) = \det(x_1, \dots, x_n)$ has also been well treated in the literature [8], as well as for *log-type* costs [14].

For starter, we have the following theorem, whose proof is rather simple:

Theorem 3.1. *If c is positive and lower semicontinuous, then there exists an optimal transport plan $\gamma^\star$ for the minimum problem* (K)*.*

Proof. The set of couplings $\Pi(\mu_1, \dots, \mu_N)$ is easily seen to be tight from the condition on the marginals. Therefore, using Prokhorov's theorem, given a minimizing sequence $(\gamma_n)_n$, there exist a subsequence $(\gamma_{n_k})_k$ and a coupling $\gamma^\star$ such that we have the weak-$\star$ convergence $\gamma_{n_k} \overset{*}{\rightharpoonup} \gamma$. From the fact that c is bounded below and l.s.c., the functional $\mu \to \int c \mathrm{d}\mu$ is l.s.c. (in the weak-$\star$ topology), and therefore $\gamma^\star$ is optimal. □

Remark 3.1. *If the marginals $\mu_1, \dots, \mu_N$ are all equal and the cost function is symmetric, then the theorem holds with $\gamma^\star$ satisfying the symmetry constraint as in* (♡)*. This is easily seen by taking an optimal solution γ and considering $\widetilde{\gamma} = \sum_{\sigma \in \mathfrak{S}_N} \sigma_\sharp \gamma$.*

As usual, one can look at the dual of (K), which in this context reads

$$\max_{(u_i)_{i=1,\dots,N}} \sum_{i=1}^N \int_{\mathcal{X}_i} u_i(x_i) \mathrm{d}\mu_i \qquad \text{(D)}$$
$$\text{s.t. } \sum_{i=1}^N u_i(x_i) \leq c(x_1, \dots, x_N),$$

and ask whether or not strong duality holds. In the case where c is lower semicontinuous and bounded above, it is a rather old result [17] that the duality gap vanishes. More recently [7, 24], the duality theory was extended for a rather large class of repulsive cost functions which are bounded from below, among which the Coulomb cost. More precisely, we have the following theorem (see [3]) :

Theorem 3.2. *Let c be a positive lower semicontinuous cost and $\mu_1 \otimes \dots \otimes \mu_N$ almost-everywhere finite. Then duality holds,* i.e. (K) = (D)*.*

In the case of the Coulomb cost, we have the following important refinement (see [7]):

Theorem 3.3. *Let c be the Coulomb cost* (2.2)*, and assume all marginals μ_i's coincide to μ. Then there exists a bounded dual maximizer $u^\star$ of* (D) (i.e. $u^\star = u_i$ *for all i) verifying*

$$u^\star(x) = \inf_{(y_i)_{i=1,\dots,N-1}} c(x, y_1, \dots, y_{N-1}) - \sum_{i=1}^{N-1} u^\star(y_i). \tag{3.1}$$

Moreover, if μ is absolutely continuous w.r.t. the Lebesgue measure, then $u^\star$ is almost-everywhere differentiable and $\nabla u^\star$ is locally bounded.

From this theorem, it follows that for two particules $N = 2$ in any dimension $d \geq 1$, the solution to (♡) is actually the unique solution to the associated Monge problem (M):

Theorem 3.4. *If $\gamma^\star$ is a solution to* (♡) *and $N = 2$, then there exists a (unique) map T such that $\gamma^\star = (Id, T)_\sharp \rho/N$.*

Proof. Let $u^\star$ be dual maximizer that verifies (3.1). We have that $\rho \otimes \rho$-a.e.

$$V(x, y) := u^\star(x) + u^\star(y) - \frac{1}{|x - y|} \leq 0$$

with equality $\gamma^\star$-a.e., so that V has a maximum on the support of $\gamma^\star$ and $\nabla_x V|_{\text{supp}(\gamma^\star)} = 0$. Therefore, from all $\gamma^\star$-a.e. $(x, y) \in \text{supp}(\gamma^\star)$, one has $y = T(x)$ where $T(x) := x + \nabla u^\star(x)/|\nabla u^\star(x)|^{3/2}$. □

In the case where $N \geq 1$ and $d = 1$, there exists a similar result [11] :

Theorem 3.5. *If $\gamma^\star$ is a solution to* (♡) *with $d = 1$, then $\gamma^\star = (Id, T, T^{(2)}, \dots, T^{(N-1)})_\sharp \rho/N$ where*

$$T(x) = \begin{cases} F_\rho^{-1}(F_\rho(x) + 1/N) & \text{if } x \leq F_\rho^{-1}(1 - 1/N) \\ F_\rho^{-1}(F_\rho(x) + 1 - 1/N) & \text{otherwise,} \end{cases}$$

where $F_\rho(x) = \frac{1}{N} \int_{-\infty}^x \rho(s) ds$.

