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15. Stability of second kind

Assume we have N electrons and M nuclei. They are interacting with each other via the Coulomb force. The electrons have charge $-e$ and are at positions $x_1, \dots, x_N$. The nuclei have charges $eZ_1, \dots, eZ_M$ and are located at $R_1, \dots, R_M \in \mathbb{R}^3$.

Since the nuclei are much heavier, we assume R_i are fixed, and therefore parameters of the system.

The many-body Hamiltonian then reads $(e=1)$

$$H_{M,N} = \sum_{i=1}^{N} (-\Delta_{x_i}) - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{Z_k}{|x_i - R_k|} + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} + \sum_{1 \le \ell < k \le M} \frac{Z_\ell Z_k}{|R_\ell - R_k|}$$

on $L^2_a(\mathbb{R}^{3N})$. The nuclear charges satisfy

$$0 < Z_k \le Z \quad \forall\, k = 1, \dots, M.$$

Let $E(M,N)$ be the ground state energy of the system, namely

$$E(M,N) = \inf_{\{R_k\}} \inf_{\|\psi\|=1} \langle \psi \,|\, H_{M,N}\, \psi \rangle$$

Stability of second kind:

$$E(M,N) \ge -C(Z)\,(M+N)$$

16. Electrostatic inequalities

The first step is to estimate the Coulomb potential by an effective one-body potential.

Thm (Baxter's electrostatic inequality, 1980)

For any $\{x_i\}_{i=1}^N$, $\{R_k\}_{k=1}^M \subset \mathbb{R}^3$ and $Z>0$ we have

$$-\sum_{i=1}^N \sum_{k=1}^M \frac{Z}{|x_i - R_k|} + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} + \sum_{1 \le \ell < k \le M} \frac{Z^2}{|R_\ell - R_k|} \ge -\sum_{i=1}^N \frac{2Z+1}{D(x_i)}$$

where $D(x) = \min_{1 \le k \le M} |x - R_k|$ is the distance to the nearest nucleus

To prove Baxter's inequality we will need Newton's theorem.

Definition Let μ be a non-negative Borel measure on $\mathbb{R}^3$. The potential function Φ associated with μ is defined as

$$\Phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|} \, d\mu(y) \in [0, \infty]$$

The Coulomb energy of μ is defined as

$$D(\mu, \mu) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{|x-y|} \, d\mu(x) \, d\mu(y) \in [0, \infty]$$

We think of μ as some charge distribution. The total charge is given by $Q = \mu(\mathbb{R}^3)$. In many cases μ is of the form $\mu(dx) = \rho(x)\,dx$ for $\rho \in L^1(\mathbb{R}^3)$. In that case we shall write $D(\rho, \rho)$. The following result is useful when computing potential functions.

Thm (Newton's thm)

Let μ be a non-negative Borel measure on $\mathbb{R}^3$ that is rotationally symmetric with respect to the origin i.e. $\mu(RA)=\mu(A)$ $\forall$ R-rotation around the origin and any Borel set A. Then

$$\Phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|}\, d\mu(y) = \frac{1}{|x|}\int_{|y|\le|x|} d\mu(y) + \int_{|y|>|x|} \frac{1}{|y|}\, d\mu(y) .$$

Proof Since μ is rotationally symmetric, so is $\Phi(x)$.

Indeed $\Phi(Rx) = \int_{\mathbb{R}^3} \frac{1}{|Rx-y|}\, d\mu(y) = \int_{\mathbb{R}^3} \frac{1}{|x-R^{-1}y|}\, d\mu(y) =$

$$= \int_{\mathbb{R}^3} \frac{1}{|x-R^{-1}y|}\, d\mu(R^{-1}y) = \int_{\mathbb{R}^3} \frac{1}{|x-\tilde{y}|}\, d\mu(\tilde{y}) = \Phi(x)$$

$\Rightarrow$ $\Phi(x) = \Phi(|x|)$.

