Stability of Matter p. 10

17. Proof of stability of second kind
18. Thermodynamic limit

17. Proof of stability of second kind

Recall

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

and

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

Thm

$$\boxed{E(M,N) \geq -C(M+N)}$$

where $C = C(Z) = C(\{Z_i\})$

Proof

Step 1

We consider the case $Z_k = Z$, $\forall k = 1,\dots,M$. We use Baxter's electrostatic inequality

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

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

$$H_{M,N} \geq \sum_{i=1}^{N} \left(-\Delta_{x_i} - \frac{2Z+1}{D(x_i)}\right).$$

Hence

$$H_{M,N} \geq \sum_{i=1}^{N} \left(-\Delta_{x_i} - \frac{2Z+1}{D(x_i)} + \mu\right) - \mu N$$

Pauli's

$$\geq \operatorname{Tr}\left(-\Delta - \frac{2Z+M}{D(x_i)} + \mu\right)_- - \mu N$$

LT

$$\geq -L_{1,3} \int_{\mathbb{R}^3} \left[\frac{2Z+1}{D(x)} - \mu\right]_+^{5/2} dx - \mu N.$$

Since $D(x) = \min_{1 \leq k \leq M} |x - R_k|$, we have

$$\left[\frac{2Z+1}{D(x)} - \mu\right]_+^{5/2} \leq \sum_{i=1}^{M} \left[\frac{2Z+1}{|x-R_k|} - \mu\right]_+^{5/2}$$

and hence

$$\int_{\mathbb{R}^3} \left[\frac{2Z+1}{D(x)} - \mu\right]_+^{5/2} dx \leq \sum_{k=1}^{M} \int_{\mathbb{R}^3} \left[\frac{2Z+1}{|x-R_k|} - \mu\right]_+^{5/2} dx =$$

$$= M \int_{\mathbb{R}^3} \left[\frac{2Z+1}{|x|} - \mu\right]_+^{5/2} dx \overset{(*)}{=} M \frac{5\pi^2}{4\sqrt{\mu}} (2Z+1)^3$$

Exercise Compute $(*)$.

$$4\pi \int_0^{\frac{A}{\mu}} x^2 \left(\frac{A}{x} - \mu\right)^{5/2} = 4\pi \int_0^{\frac{A}{\mu}} x^2 \mu^{5/2} \left(\frac{A}{\mu}\frac{1}{x} - 1\right)^{5/2} = \left(\!\left(\frac{1}{x}\frac{A}{\mu} = t, \right.\right.$$

$$\left.\left. -\frac{A}{\mu}\frac{1}{x^2}dx = dt \right)\!\right) = 4\pi \int_1^{\infty} (t-1)^{5/2} \frac{\mu}{A} \mu^{5/2} \left(\frac{A}{\mu t}\right)^4 dt = 4\pi \frac{(2Z+1)^3}{\sqrt{\mu}}.$$

$$\int_1^\infty \frac{(t-1)^{5/2}}{t^4}\,dt = 4\pi \frac{(2z+1)^3}{\sqrt{\mu}} \frac{5\pi}{16} = \frac{5}{4}\pi^2 \frac{(2z+1)^3}{\sqrt{\mu}}$$

$$\sqrt{t-1} = u$$

$$\frac{dt}{2\sqrt{t-1}} = du \Rightarrow dt = 2u\,du \qquad \int \frac{(t-1)^{5/2}}{t^4}\,dt = \int \frac{u^5\, 2u\,du}{(u^2+1)^4} \ldots$$

$\square$

Thus
$$H_{M,N} \geq -M \frac{5\pi^2 (2z+1)^3}{4\sqrt{\mu}} - \mu N$$

Step 2

The case of general $\{z_k\}$ follows from the following Proposition: (by Daubechies, Lieb 1983)

Proposition (monotonicity in nuclear charges)

Denote $E(M, N, \{z_k\})$ as the ground state energy of $H_{M,N}$ with given nuclear charges $\{z_k\}$. If $z_k \leq \tilde{z}_k$ $\forall k = 1, \ldots, M$, then
$$E(M, N, \{z_k\}) \geq E(M, N, \{\tilde{z}_k\})$$

Proof Note that for every $\ell \in \{1, 2, \ldots, M\}$, the mapping $z_\ell \longrightarrow H_{M,N}$ is linear. Therefore, the mapping $z_\ell \longrightarrow E(M, N, \{z_k\})$ is concave (concavity holds for each z_ℓ separately, not jointly).