Example 3.1 (From [15])**.** *If we introduce the artificial electronic density $\rho(x) = sech(x)/\left(2arctan(tanh(5))\right)$, we find that the co-motion T reads*

$$T(x) = 2arctanh\left(tan\left(\frac{gd(x) - sgn(x) gd(10)}{2}\right)\right), \tag{3.2}$$

where $gd(x) = arcsin(tanh(x))$ is the Gudermannian *function.*

Example 3.2. *In the case where $N = 3$ and ρ is uniform density on $[0, 1]$, one can take*

$$T(x) = \begin{cases} x + 1/3 & \text{if } x \in [0, 2/3) \\ x - 2/3 & \text{otherwise.} \end{cases}$$

If $N \geq 3$, we can (formally) extend the computation in the proof of theorem 3.4. This yields that for the dual maximizer $u^\star$, we have

$$\nabla u^\star(x_i) = -\sum_{j \neq i}^{N} \frac{x_i - x_j}{|x_i - x_j|^3}. \tag{3.3}$$

In the case where there exist co-motion maps such that $x_i = T_i(x_1)$ for all $i = 2, \dots, N$, it is then easy to check from (3.3) that the T_i's verify the group property $T_i = T_2^{(i)}$. Nevertheless, a rigorous proof of this statement is currently missing.

In the case of radial-symmetry (*i.e.* $\rho(x) = \rho(|x|)$), for any number of particles N and any dimension d, Benamou *et al.* [4, Lemma 1] proved the following theorem:

Theorem 3.6. *If c is the Coulomb cost and ρ is radially-symmetric, then*

$$(\heartsuit) = \inf_{\widetilde{\gamma} \in \Pi(\lambda, \dots, \lambda)} M(\widetilde{\gamma}) := \int_{\mathbb{R}_+^N} \widetilde{c}(r_1, \dots, r_N) d\widetilde{\gamma}, \tag{3.4}$$

where $\lambda = \lambda(r)dr$ with $\lambda(r) = \omega^d r^{d-1}\rho(r)$ (with ω^d the measure of the $(d-1)$-dimensional sphere $\mathbb{S}^{d-1}$ of $\mathbb{R}^d$), and

$$\widetilde{c}(r_1, \dots, r_N) = \inf\{c(x_1, \dots, x_N) : |x_i| = r_i, \ \forall i\}.$$

Proof. Given $\gamma^\star$ solution of ($\heartsuit$), consider its *radial component* $\widetilde{\gamma^\star}$, defined as $\pi_\sharp \gamma^\star$ where $\pi : (\mathbb{R}^d)^N \ni (x_1, \dots, x_N) \mapsto (|x_1|, \dots, |x_N|)$. Then $\widetilde{\gamma^\star} \in \Pi(\lambda, \dots, \lambda)$ and since $c(x_1, \dots, x_N) \geq \widetilde{c}(|x_1|, \dots, |x_N|)$, the solution to (3.4) is smaller than ($\heartsuit$) since $M(\widetilde{\gamma^\star}) \leq (\heartsuit)$. The converse inequality is obtained by looking at the duals of ($\heartsuit$) and (3.4) (reminiscent of theorem 3.3), and using that the Coulomb cost c is rotation-invariant. □

Example 3.3. *Suppose $N = 2$, $d = 2$ and $\rho(x) = e^{-|x|^2}/\pi$, so that $\lambda(r) = 2re^{-r^2}$. Using theorem 3.5, one can show [7] that the (unique) solution $\widetilde{\gamma}^\star$ to* (3.4) *reads $(Id, t)_\sharp \lambda$ with $t(r) = \sqrt{-\log(1 - e^{-r^2})}$.*

4. Numerics for multi-marginal problems

The problem (K), in the case where $\mathcal{X}_i = \mathbb{R}^d$ for $i = 1, \dots, N$ and the μ_i's are absolutely continuous w.r.t. the Lebesgue measure can be approached numerically as

$$\min_{\gamma \in \mathcal{C}} \sum_{j_1, \dots, j_N} c_{j_1, \dots, j_N} \gamma_{j_1, \dots, j_N} \tag{Num1}$$

where we discretize with M_d points the support of the i-th marginal as $\{x_{j_i}\}_{i=1,\dots,M_d}$, so that $\mu_{i,j_i} := \mu_i(x_{j_i})$ and $c_{j_1,\dots,j_N} := c(x_{j_1}, \dots, x_{j_N})$, and where the constraint set is defined as $\mathcal{C} := \cap_{i=1}^N \mathcal{C}_i$ where

$$\mathcal{C}_i := \left\{ \gamma \in \mathbb{R}_+^{(M_d)^N} \,\middle|\, \sum_{j_k : k \neq i} \gamma_{j_1,\dots,j_N} = \mu_{i,j_i}, \forall j_i \right\}.$$

