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The Semiclasical Limit of Thomas–Fermi Theory Forty Years After

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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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I was twenty-six, having been promoted to tenure at Princeton the summer before—while this was three years after my PhD—I was a slaggard.

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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

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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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I told Elliott his idea about TF theory really describing large Z atoms must be wrong, because large Z atoms did form molecules and Teller's theorem said TF theory didn't.

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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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Once we convinced ourselves that Teller's Theorem was not an issue, we started to work hard on developing what was needed.

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1. Existence of Solutions of the TF Equation

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1. Existence of Solutions of the TF Equation
2. Scaling and the Semiclassical Limit for the Cutoff Coulomb

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1. Existence of Solutions of the TF Equation
2. Scaling and the Semiclassical Limit for the Cutoff Coulomb
3. Dealing with the Strong Coulomb Singularity

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Elliott was at IHES for the year, but I was only there until the end of December. I was then in Marseille (CNRS) until the end of March and ETH in the spring.

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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.

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The Thomas–Fermi theory was developed by them independently (Thomas was at Columbia University and Fermi in Rome) in 1927—almost as soon as the new quantum theory was discovered.

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

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Constancy of the Fermi energy required

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

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So they got a self-consistent non-linear integral equation

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

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

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

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About the only mathematically rigorous work on TF theory when we began was the 1969 (!!) work of Hille (who was 75 in 1969!), who used ODE techniques to prove existence and uniqueness of solutions

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About the only mathematically rigorous work on TF theory when we began was the 1969 (!!) work of Hille (who was 75 in 1969!), who used ODE techniques to prove existence and uniqueness of solutions (of course, numeric solutions had been found before then).

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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For us, the key was a different approach to TF theory going back to W. Lenz (Ising's thesis advisor) in 1932. He defined the TF energy by (in suitable units)

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For us, the key was a different approach to TF theory going back to W. Lenz (Ising's thesis advisor) in 1932. He defined the TF energy by (in suitable units)

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

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For us, the TF density was the minimizer for this functional, and the minimum energy was the TF energy.

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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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I came to Bures an expert on linear functional analysis—in fact Reed-Simon, Vol. 1 appeared just before I went to Bures.

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I came to Bures an expert on linear functional analysis—in fact Reed-Simon, Vol. 1 appeared just before I went to Bures. But I knew very little non-linear functional analysis. Fortunately, many of the tools (and, in particular, what we needed!) are from the linear theory.

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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)

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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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What we used I now know is called the direct method of the calculus of variations: get minima by compactness plus lower semicontinuity.

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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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After completing existence and the quantum limit theorem, Elliott and I wrote up an announcement and sent it off to PRL (= Physical Review Letters).

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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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The paper was rejected! The report started (and I paraphrase):

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The paper took a while to write, since after our joint European jaunt, Elliott returned to MIT and I returned to Princeton. But then we lured Elliott to Princeton and things went faster. We submitted it to *Advances in Mathematics*, which solicited it and then sat on it for two years.

Existence of Solutions

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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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We pick the set of trial functions

$$\mathcal{T} = \{\rho \geq 0 \mid \rho \in L^{5/3} \cap L^1\}$$

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We pick the set of trial functions

$$\mathcal{T} = \{\rho \geq 0 \mid \rho \in L^{5/3} \cap L^1\}$$

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

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*.)

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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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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 $\mathcal{T}$.*

The proof depends on noting the minimizer obeys

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

$$\varphi(x) = V(x) - \int \frac{\rho(y)}{|x-y|} d^3y$$

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$\varphi_0 \geq 0$ because if $e(\lambda) = \min(\int \rho = \lambda)$, then $\varphi_0 = -\frac{de}{d\lambda}$ and e is decreasing.

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Thus on $\{x \mid \varphi(x) < 0\}$, ρ is zero so φ is harmonic. Given that $\varphi \to 0$ at ∞, we conclude φ must be non-negative since otherwise it would have a minimum.

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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 also proved that away from $\{R_j\}$, ρ_{TF} is C^∞ in the region where $\rho_{TF} \geq 0$ which is all of $\mathbb{R}^3$ when $Z = N$.

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We also proved that away from $\{R_j\}$, ρ_{TF} is C^∞ in the region where $\rho_{TF} \geq 0$ which is all of $\mathbb{R}^3$ when $Z = N$.

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

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We also proved

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

i.e., molecules don't bind in TF theory.

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i.e., molecules don't bind in TF theory.

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.

