Mathematical Results on The Structure of Large Atoms

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Goal: To give a mathematical explanation for the universal nature of the structure of atoms. Or why does the structure of atoms really vary *periodically* through the *periodic* table?

- Schrödinger Theory
- Hartree-Fock (HF) Theory
- Sobolev & Lieb-Thirring inequalities
- Semiclassical Weyl asymptotics & Thomas-Fermi (TF) theory
- Non-linear TF equation & TF universality
- HF universality

Basic objects:

N electrons negative charge $-e$ nucleus positive charge Ze.

Ground State Energy: $E(N, Z)$ the total binding energy

The electronic density: $\rho(x) \in L^1(\mathbb{R}^3)$
$(\int \rho = N)$.

Radius to ν last electrons: $\mathcal{R}_\nu(N, Z)$

$$\int_{|x|>\mathcal{R}_\nu(N,Z)} \rho(x)dx = \nu.$$

Main question: Why is $\mathcal{R}_\nu(Z, Z)$ bounded above and below independently of Z?

Schrödinger Theory:

Atomic State: Described by N particle wave function

$$\Psi \in \bigotimes^{N} L^2(\mathbb{R}^3;\mathbb{C}^2) = L^2(\mathbb{R}^{3N};\mathbb{C}^{2N}).$$

$\mathbb{C}^2$: spin variables

Pauli Exclusion Principle: No two electrons in the same state, i.e., restrict to antisymmetric functions

$$\Psi \in \bigwedge^{N} L^2(\mathbb{R}^3;\mathbb{C}^2) \subset L^2(\mathbb{R}^{3N};\mathbb{C}^{2N}).$$

Density:

$$\rho(x) = N \int_{\mathbb{R}^{3(N-1)}} \|\Psi(x, x_2, \ldots, x_N)\|^2_{\mathbb{C}^{2N}} dx_2 \cdots dx_N.$$

(Because of symmetry it does not matter where we put the x.) $\|\Psi\| = 1 \Rightarrow \int \rho = N$.

Energy operator:

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - Z|x_i|^{-1}\right) + \sum_{1\le i<j\le N} |x_i - x_j|^{-1}.$$

Units: Planck's constant $\hbar = 1$, Electron mass=1, Electron charge $e = 1$

Ground State Energy:

$$E(N,Z) = \inf_{\Psi \neq 0} \frac{(H_{N,Z}\Psi, \Psi)}{\|\Psi\|^2}.$$

The infimum is over antisymmetric functions Ψ.

Ground State and Ground State Density:

If the infimum is attained we say that the minimizer Ψ is a **ground state**. (Note the minimizer need not be unique.)

A minimizer Ψ is an eigenfunction of $H_{N,Z}$. The density ρ corresponding to a minimizer is the **ground state density**.

Hartree-Fock (HF) Theory:

Hartree-Fock theory simply amounts to only considering simple wedge products

$$\Psi = \phi_1 \wedge \ldots \wedge \phi_N, \tag{1}$$

of one-particle orbitals $\phi_1, \ldots, \phi_N$.

In contrast to the **linear** Schrödinger theory finding the HF energy

$$E(N,Z) = \inf_{\substack{\Psi \neq 0 \\ \text{of the form (1)}}} \frac{(H_{N,Z}\Psi, \Psi)}{\|\Psi\|^2}.$$

is a non-linear variational problem.

As before a possible minimizer is called a HF ground state and the corresponding density ρ^{HF} is a HF ground state density.

This variational problem studied in Lieb&Simon, *Commun. Math. Phys.*,(1977) The HF minimizer is **not** an eigenfunction of $H_{N,Z}$. The Euler-Lagrange equation for the HF variation is more complicated.

The Euler-Lagrange equation

Mean Field Potential: Corresponding to an HF ground state density ρ^{HF}

$$\phi^{\mathrm{HF}}(x) = Z|x|^{-1} - \int \rho^{\mathrm{HF}}(y)|x-y|^{-1}dy,$$

Mean Field Operator: Operator on $L^2(\mathbb{R}^3;\mathbb{C}^2)$

$$H_{N,Z}^{\mathrm{HF}} = -\tfrac{1}{2}\Delta - \phi^{\mathrm{HF}} - \mathcal{K}$$

Note ϕ^{HF} includes self-interaction. The **exchange operator** $\mathcal{K}$ makes up for this. Here I shall ignore $\mathcal{K}$.