Thus we can write Φ as a spherical average:

$$\Phi(x) = \frac{1}{4\pi}\int_{S^2} \Phi(|x|\omega)\, d\omega = \frac{1}{4\pi}\int_{S^2}\int_{\mathbb{R}^3} \frac{1}{\left||x|\omega-y\right|}\, d\mu(y)\, d\omega$$

$$= \frac{1}{4\pi}\int_{\mathbb{R}^3}\int_{S^2} \frac{d\omega}{\left||x|\omega-y\right|}\, d\mu(y)$$

To compute the inner integral we again use rotational symmetry to assume that $y=|y|(0,0,1)$. Then

$$\frac{1}{4\pi}\int_{S^2}\frac{d\omega}{||x|\omega-y|} = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\frac{1}{\sqrt{|x|^2+|y|^2-2|x||y|\cos\theta}}\sin\theta\, d\theta\, d\varphi$$

$$= \frac{1}{2}\int_{-1}^{1}\frac{1}{\sqrt{|x|^2+|y|^2-2|x||y|s}}\,ds = \frac{1}{2}\frac{1}{|x|}\int_{-1}^{1}\frac{ds}{\sqrt{1+\frac{|y|^2}{|x|^2}-2\frac{|y|}{|x|}s}}$$

$$= \left\| \frac{|y|}{|x|}=b \right\| = \frac{1}{2}\frac{1}{|x|}\int_{-1}^{1}\frac{ds}{\sqrt{1+b^2-2bs}} = \frac{1}{2|x|}\left(-\frac{\sqrt{b^2-2bs+1}}{b}\right)\Bigg|_{-1}^{1}$$

$$= \frac{1}{2|x|}\left(-\frac{|b-1|}{b}+\frac{|b+1|}{b}\right) = \begin{cases} b>1 & \frac{-b+1+b+1}{b} = \frac{2}{b} = \frac{2|x|}{|y|} \quad (|y|>|x|) \\ b<1 & \frac{-1+b+b+1}{b} = 2 \quad (|y|<|x|) \end{cases}$$

$$= \min\left(\frac{1}{|x|}, \frac{1}{|y|}\right) \qquad \blacksquare$$

By translational invariance, this result can be extended to rotational symmetry around a point $x_0 \in \mathbb{R}^3$

Example

$$\mu(y) = \frac{Q}{4\pi d^2}\delta(|y|-d)$$ – the uniform charge distribution of total charge Q supported on a sphere of radius d.

Then:

$$|x|>d \Rightarrow \Phi(x) = \frac{1}{|x|}\int_{|y|\le|x|} d\mu(y) = \frac{Q}{|x|}$$

i.e. from outside of the sphere the charge looks just like a point charge Q located at the origin. If $|x|<d$

$$\Phi(x) = \int_{|y|>|x|} \frac{1}{|y|} \, d\mu(y) = \frac{Q}{d}.$$

Corollary (point charges have maximal potential)

μ – non-negative, Borel measure, rotationally symmetric with respect to x_0 and $Q = \mu(\mathbb{R}^3)$. Then $\forall x \in \mathbb{R}^3$

$$\Phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|} \, d\mu(y) \leq \frac{Q}{|x-x_0|}$$

Some properties of the Coulomb energy.

Lemma

Assume $\mu = \mu_1 - \mu_2$ where μ_1, μ_2 are both non-negative Borel measures with finite Coulomb energies

$$D(\mu_i, \mu_i) < \infty \qquad i = 1, 2.$$

Then $\quad 0 \leq D(\mu, \mu) < \infty.$

Proof.

We first note that

$$\frac{1}{|x-y|} = \frac{1}{\pi^3} \int_{\mathbb{R}^3} \frac{1}{|x-z|^2} \frac{1}{|y-z|^2} \, dz. \qquad (*)$$

The fact that both sides are proportional to each other follows from the observation that both are function of $|x-y|$ and both are positive homogeneous of degree -1, i.e. $f(\lambda|x-y|) = \lambda^{-1} f(|x-y|)$

Exercise Check both statements

•) dependence on $|x-y|$ only

LHS – obvious. RHS: $\displaystyle\int_{\mathbb{R}^3} \frac{dz}{|x-z|^2|y-z|^2} = \Big\| x-y=t \Big\| =$

$$= \int \frac{dz}{|x-z|^2\,|x-t-z|^2} = \Big\| x-z=\tilde{z} \Big\| = \int_{\mathbb{R}^3} \frac{d\tilde{z}}{|\tilde{z}|^2|\tilde{z}-t|^2} = \Big\| \tilde{\tilde{z}}=\tilde{z}-\tfrac{t}{2} \Big\|$$

$$= \int_{\mathbb{R}^3} \frac{dz}{|\tilde{\tilde{z}}-\frac{t}{2}|^2|\tilde{\tilde{z}}+\frac{t}{2}|^2} = F(|t|).$$

