Recent Results in Density Functional Theory

Mathieu LEWIN

(CNRS & Paris-Dauphine University)

joint works with Elliott H. Lieb (Princeton) & Robert Seiringer (IST Austria)

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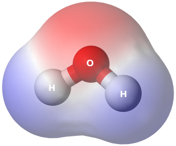
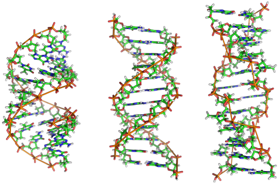
Schrödinger's equation for N electrons

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

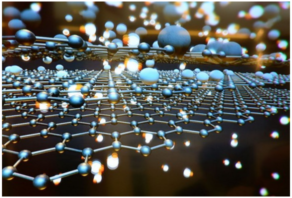
$$E^N(V) = \inf \sigma\big(H^N(V)\big) = \inf_{\substack{\Gamma=\Gamma^*\geq 0\\ \text{anti-sym.}\\ \operatorname{tr}\Gamma=1}} \operatorname{tr}\big(H^N(V)\,\Gamma\big)$$



$N = 10$ electrons in water



$N \sim 10^3$ in macromolecules



$N \sim 10^{13}$ in nano-materials

Lieb's convex formulation of DFT (1983)

$E^N(V)$ is concave in V. Its dual variable is the density: for $\Gamma = \sum_j n_j |\Psi_j\rangle\langle\Psi_j|$,

$$\rho_\Gamma(x) = N \sum_j n_j \sum_{\sigma_1,\dots,\sigma_N \in \{\uparrow,\downarrow\}} \int_{(\mathbb{R}^3)^{N-1}} |\Psi_j(x,\sigma_1,x_2,\sigma_2,\dots,x_N,\sigma_N)|^2 \, dx_2 \cdots dx_N$$

Theorem (Lieb's universal functional)

$$F[\rho] := \min_{\substack{\Gamma \text{ anti-sym.} \\ \rho_\Gamma = \rho}} \operatorname{tr}\left(H^N(0)\Gamma\right) = \min_{\substack{\Gamma \text{ anti-sym.} \\ \rho_\Gamma = \rho}} \operatorname{tr}\left(\left(-\Delta_{\mathbb{R}^{3N}} + \sum_{1\le j<k\le N} \frac{1}{|x_j - x_k|}\right)\Gamma\right)$$

is finite if and only if $\int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 < \infty$. *It is convex and we have the Legendre-Fenchel duality*

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

Hoffmann-Ostenhof '81, Harriman '81, Lieb '83

Goal of the talk:

- universal bounds on F and other functionals, valid for all densities
- local density approximation for very flat densities ($\to$ Uniform Electron Gas)

Low and high density limits

$$F\big[\lambda^3\rho(\lambda\cdot)\big] := \min_{\substack{\Gamma \text{ antisym.}\\ \rho_\Gamma=\rho}} \operatorname{tr}\Big(-\lambda^2\Delta_{\mathbb{R}^{3N}} + \lambda \sum_{1\le j<k\le N}\frac{1}{|x_j-x_k|}\Big)\Gamma$$

Theorem (Low and high density limits)

For any $\rho \in L^1(\mathbb{R}^3,\mathbb{R}_+)$ so that $\int_{\mathbb{R}^3}\rho = N$ and $\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}|^2 < \infty$, we have

$$\text{(i)}\ \lim_{\lambda\to0}\frac{F\big[\lambda^3\rho(\lambda\cdot)\big]}{\lambda} = \min_{\substack{\mathbb{P} \text{ sym.}\\ \rho_{\mathbb{P}}=\rho}}\int_{\mathbb{R}^{3N}}\sum_{1\le j<k\le N}\frac{d\mathbb{P}(x_1,\dots,x_N)}{|x_j-x_k|} =: F_{\rm cl}[\rho]$$

$$\text{(ii)}\ \lim_{\lambda\to\infty}\frac{F\big[\lambda^3\rho(\lambda\cdot)\big]}{\lambda^2} = \min_{\substack{\Gamma \text{ antisym.}\\ \rho_\Gamma=\rho}}\operatorname{tr}(-\Delta_{\mathbb{R}^{3N}})\Gamma = \min_{\substack{0\le\gamma\le1\\ \rho_\gamma=\rho}}\operatorname{tr}(-\Delta_{\mathbb{R}^3})\gamma =: T[\rho]$$

CV of minimizers holds as well.

