



Lieb-Oxford inequality: best constant, gradient correction and the homogeneous electron gas

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The many-particle Coulomb interaction

► **Coulomb many-particle interaction energy:**

$$\int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \left(\sum_{1 \leq j < k \leq N} \frac{1}{|\mathbf{x}_j - \mathbf{x}_k|} \right) \underbrace{\sum_{\sigma_i = \uparrow, \downarrow} |\Psi(\mathbf{x}_1, \sigma_1, \dots, \mathbf{x}_N, \sigma_N)|^2}_{\text{or any symmetric (no-spin) probability density on } \mathbb{R}^{3N}} d\mathbf{x}_1 \cdots d\mathbf{x}_N$$

$$\simeq \underbrace{\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{x}) \rho(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y}}_{\text{direct Coulomb energy}} + E_{\text{Ind}}(\rho)$$

where $\rho(\mathbf{x}) = N \sum_{\sigma_i = \uparrow, \downarrow} \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{x}, \sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N, \sigma_N)|^2 d\mathbf{x}_2 \cdots d\mathbf{x}_N$

► **Classical exchange-correlation / indirect energy / W_∞ :**

$$E_{\text{Ind}}(\rho) = \min_{\Psi \rightsquigarrow \rho} \left\{ \sum_{1 \leq j < k \leq N} \sum_{\sigma_i = \uparrow, \downarrow} \int \frac{|\Psi|^2}{|\mathbf{x}_j - \mathbf{x}_k|} - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{x}) \rho(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y} \right\}$$

The Lieb-Oxford bound

► **Free electron gas:** indirect energy $-\underbrace{\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}}_{\simeq 0.7386} \rho^{4/3}$ (Dirac 1926)

Theorem (Lieb-Oxford bound)

$$E_{Ind}(\rho) \geq -1.6358 \int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} dx$$

- Lieb first got 8.52 using the theory of Hardy-Littlewood maximal functions
- Lieb-Oxford decreased the constant to 1.68, proof optimized by Chan-Handy
- Classical first step in derivation of Lieb-Simon's large- Z limit
- LO bound can be used as a constraint in DFT
 - B88 does not satisfy LO
 - Perdew-Burke-Ernzerhof (PBE): 4 parameters, with one chosen to ensure LO, but $E_{xc} \simeq$ B88 in practical calculations
- Not a guarantee of success, but a guiding principle
- Estimate in classical mechanics that holds the same for bosons or fermions

Best Lieb-Oxford constant?

$$E_{\text{Ind}}(\rho) \geq - \underbrace{1.6358}_{\text{not optimal}} \int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} d\mathbf{x}$$

- best constant ≥ 1.23 [LO], but not known rigorously
- Jellium in Wigner crystal $\sim -1.4442 \rho^{4/3}$ (e.g., Perdew '91) \rightsquigarrow more on this later
- Odashima–Capelle (2007), Räsänen–Pittalis–Capelle–Proetto (2009) conjecture that 1.4442 is optimal
- for small atoms and molecules, $E_{\text{Ind}}(\rho) \geq -0.91 \int \rho^{4/3}$ (He),
- Seidl–Gori-Giorgi–Savin (2007), Räsänen–Seidl–Gori-Giorgi (2011): $N = 30$ electron droplet with $E_{\text{Ind}}(\rho) \sim -1.31 \int \rho^{4/3}$

Conjecture

The best Lieb-Oxford constant is attained at constant density and given by the Jellium energy (Wigner crystal).

Perdew, in *Electronic Structure of Solids '91* (1991)

Odashima & Capelle, *J. Chem. Phys.* **127** (2007), Räsänen, Pittalis, Capelle & Proetto, *Phys. Rev. Lett.* **102** (2009)

Seidl, Gori-Giorgi & Savin, *Phys. Rev. A* **75** (2007), Räsänen, Seidl & Gori-Giorgi, *Phys. Rev. B* **83** (2011)

A better Lieb-Oxford bound for constant densities

Lieb-Oxford-L. bound [LewLie-15]

$$E_{\text{Ind}}(\rho) \geq - \underbrace{\frac{9}{10} \left(\frac{4\pi}{3}\right)^{1/3}}_{\simeq 1.4508} \int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} \, d\mathbf{x} - \begin{cases} 0.3270 \left(\int_{\mathbb{R}^3} |\nabla \rho(\mathbf{x})| \, d\mathbf{x} \right)^{1/4} \left(\int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} \, d\mathbf{x} \right)^{3/4} \\ 1.0002 \left(\int_{\mathbb{R}^3} |\nabla \rho^{1/3}(\mathbf{x})|^2 \, d\mathbf{x} \right)^{1/3} \left(\int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} \, d\mathbf{x} \right)^{2/3} \end{cases}.$$

