On ground state of atoms and molecules and some convexity issue

Lecture 07/01/2025

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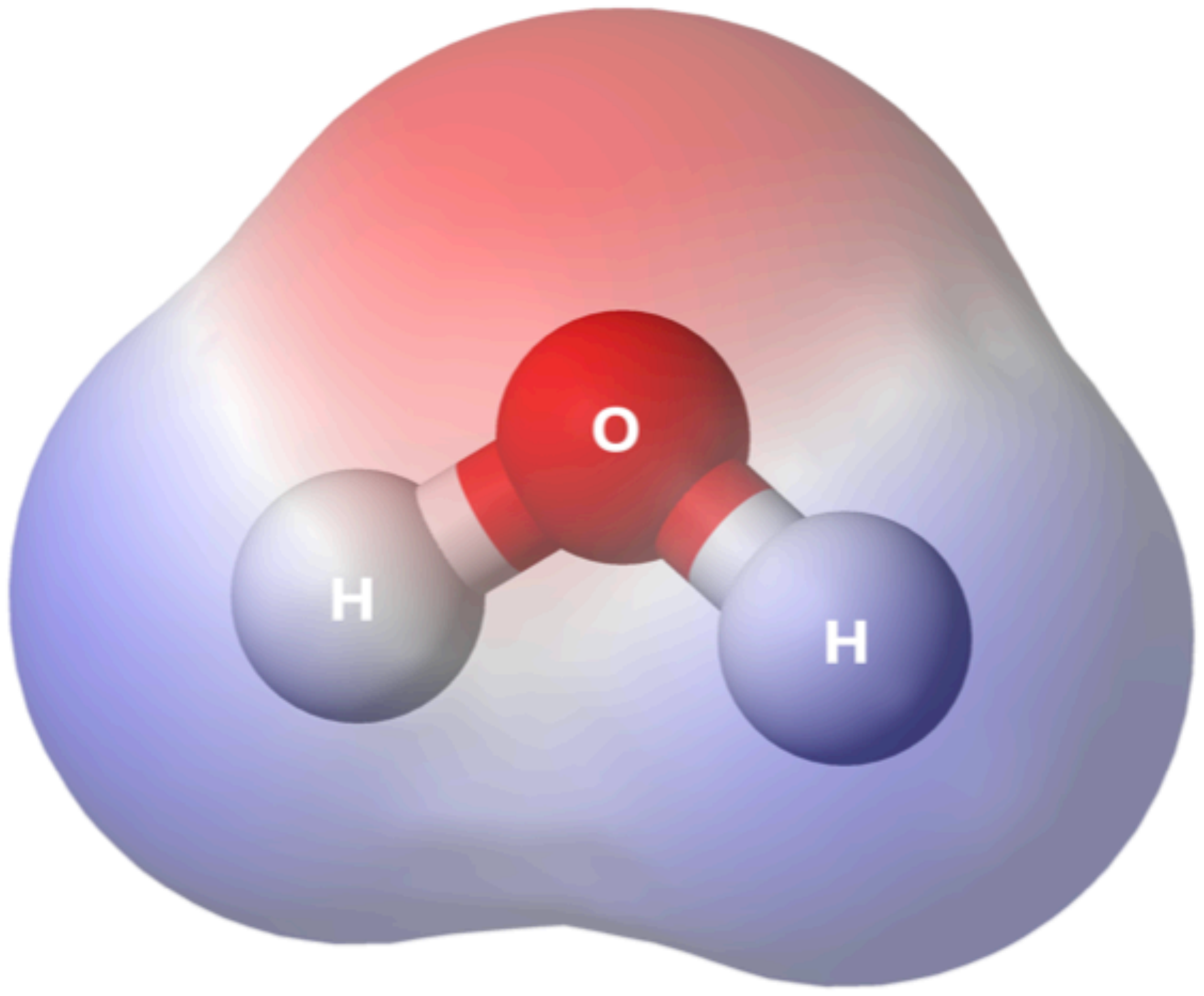
Plan for today lecture

1. Density Functional Theory: from the quantum to the classical

2. Counter-example to the convexity conjecture



Lot of calculus of variations

Some references:

- E.H. Lieb, *Density functionals for Coulomb Systems*, International Journal of Quantum Chemistry, XXIV, 243-277, 1983.
- M. Lewin, 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 Eric Cances and Gero Friesecke, Springer, 2023.
- M. Lewin *Coulomb and Riesz gases: The known and the unknown*. J. Math. Phys., 63, p. 061101, 2022.

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

Schrödinger's equation for electrons in a molecule

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

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

- N electrons: antisymmetric wave function $\psi(x_1, \ldots, x_N)$ on $(\mathbb{R}^3)^N$ with $\int_{\mathbb{R}^{3N}} |\psi|^2 = 1$

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

Problem: essentially impossible to solve numerically!

A variational principle and a double minimisation (Levy '82, Lieb '83)

Density of pure states

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

$$\rho_\Psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(x, x_2, \ldots, x_N)|^2 dx_2 \cdots dx_N$$

Pure states

$$E[N,V] = \inf_{\psi} \langle \psi, H^N(V)\psi \rangle = \inf_{\rho} \left\{ \inf_{\psi | \rho_\psi = \rho} \langle \psi, H^N(0)\psi \rangle + \int_{\mathbb{R}^3} \rho(x) V(x)\,dx \right\}$$

$F_{LL}[\rho]$ Levy-Lieb functional

Some remarks

- New unknown ρ depends on only one variable $x \in \mathbb{R}^3$ $\Rightarrow$ <u>no N-Particle space anymore!</u>
- Easy to show existence of F_{LL}
- $F_{LL} =$ "universal Levy-Lieb functional" , very nonlinear and non local, impossible to compute in practice and no-explicit formulation in terms of ρ
- It is not convex 😭
- **<u>Density Functional Theory (DFT)</u>:**
- Understand better the true F_{LL};
- Replace it with F_{app} and then $E[N, V] \approx \inf_{\rho} \left\{ F_{app}[\rho] + \int \rho V \right\}$.