The problem (Num1) is a traditional *linear program* (LP) and its dual reads

$$\max_{(u_i)_{i=1,\dots,N}} \sum_{i=1}^{N} \sum_{j_i=1}^{M_d} u_{i,j_i} \mu_{i,j_i} \tag{Num2}$$

$$\text{s.t.} \sum_{i=1}^{N} u_{i,j_i} \leq c_{j_1,\dots,j_N} \quad \forall (j_1, \dots, j_N),$$

where $u_{i,j_i} := u_i(x_{j_i})$. The problem (Num1) has $(M_d)^N$ unknowns and $M_d \times N$ linear constraints and the dual (Num2) has only $M_d \times N$ unknowns (M_d in the case where all the marginals are equal) but $(M_d)^N$ linear constraints. Therefore, both of these problems are impractical from a computational point-of-view, even for a small numbers of marginals.

Remark 4.1. *We recall that, at the very best, solving a LP of the form $\min_{Ax=b, x \geq 0} c^\intercal x$ with n variables and d constraints has worst-case complexity $\mathcal{O}^\star(\sqrt{d} \cdot nnz(A) + d^{2.5})$ where $nnz(A)$ is the number of non-zero entries in A [19, 20]. When $d = \Omega(n)$, the best complexity is $\mathcal{O}^\star(n^\omega \log(n))$ where $\omega \sim 2.37$ is the exponent of matrix multiplication [10].*

To simplify the numerical problem (Num1), as in the two-marginal setting, we can add an entropic regularization, *i.e.*

$$\min_{\gamma \in \mathcal{C}} \sum_{j_1, \dots, j_N} c_{j_1,\dots,j_N} \gamma_{j_1,\dots,j_N} - \varepsilon \text{Ent}(\gamma), \tag{Num3}$$

where $\text{Ent}(\gamma) := -\sum_{j_1,\dots,j_N} \gamma_{j_1,\dots,j_N} \log(\gamma_{j_1,\dots,j_N})$ is the entropy of the coupling γ. This makes the objective

ε-strongly convex and the solution unique. By defining the *Gibbs kernel* $\kappa^\varepsilon \in \mathbb{R}_+^{M_d^N}$ where

$$\kappa^\varepsilon_{j_1,\dots,j_N} := \exp(-c_{j_1,\dots,j_N}/\varepsilon),$$

(with $\exp -\infty = 0$) the problem (Num3) rewrites as

$$\min_{\gamma\in\mathcal{C}} \mathrm{KL}(\gamma\|\kappa^\varepsilon), \tag{Num4}$$

where $KL(\gamma\|\kappa^\varepsilon) := -\sum_{j_1,\dots,j_N} \gamma_{j_1,\dots,j_N} \log\left(\frac{\gamma_{j_1,\dots,j_N}}{\kappa^\varepsilon_{j_1,\dots,j_N}}\right)$ is the *Kullback-Leibler (KL) divergence*.

As in the two-marginal case, one can (easily) prove that the regularized solutions γ^ε to (Num4) converge to the solution of (Num1) with maximal entropy as $\varepsilon \to 0$ [25, Proposition 4.1].

Remark 4.2. *Note that even when c is the Coulomb cost, so that it blows to infinity on its diagonals, everything here is still working properly. In fact, if one is reluctant to work on the extended real line, the problem* (Num1) *can be rewritten in this context by adding the convex constraints $\gamma_{j_1,\dots,j_N} = 0$ any time there are $i \neq k$ such that $x_{j_i} = x_{j_k}$.*

The first idea to solve numerically (Num4) dates back to the seminal work of Bregman [6]. It relies on alternately projecting κ^ε on each constraint set $\mathcal{C}_i$ with respect to some « distance » (here the KL divergence), *i.e.* $\gamma^{(0)} = \kappa^\varepsilon$ and

$$\gamma^{(n)} = \mathrm{proj}^{KL}_{\mathcal{C}_{n(\mathrm{mod}N)}}(\gamma^{(n-1)}), \tag{Breg}$$

where $\mathrm{proj}^{KL}_{\mathcal{C}_i}(\gamma)$ is the projection of γ on $\mathcal{C}_i$ w.r.t. to the KL divergence. In fact, the iterates $\gamma^{(n)}$ converge to γ^ε [2]. Moreover, these projections can easily be computed :