- 1.4508 very close to the supposedly optimal 1.4442
- exact indirect energy of the Seidl-Perdew “PC model” where each electron is surrounded by a uniform sphere, which is the basic idea of the LO(L) proof
- 1.0002 based on the theory of Hardy-Littlewood maximal fns (1.1227 in [LL])

History:

- Lieb & Narnhofer (1976): energy per unit vol of Jellium $\geq -1.4508 \rho^{4/3}$
- Benguria, Bley & Loss (2012): similar with nonlocal gradient term

Discussion

New bound is of course better for constant densities. Is it useful for real systems?

► D. Feinblum, J. Kenison and K. Burke

Testing and using the Lewin-Lieb bounds in density functional theory
J. Chem. Phys. **141** (2014)

- LOL not better than LO for $Z \leq 88$
- Dividing our 0.327 by 2 would make it better for $Z \geq 2$
- New restrictions on xc enhancement factor, but satisfied for PBE

► L.A. Constantin, A. Terentjevs, F. Della Sala and E. Fabiano

Gradient-dependent upper bound for the exchange-correlation energy and application to density functional theory, *Phys. Rev. B* **91** (2014)

- Gussed from LOL the modified bound

$$E_{\text{ind}}(\rho) \geq -1.4508 \int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} \, \mathrm{d}\mathbf{x} - 0.155 \int_{\mathbb{R}^3} \rho(\mathbf{x}) |\nabla \rho(\mathbf{x})|^{1/4} \, \mathrm{d}\mathbf{x}$$

- Modified PBEsol accordingly \rightsquigarrow slight improvement for molecules and solids
- Argued that 1.4508 is optimal, not 1.4442

Classical Jellium

- N electrons and a neutralizing background in a domain Ω with $|\Omega| = N$

$$\mathcal{E}_{\text{Jel}}(\mathbf{x}_j, \Omega) = \sum_{1 \leq j < k \leq N} \frac{1}{|\mathbf{x}_j - \mathbf{x}_k|} - \sum_{j=1}^N \int_{\Omega} \frac{dy}{|\mathbf{x}_j - \mathbf{y}|} + \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{dx dy}{|\mathbf{x} - \mathbf{y}|}$$

- **Wigner crystallisation conjecture:** in thermodynamic limit $N \rightarrow \infty$, the electrons place themselves on a BCC lattice (hexagonal lattice in 2D)
- Coldwell-Horsfall & Maradudin (1960): analytical expression give that BCC energy per particle is -1.4442

- **Link with E_{Ind} ?**

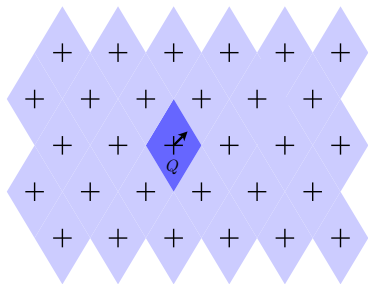
Can make a constant density with Jellium ground state: average over translations of unit cell (=uniform probability over ground states), without changing the Jellium energy.

Wigner *Phys. Rev.* **46** (1934)

Coldwell-Horsfall & Maradudin, *J. Math. Phys.* **1** (1960)

Classical Jellium and E_{Ind}

$$\mathcal{E}_{\text{Jel}}(\mathbf{x}_j, \Omega) = \sum_{1 \leq j < k \leq N} \frac{1}{|\mathbf{x}_j - \mathbf{x}_k|} - \sum_{j=1}^N \int_{\Omega} \frac{dy}{|\mathbf{x}_j - \mathbf{y}|} + \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{dx dy}{|\mathbf{x} - \mathbf{y}|}$$



- 1 put N electrons on a (finite subset of) a BCC lattice
- 2 average this state over the translations of the unit cell Q
- 3 so-obtained density ρ is constant on $\Omega = \cup$ unit cells

Indirect energy of this state

$$\mathcal{E}_{\text{Ind}}(\mathbf{x}_j, \Omega) = \sum_{1 \leq j < k \leq N} \frac{1}{|\mathbf{x}_j - \mathbf{x}_k|} - \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{dx dy}{|\mathbf{x} - \mathbf{y}|}$$

