Density functional theory and multi-marginal optimal transport: Introduction

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Consider a system of N electrons subject to an external potential

$$r_i \in \mathbb{R}^3, \quad \mathbb{R}^{3N} \ni \{r_i\}_{i=1}^N \quad \mapsto \quad \sum_{i=1}^N v(r_i).$$

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The possible states $\{\Psi_\ell\}$ of the system are described by solutions to the Schrödinger equation

$$H\Psi_\ell = E_\ell \Psi_\ell$$

with the Hamiltonian

$$H := -\sum_{i=1}^N \Delta_i + \sum_{i=1}^N v(r_i) + \sum_{1 \le i < j \le N} \frac{1}{|r_i - r_j|}$$

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Example.

A molecule is composed of M nuclei at positions $\{R_\alpha\}_{\alpha=1}^{M}$, $R_\alpha \in \mathbb{R}^3$, with charges $\{Z_\alpha\}_{\alpha=1}^{M}$, and N electrons at positions $\{r_i\}_{i=1}^{N}$, $r_i \in \mathbb{R}^3$.

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$$v(r_i) := -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{|r_i - R_\alpha|}.$$

The ground state energy: $E := \inf_\Psi \langle \Psi, H\Psi \rangle$

where

$$\langle \Psi, H\Psi \rangle = \sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_i \Psi(r)|^2 \, \mathrm{d}r + \sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} v(r_i) |\Psi(r)|^2 \, \mathrm{d}r + \sum_{1 \leq i < j < N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(r)|^2}{|r_i - r_j|} \, \mathrm{d}r, \quad r := \{r_i\}_{i=1}^{N}, \; r_i \in \mathbb{R}^3$$

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Problem. Computing E by solving the Schrödinger equation is too expensive.

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The **Levy-Lieb constrained-search functional** is

$$F_{\mathrm{LL}}(\rho) := \left\{ \inf_{\Psi : \rho_\Psi = \rho} \sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_i \Psi(r)|^2 \, \mathrm{d}r + \sum_{1 \le i < j < N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(r)|^2}{|r_i - r_j|} \, \mathrm{d}r \right\},$$

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and satisfies

$$E = \inf_{\Psi} \langle \Psi, H\Psi \rangle = \inf_{\rho} \left\{ F_{\mathrm{LL}}(\rho) + \int_{\mathbb{R}^3} \rho(x) v(x) \,\mathrm{d}x \right\}$$

because, by symmetry,
$\sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} v(r_i)|\Psi(r)|^2 \,\mathrm{d}r = \int_{\mathbb{R}^3} v(x) \rho_\Psi(x) \,\mathrm{d}x.$

Summary

To compute the ground state energy E it suffices to compute the minimum of the functional $\rho \mapsto \{F_{\mathsf{LL}}(\rho) + \langle v, \rho \rangle\}$ over the **electron densities** ρ, which depend only on $x \in \mathbb{R}^3$, instead of computing the minimum of $\langle \Psi, H\Psi \rangle$ over **wave functions** Ψ, which depend on $r \in \mathbb{R}^{3N}$.

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Problem. We have no description of

$$F_{\mathrm{LL}}(\rho) = \left\{ \inf_{\Psi : \rho_\Psi = \rho} \int |\nabla \Psi(r)|^2 \,\mathrm{d}r + \sum_{1 \le i < j \le N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(r)|^2}{|r_i - r_j|} \,\mathrm{d}r \right\}.$$

The adiabatic connection

For $\lambda \geq 0$ let

$$F_{\mathrm{LL}}^{\lambda}(\rho) := \left\{ \inf_{\Psi : \rho_\Psi = \rho} \int |\nabla \Psi(r)|^2 \, \mathrm{d}r + \lambda \sum_{1 \leq i < j \leq N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(r)|^2}{|r_i - r_j|} \, \mathrm{d}r \right\},$$

so $F_{\mathrm{LL}}^{\lambda=0}(\rho) = \inf_{\Psi : \rho_\Psi = \rho} \int |\nabla \Psi(r)|^2 \, \mathrm{d}r$ (non-interacting electrons), and $F_{\mathrm{LL}}^{\lambda=1}(\rho) = F_{\mathrm{LL}}(\rho)$.

