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23.2 Convergence of Levy-Lieb functional.

23.2. Convergence of Levy-Lieb functional

We consider the Hamiltonian

$$H_N = \sum_{i=1}^N (-h^2 \Delta_{x_i} + V(x_i)) + \lambda \sum_{i<j} w(x_i - x_j)$$

in the semiclassical mean-field regime

$$h = N^{-1/d}, \quad \lambda = N^{-1}.$$

We will prove that the rescaled Levy-Lieb density functional

$$\mathcal{E}_N(f) := \frac{\mathcal{L}_N(Nf)}{N} = \inf_{\substack{\|\Psi_N\|=1 \\ f_{\Psi_N}=f}} \frac{\langle \Psi_N, H_N \Psi_N \rangle}{N}$$

converges to the Thomas-Fermi density functional

$$\mathcal{E}^{TF}(f) := K_d^{cl} \int_{\mathbb{R}^d} f^{1+2/d} + \int Vf + \frac{1}{2} \iint f(x) f(y) w(x-y) \, dx \, dy$$

Assumptions on potentials

- $V, w \in L^p(\mathbb{R}^d) + L^q(\mathbb{R}^d)$ with $p, q \in [1+\frac{d}{2}, \infty)$
- w admits the decomposition

$$w(x) = \int_0^\infty (g_r * g_r) \, d\mu(r)$$

for a positive measure μ on $(0, \infty)$ and a family of even functions $0 \le g_r \in L^p + L^q$, $p, q \in [2+d, \infty)$

The decomposition implies that $\hat{\omega}(k) = \int_0^\infty |\hat{g}_r(k)|^2 \, d\mu(r)$

$\rightsquigarrow$ essentially $\hat{\omega}(k) \geq 0$ plus some regularity.

This holds for a large class of potentials including Coulomb, as we have the

Fefferman - de la Llave formula

$$\frac{1}{|x|} = \frac{1}{\pi} \int_0^\infty \left(1\!\!1_{B_r} * 1\!\!1_{B_r} \right)(x) \, \frac{dr}{r^5} \qquad \forall x \in \mathbb{R}^3 \setminus \{0\}$$

Thm (Gamma convergence of LL to TF)

For all $d \geq 1$, when $N \to \infty$, the Levy-Lieb functional $\mathcal{E}_N$ converges to the Thomas-Fermi functional $\mathcal{E}^{TF}$ in the following sense:

(i) (lower bound) For every sequence $0 \leq f_N \in L^1 \cap L^{1+2/d}$ such that $\int_{\mathbb{R}^d} f_N = 1$ and $f_N \to f$ in $L^{1+2/d}$, then

$$\liminf_{N \to \infty} \mathcal{E}_N(f_N) \geq \mathcal{E}^{TF}(f)$$

(ii) (upper bound) For every $0 \leq f \in L^1 \cap L^{1+2/d}$ such that $\int_{\mathbb{R}^d} f = 1$, there exists a sequence of Slater determinants $\Psi_N \in L^2_a(\mathbb{R}^{dN})$ such that $f_{\Psi_N} = f_N \to f$ strongly in $L^1 \cap L^{1+2/d}$ and

$$\limsup_{N \to \infty} \mathcal{E}_N(f_N) \leq \mathcal{E}^{TF}(f).$$

Proof (sketch)

Lower bound

Consider a normalized $\Psi_N \in L^2_a(\mathbb{R}^{dN})$ with $f_{\Psi_N} = f \to f$ in $L^{1+2/d}$. We have

$$\frac{\langle \Psi_N, H_N \Psi_N \rangle}{N} = \frac{1}{N^{1+2/d}} \langle \Psi_N, \sum_{i=1}^N (-\Delta_{x_i}) \Psi_N \rangle + \int_{\mathbb{R}^d} V \cdot f_{\Psi_N} + \frac{1}{N^2} \langle \Psi_N, \sum w(x_i - x_j) \Psi_N \rangle$$

By the convergence of the kinetic energy we have

$$\liminf_{N\to\infty} \frac{1}{N^{1+2/d}} \langle \Psi_N, \sum -\Delta_{x_i} \Psi_N \rangle \geq K_d^{cl} \int_{\mathbb{R}^d} f^{1+2/d}$$

