Density Functional Theory for two-dimensional homogeneous materials

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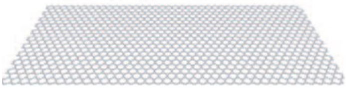
Goal: study two-dimensional materials (embedded in 3d space).



$\neq$ 2d material in 2d space (*e.g.* with the 2d Coulomb kernel).

Questions:

- What should be the size of the «simulation box»?
- What is the decay of the **electronic density** or **mean-field potential** away from the plane?

In this talk, we consider homogeneous materials, modelled by a charge density

$$\boxed{\mu(x_1, x_2, x_3) = \mu(x_3) \in L^1(\mathbb{R}).}$$

and study the properties of the electronic density in **Thomas-Fermi** and **Kohn-Sham** models.

Remarks

- Very crude approximation (we lose the microscopic details of the material);
- This model should have the correct decay properties away from the slab (the details *fade away*).

Thomas-Fermi model

Recall the (three-dimensional) Thomas-Fermi energy (assume $\mu \in C_0^\infty(\mathbb{R}^3)$)

$$\forall \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3),\ \rho \geq 0, \quad \mathcal{E}_3^{\rm TF}(\rho) := c_{\rm TF} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \mathcal{D}_3(\rho - \mu),$$

with the three-dimensional Coulomb energy

$$\mathcal{D}_3(f) := \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{f(x) f(y)}{|x-y|} {\rm d}x {\rm d}y.$$

The model is *convex* in ρ. In particular, if μ satisfies some symmetries, then ρ satisfies the same symmetries.

If μ only depends on x_3, we may assume that ρ also depends on x_3 only.

We define the Thomas-Fermi energy per unit surface

$$\boxed{\forall \rho \in L^1(\mathbb{R}) \cap L^{5/3}(\mathbb{R}), \quad \mathcal{E}_1^{\rm TF}(\rho) := c_{\rm TF} \int_{\mathbb{R}} \rho^{5/3} + \frac{1}{2} \mathcal{D}_1(\rho - \mu),}$$

with the one-dimensional Coulomb energy

$$\mathcal{D}_1(f) \overset{??}{=} -2\pi \iint_{\mathbb{R} \times \mathbb{R}} f(x) f(y) |x-y| {\rm d}x {\rm d}y.$$

First technical problem: The $\mathcal{D}_1$ functional is not convex! It will be on $\{\rho,\ \int \rho = \int \mu\}$, see later.

Thomas-Fermi minimization (for neutral systems only)

$$\boxed{\rho_{\rm TF} := \operatorname{argmin} \left\{ \mathcal{E}_1^{\rm TF}(\rho),\ \rho \in L^1(\mathbb{R}) \cap L^{5/3}(\mathbb{R}), \quad \rho \geq 0, \quad \int_{\mathbb{R}} \rho = \int_{\mathbb{R}} \mu =: Z \right\}.}$$

$$\boxed{\rho_{\rm TF} := \operatorname{argmin}\left\{ \mathcal{E}_1^{\rm TF}(\rho),\ \rho \in L^1(\mathbb{R}) \cap L^{5/3}(\mathbb{R}), \quad \rho \geq 0, \quad \int_{\mathbb{R}} \rho = Z \right\}.}$$

Key remark: It is a (very) simple model (one-dimensional, no derivatives, ...).

Proposition

There is a unique minimizer $\rho_{\rm TF}$. It is the (unique) solution to the Thomas-Fermi equation

$$\begin{cases} \frac{5}{3} c_{\rm TF} \rho_{\rm TF}^{2/3} = (\lambda - \Phi_{\rm TF})_+ \\ -\Phi_{\rm TF}'' = 4\pi(\rho_{\rm TF} - \mu), \quad \Phi_{\rm TF}'(\pm\infty) = 0, \quad \Phi_{\rm TF}(0) = 0. \end{cases}$$

Here, $\lambda \in \mathbb{R}$ is the Fermi level, chosen so that $\int_{\mathbb{R}} \rho = Z$, and $\Phi_{\rm TF}$ is defined as the unique solution of the second equation.

Remark: There is no *reference energy* in 1d (the 1d Green's function does not have a limit at infinity). Only the difference $V_{\rm TF} := \Phi_{\rm TF} - \lambda$, called the mean-field potential, makes sense.

