Theory of Inhomogeneous Classical Coulomb Systems

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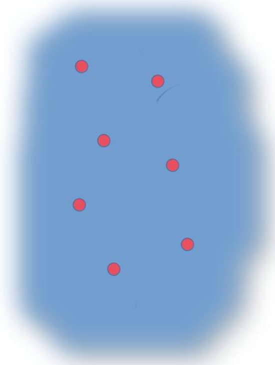
Density Functional Theory (DFT)

- fix one-particle density profile $\rho(x)$ and find the particles' positions giving this ρ and minimizing the energy



- **(Quantum) electrons in atoms, molecules and solids**
  - roots in the 30s (Thomas, Fermi)
  - theory in the 60s (Hohenberg, Kohn, Sham)
  - explosion in the 80-90s (Becke, Perdew, Burke, Yang, Parr, etc)
  - reference method for computations with many electrons
  - B3LYP cited in more than 300 000 articles and 40 000 patents on Google scholar!

- **Classical inhomogeneous systems, in particular for phase coexistence**
  - developed in the 70-80s (Ebner, Evans, etc)
  - Coulomb systems = **"Strictly Correlated Electrons"** more recent (Seidl, Gori-Giorgi, etc)
  - fits within the theory of **Optimal Transport** (Cotar-Friesecke-Kluppelberg, Buttazzo, Carlier, Champion, Colombo, De Pascale, Di Marino, Nenna, Stra, etc)

Plan

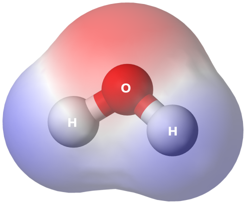
1. Density Functional Theory: from the quantum to the classical
2. Finite Coulomb systems via Optimal Transport methods
3. Counter-example to the convexity-in-N conjecture
4. Lieb-Oxford inequality
5. Local Density Approximation, Uniform Electron Gas, Wigner crystallization

- **References:**

  - M.L., E.H. Lieb & R. Seiringer. Universal functionals in Density Functional Theory. Chapter 3 in *"Density Functional Theory — Modeling, Mathematical Analysis, Computational Methods, and Applications"*, edited by Éric Cancès & Gero Friesecke, Springer, 2023.
  - M.L. Coulomb and Riesz gases: The known and the unknown. *J. Math. Phys.*, 63, p. 061101, 2022.
  - S. Di Marino, M.L. & L. Nenna. Grand-canonical Optimal Transport. *ArXiV* 2022

Part I. Density Functional Theory: from the quantum to the classical

Schrödinger's equation for electrons in a molecule



- M point nuclei of charges $z_1, ..., z_M \in \mathbb{N}$ placed at $R_1, ..., R_M \in \mathbb{R}^3$

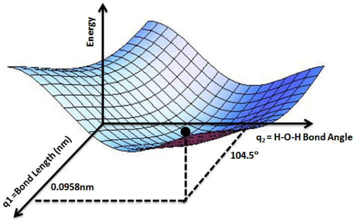
$$V(x) = -\sum_{m=1}^{M} \frac{z_m}{|x_j - R_m|}$$

- N quantum electrons: antisymmetric wavefunction $\Psi(x_1, ..., x_N)$ on $(\mathbb{R}^3)^N$ with $\int_{\mathbb{R}^{3N}} |\Psi|^2 = 1$

$$H^N(V)\Psi = E\,\Psi, \qquad H^N(V) := -\frac{1}{2}\Delta_{\mathbb{R}^{3N}} + \sum_{j=1}^{N} V(x_j) + \sum_{j<k} \frac{1}{|x_j - x_k|}$$

Equilibrium configuration of molecule: minimize

$$(R_1, ..., R_M) \mapsto E + \sum_{1 \leq \ell < m \leq M} \frac{z_\ell z_m}{|R_\ell - R_m|}$$



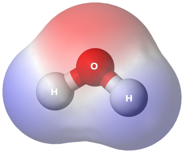
Schrödinger (essentially) impossible to solve numerically

$$H^N(V)\Psi = \left(-\frac{1}{2}\Delta + \sum_{j=1}^N V(x_j) + \sum_{j<k} \frac{1}{|x_j - x_k|} \right)\Psi = E\,\Psi$$

- $\Psi(x_1, ..., x_N) = \sum_{1 \leq j_1, \ldots, j_N \leq N_b} a_{j_1,\ldots,j_N}\, \chi_{j_1}(x_1) \cdots \chi_{j_N}(x_N)$ where $\chi_1, ..., \chi_{N_b}$ is a finite "basis" in $\mathbb{R}^3$
  - linear system with $\binom{N_b}{N}$ unknowns
  - matrix elements depend on $(N_b)^4$ numbers
  - Pople (Nobel 1998): χ_j =Gaussian $\times$ polynomial, centered at each nucleus $\Rightarrow$ exact formulas
- **Low rank approximation**, e.g. $a_{j_1,\ldots,j_N} = \sum_{1 \leq \ell_1, \ldots, \ell_N \leq N+K} b_{\ell_1,\ldots,\ell_N} c_{j_1,\ell_1} \cdots c_{j_N,\ell_N}$ (CASSCF)
  - $\binom{N+K}{N} \times N_b \times (N+K) \sim N^{K+1} N_b$ unknown
  - $K = 0$ is Hartree-Fock
  - coupled cluster (CCSD): $\propto \exp\left(\sum \alpha_{jk} a_j^\dagger a_k + \sum \alpha_{jk\ell m} a_j^\dagger a_k^\dagger a_m a_\ell\right)|HF\rangle \sim N_b^4 N^4$ unknowns

Example of numerical simulations: water molecule

cc-pVQZ basis (115 functions χ_k) on my laptop with PySCF



	HF	LDA	B3LYP	PBE	CASSCF	CCSD(T)	full CI
H O—H	-76.0530 *(1.3 s)*	-75.8998 *(1.6 s)*	-76.4253 *(2.3 s)*	-76.3776 *(2.3 s)*	-76.1126 *(13 s)*	-76.3431 *(14 s)*	failed $d \sim 10^{20}$
H O—H	-76.0655 0.9395 Å 106.22° *(19 s)*	-75.9057 0.9698 Å 104.70° *(21 s)*	-76.4325 0.9605 Å 104.88° *(26 s)*	-76.3833 0.9687 Å 103.91° *(24 s)*	-76.1185 0.9624 Å 102.88° *(75 s)*	-76.3818 0.9536 Å 104.54° *(10 min)*	**exper.** **0.958 Å** **104.48°**

HF: (restricted) Hartree-Fock. **LDA:** Dirac exchange $-c_D \int_{\mathbb{R}^3} \rho^{4/3}$ + Perdew-Wang ('92) UEG correlation.
B3LYP: hybrid with 20% of exact exchange by Becke ('93), correlation by Lee-Yang-Parr ('88). **PBE:** Perdew-Burke-Ernzerhof ('96), no exact exchange
CASSCF: linear combination of a few Slater determinants, with optimized orbitals, **CCSD(T):** coupled-cluster method
full CI: diagonalization of $H^V(N)$ in given basis

- **chemical accuracy:** precision required to make realistic chemical predictions $\approx 1 kcal/mol = 1.6 \cdot 10^{-3}$ Hartree
- requires post-Hartree–Fock methods

Legendre-Fenchel duality (Lieb '83)

$$E^N[V] = \inf_{\Psi} \langle \Psi, H^N(V)\Psi \rangle, \qquad H^N(V) := -\frac{1}{2}\Delta + \sum_{j=1}^N V(x_j) + \sum_{j<k} \frac{1}{|x_j - x_k|}$$

Legendre-Fenchel duality

$V \mapsto E^N[V]$ is **concave**, hence we can write

$$E^N[V] = \inf_{\rho} \left\{ F[\rho] + \int_{\mathbb{R}^3} \rho(x)V(x)\mathrm{d}x \right\}, \qquad F[\rho] = \sup_{V} \left\{ E^N[V] - \int_{\mathbb{R}^3} \rho(x)V(x)\mathrm{d}x \right\}$$

with $\rho : \mathbb{R}^3 \to \mathbb{R}$ "variable dual to V"

- new unknown ρ depends on only one variable $x \in \mathbb{R}^3$ $\rightsquigarrow$ no N-particle space anymore!
- F = "universal Lieb functional", very nonlinear and nonlocal, impossible to compute in practice
- **Density Functional Theory (DFT):**
  1. understand better the true F
  2. replace it with a $F_{\rm app}$ and then $E^N[V] \approx \inf_\rho \{F_{\rm app}[\rho] + \int \rho V\}$

Who is ρ? Who is $F[\rho]$?