•) homogeneity

$$\text{RHS} \int_{\mathbb{R}^3} \frac{1}{|\lambda x-z|^2}\,\frac{1}{|\lambda y-z|^2}\,dz = \frac{1}{|\lambda|^4}\int_{\mathbb{R}^3} \frac{dz}{|x-\frac{z}{\lambda}|^2\,|y-\frac{z}{\lambda}|^2} = \Big\| \frac{z}{\lambda}=\tilde{z},\ dz=\lambda^3 d\tilde{z}$$

$$= \frac{|\lambda|^3}{|\lambda|^4}\int_{\mathbb{R}^3} \frac{d\tilde{z}}{|x-\tilde{z}|^2\,|y-\tilde{z}|^2}$$

$\square$

Exercise The only positively homogeneous function of degree -1 is $\frac{1}{|x|}$.

Let $F(x)$ be another one. Then $F(x) = F(1\cdot x) = \frac{1}{|x|}\cdot F(1)$ $\square$

The constant $\frac{1}{\pi^3}$ is not important. It is clear that it has to be positive.

From the representation (*) we have

$$D(\mu,\mu) = \frac{1}{2\pi^3}\int_{\mathbb{R}^3}\left(\int_{\mathbb{R}^3}\frac{d\mu(x)}{|x-z|^2}\right)^2 dz \geq 0.$$

<u>Exercise</u> Show $D(\mu,\mu) < \infty$.

<u>Solution</u>:

From the representation we have

$$D(\mu,\nu) = \frac{1}{2\pi^3}\int_{\mathbb{R}^3}\left[\int_{\mathbb{R}^3}\frac{d\mu(x)}{|x-z|^2}\right]\left[\int_{\mathbb{R}^3}\frac{d\nu(x)}{|x-z|^2}\right]dz$$

By CS:

$$|D(\mu,\nu)|^2 \leq \frac{1}{2\pi^3}\int_{\mathbb{R}^3}\left(\int_{\mathbb{R}^3}\frac{d\mu(x)}{|x-z|^2}\right)^2 dz \int_{\mathbb{R}^3}\left(\int_{\mathbb{R}^3}\frac{d\nu(x)}{|x-z|^2}\right)^2 dz$$

$$= \frac{1}{2\pi^3} D(\mu,\mu)\, D(\nu,\nu)$$

Thus $D(\mu_1-\mu_2, \mu_1-\mu_2) \leq C\, D(\mu_1,\mu_1)\, D(\mu_2,\mu_2) < \infty$ $\blacksquare$

The next theorem allows to estimate the potential energy of an electron by the one coming from the nearest nucleus.

Thm (basic electrostatic inequality)

Let μ be a non-negative Borel measure on $\mathbb{R}^3$.

Then

$$D(\mu,\mu) - \sum_{k=1}^{M} \int_{\mathbb{R}^3} \frac{Z}{|x-R_k|} \, d\mu(x) + \sum_{1 \le i < j \le M} \frac{Z^2}{|R_i - R_j|} \ge - \int_{\mathbb{R}^3} \frac{Z}{D(x)} \, d\mu(x)$$

