The Local Density Approximation in Density Functional Theory

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Based on joint work with Mathieu Lewin and Elliott Lieb:

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Large Coulomb Systems and Related Matters

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Density Functional Theory

Formulate energy minimization in terms of the **particle density** only:

$$\Psi(x_1,\dots,x_N) \mapsto \rho_\Psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(x,x_2,\dots,x_N)|^2 dx_2 \cdots dx_N$$

Levy–Lieb formulation of the ground state energy: $\inf_\Psi = \inf_\rho \inf_{\Psi,\rho_\Psi=\rho}$:

$$E^V(N) = \inf_\Psi \left\langle \Psi \left| H_V^N \right| \Psi \right\rangle = \inf_{\rho\in\mathcal{R}_N} \left\{ F_{\mathrm{LL}}(\rho) + \int_{\mathbb{R}^3} V(x)\rho(x)dx \right\}$$

where

$$F_{\mathrm{LL}}(\rho) := \min_{\Psi,\rho_\Psi=\rho} \langle \Psi | H_0^N | \Psi \rangle = \min_{\Psi,\rho_\Psi=\rho} \left\langle \Psi \left| -\sum_{i=1}^N \nabla_{x_i}^2 + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_k|} \right| \Psi \right\rangle$$

and

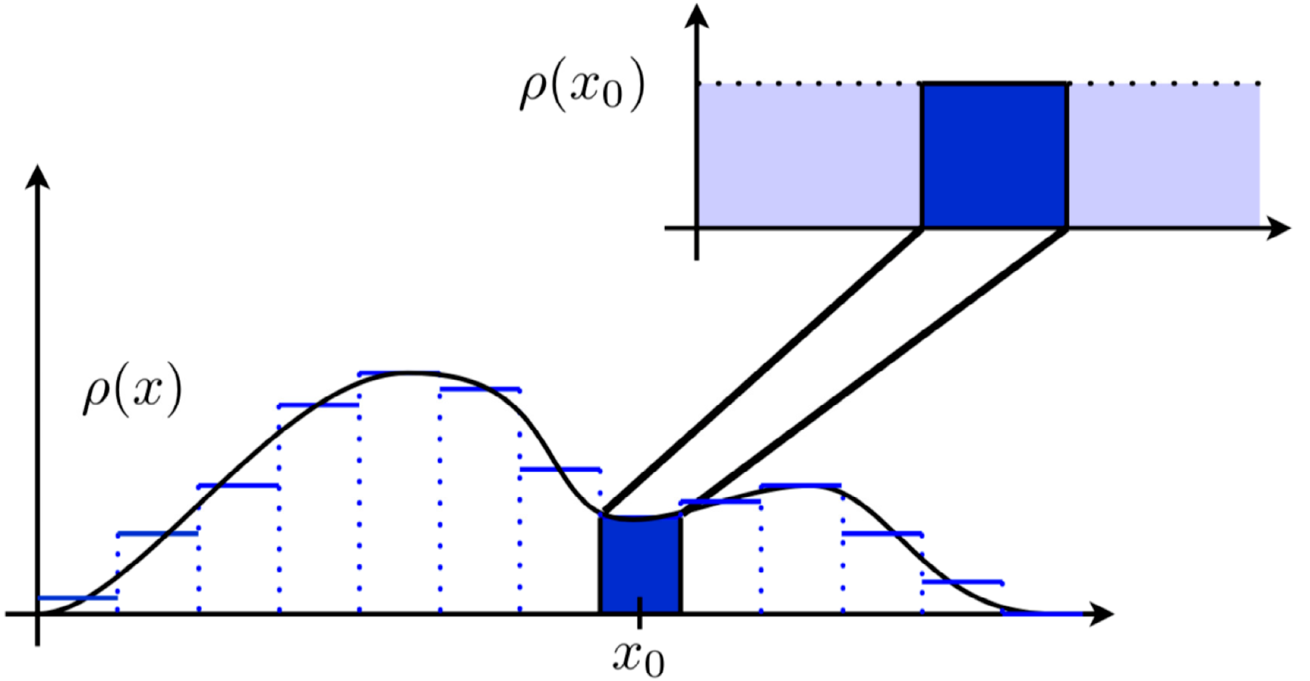
$$\mathcal{R}_N = \{\rho \ge 0, \int_{\mathbb{R}^3} \rho = N, \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 < \infty\}$$

[Lieb '83].