Density of pure states

$$\langle \Psi, H^N(V)\Psi \rangle = \langle \Psi, H^N(0)\Psi \rangle + \int_{\mathbb{R}^3} \rho_\Psi(x) V(x)\,\mathrm{d}x$$

$$\rho_\Psi(x) = N \iint_{(\mathbb{R}^3)^{N-1}} |\Psi(x, x_2, ..., x_N)|^2 \mathrm{d}x_2 \cdots \mathrm{d}x_N$$

Density of mixed states

$$\mathrm{tr}(H^N(V)\Gamma) = \mathrm{tr}(H^N(0)\Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma(x) V(x)\,\mathrm{d}x$$

$$\rho_\Gamma = \sum_j n_j\, \rho_{\Psi_j}, \qquad \Gamma = \sum_j n_j |\Psi_j\rangle\langle\Psi_j|$$

It will be important that $(V, \Gamma) \mapsto \mathrm{tr}(H^N(V)\Gamma)$ is linear in both V and Γ

Reminder: von Neumann's min-max theorem

Theorem (min-max in finite dimension)

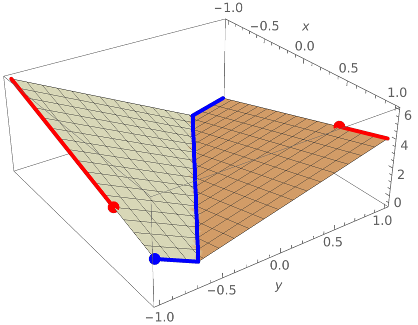
Let $f : A \times B \to \mathbb{R}$ be a continuous function with A, B compact convex sets in $\mathbb{R}^d$. Assume that $x \mapsto f(x,y)$ is convex for all $y \in B$ and that $y \mapsto f(x,y)$ is concave for all $x \in A$. Then

$$\min_{x\in A}\max_{y\in B} f(x,y) = \max_{y\in B}\min_{x\in A} f(x,y).$$

von Neumann '28, Ekeland-Teman Chap VI

- $\geq$ always true
- proof of the theorem as an exercise
- similar result in infinite dimension
- **Counter-example:** $f(x,y) = |2x+3y| - y$ on $[-1,1]^2$

  $\max\min f = 2, \qquad \min\max f = 3$



The universal functional $F[\rho]$

Theorem (Lieb '83)

The universal functional $F[\rho]$, satisfying the previous Legendre duality relations, is

$$F[\rho] := \inf_{\rho_\Gamma=\rho} \mathrm{tr}(H^N(0)\Gamma)$$

It is finite if and only if $\sqrt{\rho} \in H^1(\mathbb{R}^3)$.

- **Inf-sup argument**

$$F[\rho] := \sup_V \left\{ E^N[V] - \int_{\mathbb{R}^3} \rho V \right\} = \sup_V \inf_\Gamma \left\{ \mathrm{tr}(H^N(V)\Gamma) - \int_{\mathbb{R}^3} \rho V \right\}$$
$$= \inf_\Gamma \sup_V \left\{ \mathrm{tr}(H^N(0)\Gamma) + \int_{\mathbb{R}^3} (\rho_\Gamma - \rho) V \right\} = \inf_\Gamma \left\{ \mathrm{tr}(H^N(0)\Gamma) + \underbrace{\sup_V \int_{\mathbb{R}^3} (\rho_\Gamma - \rho) V}_{=+\infty \text{ unless } \rho_\Gamma=\rho} \right\}$$

- **Representability**
  - $F[\rho] \geq \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2$ (Hoffman-Ostenhof '77)
  - If $\sqrt{\rho} \in H^1(\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} \rho = N \in \mathbb{N}$, then there exists (nice enough) phases $\theta_1, ..., \theta_N$ such that $\varphi_j = \sqrt{\rho/N}\, e^{i\theta_j}$ are orthonormal (March-Young '58, Harriman '81, Lieb '83) $\rightsquigarrow \Psi = \varphi_1 \wedge \cdots \wedge \varphi_N$

Bounds on the universal functional $F[\rho]$

$$E^N[V] = \inf_{\substack{\sqrt{\rho}\in H^1(\mathbb{R}^3)\\ \int_{\mathbb{R}^3}\rho=N}} \left\{F[\rho] + \int_{\mathbb{R}^3}\rho(x)V(x)\mathrm{d}x\right\}, \qquad F[\rho] := \inf_{\rho_\Gamma=\rho} \mathrm{tr}(H^N(0)\Gamma)$$

Theorem (Thomas-Fermi type bounds)

There exist (explicit positive) constants such that

$$a\int_{\mathbb{R}^3}\rho^{\frac{5}{3}} + b\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}|^2 + \frac{1}{2}D(\rho,\rho) - c\int_{\mathbb{R}^3}\rho^{\frac{4}{3}} \leq F[\rho] \leq A\int_{\mathbb{R}^3}\rho^{\frac{5}{3}} + B\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}|^2 + \frac{1}{2}D(\rho,\rho)$$

where $D(\rho,\rho) := \iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}\mathrm{d}x\,\mathrm{d}y$ *is the classical Coulomb energy.*

- Hoffmann-Ostenhof '77: $b = 1/2$ and $a = 0$
- Lieb-Thirring '75: $a \leq a_{\rm sc} = \frac{3}{10}(3\pi^2)^{2/3}$ conjectured to be optimal, $b = 0$
- Frank-Hundertmark-Jex-Nam '21: $a = 0.826 a_{\rm sc}$
- Nam (JFA '18), Seiringer-Solovej '23: $a \simeq a_{\rm sc}$ if b (very) negative. ML-Lieb-Seiringer '19: $A \simeq a_{\rm sc}$ if $B \gg 1$
- Lieb-Oxford '81: $c = 1.68$, ML-Lieb-Seiringer '22: $c = 1.58$
- Cotar-Petrache '19, ML-Lieb-Seiringer '19: $c \geq -\zeta_{\rm BCC}(1) \simeq 1.44$, conjectured to be optimal
- several DFT functionals (PBE, SCAN) use c as a constraint for calibration

Low and high density regimes

$$H^N(0) = -\frac{1}{2}\Delta_{\mathbb{R}^{3N}} + \sum_{1\leq j<k\leq N} \frac{1}{|x_j - x_k|}$$

Two new functionals

$$T[\rho] = \inf_{\rho_\Gamma=\rho} \operatorname{tr}\left(\frac{-\Delta_{\mathbb{R}^{3N}}}{2}\Gamma\right) = \inf_{\substack{0\leq\gamma\leq 1\\ \rho_\gamma=\rho}} \operatorname{tr}\left(\frac{-\Delta_{\mathbb{R}^3}}{2}\right)\gamma \qquad C[\rho] := \inf_{\substack{\mathbb{P}\text{ sym.}\\ \rho_{\mathbb{P}}=\rho}} \iint_{\mathbb{R}^{3N}} \sum_{1\leq j<k\leq N} \frac{\mathbb{P}(dx_1\cdots dx_N)}{|x_j - x_k|}$$

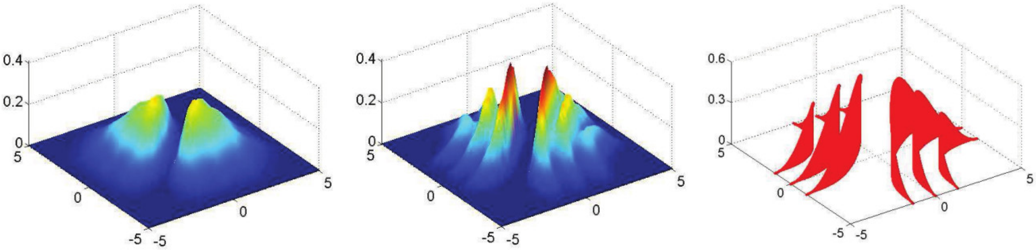
Theorem

We have the high and low density limits

$$\lim_{\lambda\to\infty} \frac{F\left[\lambda^3\rho(\lambda x)\right]}{\lambda^2} = T[\rho], \qquad \lim_{\lambda\to 0} \frac{F\left[\lambda^3\rho(\lambda x)\right]}{\lambda} = C[\rho]$$

- Convergence to $T[\rho]$ rather easy (ML-Lieb-Seiringer '22)
- Convergence to $C[\rho]$ much more complicated, due to lack of regularity of classical problem (Cotar-Friesecke-Kluppelberg '13-18, Bindini-De Pascale '18, ML '18)

The low-density limit is singular

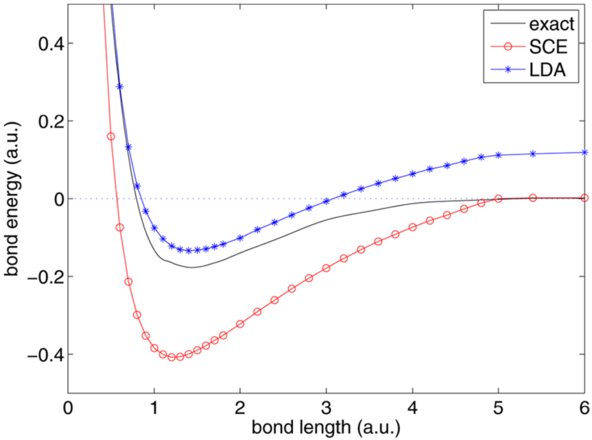


Pair density for $\lambda = 1$, $\lambda = 0.1$ and $\lambda \sim 0$ in 1D, with $N = 4$ and $\rho(x) = \frac{2}{5}(1 + \cos(\pi x/5))\mathbb{1}(-5 \le x \le 5)$

Chen-Friesecke (MMS '15)

Use of $C[\rho]$ in Kohn-Sham

- DFT typically gives huge importance to the non-interacting $T[\rho]$ (Kohn-Sham)
- $C[\rho]$ used only recently, to improve correlations: $F[\rho] \approx T[\rho] + C[\rho]$ (Malet-Gori-Giorgi '12)



Dissociation of H_2, Chen-Friesecke-Mendl (J. Chem. Theory Comput. 2014)

Part II. Finite Coulomb systems via Optimal Transport methods

Minimization problem at fixed density

$$C[\rho] := \inf_{\substack{\mathbb{P} \text{ sym.} \\ \rho_{\mathbb{P}}=\rho}} \iint_{\mathbb{R}^{3N}} \sum_{1\leq j<k\leq N} \frac{\mathbb{P}(dx_1\cdots dx_N)}{|x_j-x_k|} \qquad \rho_{\mathbb{P}}(A) = N\,\mathbb{P}(A\times(\mathbb{R}^3)^{N-1})$$

- Using $\mathbb{P} = (\rho/N)^{\otimes N}$ (uncorrelated electrons), we see that
$$C[\rho] \leq \frac{N(N-1)}{2N^2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}dx\,dy \leq \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}dx\,dy = \frac{D(\rho,\rho)}{2}$$
hence $C[\rho]$ is finite if, for instance, $\rho \in L^1 \cap L^{6/5}(\mathbb{R}^3)$ (Hardy-Littlewood-Sobolev)
- This is definitely not an optimal condition!