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Take $\lambda \to \infty$ [Seidl (1999); Seidl, Gori-Giorgi, Savin (2007)],

$$\lim_{\lambda\to\infty} \frac{F_{\mathrm{LL}}^{\lambda}(\rho)}{\lambda} = \inf_{\Psi:\rho_\Psi=\rho} \sum_{1\leq i<j\leq N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(r)|^2}{|r_i - r_j|} \,\mathrm{d}r =: V^{\mathrm{SCE}}(\rho).$$

DFT and multi-marginal optimal transport

Recall

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Typically, the infimum in $V^{\mathrm{SCE}}(\rho)$ is not attained.

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Relaxation. [Buttazzo, De Pascale, Gori-Giorgi (2012); Cotar, Friesecke, Klüppelberg (2013)]

$$\inf_{\pi:\pi_\rho=\rho}\sum_{1\le i<j\le N}\int_{\mathbb{R}^{3N}}\frac{1}{|r_i-r_j|}\,\mathrm{d}\pi(r),$$

where the infimum is over the set of probability measures π on $\mathbb{R}^{3N}$ whose marginals on $\mathbb{R}^3$ are all equal to ρ.

DFT multi-marginal optimal transport:

$$\inf_{\pi:\pi_\rho=\rho} \sum_{1\leq i<j\leq N} \int_{\mathbb{R}^{3N}} \frac{1}{|r_i - r_j|} \, \mathrm{d}\pi(r).$$

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The infimum is always attained, and moreover [Cotar, Friesecke, Klüppelberg (2013, 2018); Bindini, De Pascale (2017)],

$$\begin{aligned}
&\min_{\pi:\pi_\rho=\rho} \sum_{1\le i<j\le N} \int_{\mathbb{R}^{3N}} \frac{1}{|r_i - r_j|} \,\mathrm{d}\pi(r) \\
&= V^{\mathrm{SCE}}(\rho) \\
&= \inf_{\Psi:\rho_\Psi=\rho} \sum_{1\le i<j\le N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(r)|^2}{|r_i - r_j|} \,\mathrm{d}r.
\end{aligned}$$

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A **Monge solution** (if exists) is of much lower dimension:

$$\mathrm{d}\pi(r_1,\dots,r_N) = \left[\int_{\mathbb{R}^3} \frac{\rho(x)}{N} \prod_{i=1}^{N} \delta(r_i - f_i(x))\,\mathrm{d}x\right] \mathrm{d}r_1 \cdots \mathrm{d}r_N$$

where $f_1,\dots,f_N : \mathbb{R}^3 \to \mathbb{R}^3$ are **co-motion functions** which preserve ρ:

$$(f_i)_\sharp \rho = \rho \quad \forall\ i = 1,\dots,N.$$

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Note. Consider $f_1(x) = x$ to recover the familiar Monge solution.

The Monge problem

The DFT optimal transport problem

$$\min_{\pi:\pi_\rho=\rho} \sum_{1\leq i<j\leq N} \int_{\mathbb{R}^{3N}} \frac{1}{|r_i - r_j|} \,\mathrm{d}\pi(r)$$

becomes the Monge problem

$$\inf_{f_1,\ldots,f_N} \sum_{1\leq i<j\leq N} \int_{\mathbb{R}^3} \frac{1}{|f_i(x) - f_j(x)|} \frac{\rho(x)}{N} \,\mathrm{d}x$$

over all co-motion functions $f_1, \ldots, f_N$ which preserve ρ.

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4. For general dimension (including 3), and general N, the existence of a solution to the Monge problem is open.

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1. **No-solutions**. There exist a cost such that in dimension 1 with $N = 3$ electrons, the Monge problem has no solution.

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2. See [P15] and [DGN17] for the general theory of multi-marginal optimal transport.

