Ground-State Energies of Coulomb Systems and Reduced One-Particle Density Matrices

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I. Introduction

Atomic Schrödinger operator

$$H_{N,Z} := \sum_{n=1}^{N} \left(-\Delta_n - \frac{Z}{|x_n|} \right) + \sum_{1 \leq m < n \leq N} \frac{1}{|x_m - x_n|}$$

self-adjointly realized in

$$\mathfrak{H}_N := \bigwedge_{n=1}^{N} L^2(\mathbb{R}^3) \otimes \mathbb{C}^q.$$

Of interest is the lowest the spectral point of $H_{N,Z}$, in particular

$$E(N,Z) := \inf \sigma(H_{N,Z}).$$

(Drop N, if equal to Z. Pick $q = 1$ for notational convenience.)

In physics an asymptotic expansion for large Z was “derived” by Thomas (1927) and Fermi (1927); Scott (1952); Schwinger (1981)

$$E(Z) = E_{\mathrm{TF}}(1)Z^{7/3} + \frac{q}{8}Z^2 - \gamma_S Z^{5/3} + o(Z^{5/3}).$$

(Lieb and Simon (1977), Hughes (1986), Siedentop and Weikard (1986–1989), Fefferman and Seco (1989–1995))

Thomas-Fermi functional (Lenz 1932):

$$\mathcal{E}_{\mathrm{TF}}(\rho) := \int_{\mathbb{R}^3} \left(\frac{3}{5} \left(\frac{6\pi^2}{q}\right)^{\frac{3}{2}} \rho(x)^{\frac{5}{3}} - \frac{Z}{|x|}\rho(x) \right) \mathrm{d}x + \underbrace{\frac{1}{2}\int_{\mathbb{R}^6} \mathrm{d}x\mathrm{d}y \frac{\rho(x)\rho(y)}{|x-y|}}_{=:D[\rho]} \tag{1}$$

Thomas-Fermi energy

$$E_{\mathrm{TF}}(Z) := \inf\{\mathcal{E}_{\mathrm{TF}}(\rho) | \rho \in L^{\frac{5}{3}} \cap L^1(\mathbb{R}^3),\ \rho \geq 0\} \tag{2}$$

Scaling relation

$$E_{\mathrm{TF}}(Z) = E_{\mathrm{TF}}(1) Z^{7/3} \tag{3}$$

Thomas-Fermi functional is an example of a functional of the (electronic) density ρ. Attractive idea: $3N$ dimensions reduced to 3 dimensions paid for by non-quadratic functional. Hohenberg and Kohn (1964) triggered a rush on density functionals.
However, practically only Thomas-Fermi functional obviously related to $E(N, Z)$ (Lieb-Thirring inequality, Lieb and Simon (1977)). Reason: already the expression for the kinetic energy in ρ is not known. Remedy: use the one-particle reduced density matrix (3 instead of 6 dimensions).

II. One-Particle Reduced Density Matrix

Set $\mathcal{I}_N$ of (reduced one-particle) density matrices γ:

- $\gamma \in \mathfrak{S}^1(L^2(\mathbb{R}^3))$, $N \geq \operatorname{tr}\gamma =$ number of particles)

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Examples of γ: Pick normalized element $\psi \in \mathfrak{H}_N$. Then

$$\gamma_\psi(x,y) := \binom{N}{1} \int \mathrm{d}x_2 ... \mathrm{d}x_N \psi(x, x_2, ..., x_N)\overline{\psi(y, x_2, ..., x_N)}$$

is the reduced one-particle density matrix of ψ.

III. Functionals of the Reduced Density Matrix

During the last five years: rush on functionals of the density matrix. We discuss the two basic ones: Hartree-Fock functional and Müller functional.

Hartree-Fock functional:

$$\mathcal{E}_{\mathrm{HF}}(\gamma) := \mathrm{tr}(-\Delta - \frac{Z}{|x|})\gamma + D[\rho_\gamma] - X[\gamma] \tag{4}$$

with $\rho_\gamma(x) = \gamma(x,x)$ and

$$X[\gamma] := \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y \frac{|\gamma(x,y)|^2}{|x-y|}$$

(exchange energy).