Theorem (Finiteness)

Let ρ be a non-negative measure of integer mass $\rho(\mathbb{R}^3) = N \in \mathbb{N}$, such that $\rho(\{R\}) < 1$ for every $R \in \mathbb{R}^3$. There exists $\mathbb{P}$ with $\rho_{\mathbb{P}} = \rho$ and $\delta > 0$ such that $\min_{j\neq k}|x_j - x_k| \geq \delta > 0$ $\mathbb{P}$–a.s. In particular

$$C[\rho] \leq \frac{N(N-1)}{2\delta} < \infty.$$

Colombo-Di Marino-Stra '19, Bindini '20

Proof when $\rho \in L^1(\mathbb{R}^3)$: insert a bit of correlation

Define $R_0 = -\infty < R_1 < \cdots R_{2N-1} < R_{2N} = +\infty$ such that

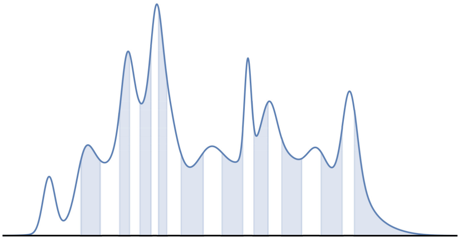
$$\rho\big((R_j, R_{j+1}] \times \mathbb{R}^2\big) = \frac{1}{2}$$

and let $\rho_j = \rho \mathbb{1}_{(R_{j-1},R_j]\times\mathbb{R}^2}$. Then write

$$\rho = \sum_j \rho_j = \frac{1}{2}\sum_{j \text{ odd}} (2\rho_j) + \frac{1}{2}\sum_{j \text{ even}} (2\rho_j)$$

and we put exactly one electron per slice

$$\mathbb{P} = \frac{1}{2}\left(\bigotimes_{j \text{ odd}}^{\text{sym}} (2\rho_j) + \bigotimes_{j \text{ even}}^{\text{sym}} (2\rho_j)\right)$$



By definition we obtain $|x_j - x_k| \geq \delta := \min_{k\neq\ell} |R_k - R_\ell| > 0$ on the support of $\mathbb{P}$ □

- if ρ is a measure without atom, $\exists \omega \in \mathbb{S}^2 \ : \ \rho(H) = 0$ for all hyperplane $H \perp \omega$ (Bindini '20)
- if ρ has atoms, need to treat the largest ones separately (exercise)
- **General case:** $C[\rho] < \infty$ if and only if $\int_{\mathbb{R}^3\setminus\{R\}} \frac{\rho(\mathrm{d}x)}{|x-R|} < \infty$ whenever $\rho(\{R\}) = 1$ (Colombo-Di Marino-Stra '19). Of course $C[\rho] = +\infty$ if $\rho(\{R\}) > 1$ for one R

Existence of an optimal plan: Kantorovich

$$C[\rho] := \inf_{\substack{\mathbb{P}\text{ sym.}\\ \rho_{\mathbb{P}}=\rho}} \iint_{\mathbb{R}^{3N}} \sum_{1\leq j<k\leq N} \frac{\mathbb{P}(dx_1\cdots dx_N)}{|x_j-x_k|} \qquad \rho_{\mathbb{P}}(A) = N\,\mathbb{P}(A\times(\mathbb{R}^3)^{N-1})$$

Theorem (Existence of a minimizer = "optimal plan")

For any measure $\rho \geq 0$ such that $\rho(\mathbb{R}^3)\in\mathbb{N}$ and $C[\rho]<\infty$, there exists a minimizer $\mathbb{P}$ (sometimes called an "optimal plan").

Proof: • $\mathbb{P}(\max_j |x_j| > R) \leq \rho(|x|>R)$, which gives some tightness
• $\mathbb{P} \mapsto$ Coulomb interaction is lower semi-continuous □

Questions:

- is $\mathbb{P}$ unique?
- how are the particles correlated on the support of $\mathbb{P}$?
- do the particles stay away from each other?
- is $\mathbb{P}$ the ground state in a well-chosen external potential V? (duality)

Strictly correlated electrons $\equiv$ "Monge" states

Definition (Monge states)

We say that $\mathbb{P}$ is a **Monge state** at density ρ if we can find a partition $\mathbb{R}^3 = \cup_{j=1}^N \Omega_j$ with $\rho(\Omega_j) = 1$ and maps $T_j : \Omega_1 \to \Omega_j$ such that $\rho \mathbb{1}_{\Omega_j} = T_j \#(\rho \mathbb{1}_{\Omega_1})$ and

$$\mathbb{P} = \int_{\Omega_1} \delta_{x_1} \otimes_s \delta_{T_2 x_1} \otimes_s \cdots \otimes_s \delta_{T_N x_1} \rho(x_1)\, dx_1$$

- Monge (1781) considered the $N = 2$ case (interaction $|x-y|^2$, asymmetric with $\rho_1 \neq \rho_2$)
- solved by Kantorovich (1942), who introduced relaxation with $\mathbb{P}$
- T_n = "transport maps" (OT) or "Seidl maps" (chemistry)

Theorem (Optimizers are sometimes Monge states)

Assume that $\rho \in L^1(\mathbb{R}^3)$.

(i) If $N = 2$, the minimizer $\mathbb{P}$ is unique and of Monge form

(ii) For every $N \geq 2$, $C[\rho]$ can be obtained by an infimum over Monge states, although minimizers are not necessarily of Monge form

(i) Cotar-Friesecke-Kluppelberg '13, (ii) Pratelli '07, Colombo-Di Marino '15

Understanding Monge states in 1D

Take a nice-enough $\rho \in L^1(\mathbb{R})$, for instance supported on (a,b) with $\rho > 0$ on (a,b).

- $N = 1$: Define $a \leq r(s) \leq b$ such that $\int_a^{r(s)} \rho(r)\,\mathrm{d}r = s \in [0,1]$. Then $r'(s)\rho(r(s)) = 1$, hence

$$\mathbb{P}(x) = \rho(x) = \int_{\mathbb{R}} \delta_r(x)\rho(r)\,\mathrm{d}r = \int_0^1 \delta_{r(s)}(x)\,\mathrm{d}s$$

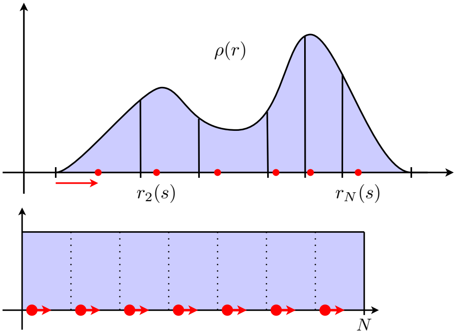
electron is moving to the right at speed $r'(s) = \rho(r(s))^{-1}$ to reproduce the desired ρ

- $N \geq 2$: Define $R_0 = a < R_1 < \cdots < R_N = b$ by $\int_{R_j}^{R_{j+1}} \rho = 1$, and $R_{j-1} \leq r_j(s) \leq R_j$ by $\int_{R_{j-1}}^{r_j(s)} \rho = s$

$$\mathbb{P}_{\rm Monge} := \int_0^1 \delta_{r_1(s)} \otimes_s \cdots \otimes_s \delta_{r_N(s)}\,\mathrm{d}s$$

The points $r_2(s), \dots, r_N(s)$ can be seen as functions of $r_1(s)$

- **Example:** for $\rho = \mathbb{1}_{[0,N]}$, $r_j(s) = j - 1 + s$ "floating crystal"



Strict correlation in 1D

Theorem (Strict correlation in 1D)

For any $\rho \in L^1(\mathbb{R})$ (no atom), the previous Monge state $\mathbb{P}_{Monge}$ is the unique optimizer for $C[\rho]$

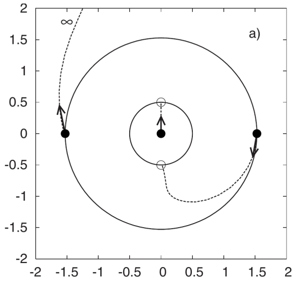
Colombo-De Pascale-Di Marino '14

- Proof only uses that $1/r$ is **positive and strictly convex**
- Should be thought of as a **crystallization result** (look again at $\rho = \mathbb{1}_{[0,N]}$)
- Ventevogel '78 proved crystallization in 1D for convex interactions (without fixing $\rho(x)$)
- One finds

$$C[\rho] = \int_0^1 \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \frac{1}{r_j(s) - r_k(s)}\, ds$$