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

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

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Also, we look at $N(\rho) = \int \rho(x)d^3x$.

We make the ansatz

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

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$N(\rho_Z) = Z^{\alpha-3\beta} N(\rho)$ so to keep neutrality $\alpha - 3\beta = 1$.

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$N(\rho_Z) = Z^{\alpha-3\beta} N(\rho)$ so to keep neutrality $\alpha - 3\beta = 1$.

Similarly

$$K(\rho_Z) = Z^{2\alpha/3} Z,\ ZA(\rho_Z) = Z(Z^{\alpha-2\beta})\, A(\rho) = Z^2 Z^{\beta} A(\rho)$$

$$R(\rho_Z) = Z^{2\alpha} Z^{-5\beta} R(\rho)$$

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For $K(\rho_Z)$ and $A(\rho_Z)$ to scale the same, we need

$$2 + \beta = 1 + \frac{2\alpha}{3}$$

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$$2 + \beta = 1 + \frac{2\alpha}{3}$$

$$3 + 3\beta = 2\alpha \,\&\, 1 + 3\beta = \alpha \Rightarrow \alpha = 2 \Rightarrow \beta = 1/3$$

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

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Thus $\mathcal{E}_Z(\rho_Z) = Z^{7/3}\mathcal{E}(\rho)$ for one center.

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Thus $\mathcal{E}_Z(\rho_Z) = Z^{7/3}\mathcal{E}(\rho)$ for one center.

For ℓ centers:

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

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Thus $\mathcal{E}_Z(\rho_Z) = Z^{7/3}\mathcal{E}(\rho)$ for one center.

For ℓ centers:

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

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

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

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An interesting observation Elliott and I made is that if $f(x) = cx^{-6}$, then $Z^2 f(Z^{1/3}x) = f(x)$.

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An interesting observation Elliott and I made is that if $f(x) = cx^{-6}$, then $Z^2 f(Z^{1/3}x) = f(x)$.

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.

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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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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!)

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

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

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 $\langle x_k, \sigma_k\rangle$.

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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.

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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 $N_{TF} = \lambda$.

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We also had results on electron densities (both one and j particle densities, j fixed—I'll only discuss the one particle result).

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We also had results on electron densities (both one and j particle densities, j fixed—I'll only discuss the one particle result).

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 $\rho_{TF}(x)$.*

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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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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.

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 $(D^+ f_n)(x_0) \to f_n(x_0)$.

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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.

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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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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 $\varphi \in Q(A)$. An interesting example is $A = -\frac{d^2}{dx^2}$ on $L^2([0,1])$ with $\varphi(0) = \varphi(1) = 0$ boundary conditions and $B = -\frac{d}{dx^2}$ on $L^2([0,1])$ with $\varphi'(0) = \varphi'(1) = 0$ boundary conditions. Then $Q(A) = \{\varphi \mid \varphi$ continuous on $[0,1]\, \varphi'$ (distributional derivatives) in L^2 with $\varphi(0) = \varphi(1) = 0\}$.

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

$$\langle \varphi, C\varphi \rangle = \int_0^1 |\varphi'(x)|^2 dx$$

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

$$\langle \varphi, C\varphi \rangle = \int_0^1 |\varphi'(x)|^2 dx$$

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

$$Q(B) \subset Q(A), \quad \varphi \in Q(B) \Rightarrow \langle \varphi, B\varphi \rangle \geq \langle \varphi, A\varphi \rangle$$

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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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Think of $\langle \varphi, A\varphi \rangle$ being defined for all φ but being ∞ if $\varphi \notin Q(A)$. Then, $B \geq A \Leftrightarrow \forall \varphi \, \langle \varphi, B\varphi \rangle \geq \langle \varphi, A\varphi \rangle$.
The point is that if $A \leq B$, then those eigenvalues are also ordered.

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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

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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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$$B_N \leq B \leq B_D$$

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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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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.

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 $\delta \downarrow 0$.

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.

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If quantum energies went to $-\infty$ at a rate faster than $Z^{7/3}$ due to collapse into the origin (or the R_j in the molecular case), these DN bracketings wouldn't see it.

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If quantum energies went to $-\infty$ at a rate faster than $Z^{7/3}$ due to collapse into the origin (or the R_j in the molecular case), these DN bracketings wouldn't see it.

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.

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Let

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

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Let

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

Let

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

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

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

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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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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 $(1-\alpha)\Delta$.

$E(A+B) \geq E(A) + E(B)$ 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 $\alpha \downarrow 0$.

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

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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!

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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

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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.