Let's try again: Legendre duality (Lieb '83)

Legendre transform and duality

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

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

where $F[\rho]$ is convex w-lsc functional defined by

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

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

Good news: F is convex!!

Bad news: Who is F?!?!

Who is ρ? Who is $F[\rho]$?

Density of mixed states

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

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

Rmk: $(V,\Gamma) \mapsto \mathrm{tr}(H^N(V)\Gamma)$ is linear both in V and Γ

Mixed states: a double minimisation approach

$$E[N,V] = \inf_\Gamma \mathrm{tr}(H^N(V)\Gamma) = \inf_\rho \left\{ \inf_{\Gamma|\rho_\Gamma=\rho} \mathrm{tr}(H^N(0)\Gamma) + \int_{\mathbb{R}^3} \rho(x)V(x)dx \right\}$$

$F[\rho]$ Lieb functional

The universal functional $F[\rho]$

Theorem (Lieb '83)

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

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

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

Inf-sup argument

$$F[\rho] = \sup_V \left\{ E[N,V] - \int \rho V \right\} = \sup_V \inf_\Gamma \left\{ \operatorname{tr}(H^N(V)\Gamma) - \int \rho V \right\}$$

$$= \inf_\Gamma \sup_V \left\{ \operatorname{tr}(H^N(0)\Gamma) + \int (\rho_\Gamma - \rho) V \right\} = \inf_\Gamma \left\{ \operatorname{tr}(H^N(0)\Gamma) + \sup_V \int (\rho_\Gamma - \rho) V \right\}$$

$= +\infty$ unless $\rho_\Gamma = \rho$

Low and high density regimes (aka some $\Gamma-$cv results)

Two new functionals

$$T[\rho] = \inf_{\rho_\Gamma=\rho} \mathrm{tr}\left(\frac{\Delta_{\mathbb{R}^{3N}}}{2}\Gamma\right)$$

$$C[\rho] = \inf_{\mathbb{P}\ \text{sym},\ \rho_{\mathbb{P}}=\rho} \int_{\mathbb{R}^{3N}} \sum_{1\leq j\leq k\leq N} \frac{d\mathbb{P}(x_1,\ldots,x_N)}{|x_j-x_k|}$$

Theorem

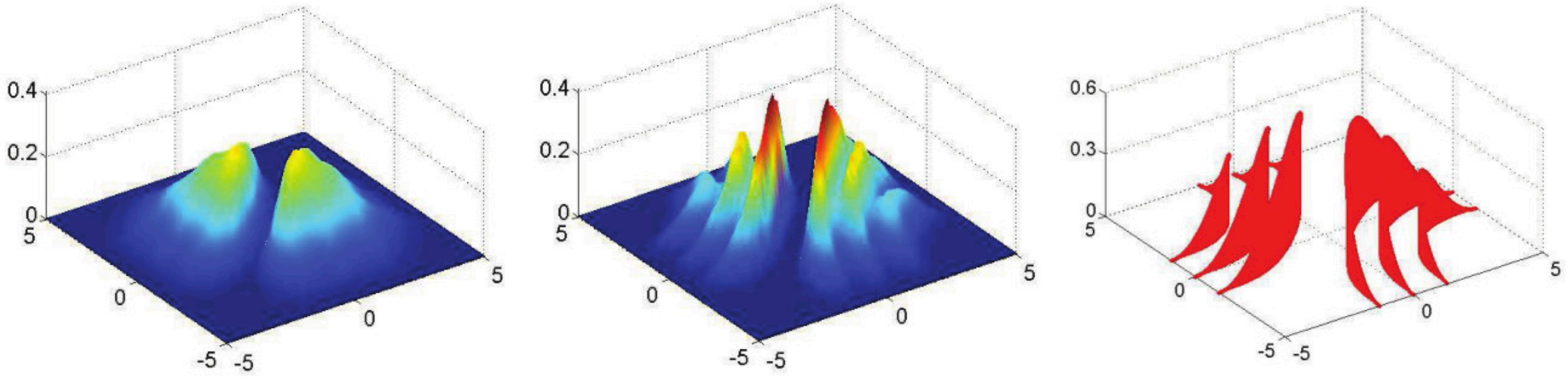
$$\lim_{\lambda\to\infty} \frac{F[\lambda^3\rho(\lambda x)]}{\lambda^2} = T[\rho]$$

$$\lim_{\lambda\to 0} \frac{F[\lambda^3\rho(\lambda x)]}{\lambda} = C[\rho]$$

Rmk:

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

The low-density limit is (very) singular



Pair density for $\lambda = 1$, $\lambda = 0.1$ and $\lambda \approx 0$ in 1D, with $N = 4$ and

$$\rho(x) = \frac{2}{5}(1 + \cos(\pi x/5))\chi_{x \in [-5,5]}(x)$$

(Chen-Friesecke '15)

Some remarks

- Existence for $F_{LL}[\rho]$ and $F[\rho]$: it follows by using the direct method fo calculus of variations. Notice that the mass constraint (e.g. $\int |\psi|^2 = 1$) helps to get some compactness.

- $\rho \mapsto F_{LL}[\rho]$ is non convex so the Legendre duality fails.

- Relation between F_{LL} and F:

$$F[\rho] = \inf \left\{ \sum_j n_j F_{LL}[\rho_j] \mid \sum_j n_j \rho_j = \rho, \ \sum_j n_j = 1, \ n_j \geq 0 \right\}$$