- Seidl '99 conjectured similar result for 3D radial ρ

  Counter-examples: Colombo-Stra '16, Di Marino-Gerolin-Nenna '17
  e.g. $\rho(x) = c_\varepsilon \mathbb{1}_{[1,1+\varepsilon]}(|x|)$ for $N = 3$ and $\varepsilon \ll 1$



Be atom, Seidl-Gori Giorgi-Savin '07

Minimal distance between particles

Theorem (Minimal distance)

Let $\rho \in L^1(\mathbb{R}^3)$ with $\int \rho = N \in \mathbb{N}$ and pick r such that $\rho(B(x,r)) \leq 1/2$ for every $x \in \mathbb{R}^3$. Then any optimal plan $\mathbb{P}$ for $C[\rho]$ must satisfy

$$\min_{j \neq k} |x_j - x_k| \geq \delta := \frac{r}{2(N-1)} > 0, \qquad \mathbb{P}\text{-almost surely.}$$

Colombo-Di Marino-Stra '19

- Many other results of the same kind by different authors, all scale badly with N
- Main tool for proving properties of $\mathbb{P}$ is

Lemma (c-monotonicity)

Let $\mathbb{P}$ be an optimizer for $C[\rho]$. Then we have

$$c(X) + c(Y) \leq c(X_1 \cup Y_2) + c(Y_1 \cup X_2) \quad \text{for } \mathbb{P} \otimes \mathbb{P}\text{–almost every } (X,Y) \in (\mathbb{R}^3)^N \times (\mathbb{R}^3)^N$$

with $c(X) = \sum_{1 \leq j < k \leq N} |x_j - x_k|^{-1}$ *and* $X_1 = (x_1, ..., x_K)$, $Y_1 = (y_1, ..., y_K)$ *for all* $1 \leq K \leq N-1$

▶ **Proof of c-monotonicity:** $A_1, B_1 \subset (\mathbb{R}^3)^K$, $A_2, B_2 \subset (\mathbb{R}^3)^{N-K}$ such that $a := \mathbb{P}(A_1 \times A_2) > 0$ and $b := \mathbb{P}(B_1 \times B_2) > 0$. Exchange the two configurations by looking at the perturbation

$$\mathbb{P}' := \mathbb{P} + \varepsilon(\mathbb{P}_{A_1} \otimes \mathbb{P}_{B_2} + \mathbb{P}_{B_1} \otimes \mathbb{P}_{A_2} - a\mathbb{P}_{B_1 B_2} - b\mathbb{P}_{A_1 A_2})$$

for $0 < \varepsilon \ll 1$, with $\mathbb{P}_{A_1 A_2} = \mathbb{P}_{|A_1 \times A_2}$ and $\mathbb{P}_{A_1}(K) = \mathbb{P}(K \times A_2)$, etc. Then $\rho_{\mathbb{P}'} = \rho_{\mathbb{P}} = \rho$

▶ **Proof of minimal distance:** for $K = 1$ one obtains

$$\sum_{j=2}^N \frac{1}{|x_1 - x_j|} + \sum_{j=2}^N \frac{1}{|y_1 - y_j|} \leq \sum_{j=2}^N \frac{1}{|y_1 - x_j|} + \sum_{j=2}^N \frac{1}{|x_1 - y_j|} \qquad \mathbb{P} \otimes \mathbb{P} \text{ a.s.}$$

For fixed x_j we have on a $\mathbb{P}$-non-negligible set $|y_j - x_1| \geq r$ and $|y_1 - x_j| \geq r$. Indeed, the probability of the complement can be estimated by

$$\mathbb{P}\Big(y_1 \in \cup_{j=1}^N B_r(x_j)\Big) + \sum_{j=2}^N \mathbb{P}\Big(y_j \in B_r(x_1)\Big) \leq \frac{1}{N} \int_{\cup_{j=1}^N B_r(x_j)} \rho + \frac{N-1}{N} \int_{B_r(x_1)} \rho < 1$$

For such y_j's we find

$$\sum_{j=2}^N \frac{1}{|x_1 - x_j|} \leq \frac{2(N-1)}{r} \Longrightarrow \min_j |x_1 - x_j| \geq \frac{r}{2(N-1)}$$

▶ **Proof of low-density limit:** Assume $\sqrt{\rho}\in H^1(\mathbb{R}^3)$ and let $\mathbb{P}$ be an optimal plan for $C[\rho]$. We can smear-out the electrons by

$$\mathbb{Q}=\mathbb{P}*(\chi^2)^{\otimes N},\qquad \rho_{\mathbb{Q}}=\rho*\chi^2$$

with $\chi_\varepsilon=\varepsilon^{-3/2}\chi(x/\varepsilon)$ and χ a radial function in C^∞_c with $\int\chi^2=1$

- Bindini-De Pascale '17 suggested to go back to ρ by letting

$$\mathbb{R}(x_1,...,x_N)=\int\prod_{k=1}^N\frac{\rho(x_k)\chi^2(x_k-z_k)}{\rho*\chi^2(z_k)}\mathbb{Q}(\mathrm{d}z_1\cdots\mathrm{d}z_N)$$

- Using that the electrons do not overlap for $\varepsilon\ll 1$, ML '18 introduced

$$\Gamma=\int_{(\mathbb{R}^3)^N}\sqrt{\rho}^{\otimes N}|\chi_{z_1}\wedge\cdots\wedge\chi_{z_N}\rangle\langle\chi_{z_1}\wedge\cdots\wedge\chi_{z_N}|\sqrt{\rho}^{\otimes N}\frac{\mathbb{Q}(\mathrm{d}z_1\cdots\mathrm{d}z_N)}{\prod_{k=1}^N\rho*\chi^2(z_k)}$$

that has a finite kinetic energy and the exact density $\rho_\Gamma=\rho$.

- When $\rho_\lambda(x)=\lambda^3\rho(\lambda x)$ we take $\varepsilon\to 0$ slowly and find $\lambda^{-1}F[\rho_\lambda]\to C[\rho]$

Existence of a dual potential

$$E_{\rm cl}^N[V] := \inf_{x_1,\dots,x_N}\left\{\sum_{1\le j<k\le N}\frac{1}{|x_j-x_k|}+\sum_{j=1}^N V(x_j)\right\}$$

for instance for $V\in C^0_b(\mathbb{R}^3)$. We have the duality formula

$$C[\rho]=\sup_{V\in C^0_b(\mathbb{R}^3)}\left\{E^N_{\rm cl}[V]-\int_{\mathbb{R}^3}\rho V\right\}=\sup_{\substack{V\in C^0_b(\mathbb{R}^3)\\ E^N_{\rm cl}[V]=0}}\left\{-\int_{\mathbb{R}^3}\rho V\right\}=\sup_{\substack{V\in C^0_b(\mathbb{R}^3)\\ \sum_{j=1}^N V(x_j)+c(X)\ge0}}\left\{-\int_{\mathbb{R}^3}\rho V\right\}$$

Theorem (Existence of a Lipschitz dual potential)

Let $\rho\in L^1(\mathbb{R}^3)$. Then there exists a dual potential $V\in C^0_b(\mathbb{R}^3)$ solving the above supremum, satisfying

$$-\frac{(N-1)^2}{r}\le V(x)\le\frac{(N-1)^3}{r},\qquad |V(x)-V(y)|\le\frac{4(N-1)^3}{r^2}|x-y|,\qquad \forall x,y\in\mathbb{R}^3$$

where r is so that $\rho(B(x,r))\le 1/2, \forall x\in\mathbb{R}^3$. Any optimal plan $\mathbb{P}$ for $C[\rho]$ is a ground state for $E^N_{cl}[V]$. If $\rho>0$ a.e., we have $V=cnst-\rho_{ext}*|x|^{-1}$ with $\rho_{ext}\ge0$ and $\int_{\mathbb{R}^3}\rho_{ext}=N-1$.

Colombo-Di Marino-Stra '19, Lelotte '22

- many other estimates in literature, all blow up badly with N
- **no result of this sort in quantum case** where V = Kohn-Sham potential

▶ **Proof of existence for a bounded Lipschitz interaction $w \geq 0$**

$$C_w[\rho] = \sup\left\{ -\int_{\mathbb{R}^3} \rho V \;\middle|\; V \in C^0_b(\mathbb{R}^3),\quad \sum_{j=1}^N V(x_j) + \sum_{1\leq j<k\leq N} w(x_j - x_k) \geq 0 \right\}$$

- For any V satisfying the constraint, we have $V(x) \geq -\frac{N-1}{2}\|w\|_\infty$. Define

$$V_1(x_1) := \sup_{x_2,\dots,x_N} \left\{ -\sum_{j=2}^N V(x_j) - \sum_{1\leq j<k\leq N} w(x_j - x_k) \right\} \leq V(x_1)$$

Then $\widetilde{V}_1 = (V_1 + (N-1)V)/N \leq V$ satisfies the constraint (exercise)
After iteration we can find a $-\frac{N-1}{2}\|w\|_\infty \leq V^* \leq V$ satisfying the constraint and such that

$$V^*(x_1) := \sup_{x_2,\dots,x_N} \left\{ -\sum_{j=2}^N V^*(x_j) - \sum_{1\leq j<k\leq N} w(x_j - x_k) \right\}$$

Then $V^*(x) \leq \frac{(N-1)^2}{2}\|w\|_\infty$ and $\|V^*\|_{\rm Lip} \leq (N-1)\|w\|_{\rm Lip}$ (exercise)

- We can replace any maximizing sequence V_n by $V_n^* \leq V_n$ and can then pass to the limit using Ascoli

▶ **Proof for Coulomb:** diagonal bounds imply that $C[\rho] = C_{w_\delta}[\rho]$ where $w_\delta(x) = \min(\delta^{-1}, |x|^{-1})$. An optimizer V_δ for w_δ is also an optimizer for Coulomb!

