The Semiclasical Limit of Thomas–Fermi Theory Forty Years After

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Introduction and History

My work with Elliott Lieb on TF theory was stretched out some, starting in the fall of 1972 with the final publication of the long paper on the subject only in 1977, but it is fair to say that the key step, where we knew we had a large Z limit theorem for atoms, took place in March 1973 (when we "pulled the Poisson Columb tooth"), so this year is the 40th anniversary of this work.

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In the fall of 1972, we were both visiting IHES near Paris. Elliott was forty—recently hired by MIT after the splash of his work on six vertex models (and the entropy of square ice), written while he was at Boston University.

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Elliott and I started talking a lot and, early on, he suggested we look at Thomas–Fermi theory, which he felt should be exact in the large Z-limit.

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Arthur passed away last January (at age 90), and I want to acknowledge my huge personal debt to him as well as the debt of the mathematical physics community.

Teller's Theorem

Fortunately, I also took a course from Arthur my first year at Princeton called "intermediate quantum mechanics," unlike any course by that name given in the U.S. in that era (Jost in Zurich and Thirring in Vienna may have given courses with an overlapping content).

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Arthur included a week on Thomas–Fermi theory, including Teller's Theorem that atoms don't bind in TF theory.

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His point, of course, is that chemistry takes place in the outer shell, and TF theory involves the core (of course this says density functionals of relevance to chemistry have to go beyond TF theory).

So Teller's Theorem is irrelevant to the $Z \to \infty$ limit result although, of course, as Lieb and Thirring realized a few years later, it was very relevant to the stability of matter!

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3. Dealing with the Strong Coulomb Singularity

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In March, I went from Marseille to Paris where Elliott had an apartment for the year. We banged our heads on the Coulomb singularity for several days and finally solved the problem.

Existence Problems

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Thomas and Fermi described their equation for the electron density ρ by supposing they were in a semiclassical limit where the local momentum of a particle at the top of the Fermi sphere was $p_F(x) = cr(x)$ while $\rho(x) = dr(x)^3$ so $p_F^2 = c_1\rho(x)^{2/3}$. The potential energy is given by

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$$\varphi(x) = V(x) - \int \rho(x)|x-y|^{-1}dy$$

Existence Problems

Constancy of the Fermi energy required

$$\begin{aligned} (2m)^{-1}p_F^2 - \varphi(x) &= \varphi_0 \quad \text{(at points when } \rho > 0) \\ &\geq \varphi_0 \quad \text{(at points when } \rho \geq 0) \end{aligned}$$

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$$c\rho^{2/3}(x) = \left(V(x) - \int |x-y|^{-1}\rho(y)dy - \varphi_0\right)_+$$

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If $V(x)$ is Coulomb with charges at $R_1, \dots, R_k$, then for $x \notin \{R_1, \dots, R_k\}$, φ obeys

$$\Delta\varphi = c(\varphi - \varphi_0)^{3/2}$$

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Hille also rigorously proved in the spherically symmetric neutral case ($\varphi_0 = 0$), $\rho_{TF}(x) \sim Cx^{-6}$, something computed by Sommerfeld in 1932.

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As a bonus, $\rho = \delta\mathcal{E}/\delta V$ so we could get convergence of derivatives using the miracle of convex functions.

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Also fortunately, as a graduate student at Princeton, I'd take a course given by Choquet (the basis of his book by Marsden et al., also students in the course) and he'd used a tool which was exactly what we needed!

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Elliott is, of course, now a leading figure in subtle uses of the direct method. I'm pleased if I helped provide his initial exposure to this subject.

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I was eventually wont to say PRL stands for Physical Review Lottery since the refereeing is so uneven. This paper is part of that story.

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Existence of Solutions

We fix $z_1, \ldots, z_\ell \geq 0$ and $R_1, \ldots, R_\ell$ and let

$$V(x; z_1, \ldots, z_\ell; R_1, \ldots, R_\ell) = \sum \frac{z_j}{|r - R_j|}$$

and

$$\mathcal{E}_{TF}(\rho, V) = \frac{3}{5} \int \rho(x)^{5/3} d^3x - \int V(x)\rho(x) d^3x + \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} d^3x \, d^3y$$

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Since $|x|^{-1} \in L^{5/2} + L^\infty$, each term in $\mathcal{E}_{TF}$ is well defined if $\rho \in \mathcal{T}$.