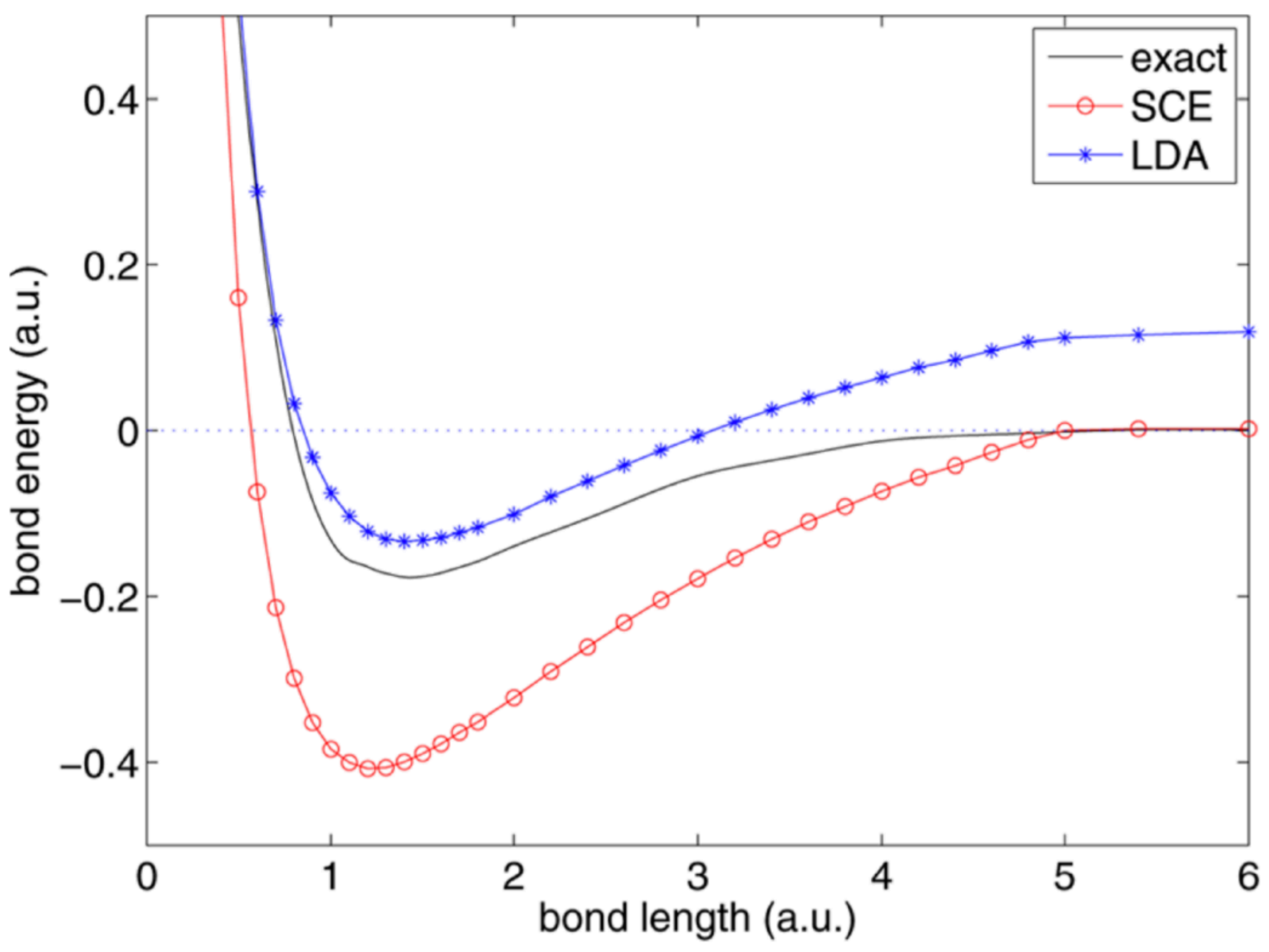
F is actually the convex hull of F_{LL}.

- I totally ignored the 3 hours speech on the functional spaces but

$$\rho \in \left\{ \int \rho = N, \sqrt{\rho} \in H^1(\mathbb{R}^3) \right\}$$ and $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ (Lieb '83).

- $C[\rho]$ is a (multi-marginal) optimal transport problem.

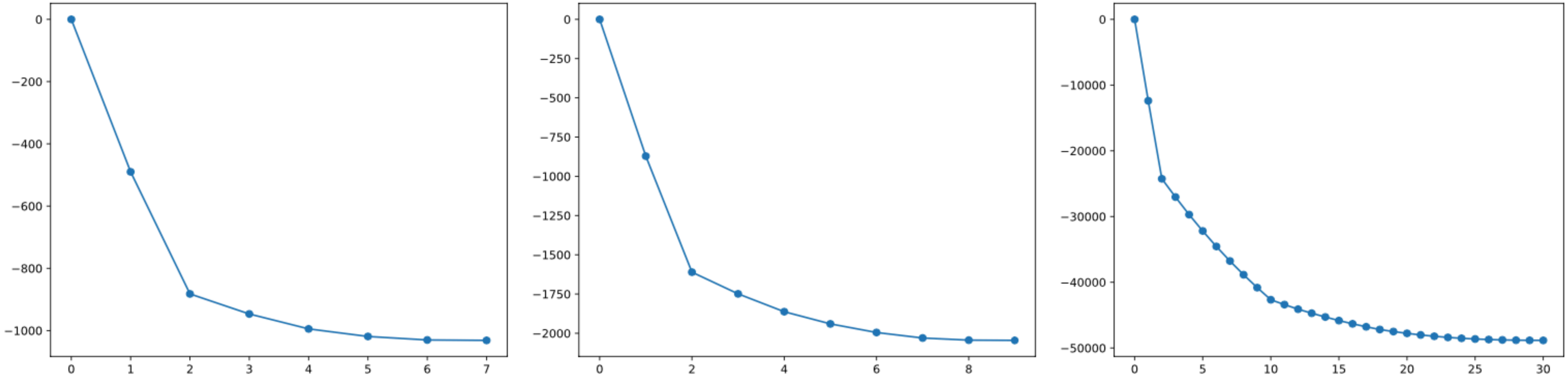
- In computational chemistry $F[\rho] \approx T[\rho] + C[\rho]$



H_2 dissociation Chen-Friesecke-Mendl '14

II. A convexity conjecture in Quantum Chemistry

Experimental energies of an atom with Z protons, in terms of the number N of electrons:



Carbon $Z = 6$ Oxygen $Z = 8$ Zinc $Z = 30$

Data from Wikipedia, NIST

Rmk #1: monotone (additional electron stays if energy decreases, or escapes to infinity)

Rmk #2: convex (valence electrons less tightly bound than core electrons)

Rmk #3: constant for $N \geq Z + 1$or $Z + 2$ (nucleus cannot bind too many electrons)

☢ Electrons described by Schrödinger's equation!

