STABILITY OF MATTER AND HARTREE-FOCK (MQM WS2016-17)

1. Lieb-Thirring and Lieb-Oxford inequalities

Theorem 1 (Lieb-Thirring). *Let $\psi \in \bigwedge_{n=1}^N H^1(\mathbb{R}^3)$ (antisymmetric, but we drop spin because it will not change the argument but will make notation heavier). Then*

eqn:lt (1.1)
$$T[\psi] := \sum_{\nu=1}^N \int_{\mathbb{R}^3} |\nabla_\nu \psi|^2 \geq L \int \rho_\psi(x)^{5/3}\, dx,$$

where

$$\rho_\psi(x) := N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots, x_N)|^2\, dx_2 \cdots dx_N.$$

The constant L is independent of ψ, and the optimal value is conjectured (Lieb-Thirring conjecture, hard!) to be $L = \frac{3}{5}\gamma_{TF} = \frac{3}{5}(6\pi^2)^{2/3}$.

This inequality is proved in homework sheet 7.

Theorem 2 (Lieb-Oxford). *Let $\psi \in H^1(\mathbb{R}^{3N})$. Then*

lieb-oxford (1.2)
$$\int_{\mathbb{R}^{3N}} \sum_{1 \leq n < m \leq N} \frac{|\psi(x)|^2}{|x_n - x_m|}\, dx \geq D[\rho_\psi] - 1.68 \int \rho_\psi^{4/3}.$$

Theorem 3. *Let*

hamiltonian (1.3)
$$H_{\mathcal{Z},\mathcal{R}} := \sum_{n=1}^N \Bigg(-\Delta_n \underbrace{- \sum_{k=1}^K \frac{Z_k}{|x_n - R_k|}}_{=:V(x_n)} \Bigg) + \sum_{1 \leq n < m \leq N} \frac{1}{|x_n - x_m|} + \underbrace{\sum_{1 \leq k < \ell \leq K} \frac{Z_k Z_\ell}{|R_k - R_\ell|}}_{\mathfrak{A}},$$

which is self adjoint in $\bigwedge_{n=1}^N L^2(\mathbb{R}^3)$. Then there exists C (depending on $N+K$ and the maximum Z_n) such that for all $R_1, \dots, R_K \in \mathbb{R}^3$ pairwise different,

(1.4)
$$\inf \sigma(H_{\mathcal{Z},\mathcal{R}}) \geq -C(N+K),$$

i.e.

$$\inf \left\{ (\psi, H_{\mathcal{Z},\mathcal{R}}\psi) : \psi \in \bigwedge_{n=1}^N C_0^\infty(\mathbb{R}^3), \|\psi\| = 1 \right\} \geq -C(N+K).$$

Proof. First note that by Teller,

$$\begin{aligned} E_{TF}(\mathcal{Z}) &\geq E_{TF}(Z_1) + \cdots + E(Z_K) = (Z_1^{7/3} + \cdots + Z_K^{7/3}) E_{TF}(1) \\ &\geq \max\{Z_1, \dots, Z_K\}^{7/3} E_{TF}(1) K. \end{aligned}$$

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Now apply Lieb-Thirring and Lieb-Oxford:

$$\begin{aligned}(\psi, H_{\mathcal{Z},\mathcal{R}}\psi) &\geq \int (\underbrace{(1-\varepsilon)L}_{:=\frac{3}{5}\gamma_{TF}} \rho_\psi^{5/3} - V(x)\rho_\psi(x))\,dx + D[\rho_\psi] + \underbrace{\mathfrak{A}}_{\text{repulsive}} + \varepsilon L \int \rho_\psi^{5/3} - 1.68 \int \underbrace{\rho_\psi(x)^{4/3}}_{=\rho_\psi^{5/6}\rho_\psi^{1/2}}\,dx \\ &\geq -\max\{Z_1,\dots,Z_K\}^{7/3} E_{TF}(1) K + \varepsilon L \int \rho_\psi^{5/3} - 2\cdot \frac{1.68}{2}\sqrt{\delta}\left(\int \rho_\psi^{5/3}\right)^{1/2}\left(\int \rho_\psi\right)^{1/2}\frac{1}{\sqrt{\delta}} \\ &\geq -CK + \varepsilon L \int \rho_\psi^{5/3} - \frac{1.68}{2}\delta \int \rho_\psi^{5/3} - \frac{1.68}{2}\frac{1}{\delta} N \\ &\geq -C(K+N),\end{aligned}$$

where we used $2ab \leq a^2 + b^2$ in the 2nd to last inequality, and chose δ so that $\varepsilon L = \frac{1.68}{2}\delta$ to obtain the last inequality. □

Remark. Goal: We want to show the actual quantum energy for saturated atoms $N = Z$ satisfies

$$E_Q(Z,Z) = E_{TF}(Z) + o(Z^{7/3}), \quad Z \to \infty, \tag{1.5}$$

so Thomas-Fermi gives the correct energies asymptotically.