Local Density Approximation

For **slowly varying** densities ρ,

$$F_{\mathrm{LL}}(\rho) \approx \underbrace{\frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy}_{\substack{\textbf{non-local} \\ \text{classical Coulomb energy}}} + \underbrace{\int_{\mathbb{R}^3} f(\rho(x))dx}_{\substack{\textbf{local} \\ \text{energy per unit volume} \\ \text{of uniform electron gas}}}$$



Main Result

THEOREM (Justification of LDA)
There exists a universal constant $C > 0$ and a universal function $f : \mathbb{R}_+ \to \mathbb{R}$ such that

$$\left| \tilde{F}_{\rm LL}(\rho) - \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx\, dy - \int_{\mathbb{R}^3} f(\rho(x)) dx \right|$$

$$\leq \varepsilon \int_{\mathbb{R}^3} \left(\rho(x) + \rho(x)^2\right) dx + \frac{C(1+\varepsilon)}{\varepsilon} \int_{\mathbb{R}^3} \left|\nabla \sqrt{\rho(x)}\right|^2 dx + \frac{C}{\varepsilon^{15}} \int_{\mathbb{R}^3} \left|\nabla \sqrt{\rho(x)}\right|^4 dx$$

for every $\varepsilon > 0$ and every $\rho \in L^1 \cap L^2(\mathbb{R}^3)$ such that $\nabla\sqrt{\rho} \in L^2 \cap L^4(\mathbb{R}^3)$.

Remarks:

- Last term can be replaced by $\varepsilon^{1-4p} \int |\nabla \rho^\theta|^p$ with $p > 3$, $\theta > 0$ and $2 \leq p\theta \leq 1 + p/2$.
- $\tilde{F}_{\rm LL}$ grand-canonical version (convex hull), but same result expected for $F_{\rm LL}$.
- For $\rho(x) = \sigma(x/N^{1/3})$ we find

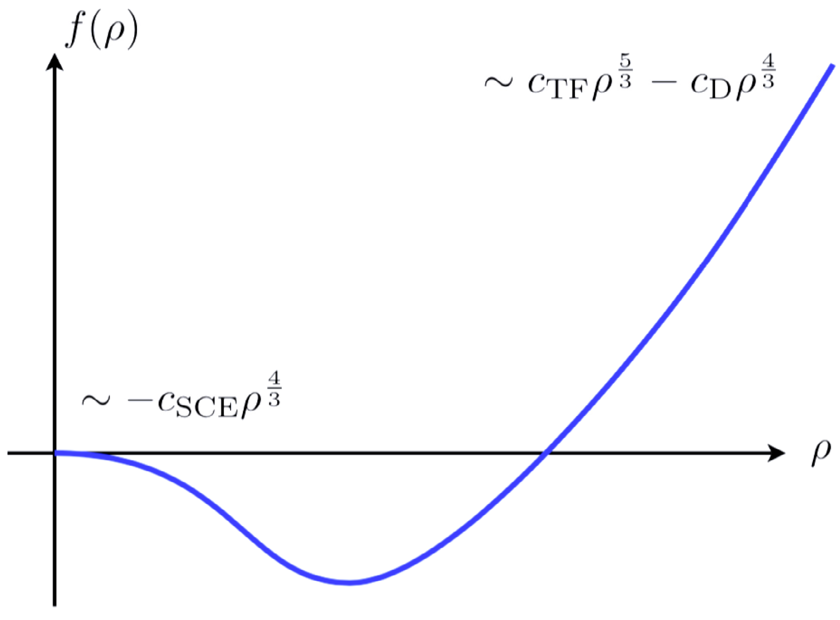
$$\tilde{F}_{\rm LL}(\rho) = \frac{N^{5/3}}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\sigma(x)\sigma(y)}{|x-y|} dx\, dy + N \int_{\mathbb{R}^3} f(\sigma(x)) dx + O(N^{11/12})$$