Some results on the Hartree-Fock functional:

Existence of minimizers For $N \in \mathbb{N}$, $N < Z + 1$ exists an minimizer γ in $\mathcal{I}_N$ with $\operatorname{tr} \gamma = N$ (Lieb and Simon (1978))

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Upper bound For $N \in \mathbb{N}$: $E(N, Z) \leq E_{\mathrm{HF}}(N, Z)$.
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Correctness of Hartree-Fock Bach (1992), Graf & Solovej (1994):

$$E_{\mathrm{HF}}(Z) = E(Z) + o(Z^{\frac{5}{3}}).$$

Müller functional:

$$\mathcal{E}_{\mathrm{M}}(\gamma) := \mathrm{tr}(-\Delta - \frac{Z}{|x|})\gamma + D[\rho_\gamma] - X[\gamma^{\frac{1}{2}}] \tag{5}$$

Note the only change $\gamma \to \gamma^{\frac{1}{2}}$ in X.
Comparison between the functionals: Assume

$$\rho_\psi^{(2)}(x,y) := \binom{N}{2} \int_{\mathbb{R}^{3(N-2)}} |\psi(x,y,x_2,...,x_N)|^2 \mathrm{d}x_3 ... \mathrm{d}x_N$$

the reduced 2-particle density of a state $\psi \in \mathfrak{H}_N$. Note, that

$$\int \rho_\psi^{(2)} = \binom{N}{2}$$

and

$$\mathcal{E}(\psi) = \mathrm{tr}(-\Delta - \frac{Z}{|x|})\gamma_\psi + \int \mathrm{d}x \int \mathrm{d}y \frac{\rho_\psi^{(2)}(x,y)}{|x-y|}.$$

Thus, two ansätze:

$$\text{HF: } \rho^{(2)}_{\mathrm{HF}}(x,y) := \tfrac{1}{2}(\gamma_\psi(x,x)\gamma_\psi(y,y) - |\gamma(x,y)|^2).$$

$$\text{Müller: } \rho^{(2)}_{\mathrm{M}}(x,y) := \tfrac{1}{2}(\gamma_\psi(x,x)\gamma_\psi(y,y) - |\gamma_\psi^{\frac{1}{2}}(x,y)|^2).$$

Thus

$$\begin{aligned}\int \rho^{(2)}_{\mathrm{HF}} &= \frac{1}{2}(N^2 - \int \gamma^2(x,x)\mathrm{d}x) \\ &\geq \underbrace{\frac{1}{2}(N^2 - \int \gamma^{\frac{1}{2}2}(x,x)\mathrm{d}x)}_{=\int \rho^{(2)}_{\mathrm{M}}} = \binom{N}{2} = \int \rho^{(2)}_\psi. \quad (6)\end{aligned}$$

Inequality strict unless γ is a projection, i.e., **HF has in general too many pairs** whereas Müller has the correct number.

Facts about the Müller functional (Frank, Lieb, Seiringer, and Siedentop (2007)) (FLSS)

HF $>$ Müller $E_{\mathrm{M}}(N, Z) \leq E_{\mathrm{HF}}(N, Z)$ (HF-minimizers are projections and $\mathcal{E}_{\mathrm{HF}}(\gamma) = \mathcal{E}_{\mathrm{M}}(\gamma)$, if $\gamma^2 = \gamma$.)

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Credo about the Müller functional (What you should believe!)

Minimizer's positivity $\gamma_{\min} > 0$. Consequences: unique minimizer.

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FLSS have tried the first two. What about the third statement?

Theorem

There is a constant c such that for all $Z \geq 1$

$$E_{\mathrm{M}}(Z) \leq E_{\mathrm{HF}}(Z) \leq E_{\mathrm{M}}(Z) + cZ^{\frac{5}{3}-\frac{1}{140}}.$$

Corollary

$$E_{\mathrm{M}}(Z) = E(Z) + o(Z^{\frac{5}{3}}) = E_{\mathrm{TF}}(Z) + \frac{1}{8}Z^2 - c_{\mathrm{S}}Z^{\frac{5}{3}} + o(Z^{\frac{5}{3}}). \quad (7)$$

The theorem's proof is inspired by Bach (1992) and Graf & Solovej (1994): The energy difference is dominated by the truncated density matrix $\gamma_{\min}(1-\gamma_{\min})$. That this difference is small will follow from the fact that $\gamma_{\min}$ is almost completely condensed into a state close to a projection.

IV. Outline of the proof

IV.1 Simple bound on the Müller energy

Reduced Hartree-Fock functional and its infimum:

$$\mathcal{E}_{\mathrm{rHF}}(\gamma) := \mathrm{tr}[(-\Delta - Z/|\cdot|)\gamma] + D[\rho_\gamma] \quad (8)$$

$$E_{\mathrm{rHF}}(N, Z) := \inf \mathcal{E}_{\mathrm{rHF}}(\mathcal{I}_N). \quad (9)$$

Lemma

Assume γ a minimizer of the Müller functional on $\mathcal{I}_N$ (short: a Müller minimizer). Then

$$E_{\mathrm{M}}(Z) \leq E_{\mathrm{HF}}(Z) \leq E_{\mathrm{rHF}}(Z) \leq \mathcal{E}_{\mathrm{rHF}}(\gamma) \leq E_{\mathrm{M}}(Z) + C\ Z^{\frac{5}{3}}. \quad (10)$$