The proof is similar to the ones of the *usual* Thomas–Fermi model (see [Lieb/Simon, Adv. Math. 23, 1977]).

Screening properties

Let $f \in C_0^\infty(\mathbb{R})$ be such that $\int_{\mathbb{R}} f = 0$. The potential generated by f is formally

$$\Phi_f(x) := -2\pi \int_{\mathbb{R}} f(y)|x-y|\mathrm{d}y.$$

We have $\Phi_f(\infty) = 2\pi \int_{\mathbb{R}} f(y)y\mathrm{d}y$ and $\Phi_f(-\infty) = -2\pi \int_{\mathbb{R}} f(y)y\mathrm{d}y$.

The difference $\Phi_f(\infty) - \Phi_f(-\infty) = 4\pi \int_{\mathbb{R}} f(y)y\mathrm{d}y$ is called the dipolar moment.

Proposition (perfect screening)

Assume $|x|\mu(x) \in L^1(\mathbb{R})$. *Then* $|x|\rho_{\mathrm{TF}}(x) \in L^1(\mathbb{R})$ *as well, and the Thomas-Fermi potential* V_{TF} *satisfies*

$$\lim_{x\to\infty} V_{\mathrm{TF}}(x) = \lim_{x\to-\infty} V_{\mathrm{TF}}(x) = 0. \quad \textit{(no dipolar moment.)}$$

Proposition (Sommerfeld estimates)

Assume μ *is compactly supported in* $[a,b]$. *Then, there is* $x_a, x_b \in \mathbb{R}$ *so that*

$$\forall x < a, \quad V_{\mathrm{TF}}(x) = \frac{-c_1}{(x-x_a)^4}, \quad \textit{and} \quad \rho_{\mathrm{TF}}(x) = \frac{c_2}{(x-x_a)^6},$$
$$\forall x > b, \quad V_{\mathrm{TF}}(x) = \frac{-c_1}{(x-x_b)^4}, \quad \textit{and} \quad \rho_{\mathrm{TF}}(x) = \frac{c_2}{(x-x_b)^6}.$$

with the constants $c_1 := \dfrac{5^5 c_{\mathrm{TF}}^3}{27\pi^2}$ *and* $c_2 := \dfrac{5^6 c_{\mathrm{TF}}^3}{27\pi^3}$.

See [Sommerfeld, Zeitschrift für Physik 78(5–6) (1932)] and [Solovej, Ann. Math., (2003)] in the *usual* case.

Proof of Sommerfeld estimates.

Assume that $V_{\rm TF} \le 0$ (this fact comes from the maximum principle).
For $x > b$, we have $\mu(x) = 0$, so the Thomas Fermi equation becomes

$$\begin{cases} \frac{5}{3} c_{\rm TF} \rho_{\rm TF}^{2/3} = -V_{\rm TF} \\ -V_{\rm TF}'' = 4\pi \rho_{\rm TF} \end{cases} \quad \text{hence} \quad \forall x > b, \quad V_{\rm TF}'' = -4\pi \left(\frac{3}{5 c_{\rm TF}} \right)^{3/2} (-V_{\rm TF})^{3/2}.$$

We now solve the *ODE*. We multiply by $V_{\rm TF}'$ and integrate:

$$\frac{1}{2} |V_{\rm TF}'|^2 = 4\pi \left(\frac{3}{5 c_{\rm TF}} \right)^{3/2} \frac{2}{5} (-V_{\rm TF})^{5/2}, \quad \text{hence} \quad \frac{V_{\rm TF}'}{(-V_{\rm TF})^{5/4}} = \frac{4\sqrt{\pi}}{\sqrt{5}} \left(\frac{3}{5 c_{\rm TF}} \right)^{3/4}.$$

We integrate a second time and get

$$\frac{4}{(-V_{\rm TF})^{1/4}} = -\frac{4\sqrt{\pi}}{\sqrt{5}} \left(\frac{3}{5 c_{\rm TF}} \right)^{3/4} (x - x_b), \quad \text{so} \quad V_{\rm TF}(x) = \frac{-c_1}{(x - x_b)^4}. \qquad \square$$

Remarks:

- Simple proof (solve an ODE) due to the one-dimensional nature of the problem.
- Highlights some features of the Thomas-Fermi model (*e.g.* perfect screening, Sommerfeld estimates)

In the Thomas Fermi model, $\rho_{\rm TF}(x) \approx |x|^{-6}$ and $V_{\rm TF}(x) \approx |x|^{-4}$ away from the slab.