Energy of the Uniform Electron Gas

For $\rho_0 > 0$ we have

$$f(\rho_0) = \lim_{\ell\to\infty} \frac{1}{|\ell\Omega|} \left(\tilde{F}_{\rm LL}(\rho_0 \mathbb{1}_{\ell\Omega} * \chi) - \frac{\rho_0^2}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\mathbb{1}_{\ell\Omega} * \chi(x) \mathbb{1}_{\ell\Omega} * \chi(y)}{|x-y|} dx\, dy \right)$$

The limit exists and is independent of Ω and χ [Hainzl-Lewin-Solovej '09].



- $c_{\rm TF} = \frac{3}{5}(3\pi^2)^{2/3}$
- $c_{\rm D} = \frac{3}{4}(3/\pi)^{1/3}$
- $1.4442 \leq c_{\rm SCE} \leq 1.4508$ (strongly correlated electrons)
- next order for large ρ believed to by $\rho \ln \rho$ [Macke '50, Bohm-Pines '53, GellMann-Brueckner '57]
- non-smooth because of phase transitions (solid/fluid, ferro/paramagnetic)

Phase Diagram

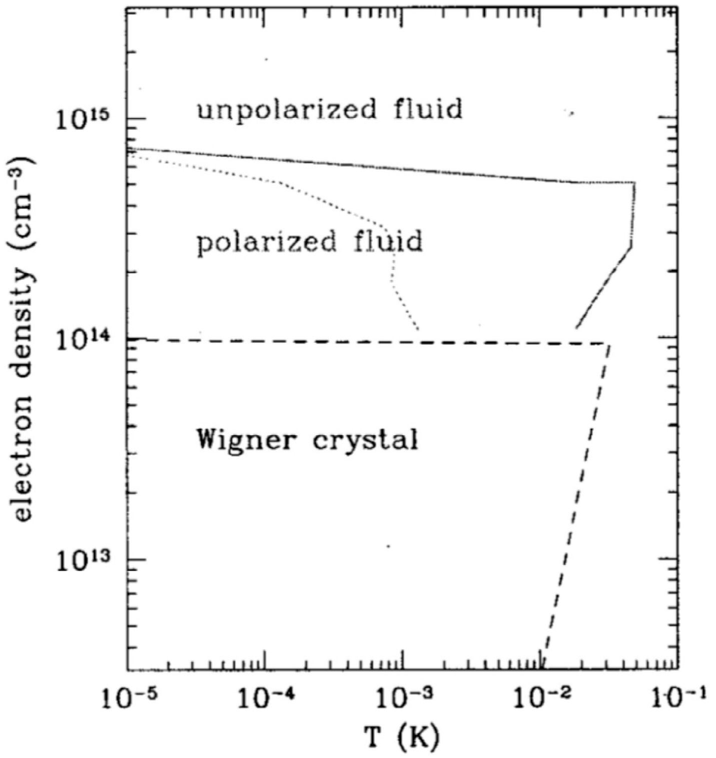


FIG. 8. The phase diagram of the electron gas. Conversion to units of cm and K was done using $a_0 = 1.3$ nm and Ry = 250 K using estimates [3] of the effective mass and the dielectric constant of SrB_6. The solid line is the mean- eld estimate of the magnetic transition temperature from the Stoner model, where the spin interaction is estimated from the zero temperature QMC data. The dotted line is the energy difference between the unpolarized and partially polarized system.