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Choose $f_1(x) := x, f_2, \ldots, f_N : \mathbb{R} \to \mathbb{R}$ such that, for each $i = 2, \ldots, N$, the amount of ρ-mass between $f_i(x)$ and $f_{i+1}(x)$ is equal to 1: $\int_{f_i(x)}^{f_{i+1}(x)} \rho(x') \, \mathrm{d}x' = 1$ for all x and i.

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Explicitly, for $i = 2, \dots, N$,

$$f_i(x) = \begin{cases} F_\rho^{-1}\left(F_\rho(x) + \frac{i-1}{N}\right) & \text{if } F_\rho(x) \le \frac{N-i+1}{N}, \\ F_\rho^{-1}\left(F_\rho(x) + \frac{i-1}{N} - 1\right) & \text{if } F_\rho(x) > \frac{N-i+1}{N}, \end{cases}$$

where F_ρ is cumulative distribution function of ρ.

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Group law. $f_i = \underbrace{f_2 \circ \cdots \circ f_2}_{i-1 \text{ times}}$ for $i = 2, \ldots, N$.

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- See Section 3 in [FGG-G22] for more information.

Quasi-Monge solutions

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with α any probability measure on $\mathbb{R}^3$, and $f_1, \ldots, f_N : \mathbb{R}^3 \to \mathbb{R}^3$ such that

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Note. If $\alpha = \frac{\rho}{N}$ then quasi-Monge is actually Monge.

Symmetric solutions

Symmetric solutions

The wave function Ψ is antisymmetric so solutions π to the DFT optimal transport problem can be assumed to be symmetric:

$$\mathrm{d}\pi(r_1, \ldots, r_N) \qquad \mapsto \qquad \frac{1}{N!} \sum_{\sigma} \mathrm{d}\pi(\sigma(r_1), \ldots, \sigma(r_N)),$$

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In particular, Monge solutions can be assumed to by symmetric:

$$\int_{\mathbb{R}^3} \frac{\rho(x)}{N} \prod_{i=1}^{N} \delta(r_i - f_i(x))\,\mathrm{d}x \mapsto \frac{1}{N!}\sum_{\sigma} \int_{\mathbb{R}^3} \frac{\rho(x)}{N} \prod_{i=1}^{N} \delta(r_{\sigma(i)} - f_{\sigma(i)}(x))\,\mathrm{d}x,$$

with $\frac{1}{N}\sum_{i=1}^{N} (f_i)_\sharp \rho = \rho$ (weaker condition)

Quasi-Monge symmetric solutions

A quasi-Monge solution

$$\left[\int_{\mathbb{R}^3} \alpha(x) \prod_{i=1}^{N} \delta(r_i - f_i(x))\,\mathrm{d}x\right] \mathrm{d}r_1 \cdots \mathrm{d}r_N,$$

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becomes a **symmetric quasi-Monge solution**:

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A coupling π of N electrons is

$$\pi = \sum_{i_1,\dots,i_N=1}^{\ell} \pi_{i_1,\dots,i_N} \left(\delta_{a_{i_1}} \otimes \cdots \otimes \delta_{a_{i_N}} \right)$$

satisfying the marginal constraint

$$\sum_{i_j, j \neq m} \pi_{i_1,\dots,i_N} = \rho_m = \frac{1}{\ell} \quad \forall\ m \in \{1, \dots, \ell\}.$$

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The optimization problem is

$$\min_{\pi} \sum_{i_1,\ldots,i_N} \left(\sum_{1 \le k < m \le N} \frac{1}{|a_{i_k} - a_{i_m}|} \right) \pi_{i_1,\ldots,i_N}.$$

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Symmetric Monge solution:
$\frac{1}{N!}\sum_{\sigma}\sum_{k=1}^{\ell}\frac{1}{\ell}\left(\delta_{f_1(a_{\sigma(k)})}\otimes\cdots\otimes\delta_{f_N(a_{\sigma(k)})}\right)$ where $f_1,\ldots,f_N$ are permutations of $\{a_1,\ldots,a_\ell\}$.

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- $N = 3$: Friesecke (2018) showed that there isn't necessarily an optimal Monge solution (already with $\ell = 3$).

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Note. The assumption that ρ is uniform is no longer needed.

