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24. Ionization in TF theory

What we did not prove exactly but what is true about the Thomas-Fermi functional is the following:

Thm (Existence of TF minimizers)
Let $\mathcal{D}_N = \{ \rho \in L^1 \cap L^{5/3} \mid \rho \geq 0 , \int \rho \leq N \}$.

There exists $\rho_* \in \mathcal{D}_N$ such that

$$\inf_{\rho \in \mathcal{D}_N} \mathcal{E}^{TF}(\rho) = \mathcal{E}^{TF}(\rho_*)$$

$\boxtimes$

The proof is a problem in calculus of variations so we omit the proof.
It turns out the minimizer is also unique which follows from convexity:

$$\mathcal{E}^{TF}(\lambda\rho_1 + (1-\lambda)\rho_2) < \lambda \mathcal{E}^{TF}(\rho_1) + (1-\lambda)\mathcal{E}^{TF}(\rho_2)$$

for $\rho_1, \rho_2 \in \mathcal{D}_N$ and $\lambda \in (0,1)$.

Another consequence of convexity is that for ρ_1 - minimizer in $\mathcal{D}_{N_1}$ and ρ_2 - minimizer in $\mathcal{D}_{N_2}$ we have

$$E^{TF}_{\lambda N_1 + (1-\lambda) N_2} \leq \mathcal{E}^{TF}(\lambda\rho_1 + (1-\lambda)\rho_2) \leq \lambda \mathcal{E}^{TF}(\rho_1) + (1-\lambda)\mathcal{E}^{TF}(\rho_2)$$

$= \lambda E_{N_1}^{TF} + (1-\lambda) E_{N_2}^{TF}$

which shows

Lemma The ground state energy of E_N^{TF} is convex, nonincreasing and bounded from below (as a fct of N)

Thus the limit $\lim_{N\to\infty} E_N^{TF} = E_\infty$ exists.

We define $N_c := \inf \{ N \mid E_N^{TF} = E_\infty \}$.

We do not know yet whether $N_c < \infty$.
Let $\mathcal{F}_N = \{ \rho \in \mathcal{D}_N : \int \rho = N \}$.
The next theorem characterizes the shape of E_N^{TF}:

Theorem For $N \leq N_c$, there exists a unique minimizer of $\mathcal{E}^{TF}$ in $\mathcal{F}_N$. The function E_N^{TF} is strictly convex and decreasing in $[0, N_c]$.
If $N_c < \infty$ and $N > N_c$, then there is no minimizer in $\mathcal{F}_N$. The function ρ_{N_c} is the unique minimizer in $\mathcal{D}_N$. Moreover, E_N^{TF} is constant in $[N_c, \infty)$.

Thus, N_c is the largest number of electrons such that there is a minimizer $\longrightarrow$ ionization conjecture!

It turns out that in Thomas-Fermi theory we have

Theorem $N_c = Z$.

24.1 Thomas-Fermi-von Weizsäcker (TFW) theory

In principle: TF purely classical and good to describe bulk of electrons at distance $O(Z^{-1/3})$ from the nucleus.

For physical and chemical applications it is important to capture contributions from innermost and outermost electrons at distances $O(Z^{-1})$ and $O(1)$.
$\rightsquigarrow$ refinements

$$\mathcal{E}^{TFW}(u) = \int_{\mathbb{R}^3} \left(c^{TF} |u|^{10/3} + c^{W} |\nabla u|^2 - \frac{Z|u|^2}{|x|} + \frac{1}{2}|u|^2 \left(|u|^2 * \frac{1}{|x|}\right)\right)$$

$$E^{TFW}(N) = \inf_{\|u\|_2^2 = N} \mathcal{E}^{TFW}(u)$$

$|u|^2$ – role of electron density and the von Weizsäcker-correction term $c^W |\nabla u|^2$ with $c^W > 0$ corresponds to the contribution of the innermost electrons.

