Large atoms and molecules

with magnetic field, including self-generated magnetic field

(Results: old, new, in progress and in perspective).

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No magnetic field case (old)

Let us consider the following operator (quantum Hamiltonian)

$$\mathsf{H} = \mathsf{H}_N := \sum_{1\le j\le N} H_{V,x_j} + \sum_{1\le j<k\le N} |x_j - x_k|^{-1} \tag{1}$$

on

$$\mathfrak{H} = \bigwedge_{1\le n\le N} \mathscr{H}, \qquad \mathscr{H} = \mathscr{L}^2(\mathbb{R}^3, \mathbb{C}^q) \simeq \mathscr{L}^2(\mathbb{R}^3 \times \{1,\dots,q\}, \mathbb{C}) \tag{2}$$

with

$$H_V = (-i\nabla)^2 - V(x) \tag{3}$$

describing N same type particles in the external field with the scalar potential $-V$ and repulsing one another according to the Coulomb law.

Here $x_j \in \mathbb{R}^3$, and $(x_1, \dots, x_N) \in \mathbb{R}^{3N}$, potential $V(x)$ is assumed to be real-valued. Except when specifically mentioned we assume that

$$V(x) = \sum_{1 \le m \le M} \frac{Z_m}{|x - \mathrm{y}_m|} \tag{4}$$

where $Z_m > 0$ and y_m are charges and locations of nuclei.

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Quantum statistics

We assume that the particles (electrons) are *fermions*. This means that the Hamiltonian should be considered on the *Fock space* $\mathfrak{H}$ defined by (2) of the functions antisymmetric with respect to all variables $(x_1, \varsigma_1), \ldots, (x_N, \varsigma_N)$ where $\varsigma_n \in \{1, \ldots, q\}$ are spin variables.

Thomas-Fermi theory

If electrons were not interacting between themselves but the field potential was $-W(x)$ then they would occupy lowest eigenvalues and ground state wave functions would be (anti-symmetrized) $\phi_1(x_1,\varsigma_1)\phi_2(x_2,\varsigma_2)\ldots\phi_N(x_N,\varsigma_N)$ where ϕ_j and λ_j are eigenfunctions and eigenvalues of $H=-\Delta-W(x)$.

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Then the local electron density would be $\rho_\Psi=\sum_{1\le j\le N}|\phi_j(x)|^2$ and according to the pointwise Weyl law

$$\rho_\Psi(x)\approx\frac{q}{6\pi^2}(W+\nu)_+^{\frac{3}{2}} \tag{5}$$

where $\nu=\lambda_N$.

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This density would generate potential $-|x|^{-1}*\rho_\Psi$ and we would have $W\approx V-|x|^{-1}*\rho_\Psi$.

Replacing all approximate equalities by a strict ones we arrive to Thomas-Fermi equations:

$$V - W^{\mathsf{TF}} = |x|^{-1} * \rho^{\mathsf{TF}}, \tag{6}$$

$$\rho^{\mathsf{TF}} = \frac{q}{6\pi^2}(W^{\mathsf{TF}} + \nu)_+^{\frac{3}{2}}, \tag{7}$$

$$\int \rho^{\mathsf{TF}}\, dx = \min(N, Z), \qquad Z = Z_1 + \ldots + Z_M \tag{8}$$

where $\nu \le 0$ is called chemical potential and in fact approximates λ_N.

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where $\nu \le 0$ is called chemical potential and in fact approximates λ_N. Thomas-Fermi theory has been rigorously justified (with pretty good error estimates).

In fact the ground state energy is given by

$$\mathsf{E}_N = \mathcal{E}^{\mathsf{TF}} + O(Z^2) \tag{9}$$

with Thomas-Fermi energy

$$\mathcal{E}^{\mathsf{TF}} := -\frac{(6\pi^2)^{\frac{5}{3}}}{10\pi^2} q^{-\frac{2}{3}} \int \rho^{\mathsf{TF}\,\frac{5}{3}}(x)\,dx - \frac{1}{2}\iint \rho^{\mathsf{TF}}(x)\rho^{\mathsf{TF}}(y)|x-y|^{-1}\,dxdy \tag{10}$$

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Names

E. Lieb, B. Simon, R. Benguria, H. Brezis, H. W. Thirring, W. Hughes, H. Siedentop, R. Weikart, C. Fefferman, L. Seco, V. Ivrii, I. M. Sigal, V. Bach, G. M. Graf, J. P. Solovej.