Interlude: the 1d Coulomb operator

For $L > 0$, we consider the $L\mathbb{Z}^2$-periodic Green's function G_L, solution to

$$-\Delta_3 G_L = 4\pi \sum_{(R_1,R_2)\in L\mathbb{Z}^2} \delta_{(R_1,R_2,0)}.$$

A computation shows that (we write $\mathbf{x} = (x_1, x_2)$)

$$\boxed{G_L(\mathbf{x}, x_3) = -\frac{2\pi}{L^2}|x_3| + \frac{2\pi}{L^2} \sum_{\mathbf{k}\in(2\pi/L)\mathbb{Z}^2\setminus\{0\}} \frac{\mathrm{e}^{-|\mathbf{k}|\cdot|x_3|}}{|\mathbf{k}|} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}.}$$

- We recognize the 1d Coulomb kernel in red.
- The other part is oscillating in $\mathbf{x}$, and exponentially decaying away from the slab («*details fade away*»).

If $f(\mathbf{x}, x_3) = f(x_3)$ only depends on the third variable, then

$$\int_{[0,L]^2\times\mathbb{R}} f(\mathbf{y}, y_3) G_L(\mathbf{x}-\mathbf{y}; x_3 - y_3) \mathrm{d}\mathbf{y}\mathrm{d}y_3 = -2\pi \int_{\mathbb{R}} f(y_3)|x_3 - y_3| \mathrm{d}y_3.$$

and, with obvious notation,

$$\boxed{\frac{1}{L^2}\mathcal{D}_{3,L}(f) = \mathcal{D}_1(f).}$$

Define the Hartree term

$$\boxed{\widetilde{\mathcal{D}_1}(f) := -2\pi \iint_{\mathbb{R}\times\mathbb{R}} f(x)f(y)|x-y|\mathrm{d}x\mathrm{d}y,}$$ (well-defined whenever $(1+|x|)f(x) \in L^1(\mathbb{R})$).

Warning: The map $f \mapsto \widetilde{\mathcal{D}_1}(f)$ is **not** convex.

$$\widetilde{\mathcal{D}_1}(tf + (1-t)g) - t\widetilde{\mathcal{D}_1}(f) - (1-t)\widetilde{\mathcal{D}_1}(g) = -t(1-t)\widetilde{\mathcal{D}_1}(f-g).$$

If $f - g =: h$ is positive pointwise, then $\widetilde{\mathcal{D}_1}(f-g) = \widetilde{\mathcal{D}_1}(h) < 0$.

We define a regularized version of the Hartree term,

$$\boxed{\mathcal{D}_1(f) := 4\pi \int_{\mathbb{R}} \frac{|\widehat{f}(k)|^2}{k^2}\mathrm{d}k = 4\pi \int_{\mathbb{R}} |W_f|^2(x)\mathrm{d}x,} \quad \text{with} \quad W_f(x) := \int_{-\infty}^{x} f(y)\mathrm{d}y.$$

This is well-defined whenever $W_f \in L^2(\mathbb{R})$. In particular, $W(\infty) = \int_{\mathbb{R}} f = 0$ (**neutral system only**).

Lemma

- *The map $f \mapsto \mathcal{D}_1(f)$ is strictly convex on $\mathcal{C} := \{f \in L^1(\mathbb{R}),\ W_f \in L^2(\mathbb{R})\}$.*
- *If $f \in \mathcal{C}$ satisfies $|x|f(x) \in L^1(\mathbb{R})$, then $\mathcal{D}_1(f) = \widetilde{\mathcal{D}_1}(f)$.*
- *If $f \in \mathcal{C}$, then $\mathcal{D}_1(f) = 4\pi \iint_{(\mathbb{R}_+)^2\cup(\mathbb{R}_-)^2} \min\{|x|,|y|\} f(x)f(y)\mathrm{d}x\mathrm{d}y = \int_{\mathbb{R}} f(x)\Phi_f(x)\mathrm{d}x$.*