Moreover, since $f_N \to f$ in $L^{1+2/d}$ and $\|f_N\|_1 = 1$, by interpolation $f_N \to f$ weakly in L^r, $r \in (1, 1+2/d]$. Under the condition $V \in L^p + L^q$, $p, q \in [1+\frac{d}{2}, \infty)$ we deduce

$$\int V f_N \to \int V f.$$

It remains to consider the interaction term. Using

$$w(x-y) = \int_0^\infty d\mu(r)\, (g_r * g_r)(x-y) = \int_0^\infty d\mu(r) \int_{\mathbb{R}^d} dz\, g_r(x-z) g_r(y-z)$$

we find that

$$\langle \Psi_N, \sum_{i<j} w(x_i - x_j) \Psi_N \rangle = \int_0^\infty d\mu(r) \int_{\mathbb{R}^d} dz\, \langle \Psi_N, \sum_{i<j} g_r(x_i - z) g_r(x_j - z) \Psi_N \rangle$$

For every $r > 0$ and $z \in \mathbb{R}^d$, by the Cauchy-Schwarz inequality we get

$$\langle \psi_N, \sum_{i<j} g_r(x_i - z) g_r(x_j - z) \psi_N \rangle =$$

$$= \frac{1}{2} \Big[\langle \psi_N, \Big(\sum_{i=1}^N g_r(x_i - z) \Big)^2 \psi_N \rangle - \langle \psi_N, \sum_{i=1}^N g_r^2(x_i - z) \psi_N \rangle$$

$$\geq \frac{1}{2} \Big[\langle \psi_N, \sum_{i=1}^N g_r(x_i - z) \psi_N \rangle^2 - \langle \psi_N, \sum_{i=1}^N g_r^2(x_i - z) \psi_N \rangle \Big]$$

$$= \frac{1}{2} \Big[N^2 (f_N * g_r)^2(z) - N (f_N * g_r^2)(z) \Big]$$

Since

$f_N \longrightarrow f$ in $L^r(\mathbb{R}^d)$ for all $1 \leq r \leq 1 + 2/d$ and $g_r, g_r^2 \in L^p + L^q$, $p, q \in [1 + \frac{d}{2}, \infty)$, we find that

$$\lim_{N \to \infty} (f_N * g_r)(z) = (f * g_r)(z)$$

$$\lim_{N \to \infty} (f_N * g_r^2)(z) = (f * g_r^2)(z).$$

Hence for every

$$\liminf_{N \to \infty} N^{-2} \langle \psi_N, \sum_{i<j} g_r(x_i - z) g_r(x_j - z) \psi_N \rangle$$

$$\geq \liminf_{N \to \infty} N^{-2} \frac{1}{2} \Big[N^2 (f_N * g_r)^2(z) - N (f_N * g_r^2)(z) \Big] =$$

$$= \frac{1}{2} (f * g_r)^2(z).$$

Therefore, by Fatou's lemma

$$\liminf_{N \to \infty} N^{-2} \langle \psi_N, \sum_{i<j} w(x_i - x_j) \psi_N \rangle =$$

$$= \liminf_{N \to \infty} \int_0^\infty dr \int_{\mathbb{R}^d} dz \, N^{-2} \langle \psi_N, \sum_{i<j} g_r(x_i - z) g_r(x_j - z) \psi_N \rangle$$

$$\geq \int_0^\infty dr \int_{\mathbb{R}^d} dz \, \frac{1}{2} (f * g_r)^2(z) = \frac{1}{2} \iint f(x) f(y) \, w(x-y) \, dx \, dy$$

Thus,

$$\liminf_{N\to\infty} \frac{\langle \Psi_N, H_N \Psi_N \rangle}{N} \geq \mathcal{E}^{TF}(f)$$