Justification: estimate from below

To justify Thomas-Fermi theory one needs to apply electrostatic inequality due to E. H. Lieb:

$$\sum_{1\le j<k\le N} \int |x_j - x_k|^{-1} |\Psi(x_1,\dots,x_N)|^2\, dx_1\cdots dx_N \ge \frac{1}{2}\mathsf{D}(\rho_\Psi,\rho_\Psi) - C\int \rho_\Psi^{\frac{4}{3}}(x)\,dx \tag{11}$$

with the spatial density

$$\rho_\Psi(x) = N\int |\Psi(x,x_2,\dots,x_N)|^2\, dx_2\cdots dx_N \tag{12}$$

and

$$\mathsf{D}(\rho,\rho') := \int |x-y|^{-1}\rho(x)\rho'(y)\, dxdy. \tag{13}$$

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$$\int \rho_{\Psi}^{\frac{4}{3}}(x)\,dx \le CN^{\frac{5}{3}} \tag{14}$$

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provided $N \asymp Z$. Then

$$\begin{aligned}
\mathsf{E}_N &\ge \sum_{1\le j\le N} \langle H_{V,x_j}\Psi,\Psi\rangle + \frac{1}{2}\mathsf{D}(\rho_\Psi,\rho_\Psi) - CN^{\frac{5}{3}}\\
&= \sum_{1\le j\le N} \langle H_{W,x_j}\Psi,\Psi\rangle - \mathsf{D}(\rho,\rho_\Psi) + \frac{1}{2}\mathsf{D}(\rho_\Psi,\rho_\Psi) - CN^{\frac{5}{3}}\\
&= \sum_{1\le j\le N} \langle H_{W,x_j}\Psi,\Psi\rangle - \frac{1}{2}\mathsf{D}(\rho,\rho) + \frac{1}{2}\mathsf{D}(\rho-\rho_\Psi,\rho-\rho_\Psi) - CN^{\frac{5}{3}}\\
&\ge \operatorname{Tr}(H^-_{W+\nu,x_j}) + \nu N - \frac{1}{2}\mathsf{D}(\rho,\rho) + \frac{1}{2}\mathsf{D}(\rho-\rho_\Psi,\rho-\rho_\Psi) - CN^{\frac{5}{3}}. \qquad (15)
\end{aligned}$$

with ρ and $\nu \le 0$ of our choice and $W = V - |x|^{-1} * \rho$.

Replacing $\mathrm{Tr}(H^-_{W+\nu,x_j})$ by its Weyl approximation (needs to be corrected and justified)

$$\mathrm{Tr}(H^-_{W+\nu,x_j}) \approx -\int T(W(x)+\nu)\,dx \tag{16}$$

with

$$T(w) = wP'(w) - P(w), \qquad P(w) := \frac{q}{15\pi^2} w^{\frac{5}{2}} \tag{17}$$

we get

$$\mathsf{E}_N \ge \underbrace{-\int T(W(x)+\nu)\,dx - 2\pi\|\nabla(W-V)\|^2 + \nu N}_{\Phi_*(W,\nu)} + \frac{1}{2}\mathsf{D}(\rho-\rho_\Psi, \rho-\rho_\Psi) - CN^{\frac{5}{3}};$$

maximizing $\Phi_*(W,\nu)$ with respect to W and $\nu \le 0$ we get $W = W^{\mathrm{TF}}$ and ν defined by Thomas-Fermi theory (6)–(8).