Proposition 4.1. *Given $\gamma \in \mathbb{R}_+^{M_d^N}$, we have*

$$proj^{KL}_{\mathcal{C}_i}(\gamma)_{j_1,\dots,j_N} = \left(\mu_{i,j_i}\frac{\gamma_{j_1,\dots,j_N}}{\sum_{k_j:j\neq i}\gamma_{k_1,\dots,k_N}}\right)_{j_i=1}^{M_d}.$$

Proof. Straightforward by writing the Lagrangian and the KKT conditions. □

At each step of (Breg), we update M_d^N entries, and each of them is computed through $M_d^{N-1}+1$ elementary operations. Therefore, the overall iteration costs $\mathcal{O}(M_d^{2N-1})$.

To reduce the computational burden, Benamou *et al.* [4] proposed to extend the famous *Sinkhorn's algorithm* (see [25, Chapter 4] for refresher) to the multi-marginal setting and to subsequently approximate the solution to (♡).

Considering the problem (Num4) in a very general setting (*i.e.* with absolutely continuous measures w.r.t. to the some reference measure), one can prove [27] that the unique solution γ^ε to (Num4) rewrites as

$$\gamma^\varepsilon(x_1,\dots,x_N) = \prod_{i=1}^N a_i(x_i)\kappa^\varepsilon(x_1,\dots,x_N),$$

where the a_i's are positive functions, which can be recover as

$$a_i(x) = \frac{\mu_i(x)}{\int \kappa^\varepsilon(x_1,\dots,x_N)\prod_{j\neq i} a_j(x_j)\mathrm{d}\widehat{x_i}},$$

where $\widehat{x_i} := (x_1,\dots,x_{i-1},x_{i+1},\dots,x_N)$. The idea of Sinkhorn's algorithm is to solve these equalities iteratively, *i.e.*

$$a_i^{(n+1)}(x) = \frac{\mu_i(x)}{\int \kappa^\varepsilon \prod_{j=1}^{i-1} a_j^{(n+1)}(x_j)\prod_{k=i+1}^N a_k^{(n)}(x_k)\mathrm{d}\widehat{x_i}},$$

given some initial conditions $a_i^{(0)}$ for $i = 2,\dots,N$. In particular, we recover the iterate approximations $\gamma^{(n)}$ of the solution to (Num4) as

$$\gamma^{(Nn+k)}(x_1,\dots,x_N) = \prod_{i=1}^k a_i^{(n+1)}(x_i)\prod_{j=k+1}^N a_j^{(n)}(x_j)\kappa^\varepsilon(x_1,\dots,x_N)$$

for all n and $k \in [\![0, N-1]\!]$. One can prove [26] that $\gamma^{(n)}$ converge to γ^ε, the unique solution of (Num4).

Note that this iterative procedure is straightforward to rewrite in a discretized setting, with $a^{(n)}_{i,j_i} = a_i^{(n)}(x_{j_i})$, $\mu_{i,j_i} = \mu_i(x_{j_i})$ and $\kappa^\varepsilon_{j_1,\dots,j_N} = \kappa^\varepsilon(x_{j_1},\dots,x_{j_N})$. In this case, computing $a_i^{(n)}$ requires updating M_d entries, each of them computed through $M_d^{N-1}(N-1)+1$ elementary operations, which makes the overall algorithm scales like $\mathcal{O}(NM_d^N)$, which is a very good improvement compared to Bregman iterative procedure. Note that we still need a huge chunk of size M_d^N to store the discretized kernel κ^ε, though this number can be reduced when the cost c displays some symmetries, as it is the case with the Coulomb cost.

5. Numerical experiments

We perform three numerical experiments, using the systems presented in examples 3.1, 3.2 and 3.3. These systems are highly artificial, in the sense that they do not represent concrete physical systems. That being said, they have the advantage of being entirely analytical, so that one can actually check that everything is working according to the theory. Indeed, it is a well-known fact that integral systems in quantum mechanics are rare commodities, and we are not aware of any of these absolute gem being well-fitted for SCE-DFT (*i.e.* they typically do not show strong correlation between particles).