Idea of the proof. $$|x| + |y| - |x-y| = \begin{cases} 2\min\{|x|,|y|\} & \text{on} \quad (\mathbb{R}_+)^2 \cup (\mathbb{R}_-)^2 \\ 0 & \text{else.} \end{cases}$$

Kohn-Sham models (reduced Hartree-Fock)

One-body density matrix: $\gamma \in \mathcal{S}(L^2(\mathbb{R}^3))$ satisfying the Pauli principle $0 \leq \gamma \leq 1$.

For *homogeneous* 2d materials, we request that γ commutes with all $\mathbb{R}^2$ translations:

$$\forall \mathbf{R} \in \mathbb{R}^2 \subset \mathbb{R}^3, \quad \tau_{\mathbf{R}} \gamma = \gamma \tau_{\mathbf{R}}, \quad \text{with} \quad \tau_{\mathbf{R}} f(\mathbf{x}, x_3) := f(\mathbf{x} - \mathbf{R}, x_3).$$

Equivalently, $\gamma(\mathbf{x}, x_3; \mathbf{y}, y_3) = \gamma(\mathbf{x} - \mathbf{y}, x_3; \mathbf{0}, y_3) =: \gamma(\mathbf{x} - \mathbf{y}, x_3, y_3)$.

For such one-body density matrix, the density $\rho_\gamma(\mathbf{x}, x_3) := \gamma(\mathbf{x}, x_3; \mathbf{x}, x_3)$ satisfies

$$\rho_\gamma(\mathbf{x}, x_3) = \rho_\gamma(x_3).$$

Trace per unit surface. Set $\Gamma := [0,1]^2 \times \mathbb{R} \subset \mathbb{R}^3$ (tube),

$$\underline{\mathrm{Tr}}(\gamma) := \mathrm{Tr}_3(\mathbb{1}_\Gamma \gamma \mathbb{1}_\Gamma) = \int_{\mathbb{R}} \rho_\gamma(x_3) \mathrm{d}x_3.$$

reduced Hartree-Fock energy per unit surface

$$\boxed{\mathcal{E}_3^{\mathrm{rHF}}(\gamma) := \frac{1}{2} \underline{\mathrm{Tr}}(-\Delta_3 \gamma) + \frac{1}{2} \mathcal{D}_1(\rho_\gamma - \mu).}$$

Remark: This energy still depends on the three-dimensional object $\gamma \in \mathcal{S}(L^2(\mathbb{R}^3))$.

Can we find a *reduced* one-dimensional model?

Minimization set = $\mathcal{P} \cap \{\gamma, \ \underline{\mathrm{Tr}}(\gamma) = Z\}$ **(neutrality condition)** with

$$\mathcal{P} := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)), \quad 0 \le \gamma \le 1, \quad \forall \mathbf{R} \in \mathbb{R}^2, \ \tau_{\mathbf{R}}\gamma = \gamma\tau_{\mathbf{R}}\right\}.$$

Theorem (DG, Lahbabi, Maichine, 2021)

Introduce $\mathcal{G} := \left\{G \in \mathcal{S}(L^2(\mathbb{R})), \quad G \ge 0, \quad \mathrm{Tr}_1(G) < \infty\right\}$. *Then, for any (representable) density* ρ,

$$\inf\left\{\frac{1}{2}\underline{\mathrm{Tr}}(-\Delta_3\gamma), \quad \gamma \in \mathcal{P}, \quad \rho_\gamma = \rho\right\} = \inf\left\{\frac{1}{2}\mathrm{Tr}_1(-\Delta_1 G) + \pi\mathrm{Tr}(G^2), \quad G \in \mathcal{G}, \quad \rho_G = \rho\right\}.$$

Remarks:

- Works for general Kohn-Sham models (assuming *no «in-plane» symmetry breaking*).
- The new minimization problem is set on operators acting on $L^2(\mathbb{R}^1)$.
- There is no Pauli principle for G. It is replaced by a penalization term $+\pi\mathrm{Tr}(G^2)$ in the energy.
- The term $\mathrm{Tr}(G^2)$ is sometime called the Tsallis or Rényi entropy.