2. Reduced density matrix functionals

We are considering states $\psi \in \bigwedge_{n=1}^{N}(L^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$ antisymmetric with spin, with norm 1. For notation, we let $x = (\mathfrak{x}, \sigma) \in \mathbb{R}^3 \times \{1,\dots,q\} =: \Gamma$ and write $\int dx = \sum_{\sigma=1}^{q} \int d\mathfrak{x}$.

Definition 1. The *one-particle reduced density matrix of* ψ is

$$\begin{aligned}\gamma_\psi : L^2(\Gamma) &\longrightarrow L^2(\Gamma) \\ f &\longmapsto \int_\Gamma \gamma_\psi(x,x') f(x')\,dx',\end{aligned}$$

where

$$\gamma_\psi(x,x') := N \int_{\Gamma^{N-1}} \psi(x,x_2,\dots,x_N)\overline{\psi(x',x_2,\dots,x_N)}\,dx_2\cdots dx_N. \tag{2.1}$$

Claim 4. $\gamma_\psi \geq 0$.

Proof.

$$\begin{aligned}(f,\gamma_\psi f) &= \int dx \int dx'\, \overline{f(x)}\gamma(x,x') f(x') \\ &= \int dx \int dx' \int dx_2\cdots dx_N\, \overline{f(x)}\psi(x,x_2,\dots,x_N)\overline{\psi(x',x_2,\dots,x_N)} f(x') \\ &= \int dx_2\cdots dx_N \left| \int dx\, \overline{f(x)}\psi(x,x_2,\dots,x_N)\right|^2 \geq 0.\end{aligned}$$

□

Fact 5. *For fermions,* $\gamma_\psi \leq 1$.

Fact 6. $\operatorname{tr}\gamma_\psi = N$*, so* $\gamma \in \mathfrak{S}^1(\Gamma)$ *the trace class operators.*

Definition 2. Any $\gamma \in \mathfrak{S}^1(\Gamma)$ with $0 \leq \gamma \leq 1$ is called a *reduced one-particle density matrix* and $N := \operatorname{tr}\gamma$ is called its *particle number*.

Remark. If γ is a one-particle density matrix with $\operatorname{tr}\gamma \in \mathbb{N}_0$, then there exists $\psi \in \bigwedge_{n=1}^{N} L^2(\Gamma)$, $\|\psi\| = 1$, such that $\gamma = \gamma_\psi$.

2.1. Slater determinant. Given $e_1, \dots, e_N \in L^2(\Gamma)$ (called orbitals by chemists) pairwise orthogonal, the simplest antisymmetric wavefunction we can form is given by a *Slater determinant*,

$$\frac{1}{\sqrt{N!}} e_1 \wedge \cdots \wedge e_N(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} e_1(x_1) & \cdots & e_1(x_N) \\ \vdots & \ddots & \vdots \\ e_N(x_1) & \cdots & e_N(x_N) \end{vmatrix}. \tag{2.2}$$

The associated one-particle reduced density matrix and its integral kernel are

$$\gamma_{\psi_{e_1,\dots,e_N}} = |e_1\rangle\langle e_1| + \cdots + |e_N\rangle\langle e_N| \tag{2.3}$$

$$\gamma_{\psi_{e_1,\dots,e_N}}(x, x') = e_1(x)\overline{e_1(x')} + \cdots + e_N(x)\overline{e_N(x')} \tag{2.4}$$

Thus the one-particle reduced density matrix of a Slater determinant is a projection onto the space spanned by its orbitals.

2.2. Hartree-Fock functional. This is also called mean-field theory. We assume our wavefunction is as simple as possible, given by a Slater determinant as above, and plug it into the Hamiltonian (eqn:hamiltonian 1.3).