- #1 easy to prove
- #2, #3 very hard to prove ⇒ **"ionisation conjecture"**

Ionization conjecture #2

Conjecture (convexity-in-N)

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

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

- **Perdew-Parr-Levy-Balduz (1982)** and Parr-Yang (1994)

  suggest conjecture true for all $V(x) = -\sum_{m=1}^{M} \frac{z_m}{|x - R_m|}$, $z_m \in \mathbb{N}$

$$E^0(N+1) - E^0(N) \geqslant E^0(N) - E^0(N-1) \qquad (4.1.14)$$

or

$$I(N+1) \geqslant I(N) \qquad (4.1.15)$$

where $I(N)$ is the ionization potential of the N-electron ground state. Equation (4.1.15) states that successive ionization potentials are not decreasing (for fixed external potential).

For atoms and molecules, no counterexample is known to (4.1.15), although a first-principles proof has never been given. As examples, in

- **Lieb (1983)** stated the conjecture for all V

While it has been conjectured that $E(N, v)$ is convex in N (for *all* v) in the case of Coulomb repulsion, this has never been proved. It has not even been proved that $E(3, v) + E(1, v) \geq 2E(2, v)$.

- **Simon (1984)** Included the conjecture for atoms in a famous list of 15 open problems

Problem 10A (Monotonicity of the Ionization Energy). Prove that

$$(\Delta E)(N-1, Z) \geqq (\Delta E)(N, Z)$$

for all N, Z.

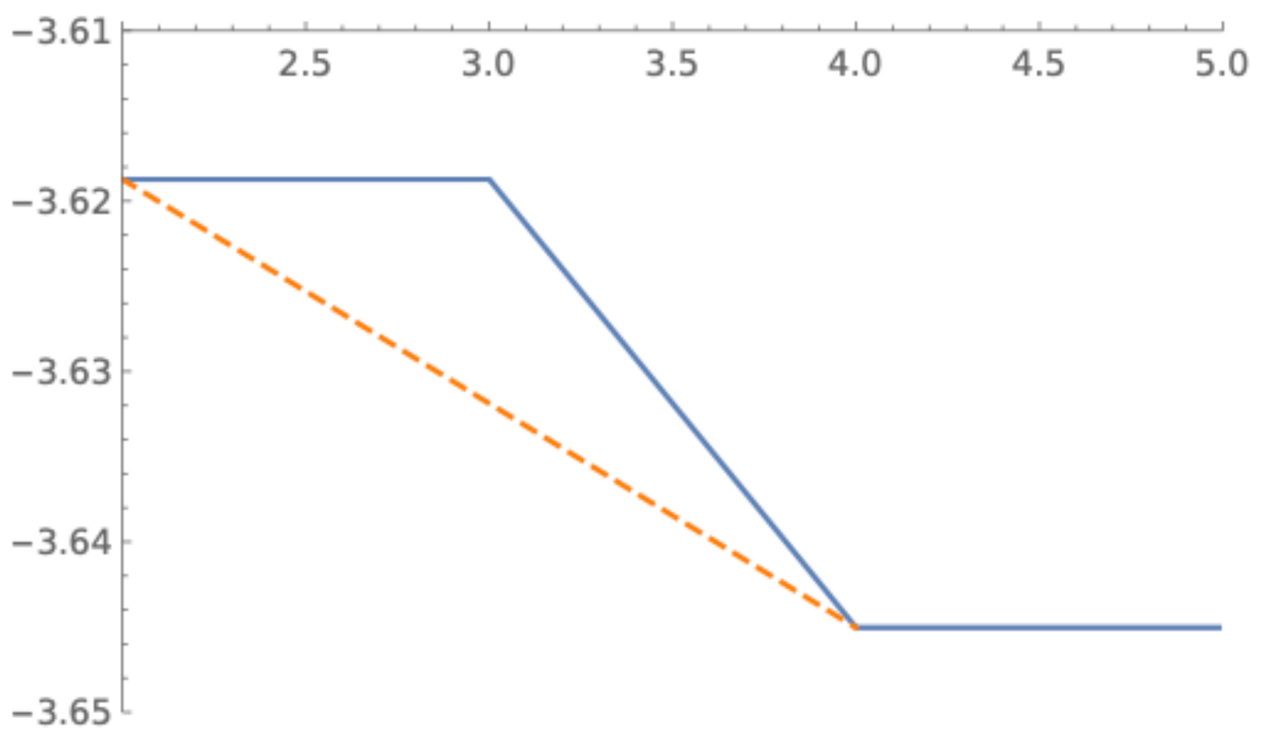
This is just the fact, almost obvious, that it takes more energy to remove inner electrons than outer ones. Since in removing electron $(N-1)$ there is one fewer electron to repel, and since the Pauli principle only makes things better this should be true. It seems to be remarkably difficult to prove.

A counter-example with nuclei of fractional charges

Theorem

There exists $R_1, \ldots, R_6 \in \mathbb{R}^3, z_1, \ldots, z_6 > 0$, and $e_4 < e_2 < e_1 < 0$ such that, for

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



We have for all $N \geq 5$

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

and hence **convexity fails at $N = 3$ for $\ell \gg 1$**.

- First counter-example for Coulomb, still open for real nuclear (integer charges)
- Follows from calculus of variations arguments for classical electrons

Back to classical $N-$body problem

Classical minimal energy

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

Conjecture (convexity-in-N)

