Indirect Coulomb Energy with Gradient Correction

Elliott Lieb
Princeton University

Joint work with
Mathieu Lewin,
C. N. R. S. Paris-Dauphine


Conference in honor of Bernard Jancovici
Analytical Results in Statistical Physics
I.H.P., Nov.5, 2015
Dedicated, with many fond memories, to my very old and valued friend

Bernard Jancovici
The electrostatic **Coulomb energy** of $N$ point particles at $\mathbf{X} = \{\mathbf{x}_1, \ldots, \mathbf{x}_N\} \in \mathbb{R}^{3N}$ is

$$U(\mathbf{X}) = \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}.$$ 

Given a (permutation symmetric) probability distribution $P(\mathbf{X}) \geq 0$ with $\int_{\mathbb{R}^{3N}} P(\mathbf{X}) \, d\mathbf{X} = 1$, the expectation value of $U$ is, of course,

$$\langle U \rangle = \int_{\mathbb{R}^{3N}} P(\mathbf{X}) U(\mathbf{X}) \, d\mathbf{X}.$$ 

We also define the one-body density $\rho(\mathbf{x}) = N \int_{\mathbb{R}^{3(N-1)}} P(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N) \, d\mathbf{x}_2 \cdots d\mathbf{x}_N$. $P$ is thought of as the square of a quantum mechanical wave function (symmetric [bosonic] or antisymmetric [fermionic]) but this does not matter in this talk. Indeed, it is an open problem to figure out the role of the bosonic or fermionic “statistics”, – but that is for another day.
A practical question in the quantum mechanics of electrons is to estimate $\langle U \rangle$, using $\rho$, as follows. Write
\[
E_{\text{ind}} := \langle U \rangle - D(\rho, \rho), \quad \text{where} \quad D(\rho, \rho) := \frac{1}{2} \int_{\mathbb{R}^6} \rho(x)|x - y|^{-1}\rho(y)dxdy.
\]

The indirect energy $E_{\text{ind}}$ (also known as exchange-correlation energy) depends on $P$ and can have either sign. The question we address is: How negative can it be, given (only) knowledge of $\rho$? I.e., how successfully can the particles avoid each other, thereby making $\langle U \rangle$ less than the simple, classical average $D(\rho, \rho)$?

One simple candidate is
\[
E_{\text{ind}} \geq -C \int_{\mathbb{R}^3} \rho(x)^{4/3}dx,
\]
which has the right scaling property, at least. Such a bound exists (L – Oxford 1981) and the sharp $C$ satisfies $1.31 < C < 1.64$.

**Variational Problem #1: What is the sharp $C$?**

Incidentally, we could let $C$ depend on $N$; it is easy to see that $C(N) \leq C(N + 1) \leq C$. When $N = 1$, $U = 0$, so $C(1) = \min_{\rho}\{D(\rho, \rho)/(\int \rho^{4/3})(\int \rho)^{2/3}\}$. This immediately leads to a Lane-Emden equation, whence $C(1) = 1.21 < C$. 
Gradient Correction

Based on a numerical example, a variational calculation for the ground state energy of ‘jellium’, physicists believe that $C \approx 1.44$. They also believe that a better bound would take into account that $E_{\text{ind}}$ also depends on the spatial variation of $\rho$.

The L-O bound harks back to Onsager’s lemma, and naturally comes in two parts:

$$E_{\text{ind}} \geq E_{\text{ind}}^{L-O} = -\frac{3}{5} \left( \frac{9\pi}{2} \right)^{1/3} \left( \int \rho^{4/3} \right) - Z \approx -1.45 \left( \int \rho^{4/3} \right) - Z$$

While $Z$ can be bounded by $(0.23) \int \rho^{4/3}$, it can be bounded instead by a quantity that depends on the spatial variation of $\rho$. We have shown how to bound it, instead, as

$$Z \leq 0.3697 \left( \int_{\mathbb{R}^3} |\nabla \rho(x)| \, dx \right)^{1/4} \left( \int_{\mathbb{R}^3} \rho(x)^{4/3} \, dx \right)^{3/4}.$$  

The challenge is to improve the constant 0.3697. We begin by defining our upper bound to $Z$ precisely.
**Definition of our bound on $Z$**