To justify Weyl approximation (16)–(17) we use a powerful machinery of Microlocal Analysis and Sharp Spectral Asymptotics paired with scaling arguments (also referred to as Multiscale Analysis) and prove that for W as regular as W^{TF} is

$$\operatorname{Tr}(H^-_{W+\nu,x_j}) = -\int P(W(x)+\nu)\,dx + \mathrm{Scott} + O(Z^{\frac{5}{3}}) \tag{18}$$

provided $a := \min_{m\neq m'} |y_m - \mathsf{y}_{m'}| \ge Z^{-\frac{1}{3}}$ where

$$\mathrm{Scott} = q \sum_{1\le m\le M} Z_m^2 \tag{19}$$

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is the Scott correction term (due to Coulomb singularities of W^{TF} at y_m). The remainder is $O(a^{-\frac{1}{2}}Z^{\frac{3}{2}})$ as $Z^{-1}\leq a\leq Z^{-\frac{1}{3}}$ and $O(Z^2)$ as $a\leq Z^{-1}$.

Improvement

Furthermore, asymptotics (18) could be improved to

$$\mathrm{Tr}(H^-_{W+\nu,x_j}) = \int P(W(x)+\nu)\,dx + \text{Scott} + \text{Schwinger} \\ + O\bigl(Z^{\frac{5}{3}}(Z^{-\delta} + (aZ^{\frac{1}{3}})^{-\delta}\bigr) \qquad (20)$$

with the Schwinger correction term

$$\text{Schwinger} = (36\pi)^{\frac{2}{3}} q^{\frac{2}{3}} \int \rho^{\mathsf{TF}\,\frac{4}{3}}\,dx \asymp Z^{\frac{5}{3}} \qquad (21)$$

is the third term in Weyl asymptotics and $\delta > 0$.

To take an advantage offered by (20) one needs to use an improved electrostatic inequality due to V. Bach, G. M. Graf, J. P. Solovej, which for the ground state boils down to

$$\sum_{1\le j<k\le N}\int |x_j-x_k|^{-1}|\Psi(x_1,\ldots,x_N)|^2\,dx_1\cdots dx_N \ge \\ \frac{1}{2}\mathsf{D}(\rho_\Psi,\rho_\Psi)-\frac{1}{2}\int |x-y|^{-1}\cdot|e(x,y,\nu)|^2\,dxdy - CZ^{\frac{5}{3}-\delta} \qquad (22)$$

where $e(x,y,\nu)$ is the Schwartz kernel of the spectral projector of H_W and

$$\frac{1}{2}\int |x-y|^{-1}\cdot|e(x,y,\tau)|^2\,dxdy = -\mathrm{Dirac}+O(Z^{\frac{5}{3}-\delta}) \qquad (23)$$

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where Dirac correction term Dirac is given by the same formula as (21) Schwinger albeit with the different numerical coefficient $-\frac{9}{2}(36\pi)^{\frac{2}{3}}q^{\frac{2}{3}}$ and it reflects that electron does not interact with itself.

Justification: estimate from above

Let us take a test function $\Psi = \Psi(x_1, \varsigma_1; \ldots; x_N, \varsigma_N)$ antisymmetrized $\phi_1(x_1, \varsigma_1) \cdots \phi_N(x_N, \varsigma_N)$ where ϕ_j are eigenfunctions of H_W corresponding to negative eigenvalues λ_j.

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If $\mathsf{N}^-(H_W) < N$ where $\mathsf{N}^-(H_W)$ is the number of the negative eigenvalues (essential spectrum occupies $[0, \infty)$) then we increase E_N replacing N by a lesser value $\mathsf{N}^-(H_W)$.

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Then

$$\mathsf{E}_N \le \sum_{1\le j\le N} \lambda_j + \frac{1}{2}\mathsf{D}(\rho_\Psi - \rho, \rho_\Psi - \rho) - \frac{1}{2}\mathsf{D}(\rho, \rho) - \frac{1}{2}\int |x-y|^{-1}\cdot |e_N(x,y)|^2\, dxdy$$

where $e_N(x,y) = e(x, y, \lambda_N + 0)$ and $\rho_\Psi(x) = \operatorname{tr} e_N(x,x)$, tr means the matrix trace.