For $V \in ?$, the map $N \mapsto e[N, V]$ is convex

Quantum conjecture for all nice-enough $V \Rightarrow$ classical one since

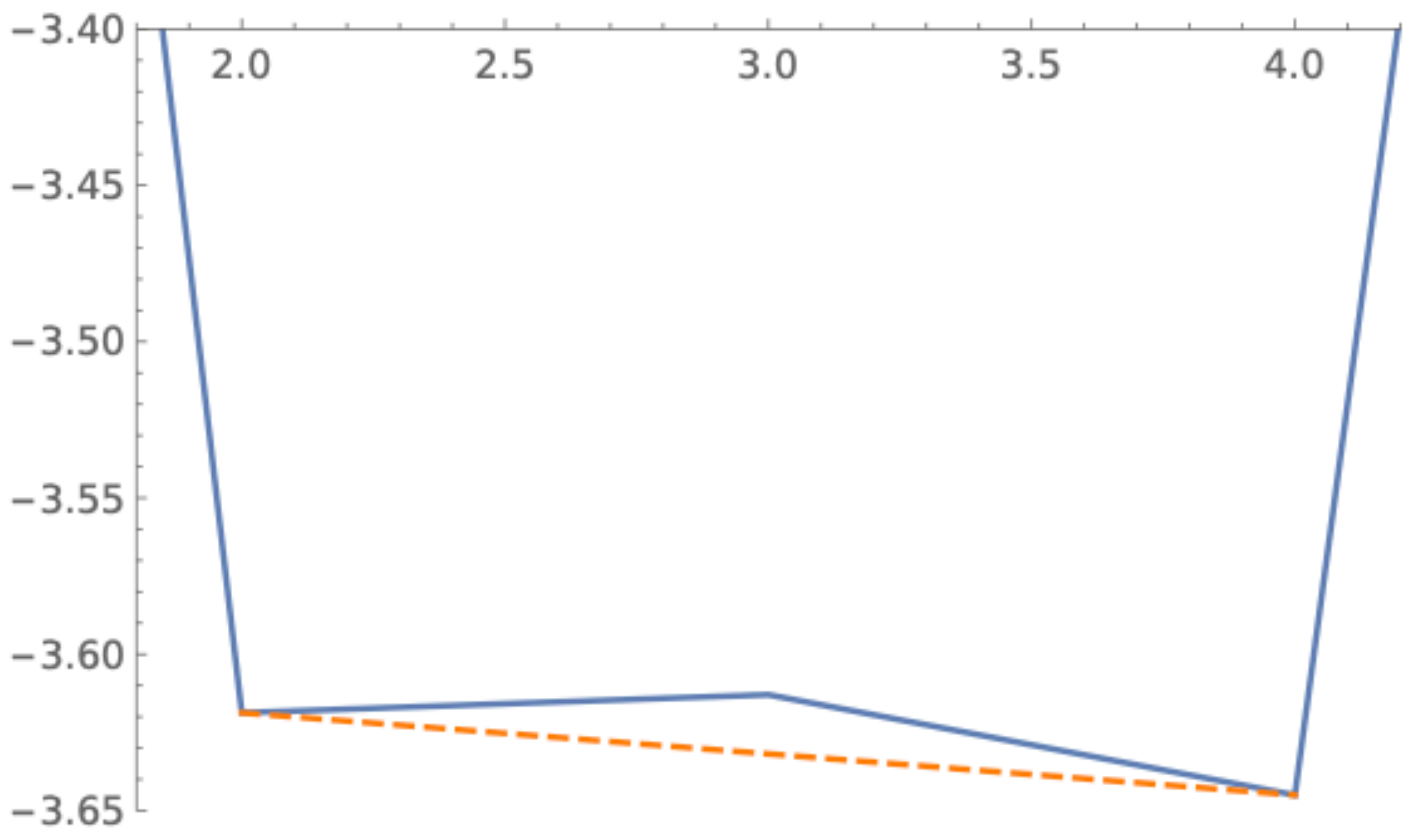
$$\lim_{\varepsilon \to 0} \frac{E[N, \varepsilon V(\varepsilon \cdot)]}{\varepsilon} = e[N, V]$$