Zong, Lin, Ceperley, PRE (2002)

Exchange-Correlation Energy

In practice one often considers the **exchange-correlation** energy

$$E_{\rm xc}(\rho) = \tilde{F}_{\rm LL}(\rho) - \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx\, dy - T(\rho)$$

where $T(\rho)$ is the (**Kohn-Sham**) kinetic energy functional

$$T(\rho) = \min_{\substack{0\leq\gamma\leq\mathbb{1} \\ \rho_\gamma = \rho}} \operatorname{Tr}(-\nabla^2)\gamma$$

Our result on the LDA applies to $E_{\rm xc}(\rho)$ as well, since

THEOREM (LDA for kinetic energy) [Nam '18, LLS '19]. For any $\varepsilon > 0$,

$$T(\rho) \geq c_{\rm TF}(1-\varepsilon)\int_{\mathbb{R}^3} \rho(x)^{5/3} dx - \frac{C}{\varepsilon^{13/3}} \int_{\mathbb{R}^3} |\nabla\sqrt{\rho(x)}|^2 dx$$

$$T(\rho) \leq c_{\rm TF}(1+\varepsilon)\int_{\mathbb{R}^3} \rho(x)^{5/3} dx + \frac{C(1+\varepsilon)}{\varepsilon} \int_{\mathbb{R}^3} |\nabla\sqrt{\rho(x)}|^2 dx$$

Upper Bound on $\boldsymbol{T(\rho)}$

Recall that

$$P_t = \mathbb{1}\left(-\nabla^2 \le \frac{5}{3} c_{\mathrm{TF}} t^{2/3}\right)$$

has density $\rho_{P_t} = t$ and kinetic energy density $c_{\mathrm{TF}} t^{5/3}$.

For the **upper bound** on $T(\rho)$, use as a trial density matrix the 'layer cake' trial state

$$\gamma = \int_0^\infty \sqrt{\eta\left(\frac{t}{\rho(x)}\right)}\mathbb{1}\left(-\nabla^2 \le \frac{5}{3} c_{\mathrm{TF}} t^{2/3}\right)\sqrt{\eta\left(\frac{t}{\rho(x)}\right)} t^{-1} dt$$

and optimize over the choice of η with $\int_0^\infty \eta(t)dt = 1$ and $\int_0^\infty \eta(t)t^{-1}dt \le 1$

Strategy of the Proof (of the Main Theorem)

The key is to prove an approximate **locality** of the **indirect energy**

$$F_{\rm ind}(\rho) = \tilde{F}_{\rm LL}(\rho) - \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}dx\,dy$$

- For a tiling $\{\Omega_{\ell,j}\}$ of $\mathbb{R}^3$ with boxes of size $\ell = \ell(\varepsilon)$,

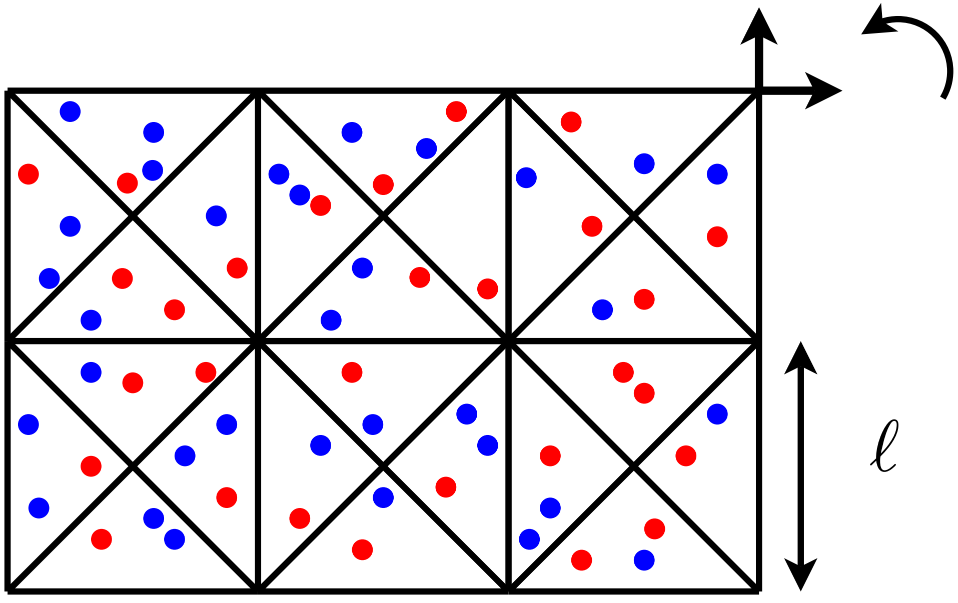
$$F_{\rm ind}(\rho) \approx \sum_j F_{\rm ind}(\rho \mathbb{1}_{\Omega_{\ell,j}} * \chi)$$