5.1. $N = 2$ and $d = 1$

We consider the artificial electronic density ρ from example 3.1, where $N = 2$ and $d = 1$. In this context, we recover the traditional Sinkhorn's algorithm in the two-marginal setting. We discretize the density ρ on $[-10, 10]$ with $M_d = 1000$ gridpoints. As $\varepsilon \to 0$, we expect γ^ε to converge to $(Id, T)_\sharp \rho(x)\mathrm{d}x$, where the co-motion map T is given by (3.2). The drawback of decreasing ε is that it takes more iterations for the algorithm to converge. In fig. 1, we display the support of γ^ε for $\varepsilon = 0.1, 0.01, 0.005$ and 0.0009 with respective number of iterations 50, 250, 500 and 2500 (we monitor the convergence by looking at $\|\gamma^{(k)}\mathbb{1}_{M_d} - \rho\|_1$).

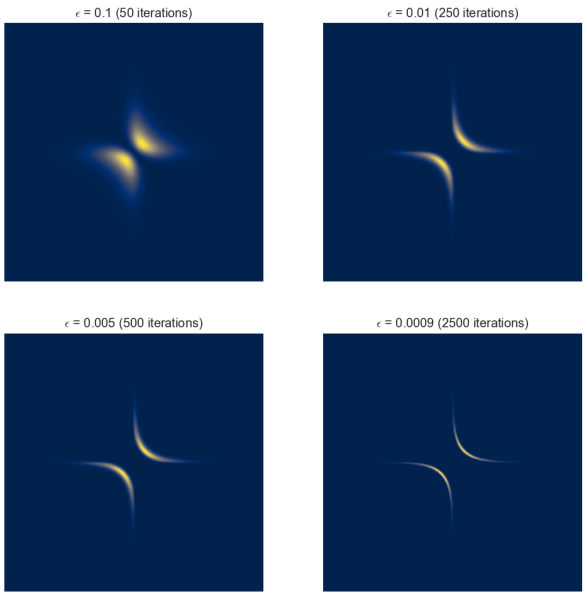

Figure 1: Color-maps of $\mathrm{supp}(\gamma^\varepsilon)$.

As expected, the regularized optimal plan γ^ε gets sparser as $\varepsilon \to 0$ and eventually converge to the graph of the analytical co-motion map T. To better see this, we compare in fig. 2 the barycenters, *i.e.*

$$\overline{T}^\varepsilon : [\![0, M_d - 1]\!] \ni i \mapsto \sum_{j=0}^{M_d-1} \gamma^\varepsilon_{ij} x_j / \rho_i$$

against the true co-motion map T, where $\{x_i\}_{i=0}^{M_d-1}$ is the uniform discretization of $[-10, 10]$ and $\rho_i := \rho(x_i)$. We observe that $\overline{T}^\varepsilon$ fits closer to T as $\varepsilon \to 0$. Note that for rather big ε, because of the high entropic noise, the projections of the two « clusters » overlap near the origin, which contaminates the barycenter near $x = 0$.

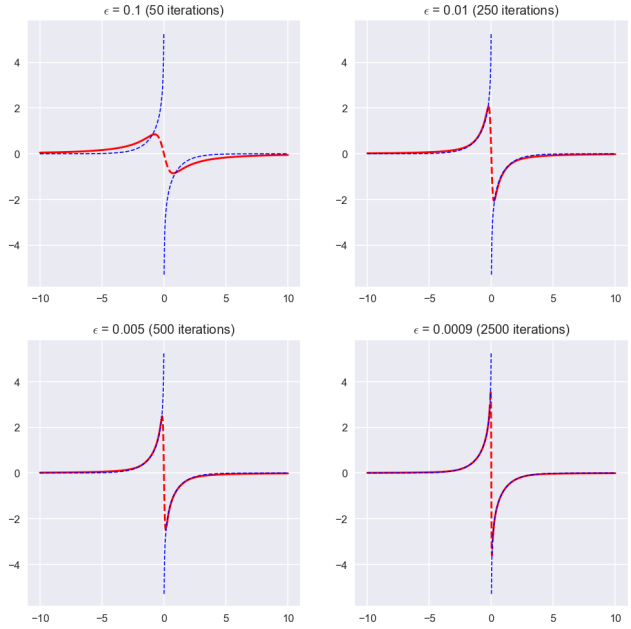

Figure 2: Barycenters $\overline{T}^\varepsilon$ (red) and T (blue).

In fact, because of the singularity of T at the origin (*e.g.* the locus of the nucleus), we don't expect any kind of uniform convergence (*i.e.* $\|\overline{T}^\varepsilon - T\|_\infty \not\to 0$), except (perhaps) away from the origin.