Note that

$$\sum_{1\le j\le N} \lambda_j \le \mathsf{Tr}(H^-_{W+\nu}) + \nu N + |\lambda_N - \nu|\cdot|\mathsf{N}^-(H_{W+\lambda_N\mp 0}) - \mathsf{N}^-(H_{W+\nu\pm 0})|$$

where the last factor estimates the number of eigenvalues in $[\lambda_N, \nu]$ (but $\nu = 0$ is excluded from this interval) and we consider both cases $\lambda_N \le \nu \le 0$ and $\nu < \lambda_N < 0$

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$$\frac{1}{2}\mathsf{D}(e_N(x,x) - \rho, e_N(x,x) - \rho) \le \mathsf{D}(e(x,x,\nu) - \rho, e(x,x,\nu) - \rho) + \mathsf{D}(e(x,x,\nu) - e_N(x,x), e(x,x,\nu) - e_N(x,x)).$$

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$$\mathsf{E}_N \le -\int T(W(x)+\nu)\,dx - \frac{1}{2}\mathsf{D}(\rho,\rho) + \nu N \\ + \mathsf{D}(P'(W+\nu)-\rho, P'(W+\nu)-\rho)$$

and minimizing the right-hand expression with respect to W,ν (recalling that $W = V - |x|^{-1} * \rho$) we again arrive to $W = W^{\mathsf{TF}}$ etc.

The semiclassical errors

$$|\mathsf{N}^-(H_{W+\nu}) - \int P'(W+\nu)\,dx| \tag{24}$$

and

$$\mathsf{D}(e(x,x,\nu) - P'(W+\nu), e(x,x,\nu) - P'(W+\nu)) \tag{25}$$

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$$\mathsf{N}^-(H_{W+\lambda_N\pm 0}) \gtrless N \qquad \text{and} \qquad \int P'(W+\nu)\,dx = \min(N,Z)$$

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we estimate $|\lambda_N - \nu|$ and then we estimate all skipped terms.

Theorem 1

1. *The following asymptotics hold:*

$$\mathsf{E}_N = \mathcal{E}^{\mathsf{TF}} + \mathsf{Tr}(H^-_{W^{\mathsf{TF}}+\nu}) - \int T(W^{\mathsf{TF}}+\nu)\,dx + O(Z^{\frac{5}{3}}), \tag{26}$$

$$\mathsf{D}(\rho_\Psi - \rho^{\mathsf{TF}}, \rho_\Psi - \rho^{\mathsf{TF}}) = O(Z^{\frac{5}{3}}), \tag{27}$$

and

$$\mathsf{E}_N = \mathcal{E}^{\mathsf{TF}} + \mathsf{Scott} + O(Z^{\frac{5}{3}}) \tag{28}$$

where the last asymptotics requires $a = \min_{m\neq m'} |\mathsf{y}_m - \mathsf{y}_{m'}| \geq Z^{-\frac{1}{3}}$*; the remainder there is* $O(a^{-\frac{1}{2}} Z^{\frac{3}{2}})$ *as* $Z^{-1} \leq a \leq Z^{-\frac{1}{3}}$ *and* $O(Z^2)$ *as* $a \leq Z^{-1}$*;*

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2. *As* $a \ge Z^{-\frac{1}{3}}$ *remainder estimates could be improved to* $O(Z^{\frac{5}{3}}(Z^{-\delta} + (aZ^{-\frac{1}{3}})^{-\delta})$, *but* (26) *should include* Dirac *and* (28) *should include both* Dirac *and* Schwinger.

Related results

Now we can employ arguments due to M. B. Ruskai, I. M. Sigal and J. P. Solovej and estimate an excessive negative charge and ionization energy I_N:

Theorem 2

1. *Let $N \geq Z$. Then*

$$\mathsf{I}_N := \mathsf{E}_{N-1} - \mathsf{E}_N > 0, \tag{29}$$

implies

$$(N-Z)_+ \leq CZ^{\frac{5}{7}} \tag{30}$$

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2. *Let $N \geq Z - C_0 Z^{\frac{5}{7}}$; then*

$$\mathsf{I}_N \leq Z^{\frac{20}{21}}; \tag{31}$$

Theorem 2 (continued)

3. *Let* $N \le Z - C_0 Z^{\frac{5}{7}}$*; then*

$$|\mathsf{I}_N + \nu| \le C(Z - N)^{\frac{17}{18}} Z^{\frac{5}{18}}; \tag{32}$$

Theorem 2 (continued)

3. *Let* $N \le Z - C_0 Z^{\frac{5}{7}}$*; then*

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It is known that $\nu \asymp (Z-N)_+^{\frac{4}{3}}$.