Mean Field Self-Consistency: If

$$\Psi = \phi_1 \wedge \ldots \wedge \phi_N$$

is an HF ground state with density ρ^{HF} then $\phi_1, \ldots, \phi_N$ span the eigenspace corresponding to the lowest N eigenvalues of $H_{N,Z}^{\mathrm{HF}}$

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The Sobolev Inequality: $\int_{\mathbb{R}^3} |\nabla\phi|^2 \geq C_{\rm S}(\int_{\mathbb{R}^3} |\phi|^6)^{1/3}$

Sobolev& Hölder: If $0 < V$

$$\left(\left(-\tfrac{1}{2}\Delta - V\right)\phi,\phi\right) = \tfrac{1}{2}\int |\nabla\phi|^2 - \int V|\phi|^2$$
$$\geq \frac{C_{\rm S}}{2}\left(\int |\phi|^6\right)^{1/3} - \left(\int V^{5/2}\int |\phi|^2\right)^{2/5}\left(\int |\phi|^6\right)^{1/5}$$
$$\geq -\frac{2}{5}\left(\frac{6}{5C_{\rm S}}\right)^{3/2}\left(\int V^{5/2}\right)\left(\int |\phi|^2\right).$$

Lowest eigenvalue of $-\frac{1}{2}\Delta - V$ bounded below by $-\frac{2}{5}\left(\frac{6}{5C_{\rm S}}\right)^{3/2}\int V^{5/2}$

Atoms: Ignoring **electron-electron repulsion** and **Pauli principle** (Ψ normalized)

$$\left(\sum_{i=1}^{N}\left(-\tfrac{1}{2}\Delta_i - \frac{Z}{|x_i|}\right)\Psi,\Psi\right)$$
$$\geq -cNZ^{5/2}\int_{|x|<R}|x|^{-5/2}dx - NZR^{-1}$$
$$= -cNZ^2,$$

$R = cZ^{-1}$. Same with electron repulsion!.

Radius: $\sim Z^{-1}$. No universality.

Lieb-Thirring inequality: Generalize Sobolev estimate to include Pauli.

$$\sum_{i=1}^{N}\int_{\mathbb{R}^{3N}}\|\nabla_i\Psi\|^2\geq C_{\mathrm{LT}}\int_{\mathbb{R}^3}(\rho(x))^{5/3}dx.$$

Ψ antisymmetric, normalized, with density ρ (Lieb&Thirring *Phys. Rev. Lett.* 1975).

$$\begin{aligned}&\left(\sum_i\left(-\tfrac{1}{2}\Delta_i-V(x_i)\right)\Psi,\Psi\right)\\ \geq\ &\tfrac{1}{2}C_{\mathrm{LT}}\int\rho^{5/3}-\int V\rho\geq-\frac{2}{5}\left(\frac{6}{5C_{\mathrm{LT}}}\right)^{3/2}\int V^{5/2},\end{aligned}$$

where $0<V$. **Sum** of neg. eigenvalues of $-\frac{1}{2}\Delta-V$ bounded below by $-\frac{2}{5}\left(\frac{6}{5C_{\mathrm{LT}}}\right)^{3/2}\int V^{5/2}$.

Atoms: With Pauli principle

$$\begin{aligned}&\left(\sum_{i=1}^{N}\left(-\tfrac{1}{2}\Delta_i-Z|x_i|^{-1}\right)\Psi,\Psi\right)\\ \geq\ &-c\int\limits_{|x|<R}(Z|x|)^{-5/2}dx-NZR^{-1}=-cN^{1/3}Z^2,\end{aligned}$$

$R=cN^{2/3}Z^{-1}(=cZ^{-1/3}$ if $N=Z)$.
Radius: $\sim Z^{-1/3}$. No universality.

Weyl semiclassical asymptotics:

Semiclassical sum of negative eigenvalues:

$$2(2\pi)^{-3} \iint\limits_{\frac{1}{2}p^2 - V(x) < 0} \left(\tfrac{1}{2}p^2 - V(x)\right) dp dx = -\frac{4\sqrt{2}}{15\pi^2} \int V^{5/2}.$$

Semiclassical density:

$$\rho^{\text{classical}}(x) = 2(2\pi)^{-3} \int\limits_{\frac{1}{2}p^2 - V(x) < 0} 1 \, dp = \frac{2\sqrt{2}}{3\pi^2} V(x)^{3/2}.$$

Theorem 1 (Weyl asymptotics)
$0 < V \in L^{5/2}(\mathbb{R}^3)$. *Let* $e_1(\lambda), e_2(\lambda), \ldots < 0$ *and* $u_1, u_2, \ldots \in L^2(\mathbb{R}^3; \mathbb{C}^2)$ *be the negative eigenvalues and corresponding eigenfunctions for* $-\frac{1}{2}\Delta - \lambda V$, $\lambda > 0$.

$$\lim_{\lambda\to\infty} \lambda^{-5/2} \sum_i e_i(\lambda) = -\frac{4\sqrt{2}}{15\pi^2} \int V^{5/2}$$

$$\lim_{\lambda\to\infty} \lambda^{-3/2} \sum_i \|u_i(x)\|^2 = \frac{2\sqrt{2}}{3\pi^2} V(x)^{3/2},$$

last limit in the sense of distributions.