Constrained-search

$$\begin{aligned}\inf_\gamma\left\{\mathcal{E}_3^{\mathrm{rHF}}(\gamma)\right\} &= \inf_\rho\left\{\frac{1}{2}\mathcal{D}_1(\rho-\mu) + \inf_{\gamma\to\rho}\left\{\frac{1}{2}\underline{\mathrm{Tr}}(-\Delta_3\gamma)\right\}\right\} \\ &= \inf_\rho\left\{\frac{1}{2}\mathcal{D}_1(\rho-\mu) + \inf_{G\to\rho}\left\{\frac{1}{2}\mathrm{Tr}_1(-\Delta_1 G) + \pi\mathrm{Tr}_1(G^2)\right\}\right\} = \inf_G \mathcal{E}_1^{\mathrm{rHF}}(G)\end{aligned}$$

with the reduced rHF model

$$\boxed{\mathcal{E}_1^{\mathrm{rHF}}(G) := \frac{1}{2}\mathrm{Tr}_1(-\Delta_1 G) + \pi\mathrm{Tr}_1(G^2) + \frac{1}{2}\mathcal{D}_1(\rho_G-\mu).}$$

Proof of the theorem

Consider $\mathcal{F} : L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ the partial Fourier transform

$$(\mathcal{F}f)(\mathbf{k}, x_3) = \frac{1}{(2\pi)} \int_{\mathbb{R}^2} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}} f(\mathbf{x}, x_3) \mathrm{d}\mathbf{x}.$$

Bloch theory. Since $\gamma \in \mathcal{P}$ commutes with $\mathbb{R}^2$-translations, there is $\{\gamma_{\mathbf{k}}\}_{\mathbf{k}\in\mathbb{R}^2}$ with $\gamma_{\mathbf{k}} \in \mathcal{S}(L^2(\mathbb{R}))$ so that

$$\boxed{\mathcal{F}\gamma\mathcal{F}^{-1} = \int_{\mathbb{R}^2}^{\oplus} \gamma_{\mathbf{k}} \mathrm{d}\mathbf{k},} \quad \text{in the sense} \quad (\mathcal{F}\gamma f)(\mathbf{k}, \cdot) = \gamma_{\mathbf{k}} \left[(\mathcal{F}f)(\mathbf{k}, \cdot) \right].$$

We have

$$0 \le \gamma_{\mathbf{k}} \le 1, \quad \rho_\gamma = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \rho_{\gamma_{\mathbf{k}}}, \quad \text{and} \quad \underline{\mathrm{Tr}}(\gamma) = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \mathrm{Tr}_1(\gamma_{\mathbf{k}}).$$

Now, we set

$$\boxed{G := \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \gamma_{\mathbf{k}} \mathrm{d}\mathbf{k},} \quad \text{in the sense} \quad Gf = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} (\gamma_{\mathbf{k}} f) \mathrm{d}\mathbf{k}.$$

We have

$$G \ge 0, \quad \rho_G = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \rho_{\gamma_{\mathbf{k}}} = \rho_\gamma, \quad \mathrm{Tr}_1(G) = \frac{1}{(2\pi)^2} \int_{\mathbb{R}^2} \mathrm{Tr}_1(\gamma_{\mathbf{k}}) = \underline{\mathrm{Tr}}(\gamma).$$

Kinetic energy

Since $\mathcal{F}(-\Delta_3)\mathcal{F}^{-1} = |\mathbf{k}|^2 + (-\Delta_1)$,

$$\underline{\mathrm{Tr}}\,(-\Delta_3\gamma) = \frac{1}{(2\pi)^2}\int_{\mathbb{R}^2}\left(|\mathbf{k}|^2\mathrm{Tr}(\gamma_{\mathbf{k}}) + \mathrm{Tr}_1(-\Delta_1\gamma_{\mathbf{k}})\right)\mathrm{d}\mathbf{k}$$

$$= \frac{1}{(2\pi)^2}\int_{\mathbb{R}^2}|\mathbf{k}|^2\mathrm{Tr}(\gamma_{\mathbf{k}})\mathrm{d}\mathbf{k} + \mathrm{Tr}_1(-\Delta_1 G).$$