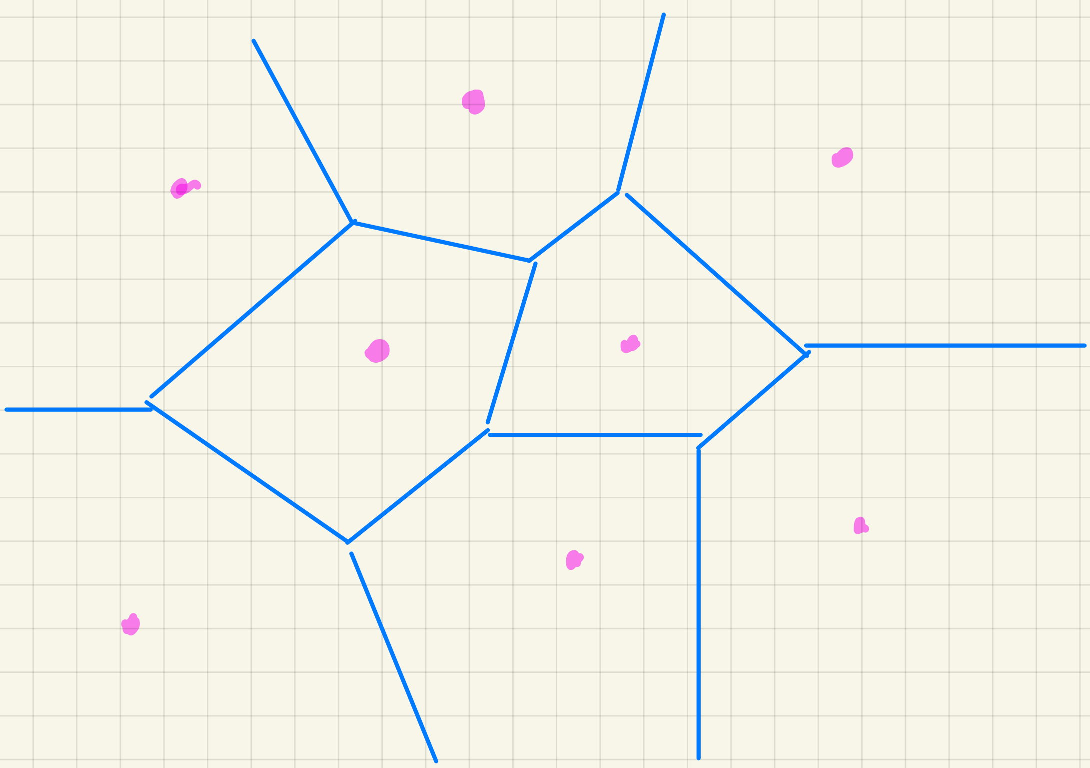
Proof.

Let $$\Phi_c(x) = \sum_{j=1}^{M} \frac{Z}{|x-R_j|} - \frac{Z}{D(x)}$$

The function $\Phi_c(x)$ is the potential generated by all nuclei apart from the nearest one.

A useful picture to keep in mind is the Voronoi cell where the nucleus at R_k is associated with the cell

$$\Gamma_k = \{ x \in \mathbb{R}^3 \;\; |x - R_k| < |x - R_\ell| \;\; \forall \ell \neq k \}$$



<u>Lemma</u> We can write $\Phi_c(x) = \int_{\mathbb{R}^3} \frac{d\nu(y)}{|x-y|}$

for some non-negative measure ν on $\mathbb{R}^3$ supported on the surfaces $\{x \in \mathbb{R}^3 : |x-R_k| = |x-R_l| \quad l \neq k\}$

<u>Proof</u> We will show that Φ_c satisfies

$$-\Delta \Phi_c = 4\pi \nu. \qquad (*)$$

Since $-\Delta (|x|^{-1}) = 0 \quad \forall \; x \neq 0$ it is clear that

$-\Delta \Phi_c(x) = 0 \quad \forall \; x \in \mathbb{R}^3$ except the surfaces

Hence, if $(*)$ holds, ν has to be supported on the surfaces. We compute $(\Phi = \Phi_c)$

$$\int_{\mathbb{R}^3} \Phi(x)\,(\Delta f)(x)\,dx = \sum_k \int_{\Gamma_k} \Phi(x)\,(\Delta f)(x)\,dx$$

$$= -\sum_k \int_{\Gamma_k} (\nabla \Phi(x))(\nabla f(x))\,dx + \sum_k \int_{\partial \Gamma_k} \Phi(x) \cdot \hat{n}_k \cdot \nabla f(x)\,dS$$

On each $\partial\Gamma_k \cap \partial\Gamma_l$ the outward normal vectors $\hat{n}_k$ and $\hat{n}_l$ point in the opposite direction.

This together with the fact that Φ and ∇f are continuous implies the boundary terms vanish. Furthermore, since

$$\int_{\Gamma_k} \nabla\Phi \nabla f = -\int_{\Gamma_k} \operatorname{div}(f \nabla \Phi) + \int_{\Gamma_j} f \,\Delta\Phi = -\int_{\Gamma_k} \operatorname{div}(f \nabla \Phi)$$

since Φ harmonic in Γ_k. By divergence theorem

$$\int_{\mathbb{R}^3} \Phi(x)\, \Delta f(x)\, dx = -\sum_k \int_{\partial\Gamma_k} f(x)\, \hat{n}_k \cdot \nabla \Phi_j(x)\, dS$$

which does not vanish as $\nabla\Phi$ is not continuous on $\mathbb{R}^3$ - as $\mathcal{D}(x)^{-1}$ is not differentiable. The contribution from $\sum_{j=1}^{M} \frac{Z}{|x-R_j|}$ is differentiable on the boundary so this contribution vanishes as before. We get

$$\int_{\mathbb{R}^3} \Phi(x)\, \Delta f(x)\, dx = \sum_k \int_{\partial\Gamma_k} f(x)\, \hat{n}_k \cdot \nabla \frac{Z}{\mathcal{D}(x)}\, dS.$$