Thomas-Fermi Theory: (Lieb&Simon CMP 1977)

Semiclassical mean field self-consistency:

$$\phi(x) = Z|x|^{-1} - \int \rho(y)|x-y|^{-1}dy \quad (2)$$

$$\rho(x) = \frac{2\sqrt{2}}{3\pi^2}\phi(x)^{3/2}. \quad (3)$$

Includes both electrostatics (2) and Pauli (3). Unique positive solution pair (Thomas-Fermi solution) $\rho^{\mathrm{TF}}, \phi^{\mathrm{TF}}$.

TF functional: ρ^{TF} is the minimizer of the functional

$$\mathcal{E}(\rho) = \tfrac{3}{10}(3\pi^2)^{2/3}\int \rho(x)^{5/3}dx - \int Z|x|^{-1}\rho(x)dx + \tfrac{1}{2}\iint \rho(x)|x-y|^{-1}\rho(y)dxdy.$$

Non-linear TF equation: ϕ^{TF} is the solution to

$$\Delta\phi^{\mathrm{TF}} = \frac{8\sqrt{2}}{3\pi}\phi^{\mathrm{TF}}(x)^{3/2} - 4\pi Z\delta_0.$$

Scaling: $\phi^{\mathrm{TF}}(x) = Z^{4/3}\phi_1(Z^{1/3}x)$, ϕ_1 independent of Z.

TF universality: For large $|x|$, Z-independent asymptotic (Sommerfeld 1932)

$$\phi^{\mathrm{TF}} \sim 3^4 2^{-3} \pi^2 |x|^{-4}.$$

Moreover,

$$\lim_{Z\to\infty} \phi^{\mathrm{TF}}(x) = 3^4 2^{-3} \pi^2 |x|^{-4}.$$

Theorem 2 (S. 1995) *$\phi \geq 0$ continuous on $\{|x| \geq r\}$ satisfies TF equation*

$$\Delta\phi(x) = \frac{8\sqrt{2}}{3\pi}\phi(x)^{3/2},$$

for $|x| > r$. Then the estimates

$$a(r)|x|^{-\eta} \leq \phi(x) - 3^4 2^{-3} \pi^2 |x|^{-4} \leq A(r)|x|^{-\tau},$$

hold for all $|x| \geq r$ if they hold for $|x| = r$. Here $\tau = (1+\sqrt{73})/2 \approx 4.8$ and $\eta = (1+\sqrt{55})/2 \approx 4.2$.

We see that a delicate balance between the nuclear attraction on one side and the electron repulsion and Pauli exclusion on the other accounts for the atomic universality, at least on the semiclassical level.

HF universality

The difficulty is to extend this to HF and Schrödinger theory. In fact, I do not know how to do it in Schrödinger theory. But for HF it is OK.

Theorem 3 (S. 1995) *There exist universal constants* $\varepsilon_1, D > 0$ *such that for* $|x| < D$

$$|\phi^{\mathrm{HF}}(x) - \phi^{\mathrm{TF}}(x)| \leq (\phi^{\mathrm{TF}}(x))^{1-\varepsilon_1}.$$

Remarks:

- $\phi^{\mathrm{TF}}(x) \approx c|x|^{-4}$ for large Z so we have asymptotics of $\phi^{\mathrm{HF}}(x)$ for large Z and small x.
- Asymptotics for small x. But note that D is large compared to the TF scale $Z^{-1/3}$.
- Universal estimate. Everything, in particular D, independent of Z.

Idea: Show that for $|x| < D$

- $\phi^{\mathrm{HF}}(x) > 0$
- ϕ^{HF} approximately satisfies the TF equation.

Tool in approximating HF by TF:

Coulomb norm

$$\|\rho^{\mathrm{HF}} - \rho^{\mathrm{TF}}\|_C = \frac{1}{2}\iint \frac{\left(\rho^{\mathrm{HF}}(x) - \rho^{\mathrm{TF}}(x)\right)\left(\rho^{\mathrm{HF}}(y) - \rho^{\mathrm{TF}}(y)\right)}{|x-y|} dxdy$$

First used by Fefferman&Seco, CMP 1990.

Problem: Coulomb norm global, depends on Z.

Iterative Scheme:

- TF approximation valid for $|x| < r$ (r may depend on Z)
- ϕ^{HF} can be found for $|x| > r$ without complete knowledge of $|x| < r$ (this step fails for Schrödinger)
- TF approximation can be established for $r < |x| < r'$