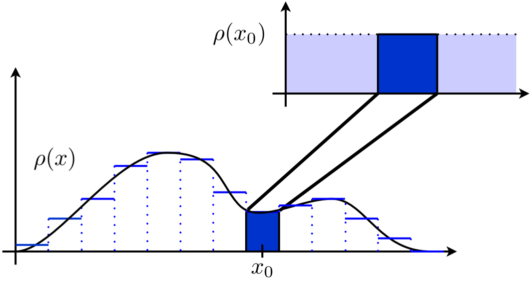
(i) Cotar-Friesecke-Kluppelberg '13-18, Bindini-De Pascale '18, M.L. '18

- $F_{\rm cl}[\rho]$ = multi-marginal optimal transport = strictly correlated electrons. Optimal $\mathbb{P}$ typically singular measure, supported on low dimension manifold
- (*ii*) is much easier than (*i*) since there is no loss of regularity
- Of course $F[\rho] \geq T[\rho] + F_{\rm cl}[\rho]$

Local Density Approximation

- simplest approximation, yet useful in many contexts
- basis for constructing better approximations
- will be shown to be valid for densities which are very flat on large sets

$$F[\rho] \approx \underbrace{\frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\,dx\,dy}_{\substack{\text{non local} \\ \text{classical Coulomb energy of } \rho}} + \underbrace{\int_{\mathbb{R}^3} f\left(\rho(x)\right)\,dx}_{\substack{\text{local} \\ f\,=\,\text{energy per unit vol.} \\ \text{of uniform electron gas}}}$$



Hohenberg-Kohn '64

Kinetic energy

$$T[\rho] = \min_{\substack{\Gamma \text{ antisym.} \\ \rho_\Gamma = \rho}} \operatorname{tr}(-\Delta_{\mathbb{R}^{3N}})\Gamma = \min_{\substack{0 \le \gamma \le 1 \\ \rho_\gamma = \rho}} \operatorname{tr}(-\Delta_{\mathbb{R}^3})\gamma$$

Theorem (Kinetic energy)

Define the Thomas-Fermi constant: $c_{\rm TF} = 3(3\pi^2)^{2/3}/5$. *For all* $\rho \in L^1(\mathbb{R}^3, \mathbb{R}_+)$ *with* $\int_{\mathbb{R}^3} \rho \in \mathbb{N}$ *and* $\int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 < \infty$, *and for all* $\varepsilon > 0$, *we have*

- **Local Density Approximation: Thomas-Fermi**

$$-\varepsilon \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} - \frac{C}{\varepsilon^{\frac{13}{3}}} \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 \le T[\rho] - c_{\rm TF} \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} \le \varepsilon \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} + \frac{C}{\varepsilon} \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2$$

- **Universal lower bound: Lieb-Thirring inequality**

$$T[\rho] \ge 0.77\, c_{\rm TF} \int_{\mathbb{R}^3} \rho(x)^{\frac{5}{3}}\, dx$$

Nam '18, M.L.-Lieb-Seiringer '19, Lieb-Thirring '75, Frank-Hundertmark-Jex-Nam '21

Example: $T[\rho(N^{-\frac{1}{3}}\cdot)] = c_{\rm TF} N \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} + O(N^{\frac{7}{8}})$