Monge states for $N = 2$

- When $N = 2$ we have (upon subtracting a constant to V to ensure $E_{\rm cl}^N[V] = 0$)

$$V(x) + V(y) + \frac{1}{|x-y|} = 0 \qquad \mathbb{P}\text{ a.e.}, \qquad V(y) = \sup_x \left\{ -V(x) - \frac{1}{|x-y|} \right\}$$

In fact, V is differentiable almost everywhere, with

$$\nabla V(x) = \frac{y-x}{|y-x|^3}$$

This implies $|\nabla V(x)| = \frac{1}{|y-x|^2}$ and

$$y = T(x) := x + \frac{\nabla V(x)}{|\nabla V(x)|^{3/2}}$$

- Not so clear how to generalize this to $N \geq 3$...

Cotar-Friesecke-Kluppelberg '13

Part III. Counter-example to the convexity-in-N conjecture

Convexity-in-N

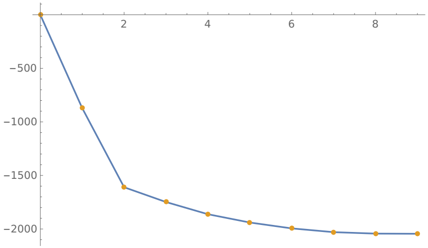
Quantum N-particle ground state energy: $E^N[V] = \min \sigma\left(-\frac{\Delta_{\mathbb{R}^{3N}}}{2} + \sum_{j=1}^N V(x_j) + \sum_{j<k} \frac{1}{|x_j - x_k|}\right)$

Conjecture (convexity-in-N)

For $V \in$ **?**, the map $N \mapsto E^N[V]$ is convex, which means (with $E^0[V] = 0$)

$$E^N[V] - E^{N-1}[V] \leq E^{N+1}[V] - E^N[V], \qquad \forall N \in \mathbb{N}$$

- **HVZ:** for $V \to 0$, $E^N[V] \leq E^{N-1}[V] = \min \sigma_{\rm ess}(H^N(V))$
- ionization energy grows when electrons are removed: core electrons more tightly bound than valence electrons
- V can bind N electrons $\Rightarrow$ can bind $N-1$ electrons
- Perdew-Levy-Balduz '82, *"Problem 7"* in Lieb '83
- Parr-Yang '88: numerical evidence for Carbon and Oxygen
- true for non-interacting systems (exercise)
- wrong for hard core (Lieb '83), $1/|x|^s$ for $s > 1.27$ (Ayers '24)



Energies (eV) of Oxygen, Parr-Yang '88

A counter-example with nuclei of fractional charges

Theorem (Di Marino-ML-Nenna '24, in preparation)

There exist $\mathbf{R}_1, ..., \mathbf{R}_6 \in \mathbb{R}^3$, $z_1, ..., z_6 > 0$ *and* $e_4 < e_2 < e_1 < 0$ *such that, for*

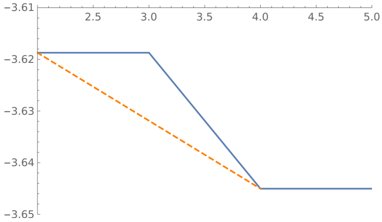
$$V_\ell(x) = -\sum_{m=1}^{6} \frac{z_m/\sqrt{\ell}}{|x - \ell\mathbf{R}_m|},$$

we have for all $N \geq 5$

$$E^1[V_\ell] = \frac{e_1}{\ell} + o(\ell^{-1}), \quad E^2[V_\ell] = E^3[V_\ell] = \frac{e_2}{\ell} + o(\ell^{-1}), \quad E^N[V_\ell] = E^4[V_\ell] = \frac{e_4}{\ell} + o(\ell^{-1})$$

and hence convexity fails at $N = 3$ *for* $\ell \gg 1$*. The corresponding Hamiltonian* $H^N(V_\ell)$ *admits a ground state for* $N = 1$, $N = 2$ *or* $N = 4$ *electrons, but not for* $N = 3$ *or* $N \geq 5$ *electrons.*

- first counter-example for Coulomb, still open for real nuclei (integer charges)
- follows from our previous study of "grand-canonical optimal transport" for classical electrons

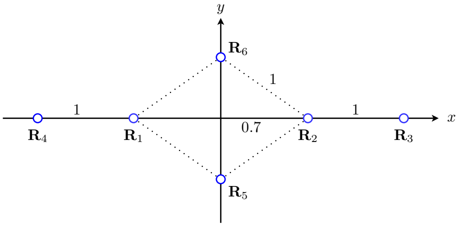


▶ Classical problem:

$$V(x) = \begin{cases} v_m & \text{if } x = \mathbf{R}_m \\ +\infty & \text{if } x \notin \{\mathbf{R}_1, ..., \mathbf{R}_6\} \end{cases}$$

$$\begin{cases} v_1 = v_2 = -2.1665 \\ v_3 = v_4 = -1.4109 \\ v_5 = v_6 = -1.9934 \end{cases}$$

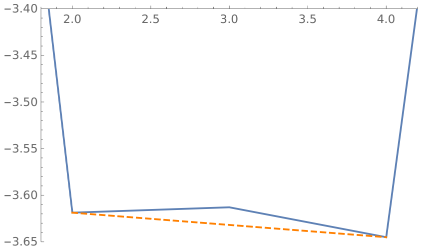
N	$E_{\rm cl}^N[V] \approx$	minimizer
1	-2.1665	$\mathbf{R}_1$
2	-3.6187	$\mathbf{R}_1, \mathbf{R}_2$
3	-3.6129	$\mathbf{R}_4, \mathbf{R}_5, \mathbf{R}_6$
4	-3.6450	$\mathbf{R}_3, ..., \mathbf{R}_6$
5	-2.3949	$\mathbf{R}_2, ..., \mathbf{R}_6$
6	-0.4304	$\mathbf{R}_1, ..., \mathbf{R}_6$



▶ Proof of quantum theorem:

$$V_\ell(x) = -\sum_{m=1}^{6} \frac{z_m/\sqrt{\ell}}{|x - \ell \mathbf{R}_m|}, \qquad z_m := \sqrt{2|v_m|}, \qquad -\frac{z_m^2}{2} = v_m$$

- each nucleus can bind 1 electron, with energy v_m/ℓ, same order as interaction $\rightsquigarrow$ classical problem to leading order
- for $N \in \{3, 5, 6\}$ additional electrons prefer to escape to infinity
- proof that $E^3[V_\ell] = E^2[V_\ell]$ and $E^6[V_\ell] = E^5[V_\ell] = E^4[V_\ell]$ uses localization techniques à la Ruskai '82, Sigal '82, Lieb-Sigal-Simon-Thirring '88



Link with grand-canonical problem

$$F_{\rm GC}[\rho] = \min_{\substack{\sum p_n=1\\ \sum_n p_n\rho_{\Gamma_n}=\rho}} \sum p_n \,{\rm tr}\,\big(H^n(0)\Gamma_n\big)$$

$$E^\lambda_{\rm GC}[V] = \inf_{\substack{\sum p_n=1\\ \sum np_n=\lambda}} \sum_n p_n \,{\rm tr}\,\big(H^n(V)\Gamma_n\big) = \inf_{\substack{\sum p_n=1\\ \sum np_n=\lambda}} \sum_n p_n E^n[V]$$

Lemma

- $\lambda \mapsto E^\lambda_{GC}[V]$ *is the* **convex hull** *of* $N \mapsto E^N[V]$*, hence they coincide when the latter is convex*
- $\rho \mapsto F_{GC}[\rho]$ *and* $V \mapsto E^\lambda_{GC}[V]$ *are Legendre-transforms to each other, where* $\lambda = \int_{\mathbb{R}^3} \rho$

convexity conjecture $\forall V, \forall N \iff F_{GC}[\rho] = F[\rho]\ \forall \rho$ *with* $\int_{\mathbb{R}^3} \rho \in \mathbb{N}$

Lemma (low density $\rightsquigarrow$ grand-canonical classical problem)

$$\lim_{\ell\to 0} \ell^{-1} F_{GC}[\ell^3\rho(\ell\cdot)] = C_{GC}[\rho] = \min_{\substack{\sum \mathbb{P}_n(\mathbb{R}^{3n})=1\\ \sum \rho_{\mathbb{P}_n}=\rho}} \sum_n \int_{(\mathbb{R}^3)^n} \sum_{1\le j<k\le n} \frac{d\mathbb{P}_n(dx_1\cdots dx_n)}{|x_j-x_k|}$$

