Indirect Coulomb Energy with Gradient Correction

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The Exchange Energy Problem

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

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

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

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

We also define the one-body density $\rho(\mathbf{x}) = N \int_{\mathbb{R}^{3(N-1)}} P(\mathbf{x}, \mathbf{x}_2, \ldots \mathbf{x}_N) \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N$. 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 ρ, as follows. Write

$$E_{ind} := \langle U\rangle - D(\rho,\rho), \qquad \text{where} \qquad D(\rho,\rho) := \frac{1}{2}\int_{\mathbb{R}^6} \rho(\mathbf{x})|\mathbf{x}-\mathbf{y}|^{-1}\rho(\mathbf{y})\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}.$$

The indirect energy E_{ind} depends on P and can have either sign. The question we address is: How negative can it be, given (only) knowledge of ρ? 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 $\boxed{E_{ind} \geq -C\int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3}\,\mathrm{d}\mathbf{x},}$ which has the right scaling property, at least. Such a bound exists (L – Oxford 1981) and the sharp C satisfies $1.43 < C < 1.64$.

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 grosomeund state energy of 'jellium', physicists believe that $C \approx 1.43$. They also believe that a better bound would take into account that E_{ind} also depends on the spatial variation of ρ.

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

$$E_{ind} = 3/5(9\pi/2)^{1/3} \left(\int \rho^{4/3}\right) - \mathbb{Z} \simeq -1.45 \left(\int \rho^{4/3}\right) - \mathbb{Z}$$

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

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

The challenge is to improve the constant 0.3697. We begin by defining our upper bound to $\mathbb{Z}$ precisely.

Definition of our bound on $\mathbb{Z}$

The upper bound on $\mathbb{Z}$ found by L-O, and which we henceforth call simply $\mathbb{Z}$, is defined as follows in terms of the nonnegative L^1 function ρ. It is clear that if ρ is almost constant then $\mathbb{Z}$ is almost zero.

$\mathbb{Z} = 2\int_{\mathbb{R}^3} \rho(\mathbf{x}) D\big(\rho - \rho(\mathbf{x}), \delta_\mathbf{x} - \mu_\mathbf{x}\big)\,\mathrm{d}\mathbf{x},$ where $\delta_\mathbf{x}$ is the Dirac delta at $\mathbf{x}$ and

$$\mu_\mathbf{x}(\mathbf{y}) := \frac{3}{4\pi R(\mathbf{x})^3}\,\mathbb{1}\Big\{|\mathbf{y}-\mathbf{x}| \le R(\mathbf{x})\Big\} = \rho(\mathbf{x})\,\mathbb{1}\Big\{|\mathbf{y}-\mathbf{x}|^3 \le \frac{3}{4\pi\rho(\mathbf{x})}\Big\} \tag{1}$$

is the normalized uniform measure of the ball centered at $\mathbf{x}$ with radius $R(\mathbf{x}) := (4\pi\rho(\mathbf{x})/3)^{-1/3}$. Note that the Coulomb potential of $\delta_\mathbf{x} - \mu_\mathbf{x}$ is positive.

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

$$(\sqrt{\rho}, |\mathbf{p}|\sqrt{\rho}) \propto \int_{\mathbb{R}^3} (\widehat{\sqrt{\rho}})^2(\mathbf{p})|\mathbf{p}|\mathrm{d}\mathbf{p}.$$

This expression is very *non*-local, however, in contrast to ours, which uses $\nabla\rho$, and is *local* and easier to compute.

Representation of $\mathbb{Z}$

The Coulomb potential of a point charge screened by a uniform distribution $\delta_{\mathbf{x}} - \mu_{\mathbf{x}}$ in a unit ball is $\Psi(r) = r^4(-r^2/2 - 1/r + 3/2) \cdot \mathbb{1}(0 \le r \le 1)$. Using this, we can write $\mathbb{Z} = \frac{3}{8\pi} \iint \Big(\rho(\mathbf{x}) - \rho(\mathbf{y})\Big) |\mathbf{x} - \mathbf{y}|^{-4} \Big[\Psi\left(|\mathbf{x} - \mathbf{y}|/R(\mathbf{x})\right) - \Psi\left(|\mathbf{x} - \mathbf{y}|/R(\mathbf{y})\right)\Big] \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{y}$.

with $R(\mathbf{x}) := (4\pi\rho(\mathbf{x})/3)^{-1/3}$.

This formula makes it clear that $\mathbb{Z}$ depends only on $|\nabla\rho|$. Our goal is to bound it from above and show that it is not too big. We could state this formally as a problem in the calculus of variations to minimize $\mathbb{Z}$ given $\int |\nabla\rho|$ and $\int \rho^{4/3}$ — or other variations on this theme.

If Ψ were monotone increasing, the integrand above would be positive, and we could go home, but it is not. $\Psi'(r)$ is negative when $r \in (r_*, 1)$ with $r_* = (\sqrt{5} - 1)/2$. To get a lower bound we can write $\Psi = \Psi_1 - \Psi_2$, both mononote nondecreasing, and ignore Ψ_1.

To proceed, we split $\mathbb{Z}$ into 2 parts $\mathbb{Z}_1$ and $\mathbb{Z}_2$ defined by a parameter $\theta > r_*$. (with $c = 4\pi/3$)

$c|\mathbf{x} - \mathbf{y}| \max\{\rho(\mathbf{x})^{\frac{1}{3}}, \rho(\mathbf{y}^{\frac{1}{3}})\} > \theta$ <u>or</u> $r_* < c|\mathbf{x} - \mathbf{y}| \max\{\rho(\mathbf{x}^{\frac{1}{3}}), \rho(\mathbf{y})^{\frac{1}{3}}\} < \theta$.