Proof: Idea: Modify Lieb's 1981 argument to control the Dirac term $\rho^{4/3}$: Pick $\epsilon \in (0,1)$. Let γ be a Müller minimizer. Then

$$
\begin{aligned}
&E_{\mathrm{rHF}}(Z,Z) \geq E_{\mathrm{HF}}(Z,Z) \geq E_{\mathrm{M}}(Z,Z) \\
&\quad = \mathrm{tr}[(-\Delta - Z/|\cdot|)\gamma] + D[\rho_\gamma] - X[\gamma^{\frac{1}{2}}] \\
&\quad = \mathrm{tr}[(-(1-\epsilon)\Delta - Z/|\cdot|)\gamma] + D[\rho_\gamma] + \epsilon\,\mathrm{tr}(-\Delta\gamma) - X[\gamma^{\frac{1}{2}}] \\
&\quad \geq \frac{1}{1-\epsilon} E_{\mathrm{rHF}}(Z) \\
&\quad + \inf\Big\{ \int_{\mathbb{R}^6} \mathrm{d}x \underbrace{\int_{\mathbb{R}^6} \epsilon |\nabla_y \gamma^{\frac{1}{2}}(x,y)|^2 - \frac{|\gamma^{\frac{1}{2}}(x,y)|^2}{2|x-y|}\mathrm{d}y}_{\geq -\frac{1}{16\epsilon}\int_{\mathbb{R}^6} |\gamma^{\frac{1}{2}}(x,y)|^2 \mathrm{d}y} \Big| \gamma \in \mathcal{I}_N \Big\} \\
&\quad \geq E_{\mathrm{rHF}}(Z) - \epsilon C\ Z^{\frac{7}{3}} - \epsilon^{-1} N/16 = E_{\mathrm{rHF}}(Z) - C\ Z^{\frac{5}{3}} \qquad (11)
\end{aligned}
$$

(By scaling of the reduced Hartree-Fock functional, by $E_{\mathrm{rHF}}(Z) = E_{\mathrm{TF}}(Z) = E_{\mathrm{TF}}(1) Z^{\frac{7}{3}} + o(Z^{\frac{7}{3}})$ (Lieb (1981)), $N = Z$, picking $\epsilon := Z^{-\frac{2}{3}}$.) $\square$

IV.2 Degree of evaporation of the Müller ground state

P semi-classical projection onto the bound states of the Thomas-Fermi potential $\phi_{\mathrm{TF}} := Z/|\cdot| - \rho_{\mathrm{TF}} * |\cdot|^{-1}$ the Thomas-Fermi potential. In detail: set

$$g(x) := \begin{cases} (2\pi R)^{-\frac{1}{2}} |x|^{-1} \sin(\pi |x|/R) & |x| \leq R \\ 0 & |x| > R \end{cases}$$

with $R = Z^{-3/5}$. Coherent states

$$f_{p,q}(x) := e^{\mathrm{i}p\cdot x} g(x-q) \tag{12}$$

with $p, q \in \mathbb{R}^3$.

$$P := (2\pi)^{-3} \int_{p^2 - \phi(q) < 0} \mathrm{d}p \mathrm{d}q |f_{p,q}\rangle\langle f_{p,q}|. \tag{13}$$

Lemma

Evaporation of Müller ground state out of P Assume γ a Müller minimizer. Then

$$\delta(\gamma, P) := \mathrm{tr}((1-P)\gamma) = O(Z^{\frac{69}{70}}). \tag{14}$$

Proof: For all $\gamma \in \mathcal{I}_Z$

$$\mathrm{tr}(\gamma(\underbrace{-\Delta - \phi}_{=:H_{\mathrm{TF}}})) \geq \mathrm{tr} \int_{\mathbb{R}^6} \mathrm{d}p\mathrm{d}q(p^2 - \phi(q))|f_{p,q}\rangle\langle f_{p,q}| - C\ Z^{\frac{7}{3}-\frac{1}{30}} \tag{15}$$

(Lieb (1981), Thirring (1981)). Thus

$$\mathcal{E}_{\mathrm{rHF}}(\gamma) \geq \mathrm{tr}(\gamma H_{\mathrm{TF}}) - D[\rho] \geq \int_{\mathbb{R}^6} \mathrm{d}p\mathrm{d}q(p^2 - \phi(q))_- - D[\rho] - C\ Z^{\frac{7}{3}-\frac{1}{30}}, \tag{16}$$

since $D[\rho - \rho_{\gamma_{\mathrm{rHF}}}] \geq 0$. Moreover,

$$\int_{-a<p^2-\phi(x)<0} \mathrm{d}p\mathrm{d}q(p^2 - \phi(q) + a) = O(a^{\frac{7}{4}}) \tag{17}$$

(Bach (1993, Graf and Solovej (1994)).