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Theorem 1. *For any* N*, there is a unique* $\rho \in \mathcal{T}$ *minimizing* $\{\mathcal{E}(\rho) \mid \rho \in \mathcal{T}, \int \rho(x) d^3x \leq N\}$*.*

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This follows from strict convexity and the direct method and the fact that $\{\rho \in \mathcal{T} \mid \int \rho \, d^3x \leq N\}$ is weakly closed. (Note: $\{\rho \in \mathcal{T} \mid \int \rho \, d^3x = N\}$ is *not*.)

No Negative Ions in TF Theory

Theorem 2. *If* $N \leq Z = \sum_{j=1}^{\ell} z_j$*, then the minimizer has* $\int \rho \, d^3x = N$*. If* $N > Z$*, the minimizer has* $\int \rho \, d^3x = Z$*. The minimizer for* $N = Z$ *is a minimizer over all of* $\mathcal{T}$*.*

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The proof depends on noting the minimizer obeys

$$\rho^{2/3}(x) = (\varphi(x) - \varphi_0)_+$$

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But $\int \varphi(r\omega) d\omega \sim \frac{Z-N}{r}$ for r large. If $Z < N$, we get a contradiction.

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But $\int \varphi(r\omega) d\omega \sim \frac{Z-N}{r}$ for r large. If $Z < N$, we get a contradiction.

Similar arguments show the absolute minimum has to have $Z = N$.

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We proved Sommerfeld's asymptotic formula, the first proof in the molecular case (Sommerfeld asked when $c|x|^{-\alpha}$ solves $\Delta\varphi = d\varphi^{3/2}$ on $\mathbb{R}^3 \setminus \{0\}$ and found $\alpha = 4$ and c in terms of d.).

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Theorem 3. *The solution ρ_{TF} in the neutral case has $|x|^{-6}\rho(x) \to 27\pi^{-3}$ as $|x| \to \infty$.*

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Theorem 3. *The solution ρ_{TF} in the neutral case has $|x|^{-6}\rho(x) \to 27\pi^{-3}$ as $|x| \to \infty$.*

The proof uses subharmonic comparison theorems and the form of the exact Sommerfeld solution of the TF ODE.

Teller's Theorem

We also proved

Theorem 4. $E(z_1, \ldots, z_{\ell+k}; R_1, \ldots, R_{\ell+k}) \geq E(z_1, \ldots, z_\ell; R_j) + E(z_{\ell+1}, \ldots, z_{\ell+k}; R_j)$

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Put more positively: TF matter is stable in the Onsager sense.

The proof followed Teller—the most important point of rigor was the existence of solutions to neutral TF.

TF Scaling

We want to see what happens to TF theory of an atom as $Z \to \infty$, so we look at

$$\mathcal{E}_Z(\rho) = \frac{3}{5}\int \rho^{5/3}(x)d^3x - Z\int \frac{\rho(x)}{|x|}d^3x + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|}d^3x d^3y$$

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We make the ansatz

$$\rho_Z(x) = Z^\alpha \rho(Z^\beta x)$$

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$$K \sim Z^{4/3+1} = Z^{7/3},\ ZA \sim Z^{2+1/3},\ R \sim Z^{4-5/3} = Z^{7/3}$$

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$$\mathcal{E}_{TF}(\rho_Z; Zz_1, \dots Zz_\ell; Z^{-1/3}R_1, \dots Z^{-1/3}R_\ell) = Z^{7/3}\mathcal{E}_{TF}(\rho; z_j, R_j)$$

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Theorem 5. *If* $E(z_j, R_j, N)$ *is the minimum*

$$E(Zz_1; Z^{-1/3}R_j; ZN) = Z^{7/3}E(z_j, R_j, N)$$

$$\rho_{TF}(x; Zz_j; Z^{-1/3}R_j; ZN) = Z^2\rho_{TF}(Z^{1/3}x; z_j; R_j; N)$$

TF Scaling

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It is important that the natural spatial scale is $Z^{-1/3}$ and the $Z^2\rho(Z^{1/3}x)$ implies in a box of sizes $Z^{-1/3}$, there are $O(Z^2(Z^{-1/3})^3) = O(Z)$ electrons. This is consistent with the notion that large Z atoms are semiclassical, i.e., large number of electrons on the natural scale.