The first part is easy. We simply bound Ψ_2 by its maximum value value $\Psi_2(r_*)$.

$$\mathbb{Z}_1 \geq -\frac{3}{4\pi}\Psi(r_*) \int \int_{\substack{\rho(\mathbf{x})^{1/3} > \frac{\theta c}{|\mathbf{x}-\mathbf{y}|} \\ \rho(\mathbf{y}) \leq \rho(\mathbf{x})}} \frac{\rho(\mathbf{x})}{|\mathbf{x}-\mathbf{y}|^4} \,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}$$

$$\geq -3\Psi(r_*) \int \rho(\mathbf{x}) \left(\int_{\theta c \rho(\mathbf{x})^{-1/3}}^{\infty} \frac{\mathrm{d}r}{r^2} \right) \mathrm{d}\mathbf{x} = -\frac{3\Psi(r_*)}{\theta c} \int \rho(\mathbf{x})^{4/3} \,\mathrm{d}\mathbf{x}.$$

The second part, $\mathbb{Z}_2$, will be proportional to $-\theta^3$, and the maximization over θ will give us the funny looking lower bound $\mathbb{Z} \geq -0.3697(\int |\nabla \rho|)^{1/4}(\int \rho^{4/3})^{3/4}$.

To bound $\mathbb{Z}_2$ we use the *fundamental theorem of calculus* to write

$$\Psi_2\left(|\mathbf{x}-\mathbf{y}|/R(\mathbf{x})\right) - \Psi_2\left(|\mathbf{x}-\mathbf{y}|/R(\mathbf{y})\right)$$

in terms of $\nabla R(\mathbf{x}) \propto \nabla \rho(\mathbf{x})^{1/3}$ as follows:

$$\Psi_2\left(\frac{|\mathbf{x}-\mathbf{y}|\rho(\mathbf{x})^{\frac{1}{3}}}{c}\right)-\Psi_2\left(\frac{|\mathbf{x}-\mathbf{y}|\rho(\mathbf{y})^{\frac{1}{3}}}{c}\right)$$
$$=\frac{|\mathbf{x}-\mathbf{y}|}{c}\int_0^1(\mathbf{x}-\mathbf{y})\cdot\nabla\rho^{\frac{1}{3}}(\mathbf{y}+t(\mathbf{x}-\mathbf{y}))\,\Psi_2'\left(\frac{|\mathbf{x}-\mathbf{y}|\rho(\mathbf{y}+t(\mathbf{x}-\mathbf{y}))^{\frac{1}{3}}}{c}\right)\,\mathrm{d}t$$

and obtain

$$\mathbb{Z}_2\geq-\frac{c^2}{2}\int_0^1\mathrm{d}t\int\int_{\frac{r_*c}{|\mathbf{x}-\mathbf{y}|}\leq\max(\rho(\mathbf{x}),\rho(\mathbf{y}))^{1/3}\leq\frac{\theta c}{|\mathbf{x}-\mathbf{y}|}}\frac{\max(\rho(\mathbf{x}),\rho(\mathbf{y}))}{|\mathbf{x}-\mathbf{y}|^2}\times$$
$$\times\,|\nabla\rho^{\frac{1}{3}}(\mathbf{y}+t(\mathbf{x}-\mathbf{y}))|\;\Psi_2'\left(c^{-1}|\mathbf{x}-\mathbf{y}|\rho(\mathbf{y}+t(\mathbf{x}-\mathbf{y}))^{\frac{1}{3}}\right)\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}.$$

After changing variables, adding a few more unenlightening inequalities, and noting that $\nabla\rho^{1/3}=\frac{1}{3}\rho^{-2/3}\nabla\rho$ we find that:

$$\mathbb{Z}_2 \geq -\frac{2\pi\theta^3 c^3}{3(r_*)^3}\left(\int_{r_*}^{1} \frac{\Psi_2'(t)}{t}\mathrm{d}t\right)\int |\nabla\rho(\mathbf{x})|\,\mathrm{d}\mathbf{x} \tag{2}$$

which concludes the derivation of the inequality since

$$\frac{2\pi\theta^3 c^3}{3(r_*)^3}\left(\int_{r_*}^{1} \frac{\Psi_2'(t)}{t}\mathrm{d}t\right) \simeq 0.11641\theta^3$$

Another bound on $\mathbb{Z}$

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

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

which is to be compared to our previous bound

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

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.

The Hardy-Littlewood type maximal function

Recall that Ψ_2 is the decreasing part of Ψ.

We define the positive function $\boxed{\chi(r) = r^{-1}\Psi_2'(r)} = -r^{-1}\Psi'(r) \cdot \mathbb{1}(r_* \leq r \leq 1)$, which is increasing on $[r_*, s_*]$ and decreasing on $[s_*, 1]$, with $s_* \simeq 0.8376$. For every square-integrable function f, we define the following Hardy-Littlewood-type function

$$\mathrm{M}_f^\chi(\mathbf{z}) := \sup_{r>0} \left\{ r^{-3} \int \chi(|\mathbf{u}|/r)\, f(\mathbf{z}+\mathbf{u})|\, \mathrm{d}\mathbf{u} \right\}. \tag{3}$$

LEMMA [Hardy-Littlewood-type inequality]: For every square-integrable function f on $\mathbb{R}^3$,

$$\left(\int \mathrm{M}_f^\chi(\mathbf{z})^2 \, \mathrm{d}\mathbf{z} \right)^{1/2} \leq 7.5831 \left(\int |f(\mathbf{z})|^2 \, \mathrm{d}\mathbf{z} \right)^{1/2}. \tag{4}$$

Homework Problem: Find a better constant than 7.5831.

THANKS FOR LISTENING!