Free nuclei model

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$$\widehat{\mathsf{E}}_N := \inf_{\mathrm{y}_1,\ldots,\mathrm{y}_m} \Big(\mathsf{E}_N(y_1, Z_1; \ldots, \mathrm{y}_M, Z_M) + \sum_{1\le m<m'\le M} \frac{Z_m Z_{m'}}{|\mathrm{y}_m - \mathrm{y}_{m'}|} \Big) \tag{33}$$

taking into account interaction between nuclei and allowing them to move.

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taking into account interaction between nuclei and allowing them to move. Then

Theorem 3

1. *Let $Z_m \asymp Z$ for all $m = 1, \dots, M$. Then in the framework of free nuclei model $a = \min_{m\ne m'} |\mathsf{y}_m - \mathsf{y}_{m'}| \ge Z^{-\frac{1}{3}+\delta}$;*

Free nuclei model

Until now positions of nuclei y_m were fixed. However if $M \geq 2$ one can replace $\mathsf{E}_N = \mathsf{E}_N(y_1, Z_1; \ldots, \mathsf{y}_M, Z_M)$ by

$$\widehat{\mathsf{E}}_N := \inf_{\mathsf{y}_1,\ldots,\mathsf{y}_m} \Bigl(\mathsf{E}_N(y_1, Z_1; \ldots, \mathsf{y}_M, Z_M) + \sum_{1\leq m<m'\leq M} \frac{Z_m Z_{m'}}{|\mathsf{y}_m - \mathsf{y}_{m'}|} \Bigr) \tag{33}$$

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Theorem 3

1. *Let $Z_m \asymp Z$ for all $m = 1, \ldots, M$. Then in the framework of free nuclei model $a = \min_{m\neq m'} |\mathsf{y}_m - \mathsf{y}_{m'}| \geq Z^{-\frac{1}{3}+\delta}$;*
2. *All results above hold for $\widehat{\mathsf{E}}_N$ and $\widehat{\mathsf{I}}_N := \widehat{\mathsf{E}}_{N-1} - \widehat{\mathsf{E}}_N$.*

Now we can employ arguments due to M. B. Ruskai, I. M. Sigal and J. P. Solovej and estimate an excessive positive charge:

Theorem 4

Let $Z_m \asymp Z$ for all $m = 1, \ldots, M$. Then in the framework of free nuclei model $a = \infty$ unless $Z - N \le CZ^{\frac{5}{7} - \delta}$.

External magnetic field case

Consider now operator with a magnetic field i. e. (3) is replaced by

$$H_{V,A} = \bigl((i\nabla - A)\cdot \boldsymbol{\sigma}\bigr)^2 - V(x) \tag{34}$$

where $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$, σ_j are Pauli matrices and we assume that $A(x)$ is linear, and therefore $\nabla \times A$ is constant.

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In this framework problem of the ground state energy (main term in the asymptotics only) was treated first in two papers of E. H. Lieb, J. P. Solovej and J. Yngvason.

Let us apply the same approach as before. In the magnetic case we need to use

$$P_B(w) = (3\pi^2)^{-1} qB\Bigl(\frac{1}{2} w_+^{\frac{3}{2}} + \sum_{j\ge 1} (w - 2jB)_+^{\frac{3}{2}}\Bigr) \tag{35}$$

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In the system (6)–(8) one should replace (7) by

$$\rho_B^{\mathsf{TF}} = P'_B(W+\nu) \tag{36}$$

and we recall that $\rho_B^{\mathsf{TF}} = 4\pi\Delta(W_B^{\mathsf{TF}} - V)$ due to (6).

Magnetic Thomas-Fermi theory distinguishes two cases: $B \lesssim Z^{\frac{4}{3}}$ and $B \gtrsim Z^{\frac{4}{3}}$ when $\mathcal{E}_B^{\mathsf{TF}} \asymp Z^{\frac{7}{3}}$ and $\mathcal{E}_B^{\mathsf{TF}} \asymp Z^{\frac{9}{5}} B^{\frac{2}{5}}$, respectively.