Under the condition $0 \le z_\ell \le \tilde{z}_\ell$ we can write

$$z_\ell = t \cdot 0 + (1-t)\, \tilde{z}_\ell \quad \text{for some } t \in [0,1]$$

Hence concavity implies

$$E(M,N,\{z_\ell\}) \ge t\, E(M,N,\{z_\ell\})\Big|_{z_\ell=0} + (1-t)\, E(M,N,\{z_\ell\})\Big|_{z_\ell=\tilde{z}_\ell}$$

On the other hand, setting $z_\ell = 0$ is equivalent to putting R_ℓ at infinity. Hence

$$E(M,N,\{z_\ell\})\Big|_{z_\ell=0} \ge E(M,N,\{z_\ell\})\Big|_{z_\ell=\tilde{z}_\ell}$$

Thus

$$E(M,N,\{z_\ell\}) \ge E(M,N,\{z_\ell\})\Big|_{z_\ell=\tilde{z}_\ell}$$

By induction:

$$E(M,N,\{z_\ell\}) \ge E(M,N,\{\tilde{z}_\ell\}).$$

$\boxtimes$

To finish the proof of the theorem we find from the lemma that $(z_\ell \le z)$

$$E(M,N,\{z_\ell\}) \ge E(M,N,\{z,z,\ldots,z\}).$$

By step 1, we have

$$E(M,N,\{z,\ldots,z\}) \ge -C_z\,(M+N)$$

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

$\boxtimes$

Remarks

•) We have not included the spin of the electron. This can be done.

•) Optimizing the final bound in μ gives

$$E(M,N) \geq -C\,(2Z+1)^2 M^{2/3} N^{1/3}$$

Taking into account all physical constants this gives a lower bound on the energy:

$$E(N,M) \geq -1{,}0732^{2/3}\,[(2Z+1)\alpha]^2 M^{2/3} N^{1/3}$$

•) One can include the dynamics of nuclei, but $E(N,M)$ is a lower bound to that as the kinetic energy is positive.

•) One can include magnetic fields:

$$-i\nabla \longrightarrow -i\nabla + A$$

then stability of second kind holds for $Z < 883$.

•) One can consider semi-relativistic kinetic energy: then stability of second kind holds for $Z < 87.2$. Open problem to improve this.

18. Thermodynamic limit

Existence of thermodynamic limit:

$$\boxed{\lim_{\substack{M,N\to\infty \\ N/(M+N)\to\eta}} \frac{E(M+N)}{M+N} = e(\eta)} \qquad (*)$$

Thm Let $Z_k = Z$ $\forall k=1,\dots,M$. For every $\eta\in(0,1)$ the limit $(*)$ above exists. Furthermore, the function $e:(0,1)\to\mathbb{R}$ is bounded and convex (consequently, it is continuous).

Proof (sketch)

-) step 1: sub-additivity

$$E(M_1+M_2, N_1+N_2) \le E(M_1,N_1) + E(M_2,N_2).$$

This is a consequence of the variational principle. More precisely, given two wave functions $\psi_{N_1}\in L^2_a(\mathbb{R}^{3N_1})$, $\psi_{N_2}\in L^2_a(\mathbb{R}^{3N_2})$ we can construct a trial wave function $\psi^{(y)}_{N_1,N_2}$ in $L^2_a(\mathbb{R}^{3(N_1+N_2)})$ by antisymmetrizing the product

$$\varphi_{N_1}(x_1, \dots, x_N)\, \varphi_{N_2}(x_{N_1+1}+y, \dots, x_{N_1+N_2}+y)$$