Remark 5.1. *It would be interesting to refine the notion of barycenter used here to deal with clusters, that is construct a* multi-valued *map $i \mapsto \widetilde{T}(i)$ where each $\overline{c} \in \widetilde{T}(i)$ is the mean-centroid of a cluster in $(\gamma_{i,j})_j$. Ideally, clusters could be retrieved in a fully unsupervised setting. In the context of high entropic noise, one could even further try to rebuild the underlying Monge solution T by retrieving topological features of the support using standard tools of* Topological Data Analysis *(TDA).*

5.2. $N = 3$ *and* $d = 1$

Let us now consider the example 3.2. We discretize $[0, 1]$ with $M_d = 120$ gridpoints. We approximate the regularized solution γ^ε with $\varepsilon = 0.1$ over 800 iteration, and we compare the overall performance of the algorithm against the solution of (Num1) computed through linear programming (LP).

Remark 5.2. *To solve the LP, we used* `cvxpy` *package with solver* `ECOS`*. Unfortunately, this package doesn't support N-tensors for $N > 2$. Therefore, we had to decompose γ into $M_d \times M_d^2$ variables, which has probably slowed down a little bit the execution.*

In fig. 3, we display a color-map of $\mathrm{supp}((\pi_{12})_\sharp \gamma^\varepsilon)$, where π_{12} is the projection on the first two marginal spaces, together with graphs of the analytical co-motion maps T and $T^{(2)}$. On the right, we display $\mathrm{supp}((\pi_{12})_\sharp \gamma^\star)$, where $\gamma^\star$ is the true (unregularized) optimal plan (*i.e.* solution to (Num1)), obtained through LP. In fig. 4, we display a 3D color-map of $(\pi_{12})_\sharp \gamma^\varepsilon$.

Remark 5.3. *We were not able to decrease ε further down without causing* underflow. *We implemented the famous loophole of carrying the computations into the log-domain, which makes the algorithm able to perform for essentially all values of ε. Nevertheless, as expected, because the iterates on the dual variables no longer can be written as simple vectors multiplications, the computational cost greatly deteriorates, especially in a multi-marginal setting. A possible strategy to alleviate this is described in [9], which consists in using a redundant parametrization,* i.e. $u_i = \widetilde{u}_i \odot \exp(\widehat{\alpha}_i/\varepsilon)$*, where the $\widehat{\alpha}_i$'s role is to occasionally absorb the large values of $(\widetilde{u}_i)_{i=1,\dots,N}$.*[1].

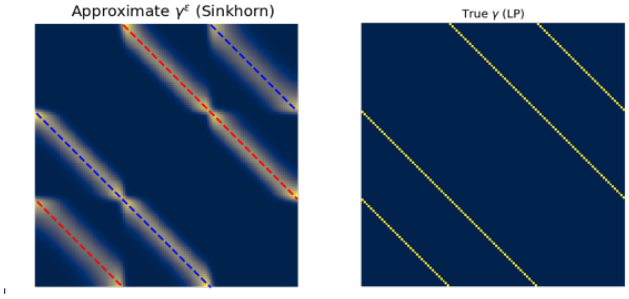

Figure 3: Color-maps of $\mathrm{supp}((\pi_{12})_\sharp \gamma^\varepsilon)$ (with T (blue) and $T^{(2)}$ (red)) and $\mathrm{supp}((\pi_{12})_\sharp \gamma^\star)$.

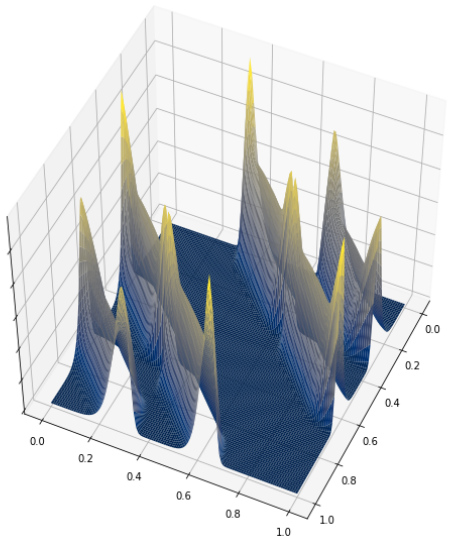

Figure 4: 3D Color-map of $(\pi_{12})_\sharp \gamma^\varepsilon$.

We can thereafter compare the performances of the two procedures. LP yielded the (true) optimal Monge map in $\sim 700s$, with associated cost ~ 892.5, while Sinkhorn's algorithm yielded an approximate solution with associated cost ~ 903.4 in $\sim 83s$, which altogether is an acceptable performance. Nevertheless, bear in mind that: *(i)* we are only considering $N = 3$ one-dimensional particles, *(ii)* the discretization that we use is rather coarse, and *(iii)* in the setting of our initial problem (Min2), we need to iterate this procedure for *all* N-representable functions ρ ! A long way is still to be traveled.