Write $G = \sum g_j|\phi_j\rangle\langle\phi_j|$, with $g_j \ge 0$ and $\sum g_j = \mathrm{Tr}_1(G)$, and define

$$\boxed{m_j(k) := \langle\phi_j, \gamma_{\mathbf{k}}\phi_j\rangle,} \quad \text{so that} \quad 0 \le m_j(\mathbf{k}) \le 1 \quad \text{and} \quad \frac{1}{(2\pi)^2}\int_{\mathbb{R}^2} m_j(\mathbf{k})\mathrm{d}\mathbf{k} = g_j.$$

Then

$$\frac{1}{(2\pi)^2}\int_{\mathbb{R}^2}|\mathbf{k}|^2\mathrm{Tr}(\gamma_{\mathbf{k}})\mathrm{d}\mathbf{k} = \frac{1}{(2\pi)^2}\sum_j\int_{\mathbb{R}^2}|\mathbf{k}|^2 m_j(\mathbf{k})\mathrm{d}\mathbf{k}$$

$$\ge \frac{1}{(2\pi)^2}\sum_j \min\left\{\int_{\mathbb{R}^2}|\mathbf{k}|^2 m(\mathbf{k})\mathrm{d}\mathbf{k},\ 0 \le m(\mathbf{k}) \le 1,\ \frac{1}{(2\pi)^2}\int_{\mathbb{R}^2} m(\mathbf{k})\mathrm{d}\mathbf{k} = g_j\right\}.$$

«Bath-tube principle»: the minimum is obtained for $m_j^*(\mathbf{k}) = \mathbb{1}(|\mathbf{k}| < k_j)$ with $k_j = 2\sqrt{\pi g_j}$.
This proves

$$\frac{1}{(2\pi)^2}\int_{\mathbb{R}^2}|\mathbf{k}|^2\mathrm{Tr}(\gamma_{\mathbf{k}})\mathrm{d}\mathbf{k} \ge 2\pi\sum_j g_j^2 = 2\pi\mathrm{Tr}_1\left(G^2\right).$$

Conversely, given $G = \sum_j g_j|\phi_j\rangle\langle\phi_j|$, we have equality for γ^* defined by

$$\gamma^* := \int_{\mathbb{R}^2}^{\oplus}\gamma^*_{\mathbf{k}}, \quad \text{with} \quad \gamma^*_{\mathbf{k}} := \sum_j m_j^*(\mathbf{k})|\phi_j\rangle\langle\phi_j|. \qquad \square$$

We now study the one-dimensional minimization problem

$$\boxed{\inf\left\{\frac{1}{2}\mathrm{Tr}_1(-\Delta G)+\pi\mathrm{Tr}_1(G^2)+\frac{1}{2}\mathcal{D}_1(\rho_G-\mu),\quad G\in\mathcal{S}(L^2(\mathbb{R})),\ G\geq 0,\ \mathrm{Tr}_1(G)=Z\right\}.}$$

Proposition

There is a unique minimizer G_*. This minimizer satisfies the Euler-Lagrange equations

$$\begin{cases} G_* = \frac{1}{2\pi}(\lambda - H_*)_+ \\ H_* := -\frac{1}{2}\Delta + \Phi_* \\ -\Phi_*'' = 4\pi(\rho_* - \mu), \quad \Phi_*'(\pm\infty) = 0, \quad \Phi_*(0) = 0. \end{cases}$$

Remarks

- The problem is **strictly** convex in G, due to the $\mathrm{Tr}_1(G^2)$ term (hence uniqueness of the minimizer).
- We have $G_* = \frac{1}{2\pi}(\lambda - H_*)_+$ instead of the *usual* $\gamma_* = \mathbb{1}(\lambda - H_* > 0)$.
- In particular, since $\lambda \mapsto \mathrm{Tr}(\lambda - H_*)_+$ is **strictly** increasing, the Fermi level is unique.