Then $$E(M_1+M_2, N_1+N_2) \le \lim_{|y|\to\infty} \langle \varphi^{(y)}_{N_1 N_2}, H_{M_1+M_2, N_1+N_2}\, \varphi^{(y)}_{N_1,N_2} \rangle$$

$$= \langle \varphi_{N_1}, H_{M_1,N_1}\, \varphi_{N_1} \rangle + \langle \varphi_{N_2}, H_{M_2,N_2}\, \varphi_{N_2} \rangle$$

(technically, if we move the nuclei $\{R_k\}_{k=1}^{M_1}$ for H_{M_1,N_1} and $\{\tilde{R}_k\}_{k=1}^{M_2}$ for H_{M_2,N_2}, then we take the nuclei

$$\{R_1, \dots, R_{M_1}, \tilde{R}_1+y, \tilde{R}_2+y, \dots, \tilde{R}_{M_2}+y\}$$

for $H_{M_1+M_2, N_1+N_2}$).

•) Step 2.

Clearly $E(M,N) \le 0$ (otherwise stability would be trivial). This and subadditivity implies $(M,N) \to E(M,N)$ is decreasing.

From stability of matter:

$$0 \ge \frac{E(M,N)}{M+N} \ge -C.$$

Hence $\forall\, \eta \in (0,1)$ $\exists$ subsequence (M_j, N_j) such that

$$M_j, N_j \to \infty, \quad \frac{N_j}{M_j+N_j} \to \eta, \quad \lim_{j\to\infty} \frac{E(M_j,N_j)}{M_j+N_j} \text{ exists}$$

One then shows using subadditivity and monotonicity that if (M_j', N_j') is such that $M_j', N_j' \to \infty$ and $\frac{N_j'}{M_j'+N_j'} \to \eta$ then

$$\lim_{j\to\infty} \frac{E(M_j', N_j')}{M_j'+N_j'} = \lim_{j\to\infty} \frac{E(M_j, N_j)}{M_j+N_j}$$

•) <u>Step 3.</u>

Clearly $e(\eta) \in [-c, 0]$.

Convexity of $e(\eta)$ is proven in the following way: take $\eta, \eta' \in (0,1)$. Let $N, M = M(N), M' = M'(N) \to \infty$ such that

$$\frac{N}{M+N} \to \eta, \quad \frac{N}{M'+N} \to \eta'$$

then

$$\frac{N(M+N) + N(M'+N)}{2(M+N)(M'+N)} = \frac{1}{2}\left(\frac{N}{M'+N} + \frac{N}{M+N}\right) \to \frac{1}{2}(\eta+\eta')$$

Note that

$$2(M+N)(M'+N) - N(M+N) - N(M'+N) = NM + NM' + 2MM'.$$

Hence
$$\frac{E(NM + NM' + 2MM', N(N+M) + N(N+M'))}{2(M+N)(M'+N)} \to e\left(\frac{\eta+\eta'}{2}\right)$$

On the other hand, by sub-additivity of $E(N,M)$

$$\leq E(NM, N^2) + E(NM', N^2) + E(MM', NM) + E(MM', NM')$$

$$\leq N\,E(M,N) + N\,E(M',N) + M\,E(M',N) + M'\,E(M,N)$$

$$= (M'+N)\,E(M,N) + (M+N)\,E(M',N).$$

Dividing both sides by $2(M+N)(M'+N)$ we obtain

$$\frac{E(NM + NM' + 2MM',\ N(N+M) + N(N+M'))}{2(M+N)(M'+N)} \leq$$

$$\leq \frac{1}{2}\left(\frac{E(M,N)}{M+N} + \frac{E(M',N)}{M'+N}\right)$$

which after taking limit gives

$$e\left(\frac{\eta+\eta'}{2}\right) \leq \frac{1}{2}\left(e(\eta) + e(\eta')\right).$$

This implies convexity.

$\blacksquare$