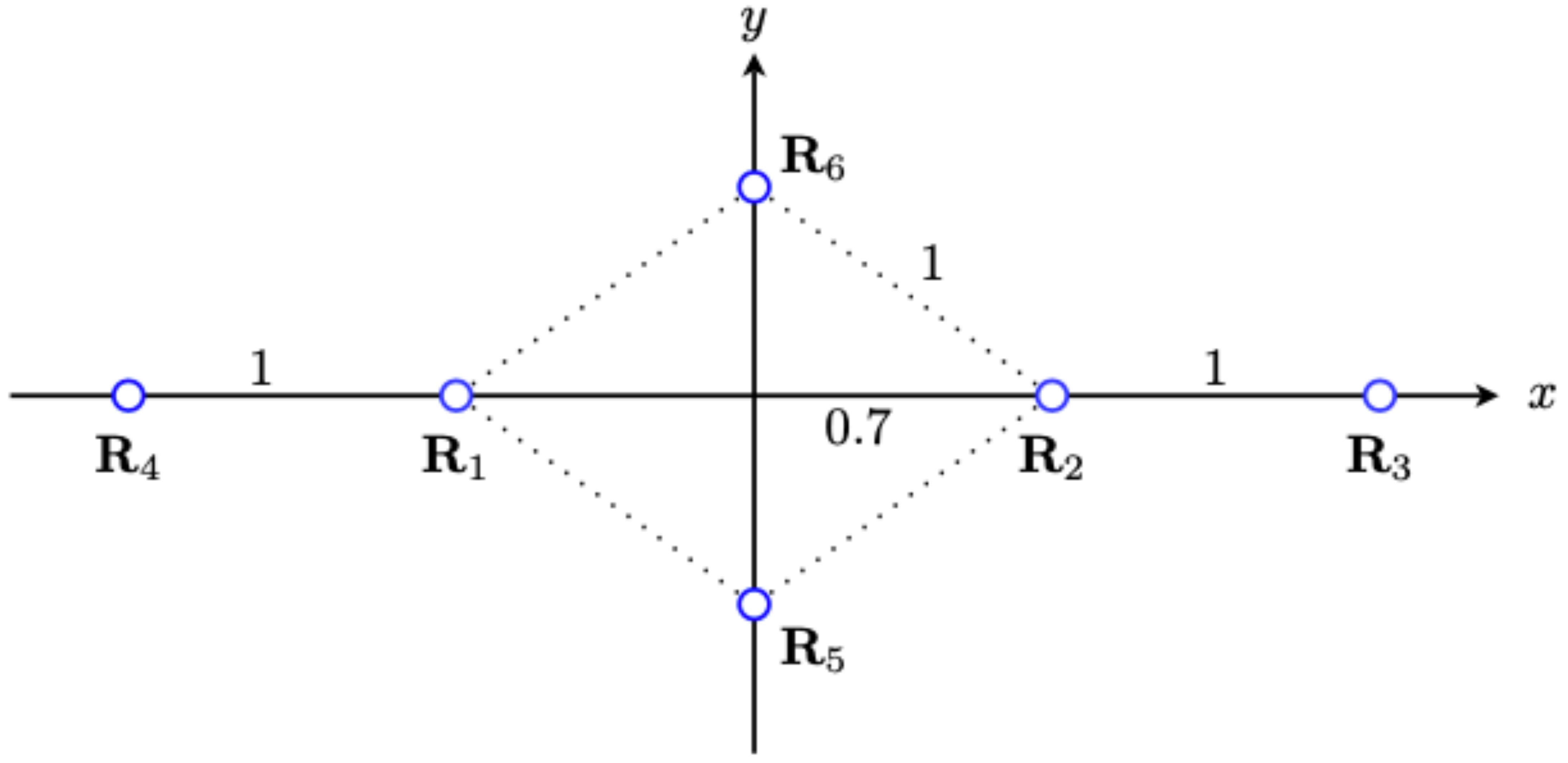
•Classical counter-example

$$V(x) = \begin{cases} v_m & \text{if } x = R_m \\ +\infty & \text{if } x \notin \{R_1, \ldots, R_6\} \end{cases}$$

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

N	$E_{\text{cl}}^N[V] \approx$	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	$\mathbf{R}_3, \ldots, \mathbf{R}_6$
5	-2.3949	$\mathbf{R}_2, \ldots, \mathbf{R}_6$
6	-0.4304	$\mathbf{R}_1, \ldots, \mathbf{R}_6$





Variational formulation for the convex hull of $N \mapsto e(N,V)$

$$e(N,V) = \inf E_N^V = \inf_{\mathbb{P}\text{ symm}} \int_{\mathbb{R}^{3N}} E_N^V d\mathbb{P}, \quad E_N^V(x_1,\dots,x_N) = \sum_{j=1}^N V(x_j) + \sum_{1\le j\le k\le N} \frac{1}{|x_j - x_k|}$$

<u>**Grand-canonical: make N random**</u>

$$e_{GC}(\lambda, V) = \inf\left\{ \sum_{n\ge 1} p_n e(n,V) \mid \sum p_n = 1, \ \sum_n n p_n = \lambda \right\}$$

That is, $\lambda \in \mathbb{R}_+ \mapsto e_{GC}(\lambda, V)$ is the **convex hull** of $N \mapsto e(N,V)$

Example: for previous counter-example V, better to have 2 and 4 particles each with proba 1/2 instead of 3.

Conjecture true for one V and all $N \ge 1$ $\iff$ $e_{GC}(N,V) = e(N,V), \forall N \ge 1$

Legendre transforms (and duality)

Let's look at the Legendre transforms of $e[N, V]$ and $e_{GC}[N, V]$!

Multi-marginal optimal transport with Coulomb cost

$$C[\rho] = \inf_{\mathbb{P}\ \text{sym},\ \rho_{\mathbb{P}}=\rho} \int_{\mathbb{R}^{3N}} \sum_{1\leq j\leq k\leq N} \frac{d\mathbb{P}(x_1,\ldots,x_N)}{|x_j - x_k|}$$

then

$$C[\rho] = \sup_V \left\{ e[N,V] - \int \rho V \right\}, \quad e[N,V] = \inf_{\int \rho = N} \left\{ C[\rho] + \int \rho V \right\}$$

Grand-canonical optimal transport with Coulomb cost

$$C_{GC}[\rho] = \inf \left\{ \sum_{n\geq 1} p_n C[\rho_n] \mid \sum p_n = 1, \sum_n p_n \rho_n = \rho \right\}$$

Conjecture true for all V and all $N \geq 1$ $\iff$ $C_{GC}[\rho] = C[\rho], \forall \rho$ with $\int \rho = N$

Support for the grand canonical aka $C[\rho] \stackrel{?}{=} C_{GC}[\rho]$

For $p = (p_n)_{n\geq 0}$ we call $\mathrm{supp}(p) = \{n \mid p_n \neq 0\}$ 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 optimiser for $C_{GC}[\rho]$ satisfies

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

Theorem (counter-example)

There exists a ρ with $\rho(\mathbb{R}^3) = 3$ such that $\mathrm{supp}(p) = \{2,4\}$, hence $C_{GC}[\rho] < C[\rho]$. Moreover, for every $k \geq 1$,

There exists $\rho^{(k)}$ with $\rho^{(k)}(\mathbb{R}^3) = \dfrac{6^k}{2}$ such that $\mathrm{supp}(p^{(k)}) = \left\{ \dfrac{6^k - 2^k}{2}, \dfrac{6^k + 2^k}{2} \right\}$