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If we are interested only in the main term with "o" remainder, for $B \ll Z^{\frac{4}{3}}$ one can ignore magnetic field and for $B \gg Z^{\frac{4}{3}}$ one can take $P_B(w) = (6\pi^2)^{-1} qBw_+^{\frac{3}{2}}$.

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Thomas-Fermi theory describes the strange world: solutions exist iff $N \leq Z$ (so no excessive negative charge) and in free nuclei model molecules do not exist. In the framework of quantum mechanical multi particle model both excessive negative charge and molecules exist inside of the magins of error of Thomas-Fermi theory.

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2. As $B \ge Z^{\frac{4}{3}}$ the atoms have radii $\asymp B^{-\frac{2}{5}} Z^{\frac{1}{5}}$ and the bulk of electrons and of their energy are in the zone $\min_m |x - \mathsf{y}_m| \asymp B^{-\frac{2}{5}} Z^{\frac{1}{5}}$.

However magnetic Thomas-Fermi theory fails as $B \gtrsim Z^3$, which is the case investigated in the first paper of E. H. Lieb, J. P. Solovej and J. Yngvason(their second paper covers the case $B \lesssim Z^3$).

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Indeed, as $B \le Z^{\frac{4}{3}}$, $M = 1$ and $N = Z$ we know that $W_B^{\mathsf{TF}} \asymp Z/|x|^{-1}$ as $|x| \le Z^{-\frac{1}{3}}$ and $W_B^{\mathsf{TF}} \asymp |x|^{-4}$ as $Z^{-\frac{1}{3}} \le |x| \le \epsilon B^{-\frac{1}{4}}$ but $W_B^{\mathsf{TF}} = 0$ as $|x| \ge cB^{-\frac{1}{4}}$; in this case main contributions to both semiclassical approximations to the number of particles and to their energy energy are delivered by zone $|x| \asymp Z^{-\frac{1}{3}}$ and here effective semiclassical parameter $\hbar = Z^{-\frac{1}{3}} \ll 1$.
However as $B \ge Z^{\frac{4}{3}}$ we have a very different picture: $W_B^{\mathsf{TF}} \asymp Z|x|^{-1}$ as $|x| \le \epsilon B^{-\frac{2}{5}} Z^{\frac{1}{5}}$ and $W_B^{\mathsf{TF}} = 0$ as $|x| \ge cB^{-\frac{2}{5}} Z^{\frac{1}{5}}$ and the main contributions are delivered by zone $|x| \asymp B^{-\frac{2}{5}} Z^{\frac{1}{5}}$ and here $\hbar = B^{\frac{1}{5}} Z^{-\frac{3}{5}}$; therefore $\hbar \ll 1$ iff $B \le Z^3$.

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My tools are Rough Microlocal Analysis (because W_B^{TF} is not very regular as $W_B^{\mathsf{TF}} + \nu - 2jB = 0$ for $j \in \mathbb{Z}^+$ we replace it by its ε-approximation with the variable scale $\varepsilon = \varepsilon(x)$), paired with the scaling arguments.

Theorem 5

The following asymptotics hold as $M = 1$:

$$\mathsf{E}_N = \mathcal{E}_B^{\mathsf{TF}} + \operatorname{Tr}(H^-_{W^{\mathsf{TF}}+\nu}) - \int T(W^{\mathsf{TF}} + \nu)\,dx + O(R), \tag{37}$$

$$\mathsf{D}(\rho_\Psi - \rho_B^{\mathsf{TF}}, \rho_\Psi - \rho_B^{\mathsf{TF}}) = O(R), \tag{38}$$

and

$$\mathsf{E}_N = \mathcal{E}_B^{\mathsf{TF}} + \mathsf{Scott} + O(R + B^{\frac{1}{3}}Z^{\frac{4}{3}}) \tag{39}$$

where $R = Z^{\frac{5}{3}}$ as $B \le Z^{\frac{4}{3}}$ and $R = Z^{\frac{3}{5}}B^{\frac{4}{5}}$ as $Z^{\frac{4}{3}} \le B \le Z^3$.

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4. As completely separate issue we can prove G. Zhislin theorem that nuclei can bind at least as many electrons as their total charge.