The upper bound on $Z$ found by L-O, and which we henceforth call simply $Z$, is defined as follows in terms of the nonnegative particle density $\rho$. It is clear that if $\rho$ is almost constant then $Z$ is almost zero.

$$Z = 2 \int_{\mathbb{R}^3} \rho(x) D(\rho - \rho(x), \delta_x - \mu_x) \, dx,$$

where $\delta_x$ is the Dirac delta at $x$ and

$$\mu_x(y) := \frac{3}{4\pi R(x)^3} 1\left\{ |y - x| \leq R(x) \right\} = \rho(x) 1\left\{ |y - x|^3 \leq \frac{3}{4\pi \rho(x)} \right\}$$

(1)

is the normalized uniform measure of the ball centered at $x$ with radius

$$R(x) := (4\pi \rho(x)/3)^{-1/3}.$$ Note that the Coulomb potential of $\delta_x - \mu_x$ is positive.

**Historical Note:** Benguria, Bley and Loss (2011) realized that $Z$ depends on the variation of $\rho$. This was an important development. They showed that $Z$ could be bounded using

$$(\sqrt{\rho}, |p|/\sqrt{\rho}) \propto \int_{\mathbb{R}^3} (\sqrt{\rho})^2(p) |p| \, dp.$$ This expression is very non-local, however, in contrast to ours, which uses $\nabla \rho$, and is local and easier to compute.
**ANOTHER BOUND ON Z**

In ‘Density Functional Theory’ people prefer $|\nabla \rho^{1/3}|^2$ (instead of $|\nabla \rho|$), which arises naturally in the high density regime of the almost-uniform electron gas. We also have an estimate of this kind, and it is

$$Z \leq 0.8035 \left( \int_{\mathbb{R}^3} |\nabla \rho^{1/3}(x)|^2 \, dx \right)^{1/3} \left( \int_{\mathbb{R}^3} \rho(x)^{4/3} \, dx \right)^{2/3},$$

which is to be compared to our previous bound

$$Z \leq 0.3697 \left( \int_{\mathbb{R}^3} |\nabla \rho(x)| \, dx \right)^{1/4} \left( \int_{\mathbb{R}^3} \rho(x)^{4/3} \, dx \right)^{3/4}.$$

The proof of this new bound is much more complicated than the previous one. It uses a Hardy-Littlewood type maximal function inequality, and it would be very nice if one could improve the known constant in this inequality.
In an appendix to our paper we discover that a supposed cornerstone of the conventional theory of the exchange-correlation energy does not hold up. Let us recall classical jellium.
**Classical Jellium and** $E_{\text{Ind}}$

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

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. the electron density $\rho$ obtained this way is constant on $\Omega := \cup$ unit cells

Indirect energy of this state

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

**Claim (due to Wigner?):**

$$\frac{1}{N} \sum_{j=1}^{N} \int_{\Omega} \frac{dy}{|x_j - y|} \xrightarrow{N \rightarrow \infty} \frac{1}{N} \int_{\Omega} \int_{\Omega} \frac{dx \, dy}{|x - y|}$$
THEOREM: [Indirect energy of Jellium]

$$\lim_{N \to \infty} \frac{1}{N} \left( \sum_{1 \leq j < k \leq N} \frac{1}{|x_j - x_k|} - \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{dx \, dy}{|x - y|} \right) = e_{Jell} + S$$

where

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

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

This shift was not noticed in the literature earlier than our paper because:

**IF ONE FIRST USES A YUKAWA POTENTIAL**

(WHICH HAS AN EXPONENTIAL CUTOFF),

TAKES THE LIMIT volume to infinity,

AND THEN REMOVES THE CUTOFF,

ONE GETS THE WRONG ANSWER.

**THE EXCHANGE OF LIMITS IS NOT VALID**

The bottom line is this: It had been assumed that the L-O bound for $\mathcal{E}_{ind}$, when the electron density was spatially constant, was at least $-1.44 \int \rho^{4/3}$, which would miraculously agree with our lower bound $-1.45 \int \rho^{4/3}$.

This was based on a miscalculation that had existed since time immemorial. The best upper bound is now only $-0.9 \int \rho^{4/3}$ for constant density. Thus, the sharp L-O constant for constant density is somewhere between 0.9 and 1.45.

**HOMEWORK PROBLEM:** Improve this state of affairs!
THANKS FOR LISTENING!