5.3. $N = 2$ *and* $d = 2$

As our last example, we consider the setting of the example 3.3, which constitutes a simple two-dimensional problem that reduces to a one-dimensional problem by invoking radial-symmetry, as shown in theorem 3.6. In the context of the Coulomb cost, the associated radial cost $\widetilde{c}$ trivially reads $\widetilde{c}(r_1, r_2) = 1/(r_1 + r_2)$.

We discretize $[0, 2]$ with $M_d = 400$ gridpoints, and we run Sinkorn's algorithm with $\varepsilon = 0.001$ across 500 iterations. In fig. 5, we display a color-map of $\mathrm{supp}(\widetilde{\gamma}^\varepsilon)$, together with the associated barycenter (left), and we com-

[1] We also implemented this strategy along with the log-domain. Unfortunately, for reasons that are still obscure to us, we were not able to make our algorithm properly works in the case of repulsive costs. We believe that either a silly mistake was made, or that the initializations $\widehat{\alpha}_i^{(0)}$ are subtle.

pare this barycenter with the true analytical radial co-motion map t (right) from example 3.3.

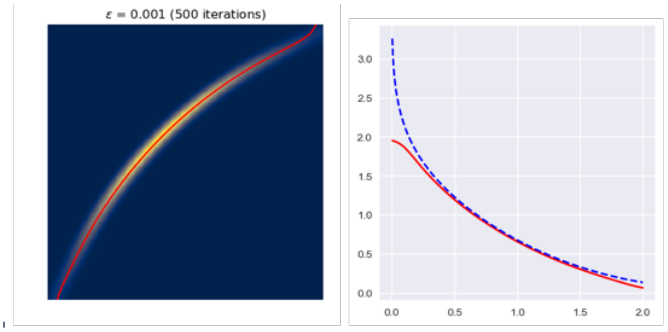

Figure 5: Color-map of supp($\widetilde{\gamma}^{\varepsilon}$), the barycenter (red) and the t (blue).

6. Conclusion

We have presented multi-marginal OT theory (section 3), together with a robust & consistent numerical scheme to approximate its solutions for a wide variety of costs (section 4), and more particularly in the case of the Coulomb cost, where the problem relates to important issues in the field of DFT (section 2).

From a theoretical point-of-view, the take-away message is that the main numerical tools to solve OT problems in the two-marginal case (*i.e.* *Bregman iteration projection* and *Sinkhorn's algorithm*) extend easily to the multi-marginal case, together with theoretical guarantees, even for repulsive costs, which in turn implies that this approach could be used in *theory* in DFT.

Nevertheless, from a *practical* point-of-view (section 5), the take-away message is that this approach is (for the moment) rather impractical. The computational cost remains very high, and at the exception of « textbook » quantum systems (*e.g.* one-dimensional, radially-symmetric), this approach is doomed to fail without further improvements.

Among those possible improvements, we may consider essentially all the classical loopholes already well-established in the traditional two-marginal setting. For instance, as proposed by Vialard & Levitt [1], one could try speeding up the overall process by resorting to *Anderson acceleration*.

References

[1] *Anderson acceleration, Sinkhorn and Multi-Marginal Euler*. `https://www.ceremade.dauphine.fr/~vialard/AndersonMultiMarginal.html`.

[2] Heinz H Bauschke and Adrian S Lewis. "Dykstras algorithm with bregman projections: A convergence proof". In: *Optimization* 48.4 (2000), pp. 409–427.

[3] Mathias Beiglboeck, Christian Leonard, and Walter Schachermayer. *A General Duality Theorem for the Monge–Kantorovich Transport Problem*. 2009. arXiv: `0911.4347 [math.OC]`.

[4] Jean-David Benamou, Guillaume Carlier, and Luca Nenna. "A numerical method to solve multi-marginal optimal transport problems with Coulomb cost". In: *Splitting Methods in Communication, Imaging, Science, and Engineering*. Springer, 2016, pp. 577–601.

[5] Ugo Bindini and Luigi De Pascale. "Optimal transport with Coulomb cost and the semiclassical limit of Density Functional Theory". In: *Journal de l'École polytechnique-Mathématiques* 4 (2017), pp. 909–934.

[6] Lev M Bregman. "The relaxation method of finding the common point of convex sets and its application to the solution of problems in convex programming". In: *USSR computational mathematics and mathematical physics* 7.3 (1967), pp. 200–217.