Support for grand-canonical optimal transport: $C[\rho] \stackrel{?}{=} C_{\rm GC}[\rho]$

For a grand-canonical state $\mathbb{P} = (\mathbb{P}_n)_{n\geq 0}$ we call $\mathrm{supp}(\mathbb{P}) = \{n\ :\ \mathbb{P}_n \neq 0\}$ its support in n

Theorem (support in n)

Let $\rho \geq 0$ with $N = \rho(\mathbb{R}^3) \in \mathbb{N}$ and $C_{GC}[\rho] \leq C[\rho] < \infty$. Any optimizer for $C_{GC}[\rho]$ satisfies

$$\mathrm{supp}(\mathbb{P}) \begin{cases} = \{N\} & \text{if } N \in \{0,1,2\}, \text{ hence } C_{GC}[\rho] = C[\rho] \\ \subset \left[N - \frac{1}{2}\sqrt{8N+9} + \frac{3}{2}\ ,\ N + \frac{1}{2}\sqrt{8N-7} - \frac{1}{2}\right] & \text{if } N \geq 3. \end{cases}$$

Di Marino-ML-Nenna '22

Method of proof: apply technique of Frank-Killip-Nam '16 (liquid drop) and Frank-Nam-Van Den Bosch '18 (TFDW) to the c-monotonicity relations

Theorem (counter-example)

There exists a ρ with $\rho(\mathbb{R}^3) = 3$ such that $\mathrm{supp}(\mathbb{P}) = \{2,4\}$, hence $C_{GC}[\rho] < C[\rho]$. In fact, for every $k \geq 1$, there exists $\rho^{(k)}$ with $\rho^{(k)}(\mathbb{R}^3) = 6^k/2$ such that $\mathrm{supp}(\mathbb{P}^{(k)}) = \left\{\frac{6^k-2^k}{2}\ ,\ \frac{6^k+2^k}{2}\right\}$.

NB: $\log 2/\log 6 \approx 0.39$

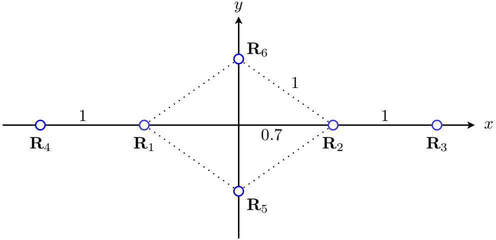
Di Marino-ML-Nenna '22

$\Longrightarrow$ convexity-in-N conjecture cannot hold!

- For the 6 points $\mathbf{R}_1, \dots, \mathbf{R}_6$ on the right, we have

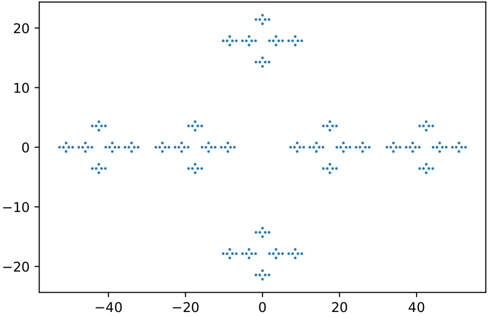
$$3.8778 \approx C_{\rm GC}\left[\frac12\sum_{m=1}^6 \delta_{\mathbf{R}_m}\right] < C\left[\frac12\sum_{m=1}^6 \delta_{\mathbf{R}_m}\right] \approx 3.9157$$

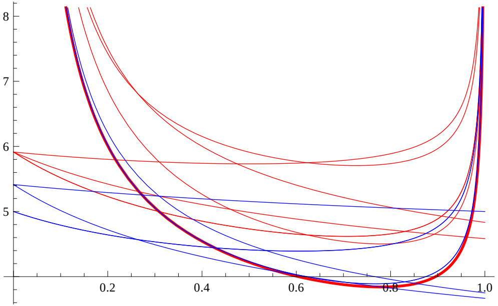
with the optimizer $\mathbb{P} = \frac12\left(\delta_{\mathbf{R}_1}\otimes_s\delta_{\mathbf{R}_2} + \delta_{\mathbf{R}_3}\otimes_s\cdots\otimes_s\delta_{\mathbf{R}_6}\right)$



- Repeating this pattern at different scales we found

$$\mathrm{supp}(\mathbb{P}^{(k)}) = \left\{\frac{6^k-2^k}{2}, \frac{6^k+2^k}{2}\right\}$$





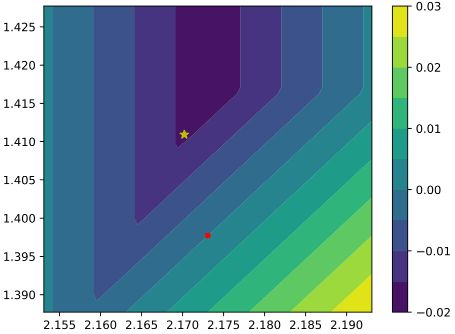
Di Marino-ML-Nenna '22

Finding the classical potential

- To find the potential V, we first solved the dual problem but got

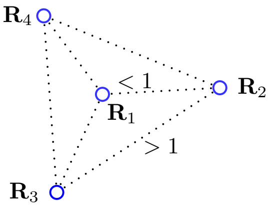
$$E_{\rm cl}^2[V_{\rm GC}] = E_{\rm cl}^3[V_{\rm GC}] = E_{\rm cl}^4[V_{\rm GC}] \quad ☹$$

- We then minimized $(v_1, \dots, v_6) \mapsto (E_{\rm cl}^2[V] + E_{\rm cl}^4[V])/2 - E_{\rm cl}^3[V]$ in a neighborhood of $V_{\rm GC}$ to get V ☺



difference as a function of $(|v_1|, |v_3|)$, Di Marino-ML-Nenna '24

Lieb's counter-example



- **Lieb '83:** 4 points with hard core interaction $w(x-y) = (+\infty)\mathbb{1}(|x-y| \leq 1)$

$$\begin{cases} v_1 = -3 \\ v_2 = v_3 = v_4 = -2 \end{cases} \qquad \begin{cases} E^1_{\rm cl}[V] = -3 \\ E^2_{\rm cl}[V] = -2 \\ E^3_{\rm cl}[V] = -6 \end{cases}$$

- **Ayers '24:** after optimizing the lengths, the same example works for the Riesz interaction $w(x-y) = |x-y|^{-s}$, whenever $s > 2\log 2/\log 3 \approx 1.26$

Theorem (convexity for Coulomb on 4 points)

If $\rho = \sum_{j=1}^4 \rho_j \,\delta_{\mathbf{R}_j}$ for any $\mathbf{R}_1, \dots, \mathbf{R}_4$ with $\sum_{j=1}^4 \rho_j \in \{1,2,3,4\}$, then we have $C_{GC}[\rho] = C[\rho]$. In particular, $N \mapsto E^N_{cl}[V]$ is convex for any V confining to 4 points or less.

Di Marino-ML-Nenna '24 (in preparation)

Proof. only $N = 3$ requires a proof, we know already that $\mathrm{supp}(\mathbb{P}) \subset \{2,3,4\}$. Use c-monotonicity to see that $\mathrm{supp}(\mathbb{P}) = \{3\}$

Part IV. Lieb-Oxford inequality

Lieb-Oxford inequality

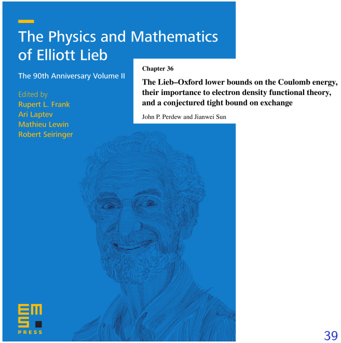
Theorem (Lieb-Oxford inequality)

For every $\rho \in L^1 \cap L^{4/3}(\mathbb{R}^3)$, we have

$$C[\rho] \geq \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} \, dx \, dy - 1.58 \int_{\mathbb{R}^3} \rho(x)^{\frac{4}{3}} \, dx$$

If ρ is constant on its support, 1.58 can be replaced by $\frac{3}{5}\left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \simeq 1.45$. The best constant in the inequality cannot be larger than $-\zeta_{BCC}(1) \approx 1.44$.

