An electrostatic inequality

The size of the Coulomb potential of a collection of nuclei and electron has two sources. It is singular close to the nuclei and it can be also large because there are many nuclei. To disentangle these two issues one resorts to an electrostatic inequality due to Lieb and Yau. Before we can describe it in detail we need the notion of a Voronoi cell with respect to a collection of nuclei. Define

$$\Gamma_j = \{x \in R^3 : |x - R_j| < |x - R_i|, i \neq j\} \ .$$

Clearly Γ_j is open and it easily seen to be convex. Further we define the nearest neighbor distance between among the nuclei by

$$\min_{i \neq j} |R_i - R_j|$$

and set

$$D_j = \frac{\min_{i \neq j} |R_i - R_j|}{2} \ .$$

The Coulomb potential due to all the nuclei that an electrons feels at the point x is

$$W(x) = Z \sum_k \frac{1}{|x - R_k|} \ .$$

Define

$$\delta(x) = \min\{|x - R_i| : 1 \leq i \leq K\} \ ,$$

and set

$$\Phi(x) = W(x) - \frac{Z}{\delta(x)} \ .$$

Thus, for $x \in \Gamma_j$ the potential $\Phi(x)$ is due to all the nuclei outside of the Voronoi cell Γ_j.

Theorem 1 *For any charge distribution* μ

$$D(\mu, \mu) - \int \Phi(x) \mu(dx) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|} \geq \frac{Z^2}{8} \sum_j \frac{1}{D_j} \ .$$

PROOF: Note that Φ is harmonic in each Voronoi cell. It is not harmonic on the whole space since the function Φ is not differentiable in the boundary of the Voronoi cells. Pick a test function f and calculate

$$\int \Delta f \Phi(x) dx = \sum_j \int_{\Gamma_j} \Delta f \Phi(x) dx = \sum_j \int_{\Gamma_j} \mathrm{div} \cdot (\nabla f \Phi)(x) dx - \sum_j \int_{\Gamma_j} \nabla f \cdot \nabla \Phi(x) dx$$

$$= \sum_j \int_{\partial \Gamma_j} N_j \cdot (\nabla f \Phi)(x) dS - \sum_j \int_{\Gamma_j} \nabla f \cdot \nabla \Phi(x) dx$$

where N_j is the outward normal to the boundar of the Voronoi cell Γ_j. Since Φ is continuous the sum of the boundary integrals add up to zero. Further

$$-\sum_j \int_{\Gamma_j} \nabla f \cdot \nabla\Phi(x)dx = -\sum_j \int_{\Gamma_j} \mathrm{div}(f \cdot \nabla\Phi)(x)dx + \sum_j \int_{\Gamma_j} f\Delta\Phi(x)dx$$

$$= -\sum_j \int_{\Gamma_j} \mathrm{div}(f \cdot \nabla\Phi)(x)dx$$

since Φ is harmonic in Γ_j.

Hence we have

$$\int \Delta f \Phi(x)dx = -\sum_j \int_{\partial\Gamma_j} (f(x)N_j \cdot \nabla\Phi)(x)dS \ .$$

The boundary $\partial\Gamma_j$ consists of two dimensional planes separating some Γ_i form Γ_j. Note that each boundary segment appears twice, as the boundary of a Voronoi cell and its neighbor. On such a segment the contribution of $W(x)$ drops out since it is differentiable and we are left with

$$\int \Delta f \Phi(x)dx = \sum_j \int_{\partial\Gamma_j} f(x)N_j \cdot \nabla \frac{1}{\delta(x)} dS \ .$$

In other words the charge density that generates the potential Φ is a measure ν that is supprted on the boundary of the Voronoi cells. More precisely, for any test function

$$\int \Delta f \Phi(x)dx = -\int f(x)\nu(dx)$$

Since every point on the common boundary of two Voronoi cells Γ_j and Γ_k has the same distance to the point R_k and R_j we get that the gradients on the common boundary but taken from the interior of Γ_j and Γ_k are of the same magnitude but of opposite direction. Thus, the density of the measure on the boundary of the Voronoi cell is given by

$$\nu(dx) = -2ZN_j\nabla|x - R_j|^{-1} \ .$$

Hence

$$\Phi(x) = \frac{1}{4\pi}\int \frac{1}{|x-y|}\nu(dy) \ ,$$

and

$$D(\mu,\mu) - \int \Phi(x)\mu(dx) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|}$$

$$= D(\mu-\nu,\mu-\nu) - D(\nu,\nu) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|}$$

$$\geq -D(\nu,\nu) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|}$$

and where we have to calculate $D(\nu,\nu)$.

$$D(\nu,\nu) = \frac{1}{2}\int \Phi(x)\nu(dx) = \frac{1}{2}\int W(x)\nu(dx) - \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx)$$

$$= \frac{Z}{2}\sum_j \Phi(R_j) - \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx)$$

$$= \sum_{k<l} \frac{Z^2}{|R_k - R_l|} - \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx) \ .$$

Hence

$$-D(\nu,\nu) + Z^2 \sum_{k<l} \frac{1}{|R_k - R_l|} = \frac{1}{2}\int \frac{Z}{\delta(x)}\nu(dx) \ .$$

The last expression reduces to

$$-\sum_j \frac{Z^2}{8\pi}\int_{\partial\Gamma_j} \frac{1}{|x-R_j|} N_j \cdot \nabla \frac{1}{|x-R_j|} dS \ .$$

note that in this expression we integrate again over each boundary twice once for each Voronoi cell. Straightforward calculation leads to

$$= -\sum_j \frac{Z^2}{16\pi}\int_{\partial\Gamma_j} N_j \cdot \nabla \frac{1}{|x-R_j|^2}$$

$$= \sum_j \frac{Z^2}{16\pi}\int_{\Lambda_j} \Delta \frac{1}{|x-R_j|^2}$$

where Λ_j is the complement of Γ_j. This causes the change in the sign. Since

$$\Delta \frac{1}{|x-R_j|^2} = \frac{2}{|x-R_j|^4} \ ,$$

it remains to calculate the integral

$$\frac{Z^2}{8\pi}\int_{\Lambda_j} \frac{1}{|x-R_j|^4} dx \ .$$

It is an integral over the complement of a convex set and hence this set contains the half space whose boundary plane touches the ball of radius D_j centered at R_j. Thus we get a lower bound by just integrating over that half space. By shifting and rotating coordinates we may assume that $R_j = 0$ and hence

$$\frac{Z^2}{8\pi}\int_{\Lambda_j} \frac{1}{|x-R_j|^4} dx \geq \frac{Z^2}{8\pi}\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{D_j}^{\infty} dx \frac{1}{(x^2+y^2+z^2)^2} = \frac{Z^2}{8D_j} \ .$$

This is what we wanted to show.