- In each box, estimate difference of $F_{\rm ind}(\rho \mathbb{1}_{\Omega_{\ell,j}} * \chi)$ and $F_{\rm ind}(\bar\rho \mathbb{1}_{\Omega_{\ell,j}} * \chi)$ in terms of derivatives of ρ
- Compare $F_{\rm ind}(\bar\rho \mathbb{1}_{\Omega_{\ell,j}} * \chi)$ with $f(\bar\rho)|\Omega_{\ell,j}|$.

Locality: Lower Bound

THEOREM (Graf-Schenker '94) Let $\{\Delta_n\}$ be a tiling of $\mathbb{R}^3$ of tetrahedra (of size 1). Then, for all $N \geq 2$, $z_j \in \mathbb{R}$ and $x_j \in \mathbb{R}^3$,

$$\sum_{1\leq i<j\leq N} \frac{z_i z_j}{|x_i - x_j|} \geq \frac{1}{\ell^3} \int_{[0,\ell]^3 \times SO(3)} \sum_n \left(\sum_{1\leq i<j\leq N} \frac{z_i z_j \mathbb{1}_{g\ell\Delta_n}(x_i) \mathbb{1}_{g\ell\Delta_n}(x_j)}{|x_i - x_j|} \right) dg - \frac{C}{\ell} \sum_{i=1}^N z_j^2$$



Tiling with tetrahedra, averaged over translations and rotations.

Local number of particles not fixed $\to$ grand-canonical description

Difficulties in the Upper Bound

For a suitable tiling we want to prove that

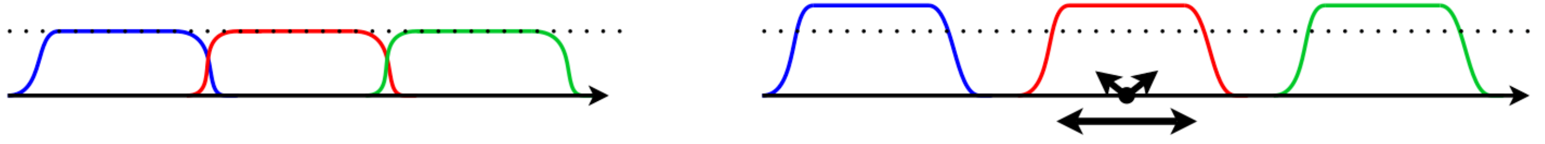
$$F_{\mathrm{ind}}(\rho) \lesssim \sum_j F_{\mathrm{ind}}(\rho \mathbb{1}_{\Omega_{\ell,j}} * \chi)$$

Difficulties:

- Need a trial state with the exact density ρ
- Tensor products work badly for fermions if the supports intersect!

Our solution:

- Partition of unity with holes, average over translations and dilations
- Averaging of the direct term gives error $\sim \delta^2 \int \rho^2$, where $\delta =$ size of holes
- Difficult to do canonically



Summary and Open Problems

- We give a mathematically rigorous justification of the **Local Density Approximation** in Density Functional Theory.
- We provide a quantitative estimate on the difference between the (grand-canonical) Levy–Lieb energy of a given density and the integral over the **Uniform Electron Gas** energy of this density.

Many **open problems** remain:

- Extension to canonical, pure state LL energy functional
- Next order correction terms, expected to scale as $N^{1/3}$ for densities of the form $\rho(x) = \sigma(N^{-1/3}x)$.
- Phase transitions, Wigner crystal, . . .