A simple trial state

Recall that the free Fermi sea $\mathbb{1}\left(-\Delta \leq 5c_{\rm TF}\,\rho^{2/3}/3\right)$ has the constant density ρ. For a nice function η with $\int_0^\infty \eta(t)\,dt = 1$ and $\int_0^\infty \eta(t)\,\frac{dt}{t} \leq 1$, we can represent

$$\rho(x) = \int_0^\infty \eta\left(\frac{t}{\rho(x)}\right)\,dt$$

$$\gamma = \int_0^\infty \sqrt{\eta\left(\frac{t}{\rho(x)}\right)}\,\mathbb{1}\left(-\Delta \leq \frac{5}{3}c_{\rm TF}\,t^{\frac{2}{3}}\right)\,\sqrt{\eta\left(\frac{t}{\rho(x)}\right)}\,\frac{dt}{t}$$

has density ρ, satisfies $\gamma \leq 1$ and has the kinetic energy

$$\mathrm{tr}(-\Delta)\gamma = A\int_{\mathbb{R}^3}|\nabla\sqrt{\rho}(x)|^2\,dx + c_{\rm TF}B\int_{\mathbb{R}^3}\rho(x)^{\frac{5}{3}}\,dx,$$

$$A = \int_0^\infty \frac{t^2\eta'(t)^2}{\eta(t)}\,dt, \qquad B = \int_0^\infty \eta(t)t^{\frac{2}{d}}\,dt$$

Taking η very concentrated at $t = 1$ proves the claimed upper bound on $T[\rho]$

Coulomb energy

Theorem (Coulomb energy)

▶ **Universal lower bound: Lieb-Oxford inequality**

$$\text{Coulomb} \geq \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy - \int_{\mathbb{R}^3}\rho(x)^{\frac{4}{3}}\,dx \times \begin{cases} 1.58 & \\ 1.45 & \textit{if } \rho \textit{ is cnst on its support,} \\ 1.25 & \textit{for HF states,} \\ 1.21 & \textit{for HF states with } \rho \textit{ cnst.} \end{cases}$$

Lieb '80, Lieb-Oxford '81, Lieb-Narnhofer '73, L.-Lieb-Seiringer '22

- used to calibrate famous functionals such as PBE, SCAN (Perdew-Sun '22)
- improves upon the previous best cnst 1.64 (Chan-Handy '99)
- first proof that exchange is much lower than full indirect energy
- conjectured best bound is 1.44 (Levy-Perdew '93, Odashima-Capelle '07)

Proof of the exchange inequality at cnst density

Consider any N-particle Γ so that

- $\rho^{(2)}_T(x,y) := \rho^{(2)}(x,y) - \rho(x)\rho(y) \leq 0$ *"negatively correlated"*

  Hartree-Fock: $\rho^{(2)}_T(x,y) = -|\gamma(x,y)|^2 \leq 0$
- $\rho(x) = \rho \mathbb{1}_\Omega$

$$
\begin{aligned}
\text{Coulomb}-\text{Direct} &= \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho^{(2)}_T(x,y)}{|x-y|}\,dx\,dy \\
&= \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \rho^{(2)}_T(x,y)\left(\frac{1}{|x-y|} - 2\lambda\rho(x)^{\frac13}\right)dx\,dy - \lambda\int_{\mathbb{R}^3}\rho^{\frac43} \\
&\geq \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \rho^{(2)}_T(x,y)\left(\frac{1}{|x-y|} - 2\lambda\rho(x)^{\frac13}\right)_+ dx\,dy - \lambda\int_{\mathbb{R}^3}\rho^{\frac43} \\
&\geq -\frac{\rho^2}{2}\iint_{\Omega\times\mathbb{R}^3} \left(\frac{1}{|x-y|} - 2\lambda\rho^{\frac13}\right)_+ dx\,dy - \lambda\rho^{\frac43}|\Omega| \\
&\geq -\left(\frac{\pi}{12\lambda^2}+\lambda\right)\rho^{\frac43}|\Omega| = -\underbrace{\frac{3}{2}\left(\frac{\pi}{6}\right)^{\frac13}}_{\simeq 1.21}\int_{\mathbb{R}^3}\rho^{\frac43} \quad \text{for best } \lambda
\end{aligned}
$$

Coulomb energy II

Theorem (Local Density Approximation)