[7] Giuseppe Buttazzo, Luigi De Pascale, and Paola Gori-Giorgi. "Optimal-transport formulation of electronic density-functional theory". In: *Physical Review A* 85.6 (2012), p. 062502.

[8] Guillaume Carlier and Bruno Nazaret. "Optimal transportation for the determinant". In: *ESAIM: Control, Optimisation and Calculus of Variations* 14.4 (2008), pp. 678–698.

[9] Lenaic Chizat, Gabriel Peyré, Bernhard Schmitzer, and François-Xavier Vialard. "Scaling algorithms for unbalanced optimal transport problems". In: *Mathematics of Computation* 87.314 (2018), pp. 2563–2609.

[10] Michael B Cohen, Yin Tat Lee, and Zhao Song. "Solving linear programs in the current matrix multiplication time". In: *Proceedings of the 51st annual ACM SIGACT symposium on theory of computing*. ACM. 2019, pp. 938–942.

[11] Maria Colombo, Luigi De Pascale, and Simone Di Marino. "Multimarginal optimal transport maps for one–dimensional repulsive costs". In: *Canadian Journal of Mathematics* 67.2 (2015), pp. 350–368.

[12] Codina Cotar, Gero Friesecke, and Claudia Klüppelberg. "Density functional theory and optimal transportation with Coulomb cost". In: *Communications on Pure and Applied Mathematics* 66.4 (2013), pp. 548–599.

[13] Wilfrid Gangbo and Andrzej Święch. "Optimal maps for the multidimensional Monge-Kantorovich problem". In: *Communications on Pure and Applied Mathematics: A Journal Issued by the Courant Institute of Mathematical Sciences* 51.1 (1998), pp. 23–45.

[14] Augusto Gerolin, Anna Kausamo, and Tapio Rajala. *Duality theory for multi-marginal optimal transport with repulsive costs in metric spaces*. 2018. arXiv: 1805.00880 [math.AP].

[15] Juri Grossi, Derk P Kooi, Klaas JH Giesbertz, Michael Seidl, Aron J Cohen, Paula Mori-Sánchez, and Paola Gori-Giorgi. "Fermionic statistics in the strongly correlated limit of Density Functional Theory". In: *Journal of chemical theory and computation* 13.12 (2017), pp. 6089–6100.

[16] P. Hohenberg and W. Kohn. "Inhomogeneous Electron Gas". In: *Phys. Rev.* 136 (3B Nov. 1964), B864–B871.

[17] Hans G Kellerer. "Duality theorems for marginal problems". In: *Zeitschrift für Wahrscheinlichkeitstheorie und verwandte Gebiete* 67.4 (1984), pp. 399–432.

[18] Walter Kohn and Lu Jeu Sham. "Self-consistent equations including exchange and correlation effects". In: *Physical review* 140.4A (1965), A1133.

[19] Yin Tat Lee and Aaron Sidford. *Path Finding I :Solving Linear Programs with $\tilde{O}$(sqrt(rank)) Linear System Solves*. 2013. arXiv: 1312.6677 [cs.DS].

[20] Yin Tat Lee and Aaron Sidford. *Efficient Inverse Maintenance and Faster Algorithms for Linear Programming*. 2015. arXiv: 1503.01752 [cs.DS].

[21] Mel Levy. "Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem". In: *Proceedings of the National Academy of Sciences* 76.12 (1979), pp. 6062–6065.

[22] Mathieu Lewin. "Semi-classical limit of the Levy–Lieb functional in density functional theory". In: *Comptes Rendus Mathématiques* 356.4 (2018), pp. 449–455.

[23] Elliott H. Lieb. "Density functionals for coulomb systems". In: *International Journal of Quantum Chemistry* 24.3 (1983), pp. 243–277.

[24] Luigi De Pascale. *Optimal Transport with Coulomb cost. Approximation and duality*. 2015. arXiv: 1503.07063 [math.AP].

[25] Gabriel Peyré, Marco Cuturi, et al. "Computational optimal transport". In: *Foundations and Trends® in Machine Learning* 11.5-6 (2019), pp. 355–607.

[26] Ludger Ruschendorf et al. "Convergence of the iterative proportional fitting procedure". In: *The Annals of Statistics* 23.4 (1995), pp. 1160–1174.

[27] Ludger Rüschendorf and Wolfgang Thomsen. "Closedness of sum spaces andthe generalized schrödinger problem". In: *Theory of Probability & Its Applications* 42.3 (1998), pp. 483–494.

[28] Michael Seidl, John P Perdew, and Mel Levy. "Strictly correlated electrons in density-functional theory". In: *Physical Review A* 59.1 (1999), p. 51.