Self-generated magnetic field case

In several papers recently L. Erdös, S. Fournais, and J. P. Solovej introduced and investigated the same operator as before, albeit with unknown magnetic potential A and included an energy of the magnetic field in the total energy:

$$\mathsf{E}^*_N = \inf_A \Bigl(\mathsf{E}_N(A) + \frac{1}{\alpha}\int |\nabla \times A|^2\, dx\Bigr) \tag{40}$$

with

$$0 < \alpha \le \kappa^* Z^{-1} \tag{41}$$

with sufficiently small constant $\kappa^* > 0$.

Theorem 6

Under assumption (41) *as* $N \geq Z - CZ^{-\frac{2}{3}}$

$$\mathsf{E}_N^* = \mathcal{E}_N^{\mathsf{TF}} + \sum_{1\leq m\leq M} qZ_m^2 S(\alpha Z_m) + O\bigl(Z^{\frac{16}{9}} + \alpha a^{-3} Z^2\bigr) \tag{42}$$

provided $a \geq Z^{-\frac{1}{3}}$ *where* $\mathcal{E}_N^{\mathsf{TF}}$ *is a Thomas-Fermi energy and* $qS(Z_m)Z_m^2$ *are magnetic Scott correction terms.*

Combining with the properties of the Thomas-Fermi energy we arrive to

Corollary 7

Let us consider $\mathsf{y}_m = \mathsf{y}_m^*$ *minimizing the full energy*

$$\mathsf{E}_N^* + \sum_{1\le m<m'\le M} \frac{Z_m Z_{m'}}{|\mathsf{y}_m - \mathsf{y}_{m'}|}. \tag{43}$$

Assume that $Z_m \asymp N \ \forall m = 1, \dots, M$.
Then $a \ge Z^{-\frac{1}{4}}$ *and the remainder estimate in* (42) *is* $O\bigl(Z^{\frac{16}{9}}\bigr)$.

The proof is based on reduction to one-particle theory (as we did), then minimization with respect to A of

$$\operatorname{Tr}(H^{-}_{A,W}) + \frac{1}{\alpha}\int |\nabla \times A|^2\,dx \tag{44}$$

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While minimizer A exists we do not know if it is unique (under assumptions $\nabla \cdot A = 0$ and $A = O(1)$ as $|x| \to \infty$). If the minimizer was unique , it would be 0 at least as $M = 1$.

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While minimizer A exists we do not know if it is unique (under assumptions $\nabla \cdot A = 0$ and $A = O(1)$ as $|x| \to \infty$). If the minimizer was unique , it would be 0 at least as $M = 1$. Then $S(.) = S(0)$ even for $M \geq 2$.

Any minimizer A should satisfy equation

$$\frac{1}{\kappa h^2}\Delta A_j(x) = \Phi_j(x) := \\ -\operatorname{Re}\operatorname{tr}\Bigl(\upsigma_j\bigl((hD-A)_x\cdot\boldsymbol{\sigma}\bigr)\bigl(\psi(x)e(x,y,0)\psi(y)\bigr)\Bigr)\Bigr|_{y=x} \tag{45}$$

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If we apply Weyl approximation to the right-hand expression, we get 0. Therefore right-hand expression is a remainder in the Weyl approximation. Using this observation we recover by the means of the Rough Microlocal Analysis and Sharp Spectral Asymptotics the series of improving estimates to A and the best of them would be almost

$$|\nabla^\beta A| \le CZ^{\frac{1}{2}}\ell(x)^{-\frac{1}{2}-|\beta|} \qquad \ell(x)\le Z^{-\frac{1}{3}}, \qquad (46)$$

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with $\ell(x)=\min_m|x-y_m|$.

Applying rough Microlocal Analysis and Sharp Spectral Asymptotics again we recover all necessary estimates.

Remark

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2. As completely separate issue we can prove G. Zhislin theorem that nuclei can bind at least as many electrons as their total charge.

Combined magnetic field

Currently I am working on combined magnetic field when $A = \bar{A} + A'$ with constant magnetic field $\bar{A}$ of intensity B and unknown self-generated magnetic field and only its energy is counted:

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Luckily I already investigated in Chapter 16 of [V. Ivrii, Future Book] pointwise spectral asymptotics for magnetic Schrödingier operator where short loops play crucial role.