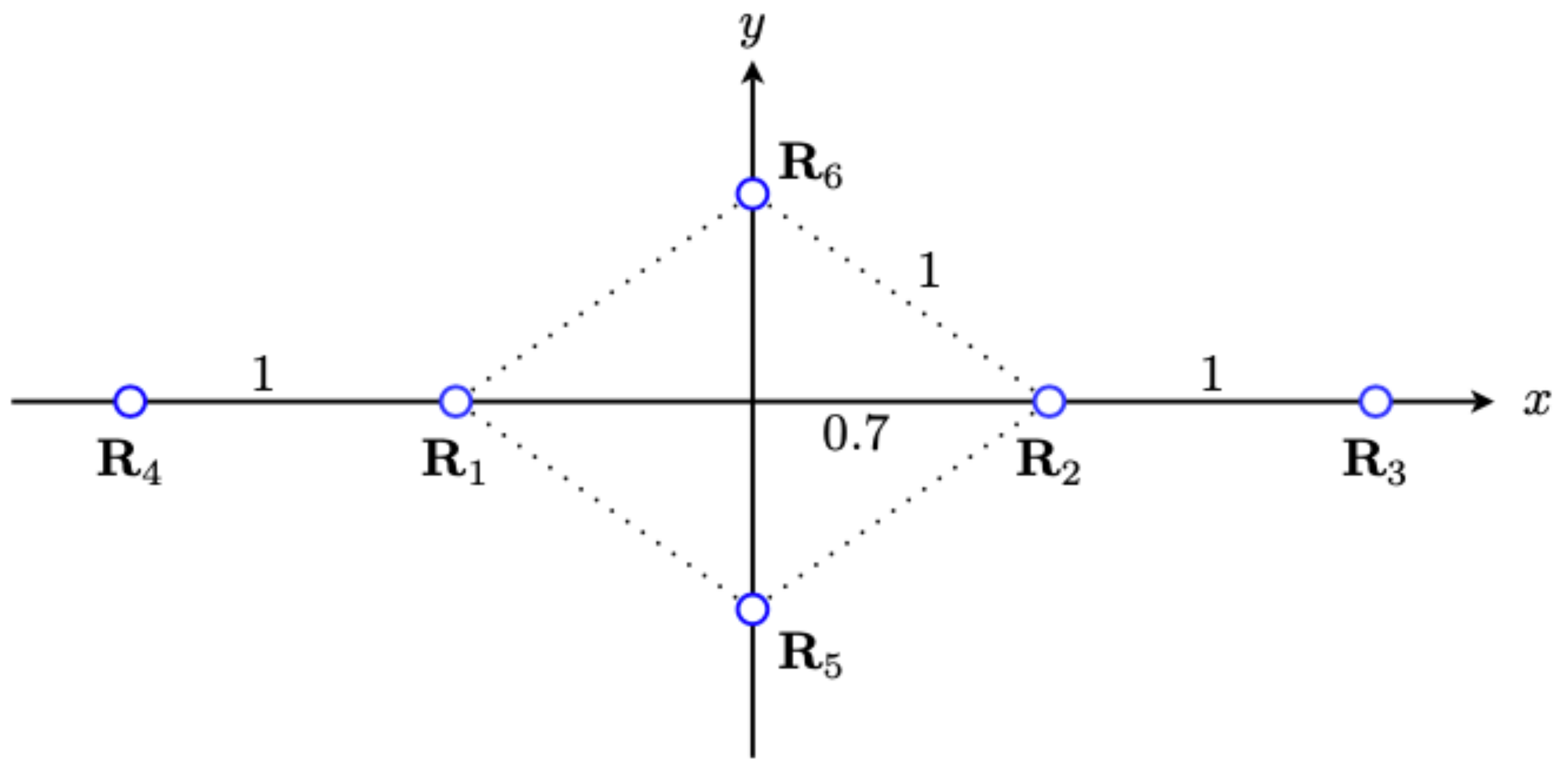
$\Rightarrow$ convexity in N conjecture cannot hold!

- For the 6 points $R_1, \ldots, R_6$ below-right we have

$$3.8778 \approx C_{GC}\left[\frac{1}{2}\sum_{m=1}^{6}\delta_{R_m}\right] < C\left[\frac{1}{2}\sum_{m=1}^{6}\delta_{R_m}\right] \approx 3.9157$$

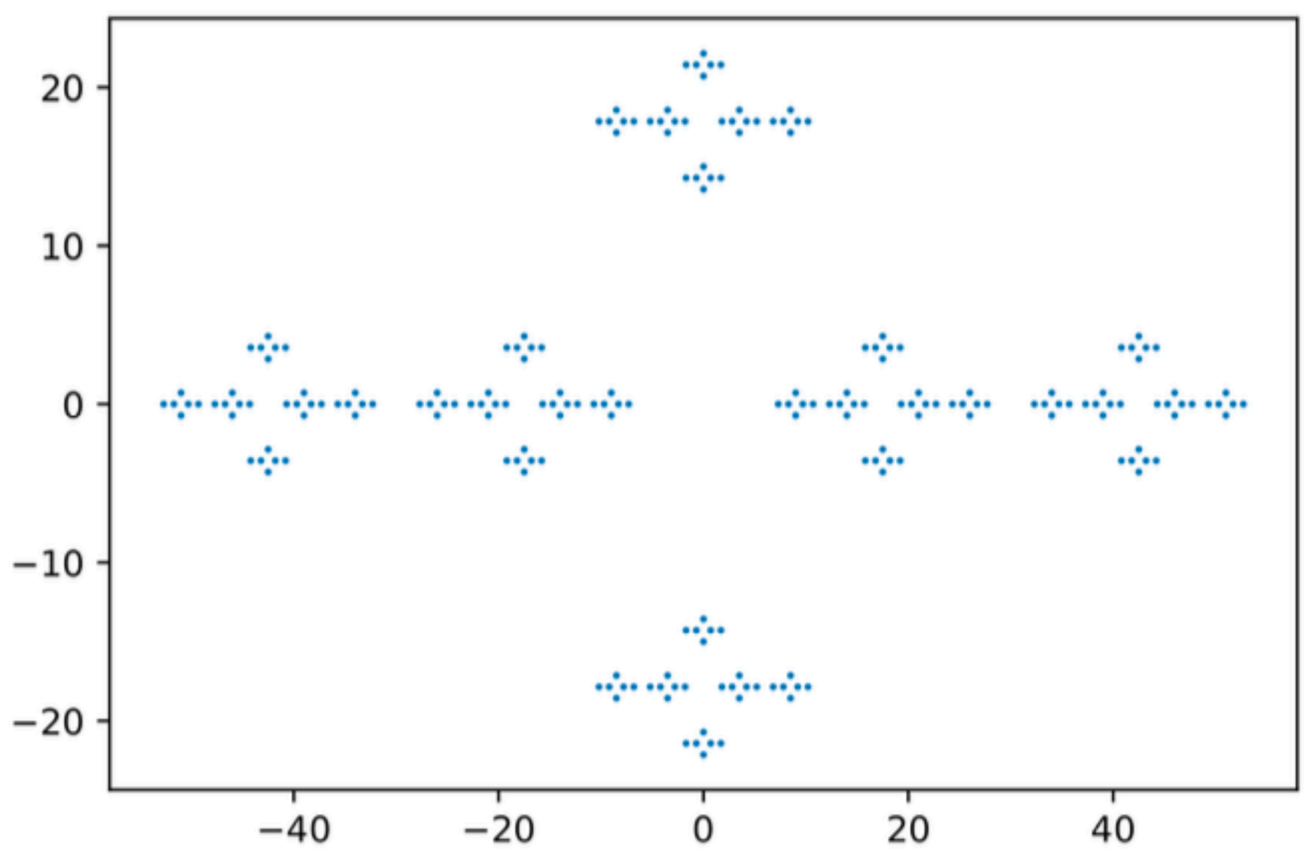
With the optimiser

$$\mathbb{P} = \frac{1}{2}\left(\delta_{R_1}\otimes\delta_{R_2} + \delta_{R_3}\otimes\ldots\otimes\delta_{R_6}\right)$$