Set

$$\mathcal{E}_{\mathrm{M},a}(\gamma) := \mathcal{E}_{\mathrm{M}}(\gamma) - a\,\mathrm{tr}(1-P)\gamma.$$

Then

$$a\,\mathrm{tr}(1-P)\gamma = E_{\mathrm{M}}(Z) - \mathcal{E}_{\mathrm{M},a}(\gamma) \underbrace{\leq}_{(\mathbf{??})} E_{\mathrm{rHF}}(Z) - [\mathcal{E}_{\mathrm{rHF}}(\gamma) - a\,\mathrm{tr}((1-P)\gamma)]$$

$$\leq E_{\mathrm{rHF}}(Z) + aZ - \mathrm{tr}((H_{\mathrm{TF}} + aP)\gamma) + D[\rho] + C\ Z^{\frac{5}{3}}$$

$$\leq \int_{\mathbb{R}^6} \mathrm{d}p\mathrm{d}q(p^2 - \phi(x) + a)_- - D[\rho] - \int_{\mathbb{R}^6} \mathrm{d}p\mathrm{d}q(p^2 - \phi(x) + a\chi_M(x))_- + D[\rho]$$

$$= \int_{-a<p^2-\phi(x)<0} \mathrm{d}p\mathrm{d}q(p^2 - \phi(x) + a) + O(Z^{\frac{69}{30}}) \leq C\,(a^{\frac{7}{4}} + Z^{\frac{69}{30}}), \tag{18}$$

i.e., with $a = Z^{\frac{138}{105}}$ we get

$$\delta(\gamma, P) = O(Z^{\frac{69}{70}}), \tag{19}$$

which is the desired estimate on the degree of evaporation.

Corollary

Again, γ a Müller minimizer. Then

$$\operatorname{tr}(\gamma(1-\gamma)) \le C\, Z^{\frac{69}{70}}. \tag{20}$$

Proof.

Since $0 \le \gamma \le 1$ and $\operatorname{tr}\gamma = \operatorname{tr} P = Z$, we have

$$\begin{aligned}
&\operatorname{tr}(\gamma(1-\gamma)) = \operatorname{tr}(P\gamma(1-\gamma)) + \operatorname{tr}((1-P)\gamma(1-\gamma)) \\
\le &\operatorname{tr}(P(1-\gamma)) + \operatorname{tr}((1-P)\gamma) = Z - \operatorname{tr}(P\gamma) + \operatorname{tr}((1-P)\gamma) \\
= &2\operatorname{tr}((1-P)\gamma) = 2\delta(\gamma, P) = O(Z^{\frac{69}{70}}).
\end{aligned}$$

$\square$

IV.3 Bound on the Müller energy through truncated density matrix

Lemma

Again, γ a Müller minimizer. Then

$$0 \leq E_{\mathrm{HF}}(Z) - E_{\mathrm{M}}(Z) \leq C\ Z^{\frac{7}{6}} (\mathrm{tr}\,\gamma(1-\gamma))^{\frac{1}{2}}.$$

Proof.

By the variational principle

$$0 \leq E_{\mathrm{HF}}(Z) - E_{\mathrm{M}}(Z) \leq \frac{1}{2} \int \mathrm{d}x \int \mathrm{d}y \frac{|\gamma^{\frac{1}{2}}(x,y)|^2 - |\gamma(x,y)|^2}{|x-y|} \tag{21}$$

$$= \frac{1}{2} \int \mathrm{d}x \int \mathrm{d}y \frac{(\gamma^{\frac{1}{2}}(x,y) + \gamma(x,y))\overline{(\gamma^{\frac{1}{2}}(x,y) - \gamma(x,y))}}{|x-y|} \tag{22}$$

$$\leq \frac{1}{2} \sqrt{\int_{\mathbb{R}^6} \mathrm{d}x \int_{\mathbb{R}^6} \mathrm{d}y \frac{|\gamma^{\frac{1}{2}}(x,y) + \gamma(x,y)|^2}{|x-y|^2}} \sqrt{\mathrm{tr}\, |\gamma^{\frac{1}{2}}(1-\gamma^{\frac{1}{2}})|^2} \tag{23}$$

$$\leq 2\sqrt{\mathrm{tr}(-\Delta\gamma)}\sqrt{\mathrm{tr}[\gamma(1-\gamma)]} \leq C\ Z^{\frac{7}{6}} \sqrt{\mathrm{tr}[\gamma(1-\gamma)]}. \tag{24}$$

$\square$

Proof of Theorem 1.

The upper bound is trivial. The lower bound is follows from the above lemmata. $\square$