Since the only condition on $\Psi_N \in L^2_a$ is $f_{\Psi_N} = f$ we get

$$\liminf_{N\to\infty} \mathcal{E}_N(f_N) \geq \mathcal{E}^{TF}(f).$$

<u>Upper bound</u>

Let $0 \leq f \in L^1 \cap L^{1+2/d}$ with $\int f = 1$. By the thm about the convergence of the kinetic energy, there exist Slater determinants $\Psi_N \in L^2_a(\mathbb{R}^{dN})$ such that $f_{\Psi_N} = f_N \longrightarrow f$ strongly in $L^1 \cap L^{1+2/d}$ and

$$\limsup_{N\to\infty} \frac{1}{N^{1+2/d}} \langle \Psi_N, \sum_{i=1}^{N} (-\Delta_i) \Psi_N \rangle \leq K_d^{cl} \int_{\mathbb{R}^d} f^{1+2/d}$$

Convergence of external potential term works as for lower bound.

Now the interaction term. Since Ψ_N is a Slater we have

$$\langle \Psi_N, \sum_{i<j} w(x_i - x_j) \Psi_N \rangle \stackrel{(*)}{=} \frac{1}{2} \iint_{\mathbb{R}^d \, \mathbb{R}^d} \left(\rho_{\Psi_N}(x) \rho_{\Psi_N}(y) - |\gamma_{\Psi_N}(x,y)|^2 \right) w(x-y) \, dx \, dy$$

Problem: check $(*)$.

we will leave this computation for a second and use $w \geq 0$ to get

$$\langle \varphi_N, \sum_{i \neq j} w(x_i - x_j)\, \varphi_N \rangle \leq \frac{1}{2} \iint \rho_{\varphi_N}(x)\, \rho_{\varphi_N}(y)\, w(x-y)\, dx\, dy$$

$$= \frac{N^2}{2} \iint f_N(x)\, f_N(y)\, w(x-y)\, dx\, dy$$

The convergence $f_N \to f$ in $L^1 \cap L^{1+2/3}$ and the assumption $w \in L^p + L^q$, imply that

$$f_N * w \longrightarrow f * w \quad \text{in } L^\infty$$

by Young's inequality: $\| f * g \|_\infty \leq \| f \|_p \| g \|_q$

Hence

$$N^{-2} \langle \varphi_N, \sum_{i \neq j} w(x_i - x_j)\, \varphi_N \rangle \leq \frac{1}{2} \iint f_N(x) f_N(y)\, w(x-y)$$

$$\xrightarrow[N \to \infty]{} \frac{1}{2} \iint f(x) f(y)\, w(x-y)\, dx\, dy$$

All together

$$\limsup_{N \to \infty} \frac{\langle \varphi_N, H_N \varphi_N \rangle}{N} \leq \mathcal{E}^{TF}(f)$$

$\boxtimes$

Solution of $(*)$

recall Slater: $u_1 \wedge \dots \wedge u_N (x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_\sigma \operatorname{sign} \sigma \, u_{\sigma(1)}(x_1) \cdots u_{\sigma(N)}(x_N)$

$$\langle \psi_N , \sum_{i<j} w(x_i - x_j)\, \psi_N \rangle =$$

$\downarrow$ Slater

$$= \frac{1}{2N!} \sum_{\sigma,\tau} \operatorname{sgn} \sigma \cdot \operatorname{sgn} \tau \sum_{i\neq j} \langle u_{\sigma(1)}(x_1) \cdots u_{\sigma(N)}(x_N), w(x_i - x_j)\, u_{\tau(1)}(x_1) \cdots u_{\tau(N)}(x_N) \rangle$$

// Now $\quad \tau = \tau \circ \sigma^{-1} \circ \sigma \quad$ and denote $\quad \tau' = \tau \circ \sigma^{-1}$ //

$$= \frac{1}{2N!} \sum_{i\neq j} \sum_{\sigma, \tau' \in S_N} \operatorname{sgn} \tau' \iint \cdots \int dx_1 \cdots dx_N$$

$$\overline{u_1(x_1) \cdots u_N(x_N)}\; w(x_i - x_j)\, u_{\tau'(1)}(x_1) \cdots u_{\tau'(N)}(x_N) =$$