Lieb '80, Lieb-Oxford '81, Lieb-Narnhofer '73, Cotar-Petrache '19, ML-Lieb-Seiringer '19, '22



- used to calibrate famous functionals, e.g. PBE, SCAN (Perdew-Sun '22)
- previous constants were 8.52 (Lieb '79), 1.68 (Lieb-Oxford '81), 1.64 (Chan-Handy '99)
- we used heavy numerics to optimize two probability measures appearing in the proof, to push 1.64 down to 1.58
- conjectured best cnst $-\zeta_{\rm BCC}(1) \approx 1.44$ (Levy-Perdew '93, Odashima-Capelle '07)

Idea of proof

▶ **Onsager lemma:** two-particle interaction $\geq$ one-particle term (using Newton + $\widehat{|x|^{-1}} \geq 0$)

- For any radial probability measures μ_{x_1} and μ_{x_2} centered at x_1, x_2, we have

$$\frac{1}{|x_1 - x_2|} \geq D(\mu_{x_1}, \mu_{x_2}) := \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\mu_{x_1}(dy)\mu_{x_2}(dz)}{|y-z|} \qquad \text{(Newton)}$$

- For a "field" of radial probability densities $x \mapsto \mu_x$, we obtain

$$\sum_{1\leq j<k\leq N} \frac{1}{|x_j - x_k|} \geq \sum_{1\leq j<k\leq N} D(\mu_{x_j}, \mu_{x_k}) = \underbrace{\frac{1}{2} D\left(\sum_{j=1}^N \mu_{x_j}, \sum_{j=1}^N \mu_{x_j}\right)}_{\geq D\left(\sum_{j=1}^N \mu_{x_j}, \eta\right) - \frac{1}{2}D(\eta,\eta)} - \frac{1}{2}\sum_{j=1}^N D(\mu_{x_j}, \mu_{x_j})$$

$$\left\langle \sum_{1\leq j<k\leq N} \frac{1}{|x_j - x_k|} \right\rangle_{\mathbb{P}} \geq D\left(\int_{\mathbb{R}^3} \rho(x)\mu_x(\cdot)\, dx, \eta\right) - \frac{1}{2}D(\eta,\eta) - \frac{1}{2}\int_{\mathbb{R}^3} D(\mu_x, \mu_x)\rho(x)\, dx$$

- The best is $\eta = \int_{\mathbb{R}^3} \rho(x)\mu_x(\cdot)\, dx \rightsquigarrow$ optimization problem in $\mu_x \overset{?}{\geq} D(\rho,\rho)/2 - \text{cnst} \int \rho^{4/3}$
- **Lieb-Oxford:** $\mu_x(y) := \rho(x)\mu\left(\rho(x)^{\frac{1}{3}}(y-x)\right)$ (rescale according to local value of ρ) and $\eta = \rho$
- **We took:** same μ_x and $\eta = \int_{\mathbb{R}^3} \rho(x)\nu_x(\cdot)\, dx$, then optimized numerically in μ, ν

$$C[\rho] \geq \frac{1}{2}D(\rho,\rho) - \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\Psi_{\mu\nu}\left(|x-y|\rho(x)^{\frac13}, |x-y|\rho(y)^{\frac13}\right)}{|x-y|^7}\,\mathrm{d}x\,\mathrm{d}y - \frac{D(\mu,\mu)}{2}\int_{\mathbb{R}^3}\rho(x)^{\frac43}\,\mathrm{d}x$$

where $\Psi_{\mu\nu}(a,b) = a^3b^3(1 - D(\mu_{0,a},\nu_{e_1,b}) - D(\nu_{0,a},\mu_{e_1,b}) + D(\nu_{0,a},\nu_{e_1,b}))$ and $\mu_{v,a}(y) = a^3\mu(a(y-v))$.

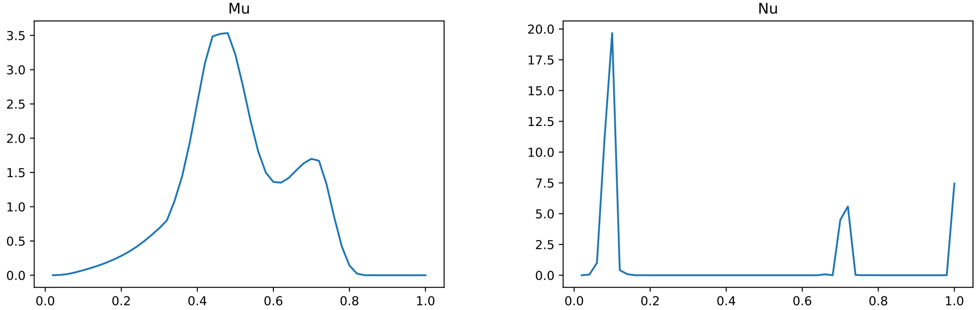
- If $\Psi_{\mu\nu}(a,b) \leq f(a) + f(b)$, then

$$\frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\Psi_{\mu\nu}\left(|x-y|\rho(x)^{\frac13}, |x-y|\rho(y)^{\frac13}\right)}{|x-y|^7}\,\mathrm{d}x\,\mathrm{d}y \leq \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{f\left(|x-y|\rho(x)^{\frac13}\right)}{|x-y|^7}\,\mathrm{d}x\,\mathrm{d}y$$
$$= \left(\int_{\mathbb{R}^3}\rho(x)^{\frac43}\,\mathrm{d}x\right)\left(\int_{\mathbb{R}^3}\frac{f(|z|)}{|z|^7}\,\mathrm{d}z\right)$$

hence we get the Lieb-Oxford bound with the constant

$$\int_{\mathbb{R}^3}\frac{f(|z|)}{|z|^7}\,\mathrm{d}z + \frac{1}{2}D(\mu,\mu)$$

We numerically minimized over μ,ν,f. For f, looks like dual of a 1D optimal transport problem! We used $f_1(a) = \sup_b\{\Psi_{\mu\nu}(a,b) - f(b)\}$, then $f_2 = (f+f_1)/2$ and iterate finitely many times



Optimal measures $r \mapsto r^2\mu(r)$ and $r \mapsto r^2\nu(r)$ found in ML-Lieb-Seiringer '22, that yield $c_{\rm LO} \leq 1.58$
(combination 50 concentric Dirac measures on spheres)

Part V. Local Density Approximation, Uniform Electron Gas, Wigner crystallization

Uniform Electron Gas

Definition (Uniform Electron Gas)

The **UEG** is an infinite system of electrons at equilibrium, with the constraint that their density is exactly constant, $\rho(x) = \rho_0$, in the whole of $\mathbb{R}^3$.

- in Physics, often confused with **Jellium** where the electrons evolve in a constant background without any constraint on their density ($\approx$ dual)
- (long range) Coulomb interaction: energy **not extensive** (does not scale like the volume), but it does if one removes the direct term $D(\rho, \rho)$

Definition (Indirect energy)

The **indirect energy** is

$$E_{\rm ind}[\rho] := C[\rho] - \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} \mathrm{d}x \, \mathrm{d}y$$

and it satisfies by Lieb-Oxford

$$-1.58 \int_{\mathbb{R}^3} \rho^{4/3} \leq E_{\rm ind}[\rho] \leq 0$$

Thermodynamic limit

Theorem (Thermodynamic limit)

For any $\rho_0 > 0$ *and* $\Omega_n \nearrow \mathbb{R}^3$ *in the sense of Fisher, with* $\rho_0|\Omega_n| \in \mathbb{N}$ *we have*

$$\lim_{n\to\infty} \frac{E_{\rm ind}[\rho_0 \mathbb{1}_{\Omega_n}]}{|\Omega_n|} = e_{\rm UEG}\, \rho_0^{4/3}$$

In particular, the best Lieb-Oxford constant must be $\geq -e_{\rm UEG}$

ML-Lieb-Seiringer '18

Proof: • $E_{\rm ind}$ is exactly **subadditive**

$$E_{\rm ind}[\rho_1+\rho_2] \leq E_{\rm ind}[\rho_1] + E_{\rm ind}[\rho_2]$$

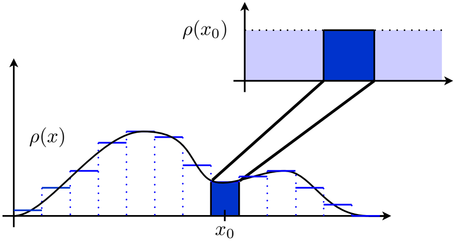
hence limit follows from standard arguments à la Ruelle-Fischer '60s

• Proof of subadditivity: let $\mathbb{P}_1$ and $\mathbb{P}_2$ be optimal plans for $C[\rho_1]$ and $C[\rho_2]$, then

$$C[\rho_1+\rho_2] \leq \left\langle \sum_{1\leq j<k\leq N_1+N_2} \frac{1}{|x_j-x_k|}\right\rangle_{\mathbb{P}_1\otimes_s\mathbb{P}_2} = C[\rho_1]+C[\rho_2] + \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho_1(x)\rho_2(y)}{|x-y|}\,dx\,dy$$

• Exact scaling: $E_{\rm ind}[\rho_0\mathbb{1}_\Omega] = \ell^{-1}E_{\rm ind}[\rho_0\ell^3\mathbb{1}_{\ell\Omega}]$ gives $\rho_0^{4/3}$

Local Density Approximation



Simplest approximation in (classical) DFT

$$C[\rho] \approx \frac{1}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy + e_{\rm UEG}\int_{\mathbb{R}^3} \rho(x)^{4/3}dx$$

Theorem (Local Density Approximation)

Fix any function $\rho \in L^1 \cap L^{4/3}$ with $\int_{\mathbb{R}^3}\rho \in \mathbb{N}$. Then we have for all $N \in \mathbb{N}$ and all $\varepsilon > 0$

$$C[\rho(N^{-\frac13}\cdot)] = \frac{N^{5/3}}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy + N\, e_{\rm UEG}\int_{\mathbb{R}^3} \rho(x)^{4/3}dx + o(N)$$

$$\left|C_{\rm GC}[\rho] - \frac{1}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy - e_{\rm UEG}\int_{\mathbb{R}^3} \rho(x)^{4/3}dx\right| \le \varepsilon\int_{\mathbb{R}^3}(\rho+\rho^{4/3}) + \frac{C}{\varepsilon^7}\int_{\mathbb{R}^3}|\nabla\rho^{\frac13}|^4$$

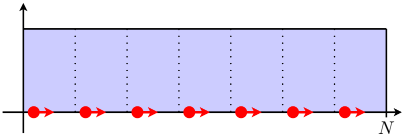
ML-Lieb-Seiringer '18 '19

- idea is to split space into regions of size $1 \ll \ell \ll N^{1/3}$ and show interactions are small
- universal bound involving gradients in canonical case?