Definition 3. The *Hartree-Fock functional* is

$$\begin{aligned} E^C_{HF}(e_1, \dots, e_N) :=& (\psi_{e_1,\dots,e_N}, H_{\mathcal{Z},\mathcal{R}} \psi_{e_1,\dots,e_N}) \\ =& \sum_{n=1}^N (e_n, (-\Delta - V)e_n) + \frac{1}{2}\int_\Gamma dx \int_\Gamma dy \left[\frac{(|e_1(x)|^2 + \cdots |e_N(x)|^2)(|e_1(y)|^2 + \cdots + |e_N(y)|^2)}{|\mathfrak{x} - \mathfrak{y}|} - \right. \\ & \left. - \frac{|e_1(x)\overline{e_1(y)} + \cdots + e_N(x)\overline{e_N(y)}|}{|\mathfrak{x} - \mathfrak{y}|} \right] + \underbrace{\mathfrak{A}}_{\text{repulsion}} \end{aligned}$$

The Hartree-Fock functional (omitting the repulsive term) can also be written

$$\begin{aligned} E^C_{HF}(e_1, \dots, e_N) = \operatorname{tr}((-\Delta - V)\gamma_{\psi_{e_1,\dots,e_N}}) + & \underbrace{\frac{1}{2}\int_\Gamma dx \int_\Gamma dy \frac{\gamma_{\psi_{e_1,\dots,e_N}}(x,x)\gamma_{\psi_{e_1,\dots,e_N}}(y,y)}{|\mathfrak{x} - \mathfrak{y}|}}_{=:D[\rho_\psi]} - \\ & - \underbrace{\frac{1}{2}\int_\Gamma dx \int_\Gamma dy \frac{|\gamma_{\psi_{e_1,\dots,e_N}}(x,y)|^2}{|\mathfrak{x} - \mathfrak{y}|}}_{=:X[\gamma_{\psi_{e_1,\dots,e_N}}] \text{ exchange term}} \end{aligned} \tag{2.5}$$

(Recall for trace class operators the *trace* can be computed as

$$\operatorname{tr} A = \sum_n \langle \varphi_n, A\varphi_n \rangle, \qquad \text{for } (\varphi_n)_n \text{ orthonormal basis,} \tag{2.6}$$

which is finite and independent of the orthonormal basis. Thus for $\gamma = \sum_{n=1}^N |e_n\rangle\langle e_n|$,

$$\begin{aligned} \operatorname{tr} A\gamma &= \sum_{k=1}^\infty (e_k, A \sum_{n=1}^N |e_n\rangle\langle e_n|e_k) \\ &= \sum_{k=1}^\infty (e_k, \sum_{n=1}^N Ae_n)(e_n, e_k) = \sum_{n=1}^N (e_n, Ae_n). \end{aligned}$$

2.3. **Hartree-Fock for trace class operators.** Define

$$S := \{\gamma \in \mathfrak{S}^1(L^2(\mathbb{R}^3 : C^q)) : \langle p\rangle\gamma\langle p\rangle \in \mathfrak{S}^1, 0 \le \gamma \le 1\},$$

where $\langle p\rangle = \sqrt{p^2+1}$ the Japanese bracket. This condition essentially says that we have finite kinetic energy and particle number, since we require

$$\operatorname{tr}\sqrt{p^2+1}\gamma\sqrt{p^2+1} = \operatorname{tr} p^2\gamma + \operatorname{tr}\gamma < \infty.$$

For any $\gamma \in \mathfrak{S}^1$ with $\gamma \ge 0$ (which implies self-adjoint), we can write (spectral theorem for compact operators and integral kernel[1])

$$\gamma = \sum_{\nu=1}^{\infty} \lambda_\nu |\xi_\nu\rangle\langle\xi_\nu|, \quad \xi_j \text{ ON} \tag{2.7}$$

$$\gamma(x,y) = \sum_{\nu=1}^{\infty} \lambda_\nu \xi_\nu(x)\overline{\xi_\nu(y)}. \tag{2.8}$$

Definition 4. For any $\gamma \in S$, the *Hartree-Fock functional* is

$$\mathcal{E}_{HF}(\gamma) := \operatorname{tr}((-\Delta - V)\gamma) + D[\rho_\gamma] - X[\gamma], \tag{2.9}$$

$$\text{where} \quad \rho_\gamma(\mathfrak{x}) := \sum_{\sigma=1}^{q}\sum_{\nu} \lambda_\nu |\xi_\nu(\mathfrak{x},\sigma)|^2 \text{ ``}=\text{''} \sum_{\sigma=1}^{q} \gamma(x,x). \tag{2.10}$$

Here

$$D[\rho_\gamma] := \frac{1}{2}\int d\mathfrak{x}\, d\mathfrak{y}\, \frac{\rho_\gamma(\mathfrak{x})\rho_\gamma(\mathfrak{y})}{|\mathfrak{x}-\mathfrak{y}|}$$
$$X[\gamma] := \frac{1}{2}\int_\Gamma dx \int dy\, \frac{|\gamma(x,y)|^2}{|\mathfrak{x}-\mathfrak{y}|}$$