For a universal constant $1.44 \leq e_{\rm UEG} \leq 1.45$,

$$\left|\widetilde{F}_{\rm cl}[\rho] - \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\,dx\,dy + e_{\rm UEG}\int_{\mathbb{R}^3}\rho(x)^{\frac{4}{3}}\,dx\right| \leq \varepsilon\int_{\mathbb{R}^3}\left(\rho(x)+\rho(x)^{\frac{4}{3}}\right)dx + \frac{C}{\varepsilon^7}\int_{\mathbb{R}^3}|\nabla\rho^{\frac{1}{3}}(x)|^4\,dx$$

M.L.-Lieb-Seiringer '19

- Lower bound $e_{\rm UEG} \gtrsim 1.44$ (BCC Wigner crystal) surprisingly hard to prove (M.L.-Lieb '15, M.L.-Lieb-Seiringer '19, Cotar-Petrache '19)
- $\widetilde{F}_{\rm cl}$ is the grand-canonical version of $F_{\rm cl}$. For the latter we can only prove

$$\lim_{N\to\infty}\frac{1}{N}\left(F_{\rm cl}\left[\rho(N^{-\frac{1}{3}}\cdot)\right] - \frac{N^{\frac{5}{3}}}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho(x)\,\rho(y)}{|x-y|}\,dx\,dy\right) = -e_{\rm UEG}\int_{\mathbb{R}^3}\rho(x)^{\frac{4}{3}}\,dx$$

M.L.-Lieb-Seiringer '18

Full quantum case

From previous bounds we obtain

$$F[\rho] \geq 4.47 \int_{\mathbb{R}^3} \rho(x)^{\frac{5}{3}}\, dx + \frac{1}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\, dx\, dy - 1.58 \int_{\mathbb{R}^3} \rho(x)^{\frac{4}{3}}\, dx$$

(Thomas-Fermi-Dirac)

$$F[\rho] \leq (1+\varepsilon) c_{\rm TF} \int_{\mathbb{R}^3} \rho(x)^{\frac{5}{3}}\, dx + \frac{C}{\varepsilon} \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}(x)|^2\, dx + \frac{1}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\, dx\, dy$$

(Thomas-Fermi-von Weizäcker)

Theorem (LDA in full quantum case)

For a universal function f, we have for the grand-canonical $\widetilde{F}[\rho]$

$$\left|\widetilde{F}[\rho] - \left(\frac{1}{2} \iint_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\, dx\, dy + \int_{\mathbb{R}^3} f\left(\rho(x)\right) dx\right)\right|$$

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

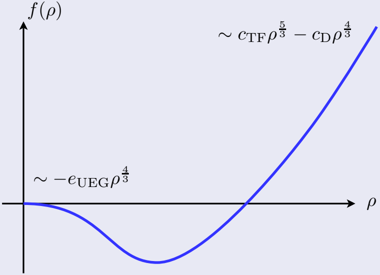
for every $\varepsilon > 0$ and every ρ.

M.L.-Lieb-Seiringer '19

The uniform electron gas energy $f(\rho)$

Theorem (The UEG≡Jellium energy $f(\rho)$)

The function f from the last theorem is Lipschitz-continuous on $\mathbb{R}_+$. It satisfies



- $c_{TF} = \frac{3}{5}\left(3\pi^2\right)^{\frac{2}{3}}$ *(Thomas-Fermi constant)*
- $c_D = \frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$ *(Dirac constant)*
- $1.44 \leq e_{UEG} \leq 1.45$ *(strongly correlated electrons)*

Graf-Solovej '94, Lieb-Narnhofer '73

- Derivative of f believed to have at least one jump = solid/fluid phase transition. Still unknown if there is a para.→ferromagn. transition in fluid (Cerperley-Alder '80, Zong-Lin-Ceperley '02, Holzmann-Moroni '20)
- Next order believed to be $\rho \log \rho$ for $\rho \to \infty$ (Macke '50, Bohm-Pines '53, GellMann-Brueckner '57)
- Famous numerical parametrizations of f (Perdew-Wang '92)

Conclusion

- Universal Lieb functional $F[\rho]$ is basis of DFT
- Complicated fully non-local functional of the density ρ
- Exact bounds known in some cases, important for calibration of empirical functionals
- Model simplifies in slowly-varying regime (local density approximation) but limiting f is not yet fully understood