Case $B \le Z^{\frac{4}{3}}$

Theorem 8

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1. *As* $B \le Z$

$$\mathsf{E}^*_N = \mathcal{E}^{\mathsf{TF}}_N + 2Z^2 S(\alpha Z) + O\bigl(Z^{\frac{5}{3}} + \alpha |\log(\alpha Z)|^{\frac{1}{3}} Z^{\frac{25}{9}}\bigr); \qquad (48)$$

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2. *As $Z \le B \le Z^{\frac{4}{3}}$*
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Theorem 9

As as $B \ll Z$ estimate (48) could be improved to

$$\mathsf{E}_N^* = \mathcal{E}_N^{\mathsf{TF}} + 2Z^2 S(\alpha Z) + \text{Dirac} + \text{Schwinger} \\ + O\bigl(Z^{\frac{5}{3}-\delta}(1+B^\delta) + \alpha|\log(\alpha Z)|^{\frac{1}{3}} Z^{\frac{25}{9}}\bigr). \quad (50)$$

Case $Z^{\frac{4}{3}} \le B \le Z^3$

Theorem 10

Let $M = 1$, $N \asymp Z$, $Z^{\frac{4}{3}} \le B \le Z^3$ *and* $\alpha \le \kappa^* Z^{-1}$, $\alpha \le B^{-\frac{4}{5}} Z^{\frac{2}{5}} |\log Z|^{-K}$. *Then*

$$\mathsf{E}^*_N = \mathcal{E}^*_N + 2Z^2 S(0) + O\bigl(B^{\frac{1}{3}} Z^{\frac{4}{3}} + B^{\frac{4}{5}} Z^{\frac{3}{5}} + \alpha Z^3 + \alpha^{\frac{16}{9}} B^{\frac{82}{45}} Z^{\frac{49}{45}} + \alpha^{\frac{40}{27}} B^{\frac{74}{45}} Z^{\frac{139}{135}}\bigr). \quad (51)$$

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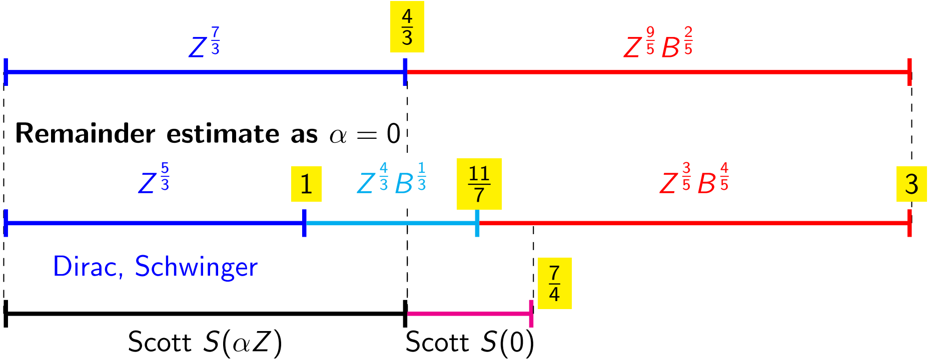
Main term



Numbers in yellow boxes show $B = Z^{\star}$ thresholds.

Future plans

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7. May be consider 2D-theory (quantum dots).

Reference

Microlocal Analysis, Sharp Spectral, Asymptotics and Applications (in progress)
http://weyl.math.toronto.edu/victor2/futurebook/futurebook.pdf

- Chapter 24. Asymptotics of the ground state energy of heavy molecules, pp 2153–2217;
- Chapter 25. Asymptotics of the ground state energy of heavy molecules in magnetic field, pp 2218–2349;
- Chapter 26. Asymptotics of the ground state energy of heavy molecules in self-generated magnetic field, pp 2350–2424;
- Chapter 27. Asymptotics of the ground state energy of heavy molecules in combined magnetic field, (in progress);
- Chapter 28. Asymptotics of the ground state energy of heavy molecules in super strong magnetic field, (in perspective).

Semiclassical theory with self-generated magnetic field
http://weyl.math.toronto.edu/victor2/preprints/Talk_11.pdf