Since on $\partial\Gamma_j \cap \partial\Gamma_k$ every point has the same distance to R_k and R_j the gradients of $\mathcal{D}(x)^{-1}$ have the same magnitude but opposite orientation, i.e.

$$\hat{n}_j \cdot \nabla \frac{1}{|x-R_j|} = \hat{n}_k \cdot \nabla \frac{1}{|x-R_k|}$$

It follows that

$$\int_{\mathbb{R}^3} \Phi(x)\, \Delta f(x)\, dx = 2Z \sum_k \int_{\partial\Gamma_k} f(x)\, \hat{n}_k \cdot \nabla \frac{1}{|x-R_k|}\, dS$$

Thus ν is a measure concentrated on the segments joining the Voronoi cells. In particular on $\partial\Gamma_k \cap \partial\Gamma_j$ it has magnitude

$$-\frac{Z}{2\pi}\, \hat{n}_j \cdot \nabla \frac{1}{|x-R_j|} = -\frac{Z}{2\pi}\, \hat{n}_k \cdot \nabla \frac{1}{|x-R_k|}$$

which implies

$$4\pi\, d\nu(x) = 2Z \sum_k \mathbb{1}(x\in\partial\Gamma_k)\, \frac{\hat{n}_k\cdot(x-R_k)}{|x-R_k|^3} \geq 0$$

because

$n_k\,(x-R_k) \geq 0$ on $x\in\partial\Gamma_k$ by convexity of Γ_k. ▨

We move back to the proof of the basic electrostatic inequality which using the definition of Φ_c can be rewritten as

$$D(\mu,\mu) - \int \Phi_c(x)\, d\mu(x) + \sum_{1\leq l<k\leq M} \frac{Z^2}{|R_l-R_k|} \geq 0.$$

By the previous lemma we have

$$D(\mu,\mu) - \int \Phi_c(x)\, d\mu(x) = D(\mu,\mu) - 2D(\mu,\nu) \geq -D(\nu,\nu)$$

by $D(\mu-\nu,\mu-\nu)\geq 0$. It remains to compute $D(\nu,\nu)$.

We have

$$\Phi_c(x) = \sum_{k=1}^{M} \frac{Z}{|x-R_k|} - \frac{Z}{\mathcal{D}(x)} \leq \sum_{k=1}^{M} \frac{Z}{|x-R_k|} = Z\sum_{k=1}^{M}\int_{\mathbb{R}^3} \delta(y-R_k)\frac{dy}{|x-y|}$$

Since $d\nu(x)$ is positive

$$D(\nu,\nu) = \frac{1}{2}\int \Phi(x)\, d\nu(x) \leq \frac{Z}{2}\sum_{k=1}^{M}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \delta(y-R_k)\frac{dy}{|x-y|}\, d\nu(x)$$

$$= \frac{Z}{2}\sum_{k=1}^{M}\int_{\mathbb{R}^3} \delta(y-R_k)\left(\int_{\mathbb{R}^3}\frac{1}{|x-y|}\, d\nu(x)\right)dy = \frac{Z}{2}\sum_{k=1}^{M}\int_{\mathbb{R}^3}\delta(y-R_k)\,\Phi(y)\,dy$$

$$= \frac{Z}{2}\sum_{k=1}^{M}\Phi(R_k) = \sum_{1\leq l<k\leq M}\frac{Z^2}{|R_l-R_k|}$$

▨

Proof of Baxter's electrostatic inequality

Recall $\mathcal{D}(x) = \min_k |x-R_k|$.

We have

$$D(\mu,\mu) - \sum_{k=1}^{M} \int_{\mathbb{R}^3} \frac{Z}{|x-R_k|}\, d\mu(x) + \sum_{1\le i<j\le M} \frac{Z^2}{|R_i-R_j|} \ge -\int_{\mathbb{R}^3} \frac{Z}{\mathcal{D}(x)}\, d\mu(x) \quad (*)$$

but want to prove

$$-\sum_{i=1}^{N}\sum_{k=1}^{M} \frac{Z}{|x_i-R_k|} + \sum_{1\le i<j\le N} \frac{1}{|x_i-x_j|} + \sum_{1\le l<k\le M} \frac{Z^2}{|R_l-R_k|} \ge -\sum_{i=1}^{N} \frac{2Z+1}{\mathcal{D}(x_i)}.$$

if we would choose $\mu = \sum_{i=1}^{N} \delta(|x-x_i|)$ in $(*)$

we would be almost there. Unfortunately, $D(\mu,\mu) = \infty$.