Proposition

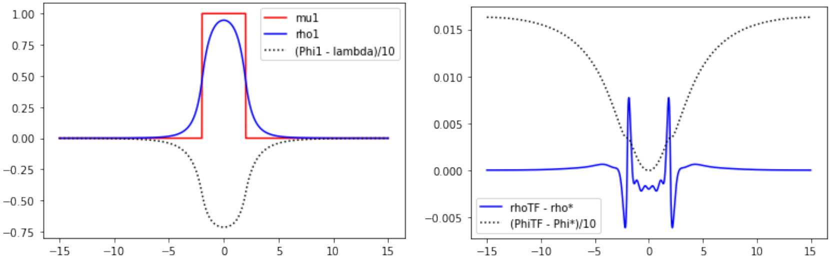
Assume $|x|^3\mu(x)\in L^1(\mathbb{R})$. Then, if $|x|^3\rho(x)\in L^1(\mathbb{R})$ as well, G_* is finite rank, and its density ρ_* is exponentially decaying away from the slab.

The proof relies on Bargmann's bound (very specific to one-dimension):
If $V:\mathbb{R}\to\mathbb{R}$ satisfies $\int_{\mathbb{R}}|x|V_-(x)<\infty$, then $-\partial_{xx}^2+V$ has a finite number of negative eigenvalues.

Numerical illustrations

Numerical results 1

$$\mu_1(x) = \mathbb{1}(|x| < 2)$$

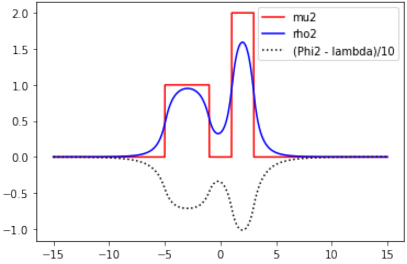


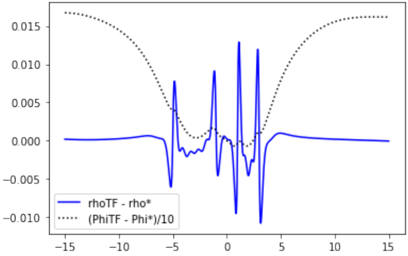
Remarks

- The Thomas-Fermi density ρ_{TF} and rHF density ρ_* are **very** close!
- The optimal G_* has 15 positive eigenvalues. The largest one is around 1.07.

Numerical results 2 (with dipolar moment)

$$\mu_2(x) = \mathbb{1}(-5 < x < -2) + 2 \cdot \mathbb{1}(1 < x < 3)$$



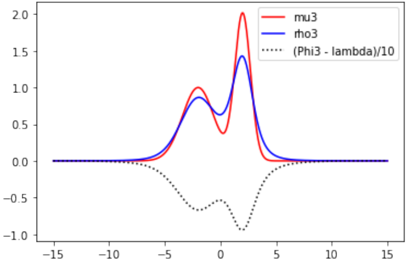


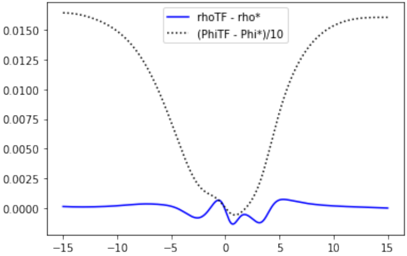
Remarks

- The Thomas-Fermi density ρ_{TF} and rHF density ρ_* are **very** close!
- The optimal G_* has 17 positive eigenvalues. The largest one is around 1.44.
- The *screening* in the rHF model is close to perfect!

Numerical results 3 (smooth case)

$$\mu_3(x) = \mathrm{e}^{-\frac{1}{4}(x+2)^2} + 2 \cdot \mathrm{e}^{-(x-2)^2}.$$





Remarks

- The Thomas-Fermi density ρ_{TF} and rHF density ρ_* are **extremely** close!
- The optimal G_* has 19 positive eigenvalues. The largest one is around 1.32.
- The *screening* in the rHF model is close to perfect!

Bonus: a Lieb-Thirring type inequality

General dimension

Let $\gamma \in \mathcal{S}(L^2(\mathbb{R}^{s+d}))$ be translationally invariant in its first s variables, and so that $0 \leq \gamma \leq 1$. Then there is $G \in \mathcal{S}(L^2(\mathbb{R}^d))$ so that $\rho_\gamma = \rho_G$ and

$$\boxed{\underline{\mathrm{Tr}}\left(-\Delta_{s+d}\gamma\right) \geq \mathrm{Tr}_d\left(-\Delta_d G\right) + 2c_{\mathrm{TF}}(s)\mathrm{Tr}_d(G^{1+\frac{2}{s}}).}$$

Conversely, for each G, there is a γ such that we have equality.