Wigner crystallization conjecture

Recall (Colombo-De Pascale-Di Marino '14)

- optimal 1D Monge state at constant density $\rho(x) = \mathbb{1}_{[0,N]}$
- called a "floating crystal" in physics

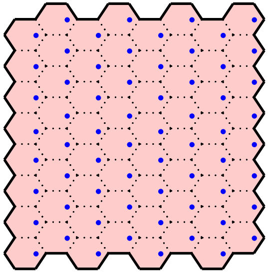


Conjecture (Wigner crystallization in 3D)

In the thermodynamic limit, the optimal $\mathbb{P}_N$ converges locally to the **BCC floating crystal**. The UEG energy must be

$$e_{\rm UEG} \overset{?}{=} \zeta_{\rm BCC}(1) \approx -1.4442$$

where $\zeta_{\mathcal{L}}(s) = \frac{1}{2}\sum_{z\in\mathcal{L}\setminus\{0\}} |z|^{-s}$ for $\Re(s) > 3$, analytically continued to $\mathbb{C}\setminus\{3\}$ **(Epstein Zeta function)**



Conjecture (Lieb-Oxford best constant)

The Lieb-Oxford best constant is attained at constant density, that is, $c_{\rm LO} \overset{?}{=} -e_{\rm UEG}$

Levy-Perdew '93, Odashima-Capelle '07

A surprising calculation

Lemma (indirect energy of floating crystals)

Let $\mathcal{L} = v_1\mathbb{Z} + v_2\mathbb{Z} + v_3\mathbb{Z}$ *be any lattice of unit cell* Q *satisfying* $|Q| = 1$, $\int_Q x\,dx = 0$ *and* $\int_Q xx^T\,dx = \frac{I_3}{3}\int_Q |x|^2\,dx$. *Then the indirect energy per unit volume of the floating crystal converges to*

$$\lim_{L\to\infty} \frac{1}{|\Omega_L|}\left(\frac12 \sum_{z\neq z'\in\mathcal{L}\cap(0,L)^3} \frac{1}{|z-z'|} - \frac12 \iint_{\Omega_L^2} \frac{dx\,dy}{|x-y|}\right) = \zeta_{\mathcal{L}}(1) + \frac{2\pi}{3}\int_Q |x|^2\,dx$$

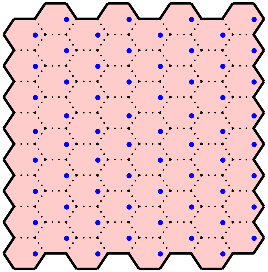
where $\Omega_L = \cup_{z\in\mathcal{L}\cap(0,L)^3}(Q+z)$.

ML-Lieb '15

- **Very specific to Coulomb:** for $1 < s < 3$

$$\lim_{L\to\infty} \frac{1}{|\Omega_L|}\left(\frac12 \sum_{z\neq z'\in\mathcal{L}\cap(0,L)^3} \frac{1}{|z-z'|^s} - \frac12 \iint_{\Omega_L^2} \frac{dx\,dy}{|x-y|^s}\right) = \zeta_{\mathcal{L}}(s)$$

- similar calculations by Borwein *et al* '88
- has raised a small controversy in DFT, that was eventually solved in Cotar-Petrache '19, ML-Lieb-Seiringer '19



A simple explanation

Lemma (Integral of screened Coulomb potential)

Let $Q \subset \mathbb{R}^3$ be any set satisfying $|Q| = 1$, $\int_Q x\,\mathrm{d}x = 0$ and $\int_Q xx^T\,\mathrm{d}x = \frac{I_3}{3}\int_Q |x|^2\,\mathrm{d}x$. Then we have

$$\int_{\mathbb{R}^3}\left(\frac{1}{|x|^s} - \mathbb{1}_Q * \frac{1}{|x|^s}\right)\mathrm{d}x = \begin{cases} 0 & \text{for } 1 < s < 3 \\ \frac{2\pi}{3}\int_Q |x|^2\,\mathrm{d}x & \text{for } s = 1 \end{cases}$$

Proof: No-dipole and no-quadrupole conditions ensure the function is integrable. Then

$$\mathcal{F}\left(\frac{1}{|x|^s} - \mathbb{1}_Q * \frac{1}{|x|^s}\right)(k) \propto \frac{(2\pi)^{-\frac{3}{2}} - \widehat{\mathbb{1}_Q}(k)}{|k|^{3-s}} \propto \frac{|k|^2(1+o(1))}{|k|^{3-s}}$$

$$\widehat{\mathbb{1}_Q}(k) = (2\pi)^{-\frac{3}{2}}\int_Q e^{-ik\cdot x}\,\mathrm{d}x = (2\pi)^{-\frac{3}{2}}\left(1 - \frac{|k|^2}{6}\int_Q |x|^2\,\mathrm{d}x + o(|k|^2)\right)$$

Computation for the floating crystal

$$\frac{1}{2}\sum_{z\neq z'\in\mathcal{L}\cap(0,L)^3}\frac{1}{|z-z'|^s}-\frac{1}{2}\iint_{\Omega_L^2}\frac{dx\,dy}{|x-y|^s}$$
$$=\frac{1}{2}\sum_{z\neq z'\in\mathcal{L}\cap(0,L)^3}\left(\frac{1}{|x|^s}-\mathbb{1}_Q*\mathbb{1}_Q*\frac{1}{|x|^s}\right)(z-z')-\frac{N}{2}\iint_{Q^2}\frac{dx\,dy}{|x-y|^s}$$

hence the limit per particle is

$$\frac{1}{2}\sum_{z\in\mathcal{L}}\left(\frac{\mathbb{1}(|x|\neq 0)}{|x|^s}-\mathbb{1}_Q*\mathbb{1}_Q*\frac{1}{|x|^s}\right)(z)$$
$$=\frac{1}{2}\sum_{z\in\mathcal{L}}\left(\frac{\mathbb{1}(|x|\neq 0)}{|x|^s}-2\mathbb{1}_Q*\frac{1}{|x|^s}+\mathbb{1}_Q*\mathbb{1}_Q*\frac{1}{|x|^s}\right)(z)+\underbrace{\sum_{z\in\mathcal{L}}\mathbb{1}_Q*\left(\frac{1}{|x|^s}-\mathbb{1}_Q*\frac{1}{|x|^s}\right)(z)}_{=\int_{\mathbb{R}^3}\left(\frac{1}{|x|^s}-\mathbb{1}_Q*\frac{1}{|x|^s}\right)=\cdots}$$

Lemma

For $0<s<3$ the first term is $\zeta_{\mathcal{L}}(s)$.

Borwein *et al* '88, Blanc-ML '15, ML-Lieb '15, Lauritsen '21

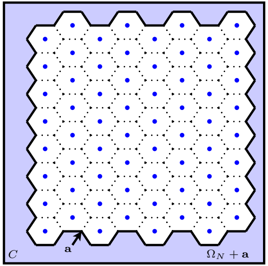
Making the crystal (really) float

Theorem (Upper bound)

We have $-1.4508 \simeq \frac{3}{5}\left(\frac{9\pi}{2}\right)^{\frac{1}{3}} \leq e_{\rm UEG} \leq \zeta_{\rm BCC}(1) \simeq -1.4442.$

Lieb-Narnhofer '75, Cotar-Petrache '19, ML-Lieb-Seiringer '19

- $\zeta_{\rm FCC}(1) \approx -1.4441$, $\zeta_{\mathbb{Z}^3}(1) \approx -1.4187$
- Cotar-Petrache '19: continuity in $s > 1$ for interaction $|x|^{-s}$
- ML-Lieb-Seiringer '19: better trial state by adding a layer of fluid to suppress boundary charge fluctuations
- would be interesting to investigate numerically whether the true minimizer $\mathbb{P}$ is a fluid close to the boundary and a solid in the bulk



Theorem (Dimensions $d \in \{1, 8, 24\}$)

In $d = 1$ *with the potential* $w(x) = -|x|$*, the UEG is crystallized with the energy* $\zeta(-1) + \frac{1}{12}$
In $d = 8, 24$ *with* $w(x) = |x|^{2-d}$*, we have* $e_{\rm UEG} = \zeta_{\mathcal{L}}(d-2)$ *with* $\mathcal{L}$ *the E8 and Leech lattices.*

Colombo-De Pascale-Di Marino '14, Cohn-Kumar-Miller-Radchenko-Viazovska '22, Petrache-Serfaty '20

Open problems

- understand better the existence of the dual (Kohn-Sham) potential in the quantum case
- find a counter-example to the convexity-in-N with nuclei of integer charges
- what is the largest possible length of supp($\mathbb{P}$) in the grand-canonical case?
- understand Lieb-Oxford inequality for exchange (Perdew-Sun '22)
- get N-independent bounds on the distance between particles in the thermodynamic limit
- existence of a dual potential for the infinite system?
- better justify the LDA in the canonical case
- prove crystallization