This is why we will smear out charges. Define

$$d\mu_i(x) = \frac{1}{\pi \mathcal{D}(x_i)^2}\, \delta\big(|x-x_i| - \mathcal{D}(x_i)/2\big) \qquad i=1,\dots,N$$

uniform, normalized measure

Picture

We make two observations:

(1) the electrostatic interaction between the electrons

is reduced because the interaction energy between two spheres is less than two points:

$$\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{d\mu_i(x)\, d\mu_j(y)}{|x-y|} \leq \int_{\mathbb{R}^3} \frac{1}{|x_i-y|}\, d\mu_j(y) \leq \frac{1}{|x_i-x_j|}$$

by Corollary after Newton's thm.

② Again by Newton's thm, the interaction between the smeared out electrons and nuclei is not changed as $D(x_i)/2 < |x-R_j|\ \forall j$ and thus

$$\int_{\mathbb{R}^3} \frac{Z}{|x-R_j|}\, d\mu_i(x) = \frac{Z}{|x_i-R_j|}$$

As a consequence we obtain the lower bound

$$\sum_{1\leq i<j\leq N} \frac{1}{|x_i-x_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z}{|x_i-R_j|} \geq \sum_{1\leq i<j\leq N} \int_{\mathbb{R}^6} \frac{d\mu_i(x)\, d\mu_j(y)}{|x-y|}$$

$$- \sum_{j=1}^{M}\sum_{i=1}^{N} \int_{\mathbb{R}^3} \frac{Z\, d\mu_i(x)}{|x-R_j|} = D(\mu,\mu) - \sum_{j=1}^{M} \int_{\mathbb{R}^3} \frac{Z}{|x-R_j|}\, d\mu(x) - \sum_{i=1}^{N} \frac{1}{D(x_i)}$$

$\mu = \sum \mu_i$

Here we used that

Exercise $D(\mu_i,\mu_i) = \frac{1}{D(x_i)}$

$$d\mu_i(x) = \frac{1}{\pi D(x_i)^2}\, \delta\big(|x-x_i| - D(x_i)/2\big)$$

$$\mathcal{D}(\mu_i,\mu_i) = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{d\mu_i(y)\, d\mu_i(x)}{|x-y|} = \frac{1}{2}\int_{\mathbb{R}^3} d\mu_i(y)\left[\int_{\mathbb{R}^3} \frac{d\mu_i(x)}{|x-y|}\right]$$

Newton

$$\overset{\downarrow}{=} \frac{1}{2}\int_{\mathbb{R}^3} d\mu_i(y) \begin{cases} \dfrac{2}{D(x_i)} & |y-x_i| < \dfrac{D(x_i)}{2} \\[2ex] \dfrac{1}{|y-x_i|} & |y-x_i| > \dfrac{D(x_i)}{2} \end{cases}$$

$$= \frac{1}{2}\,\frac{2}{D(x_i)} = \frac{1}{D(x_i)}$$

$\boxtimes$

Using the basic electrostatic inequality we get

$$\sum_{1\le i<j\le N} \frac{1}{|x_i-x_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z}{|x_i-R_j|} + \sum_{1\le k<l\le M} \frac{Z^2}{|R_k-R_l|} \geq$$

$$\geq -\sum_{i=1}^{N}\left(\int_{\mathbb{R}^3} \frac{Z\, d\mu_i(x)}{D(x)} + \frac{1}{D(x_i)}\right)$$

To finish the proof we need to show that

$$\int_{\mathbb{R}^3} \frac{d\mu_i(x)}{D(x)} \leq \frac{2}{D(x_i)}$$

This will be true if $D(x) = \min_{j=1,\dots,M} |x-R_j| \geq \frac{D(x_i)}{2}$

for any x in the support of μ_i (that is $|x-x_i| = \frac{D(x_i)}{2}$)

This is a consequence of the fact that

$$|x-R_j| \geq |x_i-R_j| - |x_i-x| \geq D(x_i) - \frac{D(x_i)}{2} = \frac{D(x_i)}{2}$$

$\boxtimes$