$$= \{ \tau' \in S_{\{i,j\}} \} = \frac{1}{2} \sum_{\tau' \in S_{\{i,j\}}} \operatorname{sgn}(\tau') \int_{\mathbb{R}^d} dx \int_{\mathbb{R}^d} dy\; \overline{u_i(x)\, u_j(y)}$$

$$w(x-y)\, u_{\tau'(1)}(x)\, u_{\tau'(N)}(y) =$$

$$= \frac{1}{2} \sum_{i\neq j} \int dx\, dy\; \overline{u_i(x)\, u_j(y)}\; w(x-y) \left(u_i(x) u_j(y) - u_j(x) u_i(y) \right)$$

$$= \frac{1}{2} \left(\int dx \int dy\; \rho(x) \rho(y)\, w(x-y) - \int dx \int dy\; \gamma(x,y)\, \overline{\gamma}(x,y)\, w(x-y) \right)$$

$$= \frac{1}{2} \iint \rho(x)\rho(y)\, w(x-y)\, dx\, dy - \frac{1}{2} \iint |\gamma(x,y)|^2\, w(x-y)\, dx\, dy$$

where, recall,

$$\gamma(x,y) = \sum_{i=1}^{N} u_i(x)\overline{u_i(y)}, \quad \rho(x) = \gamma(x,x).$$

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23.3. Convergence of ground state and ground state energy

Thm Let $d \geq 1$. The ground state energy E_N of H_N converges to the Thomas-Fermi energy:

$$\lim_{N\to\infty} \frac{E_N}{N} = E^{TF}$$

$\uparrow$ with $\int f = 1$ (rescaled)

Moreover, if $\Psi_N \in L^2_a(\mathbb{R}^{dN})$ is a ground state of H_N or more generally

$$\lim_{N\to\infty} \frac{\langle \Psi_N, H_N \Psi_N\rangle}{N} \to E^{TF},$$

then

$$f_{\Psi_N} \rightharpoonup f^{TF} \quad \text{weakly} \quad \text{in } L^{1+2/d}(\mathbb{R}^d)$$

where f^{TF} is the unique Thomas-Fermi minimizer of

$$\mathcal{E}^{TF}(f) = K_d^{cl} \int f^{1+2/d} + \int Vf + \frac{1}{2} \iint f(x) f(y)\, w(x-y)\, dx\, dy$$

satisfying $\int f^{TF} \leq 1$.

Remarks:

•) It may happen that $\mathcal{E}_N$ has no minimizer and/or $\mathcal{E}^{TF}$ has no minimizer satisfying $\int f^{TF}=1$. Nevertheless the convergence of the ground state is valid.
In fact it is valid under more general assumptions on w, e.g. $w(x) = \frac{1}{|x|}$.

•) This result justifies Thomas-Fermi theory in the atomic case. This was first proven by Lieb and Simon in 1973.

Proof (sketch)
Energy upper bound:

Recall the variational principle:

$$E_N = \inf_{\|\varphi_N\|=1} \langle \varphi_N, H_N \varphi_N \rangle = \inf_{\substack{f\geq 0 \\ \int f=1}} \; \inf_{\substack{\|\varphi_N\|=1 \\ f_{\varphi_N}=f}} \langle \varphi_N, H_N \varphi_N \rangle$$

which can be rewritten as

$$\frac{E_N}{N} = \inf_{\substack{f\geq 0 \\ \int f=1}} \mathcal{E}_N(f) \; ; \quad \mathcal{E}_N(f) = \inf_{\substack{\|\varphi_N\|=1 \\ f_{\varphi_N}=f}} \frac{\langle \varphi_N, H_N \varphi_N \rangle}{N}$$

Recall

Ex: $\int f \leq 1$

$$E^{TF} = \inf \{ \mathcal{E}^{TF}(f) : 0 \leq f \in L^1 \cap L^{1+2/d}, \int f = 1 \}$$

For every $0 \leq f \in L^1 \cap L^{1+2/d}$ s.t. $\int f = 1$, by Gamma conv.