Define

$$S_N := \{\gamma \in S : \operatorname{tr}\gamma \le N\}$$
$$S_{\partial N} := \{\gamma \in S : \operatorname{tr}\gamma = N\}$$

Proposition 1. *$\mathcal{E}_{HF}(S_N) \ge -cN$.*

Proof. Recall $V(\mathfrak{x}) = \sum_{k=1}^{K} \frac{Z_k}{|\mathfrak{x}-R_k|}$, and compute

$$\begin{aligned}\operatorname{tr}((-\Delta - V)\gamma) &= \operatorname{tr}[(-\Delta - V)\sum_\nu \lambda_\nu|\xi_\nu\rangle\langle\xi_\nu|] = \sum_\mu \langle\xi_\mu, (-\Delta - V)(\sum_\nu \lambda_\nu|\xi_\nu\rangle\langle\xi_\nu), \xi_\mu\rangle \\ &= \sum_\nu \lambda_\nu(\xi_\nu, (-\Delta - V)\xi_\nu) \ge -\sum_\nu \lambda_\nu|E_0| \ge -N|E_0|,\end{aligned}$$

where $E_0 := \inf\sigma(-\Delta - V) > -\infty$ (Kato-Rellich? $-\Delta - V \ge -K$?). The remaining term to bound is $Q(\gamma,\gamma) = D[\rho_\gamma] - X[\gamma]$, which we can bound via

$$\begin{aligned}&\frac{1}{2}\int_\Gamma dx \int_\Gamma dy\, \frac{\sum_\nu \lambda_\nu|\xi_\nu(x)|^2 \sum_\mu \lambda_\mu|\xi_\mu(y)|^2 - \left|\sum_\nu \lambda_\nu \xi_\nu(x)\overline{\xi_\nu(y)}\right|^2}{|\mathfrak{x}-\mathfrak{y}|} \\ &\ge \frac{1}{2}\int_\Gamma dx \int_\Gamma dy\, \frac{1}{|\mathfrak{x}-\mathfrak{y}|}\left(\sum_\nu \lambda_\nu|\xi_\nu(x)|^2 \sum_\mu \lambda_\mu|\xi_\mu(x)|^2 - \left(\sqrt{\sum_\nu \lambda_\nu|\xi_\nu(x)|^2}\sqrt{\sum_\mu \lambda_\mu|\xi_\mu(y)|^2}\right)^2\right) \\ &= 0.\end{aligned}$$

[1] The Schatten p-classes are increasing so $\mathfrak{S}^1 \subset \mathfrak{S}^2$.

Thus $\mathcal{E}_{HF}(S_N) \geq -cN$. □

Lemma 1 (Lieb, Bach). *Let $\gamma \in S_N$, $\gamma = \sum \lambda_\nu |\xi_\nu\rangle\langle\xi_\nu|$ with $\lambda_1, \lambda_2 \in (0,1)$. Then there exists $\gamma' \in S_N$ such that*

* $\operatorname{tr}\gamma = \operatorname{tr}\gamma'$
* $\mathcal{E}_{HF}(\gamma') < \mathcal{E}_{HF}(\gamma)$
* *$\gamma = \gamma'$ on the space $\{\xi_1, \xi_2\}^\perp$, and on the space generated by $\{\xi_1, \xi_2\}$,*

$$\gamma' = \delta|\xi_1\rangle + \lambda_2'|\xi_2\rangle\langle\xi_2|$$

$$\text{OR} \qquad \gamma' = \lambda_1'|\xi_1\rangle\langle\xi_1| + \delta|\xi_2\rangle\langle\xi_2|,$$

where $\delta \in \{0,1\}$.

So we have one less eigenvalue in $(0,1)$ than before.