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There is more to the story...

Proof sketch

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- The space of symmetric couplings $\frac{1}{N!}\sum_{\sigma}\sum_{i_1,\ldots,i_N=1}^{\ell}\pi_{i_{\sigma(1)},\ldots,i_{\sigma(N)}}\left(\delta_{a_{i_{\sigma(1)}}}\otimes\cdots\otimes\delta_{a_{i_{\sigma(N)}}}\right)$ forms a polytope.

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- The marginal constraints $\frac{1}{N!}\sum_{\sigma}\sum_{i_j,j\neq m}\pi_{i_{\sigma(1)},\dots,i_{\sigma(N)}}=\rho_m\ \forall\ m\in\{1,\dots,\ell\}$ correspond to intersecting the polytope with $(\ell-1)$ hyperplanes.

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- Optimal values of linear objectives are attained at extreme points.

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Some mathematical aspects of density functional theory

Foundations of DFT

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The map

$$v \mapsto H(v) := -\sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} v(r_i) + \sum_{1 \le i < j \le N} \frac{1}{|r_i - r_j|}$$

is injective.

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is injective.

Hohenberg-Kohn (1964): The map $v \mapsto \rho_v$ is injective, where

$$\rho_v(x) := \rho_\Psi(x) := \int |\Psi(x, r_2, \ldots, r_N)|^2 \, \mathrm{d}r_2 \cdots \mathrm{d}r_N,$$

with Ψ the *ground state* of $H(v)$.

The Hohenberg-Kohn Theorem

If ρ is *ground state representable*, then

$\rho \mapsto v_\rho \mapsto H(v_\rho) \mapsto \Psi_\rho$ where Ψ_ρ is the ground state of $H(v_\rho)$.

In words: **The one-electron marginal ρ uniquely determines the multi-electron ground state Ψ.**

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In words: **The one-electron marginal ρ uniquely determines the multi-electron ground state Ψ.**

In particular, $E = \inf_\Psi \langle \Psi, H\Psi \rangle$ is a function of *just* ρ.

The Hohenberg-Kohn variational principle

Let ρ be ground state representable and define the *universal functional*

$$F_{\mathsf{HK}}(\rho) := E(v_\rho) - \langle \rho, v_\rho \rangle \quad \text{where} \quad \langle \rho, v_\rho \rangle := \int v_\rho(x)\,\mathrm{d}\rho(x).$$

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Then, for any v such that $H(v)$ has a ground state,

$$E(v) = \inf \left\{ F_{\mathsf{HK}}(\rho) + \langle \rho, v \rangle : \rho \text{ is ground state representable} \right\}.$$

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Problem 1. The form of F_{HK} is unknown, and F_{HK} is non-convex.

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Problem 3. The form of the space of potentials whose corresponding Hamiltonian has a ground state is unknown.

Levy-Lieb constrained-search functional and variational principle

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Levy-Lieb constrained-search functional and variational principle

Let

$$F_{\mathrm{LL}}(\rho) := \left\{ \inf_{\Psi:\rho_\Psi=\rho} \sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_i \Psi(r)|^2 \,\mathrm{d}r + \sum_{1\le i<j<N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(r)|^2}{|r_i - r_j|} \,\mathrm{d}r \right\}.$$

Then, for any $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$,

$$E(v) = \inf \{ F_{\mathrm{LL}}(\rho) + \langle \rho, v \rangle : \rho = \rho_\Psi \text{ for some } \Psi \}$$

Problem 1. The form of F_{LL} is unknown, and F_{LL} is non-convex.

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Note. When ρ is ground state representable, $F_{\mathrm{LL}}(\rho) = F_{\mathrm{HK}}(\rho)$.

The Lieb functional and variational principle

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Observation. The map $L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \ni v \mapsto E(v)$ is strictly concave.

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$$F_L(\rho) := \sup\{E(v) - \langle v, \rho \rangle : v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)\}.$$

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Note. When $\rho = \rho_\Psi$ for some Ψ, $F_\mathrm{L}(\rho) = F_\mathrm{LL}(\rho)$.