- Repeating this pattern at different scales we found

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

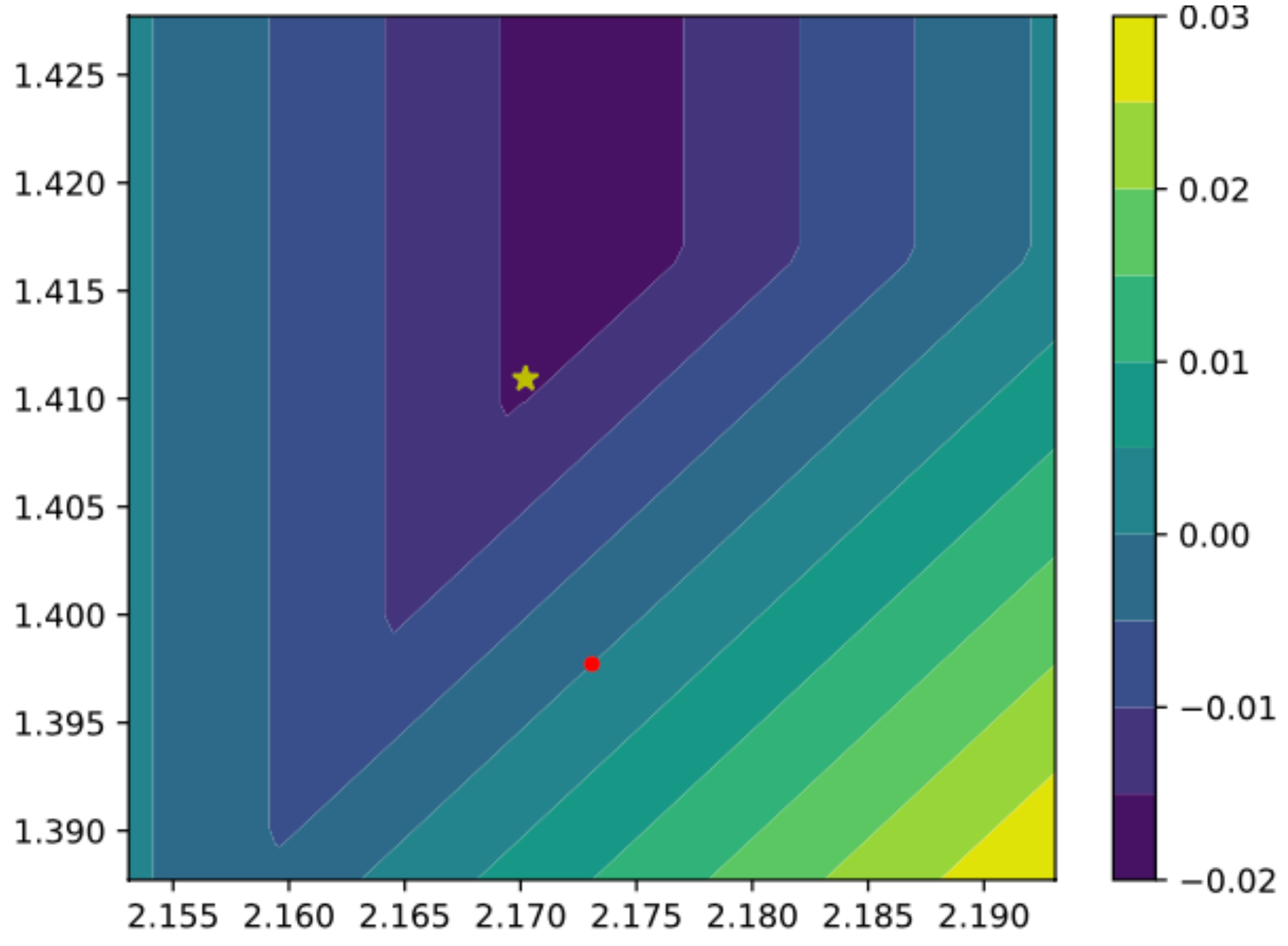


Finding the potential V

- To find the potential V, we first solve the dual problem to C_{GC} bu we get

$$e[2,V_{GC}] = e[3,V_{GC}] = e[4,V_{GC}]$$ 😭

- Idea: minimize $V \mapsto (e[2,V] + e[4,V])/2 - e[3,V]$ in a neighbourhood of V_{GC} to get V. 😊



difference as a function of $(|v_1|, |v_3|)$

Conclusion

- convexity-in-N conjecture wrong for general Coulomb potentials
- still open for atoms and molecules
- experiments and numerics say it is true for atoms, but no (mathematical) intuition why
- very helpful to work with tools from calculus of variations (Legendre transform)
- Schrödinger equations is 100 years old in 2025 but still poses many interesting mathematical questions with large impact in applications

Not yet the end (Exam on 17/01/2025 room 0A7)

- Existence: use the direct method of calculus of variations so look for (1) compactness and (2) lower semi-continuity.

- Uniqueness follows from strict convexity of the functional.

- Euler-Lagrange equations hold usually in the sense of distributions: prove that they hols in a stringer sense demands some additional work (remember the one dimensional case).

- Legendre transform and duality can help to understand better the problem, that is the properties of the minimiser (regularity).

- Variational convergence, aka $\Gamma-$convergence, helps to understand better a problem if we approximate it with a suitable optimization problem.

Happy 2025! And good luck (especially if you go for a Ph.D. whatever the topic😉)!