(upper bound), we can find Slater determinants φ_N such that $f_{\varphi_N} = f_N \to f$ strongly in $L^1 \cap L^{1+2/d}$ and

$$\limsup_{N\to\infty} \frac{E_N}{N} \leq \limsup_{N\to\infty} \mathcal{E}_N(f_N) \leq \mathcal{E}^{TF}(f)$$

Optimizing over f we obtain

$$\limsup_{N\to\infty} \frac{E_N}{N} \leq E^{TF}.$$

<u>Energy lower bound</u>:

Using $w \geq 0$ we have

$$H_N \geq \sum_{i=1}^N \left(-N^{2/d} \Delta_{x_i} + V(x_i)\right)$$

which by Lieb–Thirring gives

$$\frac{\langle \varphi_N, H_N \varphi_N\rangle}{N} \geq \frac{\langle \varphi_N, \sum -\Delta_i \varphi_N\rangle}{N^{1+2/d}} + \int V f_{\varphi_N} \geq K_d \int f_{\varphi_N}^{1+2/d} + \int V f_{\varphi_N}$$

for a constant $K_d > 0$. Since $V \in L^p + L^q$, $p,q \in [1+\frac{d}{2}, \infty)$ we have

$$\frac{\langle \varphi_N, H_N \varphi_N\rangle}{N} \overset{(*)}{\geq} \frac{K_d}{2} \int f_{\varphi_N}^{1+2/d} - C$$

thus $\frac{E_N}{N}$ is bounded from below. Moreover, if the wave function satisfies $\langle \varphi_N, H_N \varphi_N\rangle = E_N + o(N)$ then $f_N := f_{\varphi_N}$ is bounded in $L^{1+2/d}(\mathbb{R}^d)$.

Up to a subsequence, we can assume

$$f_N \rightharpoonup f \quad \text{in} \quad L^{1+2/d}(\mathbb{R}^d).$$

Hence, by Gamma convergence (lower bound) we have

$$\liminf_{N\to\infty} \frac{E_N}{N} = \liminf_{N\to\infty} \frac{\langle \Psi_N, H_N \Psi_N \rangle}{N} \geq \liminf_{N\to\infty} \mathcal{E}_N(f_N) \geq \mathcal{E}^{TF} \geq E^{TF}$$

$\boxtimes$

Exercise:

Show $\int f^{TF} = 1$

Solution:

Assume by contradiction that $\int f^{TF} < 1$.

$\forall\, 0 \leq \varphi \in C_c^\infty(\mathbb{R}^3)$, $t > 0$ small we have

$$f^{TF} + t\varphi \geq 0, \quad \int_{\mathbb{R}^3} (f^{TF} + t\varphi) \leq 1$$

$\mathcal{E}^{TF}(f^{TF}) \leq \mathcal{E}^{TF}(f^{TF} + t\varphi)$. Consequently

$$0 \leq \frac{d}{dt}\left(\mathcal{E}^{TF}(f^{TF} + t\varphi)\right)\Big|_{t=0^+} = \int_{\mathbb{R}^3}\left(K f^{TF}(x)^{2/3} - \frac{1}{|x|} + f^{TF} * \frac{1}{|x|}\right)\varphi(x)\, dx$$

Since this holds $\forall \varphi \geq 0$ we get

$$K(f^{TF})^{2/3} - \frac{1}{x} + f^{TF} * \frac{1}{|x|} \geq 0 \qquad \text{a.e. } x \in \mathbb{R}^3.$$

By Newton's theorem

$$\left(f^{TF} * \frac{1}{|\cdot|}\right)(x) = \int_{\mathbb{R}^3} \frac{f^{TF}(y)}{|x-y|}\, dy = \int_{\mathbb{R}^3} \frac{f^{TF}(y)}{\max\{|x|,|y|\}}\, dy$$

$$\leq \int_{\mathbb{R}^3} \frac{f^{TF}(y)}{|x|}\, dy = \frac{\int f^{TF}}{|x|}.$$

Thus $\quad K f^{TF}(x)^{2/3} \geq \frac{1}{|x|} - f^{TF} * \frac{1}{|x|} \geq \left(1 - \int f^{TF}\right)\frac{1}{|x|} \quad$ a.e. x

This implies

$$f^{TF}(x) \geq \frac{c_0}{|x|^{3/2}}$$ which contradicts $\int f^{TF} < \infty$.

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