Quantum Limit Theorem

For $\frac{3}{5}\int \rho^{5/3}(x)d^3x$ to be semiclassical limit of the quantum kinetic energy requires a certain value of $\hbar$ and that value depends on the number of electrons allowed and the mass (as in $\hbar^2/2m$) under the Pauli principle (i.e., 2 spin states in nature!)

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By $H_Q(z_j, R_j)$ we mean the quantum Hamiltonian

$$H_Q = -\frac{\hbar^2}{2m}\sum_{k=1}^{N}\Delta_k - \sum_{k=1}^{N}\sum_{j=1}^{\ell}\frac{z_j}{|x_k - R_j|} + \sum_{1\leq k<q\leq N}\frac{1}{|x_k - x_j|}$$

as an operator on $L^2(\mathbb{R}^{3N}; (\mathbb{C}^2)^N)$.

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as an operator on $L^2(\mathbb{R}^{3N};(\mathbb{C}^2)^N)$.

$E_Q(z_j, R_j)$ is the inf of $\langle\varphi, H_Q\varphi\rangle$ over all φ antisymmetric in $\langle x_k, \sigma_k\rangle$.

Quantum Limit Theorem

Our main result was

Theorem 6. *With the above value of* $\hbar$

$$\lim_{Z\to\infty} E_Q(z_j Z, R_j Z^{-1/3})/Z^{7/3} = E_{TF}(z_j, R_j)$$

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There were subsequent results on the $O(Z^2)$ (Scott) correction by Hughes and Siedentop and $O(Z^{5/3})$ by Fefferman–Seco.

In this result, $N = \lambda Z\,(\lambda \leq 1)$ and E_{TF} is for $N_{TF} = \lambda$.

Quantum Limit Theorem

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Theorem 7. *Let $N \leq Z$. If ρ^Q is the one particle density (normalized to $\int \rho^Q(x) d^3x = N$), then $Z^{-2}\rho^Q(Z^{-1/3}x)$ converges weakly (in L^∞-sense) to $\rho_{TF}(x)$.*

Quantum Limit Theorem

This result is actually a simple corollary of the energy result when $Z|x|^{-1}$ is replaced by $Z|x|^{-1} + Z^{4/3}V(Z^{1/3}x)$, so $\rho^Q(x) = \delta E_Q / \delta V(x)$ after scaling.

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Normally, convergence of functions does not imply convergence of derivatives—we use the fact that $f_n(x) \to f(x)$, all f_n convex, and f differentiable at x_0 implies $(D^+ f_n)(x_0) \to f_n(x_0)$.

The Magic of Quadratic Forms

There is a classic technique used to prove the Weyl limit theorem (on number of eigenvalues in a region) which had been used by Martin, Robinson, and Tamura shortly before our work to prove WKB asymptotics for the number of negative eigenvalues of $-\frac{\hbar^2}{2m}\Delta + V$ as $\hbar \downarrow 0$ where $V \leq 0$, C^∞, and goes to zero rapidly at ∞.

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It relies on a beautiful subtlety of Hilbert space unbounded operator theory. Operators have a domain, $D(A)$, and self-adjoint operators, A, B, cannot have $D(B) \supset D(A)$ and $B \restriction D(A) = A$ (B is an extension of A), unless $B = A$.

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If A is positive and self-adjoint, $Q(A) = A^{1/2}$ and $\langle \varphi, A\varphi \rangle \equiv \|A^{1/2}\varphi\|^2$ for $\varphi \in Q(A)$.

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$Q(B)$ is the same but with no boundary condition. In each case (for $C = A$ or B)

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Thus $Q(A) \subset Q(B)$ and $B \restriction Q(A) = A$!

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We say for A, B positive and self-adjoint that $A \leq B$ if and only if

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Think of $\langle \varphi, A\varphi \rangle$ being defined for all φ but being ∞ if $\varphi \notin Q(A)$. Then, $B \geq A \Leftrightarrow \forall \varphi \, \langle \varphi, B\varphi \rangle \geq \langle \varphi, A\varphi \rangle$.

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The point is that if $A \leq B$, then those eigenvalues are also ordered.