Proof. For some $\varepsilon \in \mathbb{R}$, write

$$\begin{aligned}\gamma' &= \gamma + \varepsilon|\xi_1\rangle\langle\xi_1| - \varepsilon|\xi_2\rangle\langle\xi_2| \\ &=: \gamma + \varepsilon P.\end{aligned}$$

Then $\operatorname{tr}\gamma = \operatorname{tr}\gamma'$ and $\gamma' \in S_N$ if ε is close enough to 0. (We need $0 \leq \lambda_1 + \varepsilon \leq 1$ and $0 \leq \lambda_2 - \varepsilon \leq 1$.) Then

-bach-proof

$$\begin{aligned}\mathcal{E}_{HF}(\gamma') - \mathcal{E}_{HF}(\gamma) &= \operatorname{tr}[(-\Delta - V)(\gamma' - \gamma)] + Q(\gamma + \varepsilon P, \gamma + \varepsilon P) - Q(\gamma, \gamma) \\ &= \varepsilon \operatorname{tr}[(-\Delta - V)P] + \varepsilon(Q(\gamma, P) + Q(P, \gamma)) + \varepsilon^2 Q(P,P)\end{aligned} \tag{2.11}$$

Now we show $Q(P,P) < 0$, so that $\varepsilon^2 Q(P,P) < 0$. Then by choosing ε appropriately, we can force the above expression (eqn:lieb-bach-proof 2.11) $\varepsilon[\cdots] + \varepsilon^2 Q(P,P)$ negative.

$$\begin{aligned}Q(P,P) &= \frac{1}{2}\int dx\,dy\,\frac{1}{|\mathfrak{x} - \mathfrak{y}|}\left((|\xi_1(x)|^2 - |\xi_2(x)|^2)(|\xi_1(y)|^2 - |\xi_2(y)|^2) - |\xi_1(x)\overline{\xi_1(y)} - \xi_2(x)\overline{\xi_2(y)}|^2\right) \\ &= \frac{1}{2}\int dx\,dy\,\frac{1}{|\mathfrak{x} - \mathfrak{y}|}\Big(\underbrace{|\xi_1(x)|^2|\xi_1(y)|^2} + \underline{|\xi_2(x)|^2|\xi_2(y)|^2} - 2|\xi_1(x)|^2|\xi_2(y)|^2 - \\ &\qquad - \underbrace{|\xi_1(x)|^2|\xi_1(y)|^2} - \underline{|\xi_2(x)|^2|\xi_2(y)|^2} + 2\,\mathfrak{Re}\,\xi_1(x)\overline{\xi_2(x)\xi_1(y)}\xi_2(y)\Big) \\ &\overset{\text{Schwarz}}{\leq} 0,\end{aligned}$$

using Cauchy-Schwarz to obtain

$$\begin{aligned}&\int dx\,dy\,\frac{1}{|\mathfrak{x} - \mathfrak{y}|}\cdot 2\,\mathfrak{Re}\,\underline{\xi_1(x)\,\underline{\overline{\xi_2(x)\xi_1(y)}}\,\xi_2(y)} \\ &\leq 2\sqrt{\int dx\,dy\,\frac{1}{|\mathfrak{x} - \mathfrak{y}|}|\xi_1(x)|^2|\xi_2(y)|^2}\sqrt{\int dx\,dy\,\frac{1}{|\mathfrak{x} - \mathfrak{y}|}|\xi_2(x)|^2|\xi_1(y)|^2} \\ &= 2\int dx \int dy\,\frac{1}{|\mathfrak{x} - \mathfrak{y}|}|\xi_1(x)|^2|\xi_2(y)|^2.\end{aligned}$$

Moreover, equality in $Q(P,P) \geq 0$ is not possible, since one would require $\xi_1(x)\xi_2(y) = c\overline{\xi_2(x)\xi_1(y)}$, which is not possible since ξ_1, ξ_2 are orthogonal. So we obtain $Q(P,P) > 0$.

Going back to $\varepsilon[\cdots] + \varepsilon^2 Q(P,P)$:

* If $[\cdots] < 0$ choose $\varepsilon > 0$
* If $[\cdots] > 0$ choose $\varepsilon < 0$
* If $[\cdots] = 0$ choose $\varepsilon \neq 0$

This ensures (eqn:lieb-bach-proof 2.11) $\varepsilon[\cdots] + \varepsilon^2 Q(P,P) < 0$. In fact, we can increase or decrease ε until $\lambda_1 + \varepsilon$ reaches 0 or 1, or until $\lambda_2 - \varepsilon$ reaches 0 or 1. □

Corollary 1. *Assume* γ *minimizes* $\mathcal{E}_{HF}(S_{\partial N})$, N *an integer. Then* $\gamma = \gamma^2$ *a projection.*

Proof. Suppose $\gamma = \sum \lambda_\nu |\xi_\nu\rangle\langle\xi_\nu|$, and there is $0 < \lambda_\nu < 1$. Then there exists a second $\mu \neq \nu$ such that $0 < \lambda_\mu < 1$. Then γ' as constructed before yields $\mathcal{E}_{HF}(\gamma') < \mathcal{E}_{HF}(\gamma)$. □