If there is equality, the «Lieb-Thirring» inequality for γ gives

$$\mathrm{Tr}_d\left(-\Delta_d G\right) + 2c_{\mathrm{TF}}(s)\mathrm{Tr}_d(G^{1+\frac{2}{s}}) = \underline{\mathrm{Tr}}\left(-\Delta_{s+d}\gamma\right) \geq K_{\mathrm{LT}}(d+s)\int_{\mathbb{R}^d} \rho_G^{1+\frac{2}{d+s}}.$$

After optimization over scaling $\lambda \mapsto \lambda G$, we obtain

Theorem (Lieb-Thirring type inequality)

There is a constant K so that, for all $G \in \mathcal{S}(L^2(\mathbb{R}^d))$ with $G \geq 0$, and for all $s \in \mathbb{N}$,

$$K\left(\int_{\mathbb{R}^d} \rho_G^{1+\frac{2}{s+d}}\right)^{1+\frac{s}{d}} \leq \left(\mathrm{Tr}_d(G^{1+\frac{s}{d}})\right)^{s/d} \mathrm{Tr}_d\left(-\Delta_d G\right).$$

This type of inequalities was recently studied in [Frank/Gontier/Lewin, Commun. Math. Phys. 384 (2021)].

Theorem (Frank, DG, Lewin, 2021)

For all $d \geq 1$ and all $1 \leq p \leq 1 + \frac{2}{d}$, there is an optimal constant $K_{p,d}$ so that, for all $G \in \mathcal{S}(L^2(\mathbb{R}^d))$,

$$K_{p,d} \left(\int_{\mathbb{R}^d} \rho_G^p \right)^{\theta_1} \leq \left(\mathrm{Tr}_d(G^q) \right)^{\theta_2} \mathrm{Tr}_d \left(-\Delta_d G \right), \quad \textit{where} \quad q := \frac{2p + d - dp}{2 + d - dp}.$$

In addition, $K_{p,d}$ is the **dual constant** *of the usual Lieb-Thirring constant $L_{\gamma,d}$, in the sense*

$$K_{p,d} \left(L_{\gamma,d} \right)^{\frac{2}{d}} = \left(\frac{\gamma}{\gamma + \frac{d}{2}} \right)^{\frac{2\gamma}{d}} \left(\frac{d}{2\gamma + d} \right), \quad \textit{with} \quad \gamma + \frac{d}{2} = \frac{p}{p-1}, \quad \textit{so that} \quad \frac{\gamma}{\gamma - 1} = q.$$

The previous case corresponds to $p = 1 + \frac{2}{d+s}$, which gives $\gamma = 1 + \frac{s}{2}$.
In particular, $\gamma \geq \frac{3}{2}$: the best constant is the semi-classical one.

In other words, for all $d \in \mathbb{N}$ and $s \in \mathbb{N}$,

$$\frac{1}{2} \mathrm{Tr}_d \left(-\Delta_d G \right) + c_{\mathrm{TF}}(s) \mathrm{Tr}_d (G^{1 + \frac{2}{s}}) \geq c_{\mathrm{TF}}(d+s) \int_{\mathbb{R}^d} \rho_G^{1 + \frac{2}{d+s}}.$$

The reduced rHF energy is greater than the reduced Thomas–Fermi one.

Conclusion

For Homogeneous two-dimensional slab in three-dimensional space:

Thomas–Fermi

- ρ_{TF} decays as $|x|^{-6}$ away from the slab;
- perfect screening.

reduced Hartree-Fock

- ρ_* decays exponentially fast away from the slab (up to some technical assumption)
- ρ_* and ρ_{TF} are very close.
- Very good screening property.

The Pauli principle is replaced by a Tsallis entropy term through the collapse of dimensions.

Reference: Gontier/Lahbabi/Maichine, Commun. Math. Phys (2021).

Thank you for your attention