► **Claim (Wigner?):** $\frac{1}{N} \sum_{j=1}^N \int_{\Omega} \frac{dy}{|\mathbf{x}_j - \mathbf{y}|} \underset{N \rightarrow \infty}{\sim} \frac{1}{N} \int_{\Omega} \int_{\Omega} \frac{dx dy}{|\mathbf{x} - \mathbf{y}|}$

An unexpected shift

Theorem (Indirect energy of Jellium)

$$\lim_{N \rightarrow \infty} \frac{1}{N} \left(\sum_{1 \leq j < k \leq N} \frac{1}{|\mathbf{x}_j - \mathbf{x}_k|} - \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{dx dy}{|\mathbf{x} - \mathbf{y}|} \right) = \underbrace{e_{Jell}}_{\simeq -1.4442} + S$$

$$\lim_{N \rightarrow \infty} \frac{1}{N} \left(- \sum_{j=1}^N \int_{\Omega} \frac{dy}{|\mathbf{x}_j - \mathbf{y}|} + \int_{\Omega} \int_{\Omega} \frac{dx dy}{|\mathbf{x} - \mathbf{y}|} \right) = -S$$

$$\text{where } S = \int_{\mathbb{R}^3} \left(\frac{1}{|\mathbf{x}|} - \int_Q \frac{dy}{|\mathbf{x} - \mathbf{y}|} \right) dx = \frac{2\pi}{3} \int_Q x^2 dx = \begin{cases} 0.5236 & (SC) \\ 0.4948 & (FCC) \\ 0.4935 & (BCC) \end{cases}$$

- $S = 0$ for any potential that decays faster than Coulomb at infinity
- Similar shift in slightly different context by Borwein et al

A simple calculation

$$-\sum_{j=1}^N \int_{\Omega} \frac{dy}{|\mathbf{x}_j - \mathbf{y}|} + \int_{\Omega} \int_{\Omega} \frac{dx dy}{|\mathbf{x} - \mathbf{y}|} = -\sum_{i=1}^N \int_{\Omega} W(\mathbf{x}_i - \mathbf{y}) \sim_{N \rightarrow \infty} -N \int_{\mathbb{R}^3} W(\mathbf{x}) dx$$

$$W(\mathbf{x}) = \frac{1}{|\mathbf{x}|} - \int_Q \frac{dy}{|\mathbf{x} - \mathbf{y}|} = \text{fastly decaying screened Coulomb potential}$$

$$\begin{aligned} S &= \int_{\mathbb{R}^3} W(\mathbf{x}) dx = (2\pi)^{3/2} \lim_{\mathbf{k} \rightarrow 0} \widehat{W}(\mathbf{k}) \\ &= 4\pi \lim_{\mathbf{k} \rightarrow 0} \frac{1}{|\mathbf{k}|^2} \left(1 - \int_Q e^{-i\mathbf{k} \cdot \mathbf{x}} dx \right) = \frac{2\pi}{3} \int_Q x^2 dx. \end{aligned}$$

► Shift missed in the literature so far:

- Coldwell-Horsfall & Maradudin: $1/|\mathbf{x}| \rightsquigarrow e^{-\nu|\mathbf{x}|}/|\mathbf{x}|$ in whole space, then $\nu \rightarrow 0$

$$\int_{\mathbb{R}^3} \left(\frac{e^{-\nu|\mathbf{x}|}}{|\mathbf{x}|} - \int_Q \frac{e^{-\nu|\mathbf{x}-\mathbf{y}|}}{|\mathbf{x}-\mathbf{y}|} dy \right) dx = \int_{\mathbb{R}^3} \frac{e^{-\nu|\mathbf{x}|}}{|\mathbf{x}|} dx - \int_Q \left(\int_{\mathbb{R}^3} \frac{e^{-\nu|\mathbf{x}-\mathbf{y}|}}{|\mathbf{x}-\mathbf{y}|} dx \right) dy = 0$$

- Ceperley & Alder (1980): quantum Monte Carlo with **periodic** boundary conditions

Conclusion

- ▶ Rigorous bounds are useful in DFT
- ▶ Careful numerical investigation of best constants needed
- ▶ Unknown best Lieb-Oxford constant is between 1.31 and 1.6358
- ▶ At constant density, the best constant is between 1.31 and 1.4508, **not clear anymore** if it is given by Wigner crystal
- ▶ The indirect energy of Jellium seems to have **an unexpected shift** due to the long range of Coulomb, missed in the literature so far
- ▶ Given that Jellium is used as a reference system in DFT, this **requires more investigation!**