In the above example, $\left(-\frac{d^2}{dx^2}\right)_D \geq \left(-\frac{d^2}{dx^2}\right)_N$

Dirichlet–Neumann Bracketing

If B is $-\Delta + V$ on $\mathbb{R}^\nu$ and we put in some D b.c., then the resulting operator has a smaller form domain since φ's are forced to vanish on the Dirichlet boundary. If we put in Neumann b.c. functions can be discontinuous across N boundary, so the domain is bigger and

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$$B_N \leq B \leq B_D$$

The Semiclassical Limit

So, for example, to treat the number of negative eigenvalues of $-\Delta + \lambda V$ when $\lambda \to \infty$ and $V \in C_0^\infty(\mathbb{R}^{3N})$, cover $\mathrm{supp}(V)$ by rectangular boxes of side δ, let $H_-(\lambda)$ have N b.c. and V in each but replaced by its minimum, and $H_+(\lambda)$ have D b.c. and V replaced by its max.

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Then we need only count eigenvalues in a box with constant potential $\alpha\lambda$ where $\alpha < 0$, the control $\overline{\lim}\,(\lambda V)/\lambda^{3/2}$ and $\underline{\lim}\,N(\lambda V)/\lambda^{3/2}$. Then take $\delta \downarrow 0$.

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If $Z/|x|$ is replaced by $Z^{4/3}V(Z^{1/3}x)$ with V bounded and continuous (go to 0 at ∞), the same argument with boxes in $\mathbb{R}^{3N}$ proves the TF limit theorem.

The Coulomb Singularity

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The upper bound is fine but since $V = -\infty$ in the boxes near the R_j's, we need another way to handle the lower bound.

Reduction to One Body Problem

Let

$$V(x;R) = \begin{cases} |x|^{-1} & |x| \leq R \\ 0 & |x| > R \end{cases}$$

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$$e_N(Z;R,\alpha) = \text{ gd state energy of } H_N(Z;R,\alpha)$$

$$H_N(Z;R,\alpha) = -\alpha \sum_{i=1}^{N} \Delta_i - Z \sum_{i=1}^{N} V(x_i;R)$$

on $L^2(\mathbb{R}^{3N};\mathbb{C}^{2N})_{\text{anti}}$

Reduction to One Body Problem

If we show for each $\alpha > 0$ and

$$\lim_{\delta\downarrow 0} \overline{\lim}_{Z\to\infty} \sup_N \left[Z^{-7/3} \left| e_N(Z; \delta Z^{-1/3}, \alpha) \right| \right] = 0$$

for $H_Q = \widetilde{H}_Q + H_N(Z; \delta Z^{-1/3} R; \alpha)$ where $\widetilde{H}_Q$ has the Coulomb tooth pulled and Δ replaced by $(1-\alpha)\Delta$.

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$E(A+B) \geq E(A) + E(B)$ so we get a lower bound for α, δ fixed on $\underline{\lim}\, E_Q/Z^{7/3}$ by one term involving $\overline{\lim}_{Z\to\infty} Z^{-7/3} e_N(Z; \delta Z^{-1/3}; \alpha)$ and one term controlled by cutoff Coulomb TF. Then take $\delta \downarrow 0$ and $\alpha \downarrow 0$.

Reduction to One Body Problem

So we are now dealing with a one body problem!

If λ_j are the negatives ev. of $-\alpha\Delta - ZV(x;R)$, then (2 spin states)

$$|e_N| \leq 2\sum_j \lambda_j$$

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We proved

$$\frac{1}{2}|e_N| \leq Z^2\alpha^{-1} + Z^{5/2}\alpha^{-3/2}R^{1/2}$$

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Picking $R = \delta Z^{-1/3}$ and using $Z^{5/2}Z^{-1/6} = Z^{7/3}$ (!) and we see

$$|e_N(Z;\delta Z^{-1/3}\alpha)| \leq Z^2\alpha^{-1} + \delta^{1/2}Z^{7/3}\alpha^{-3/2}$$

finishing the result.

Lieb–Thirring!

Of course, Lieb–Thirring faced the same problem and found a general solution that gives the inequality we need very quickly. They showed

$$\sum \lambda_j(-\alpha\Delta + V) \leq c\alpha^{-3/2} \int |V(x)|^{5/2} dx$$

for any V and in our case $\int |V(x;R)|^{5/2} dx = cR^{1/2}$ so they give $|e_N| \leq cZ^{5/2}\alpha^{-3/2}R^{1/2}$.

Pedestrian Approach

We used a simple argument. For the truncated Coulomb to beat the central $\ell(\ell+1)$ barrier, we know that only ℓ's below $L = O(Zr/\alpha)^{1/2} + 1$ entered. For allowed ℓ's, we used the full Coulomb and we got the bound we needed.