In the context of the ionization conjecture

Thm The variational problem $E^{TFW}(N)$ has a minimizer iff $N \leq N_c(Z)$ with
$Z < N_c(Z) \leq Z + C.$

Other extensions TFDW theory (D for Dirac)

additional term $-c^D \int_{\mathbb{R}^3} \rho(x)^{4/3}$

Thm If $E_Z^{TFDW}(N)$ has minimizer $\Rightarrow N \leq Z + C.$

2.5. Hartree-Fock theory

$$E^{HF} := \inf_{\substack{\psi\text{- Slater}\\ \text{determinants}}} \langle \psi, H_N \psi \rangle$$

As already derived last time:

direct term

$$\mathcal{E}^{HF}(\gamma) := \operatorname{Tr}\left((-h^2\Delta + V)\gamma\right) + \frac{\lambda}{2} \int_{\mathbb{R}^d}\int_{\mathbb{R}^d} \left(\rho_\gamma(x)\rho_\gamma(y) - |\gamma(x,y)|^2\right) w(x-y)$$

exchange term

In fact:

$$\mathcal{E}^{HF}(\gamma) = \mathcal{E}^{HF}(\gamma_{\psi_N}^{(1)}) \quad , \quad \gamma_{\psi_N}^{(1)} = \sum_{i=1}^{N} |u_i\rangle\langle u_i|$$

Exercise: show that

$$\rho_\gamma(x)\,\rho_\gamma(y) - |\gamma(x,y)|^2 \geq 0 \quad \forall x,y \in \mathbb{R}^d$$

recall,

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

By Cauchy-Schwarz

$$|\gamma(x,y)| \leq \sum_{i=1}^{N} |u_i(x)|\,|u_i(y)| \leq \Big(\sum_{i=1}^{N} |u_i(x)|^2\Big)^{1/2}\Big(\sum_{i=1}^{N} |u_i(y)|^2\Big)^{1/2}$$

$$\Rightarrow \quad |\gamma(x,y)|^2 \leq \rho_\gamma(x)\,\rho_\gamma(y)$$

$\square$

Thus the Hartree-Fock energy can be rewritten as

$$E^{HF} = \inf_{\substack{0 \leq \gamma = \gamma^2 \leq 1 \\ \mathrm{Tr}\,\gamma = N}} \mathcal{E}^{HF}(\gamma)$$

Here the condition $\gamma = \gamma^2$ is to ensure that γ is a projection. For some computations it is more convenient to ignore this condition. Since the set $\{0 \leq \gamma \leq 1 \,,\ \mathrm{Tr}\,\gamma = N\}$ is convex.

Actually it is possible to do that without losing anything, provided that the interaction potential is non-negative.

Thm (Lieb's variational principle)

If $w \geq 0$, then

$$E^{HF} = \inf_{\substack{0 \leq \gamma \leq 1 \\ \mathrm{Tr}\,\gamma = N}} \mathcal{E}^{HF}(\gamma).$$

(Here V is supposed to be regular enough) $\square$

In some situations: reduced Hartree-Fock:

$$E^{rHF} = \inf_{\substack{0 \leq \gamma \leq 1 \\ \mathrm{Tr}\,\gamma = N}} \mathcal{E}^{rHF}$$

$$\mathcal{E}^{rHF}(\gamma) := \mathrm{Tr}\left((-\hbar^2\Delta + V)\gamma\right) + \frac{1}{2}\iint \rho_\gamma(x)\rho_\gamma(y)\, w(x-y)\,dx\,dy$$

Thus, keep direct term, ignore the exchange term. Mathematically easier to analyze since if $\hat{w} \geq 0$ then $\gamma \mapsto \mathcal{E}^{rHF}(\gamma)$ is convex. Also if $w \geq 0$

$$E_N \leq E^{HF} \leq E^{rHF}$$

Atomic case: (H_N – semi-classical mean-field)

$$E_N = \underbrace{-c_1 N}_{\text{TF theory (Lieb-Simon 1970's)}} + \underbrace{c_2 N^{2/3}}_{\substack{\text{Scott's correction} \\ \text{Siedentop-Weikard 1987}}} - \underbrace{c_3 N^{1/3}}_{\substack{\text{Dirac-Schwinger} \\ \text{Fefferman-Seco 1990s}}} + o(N^{1/3})_{N \to \infty}$$