Asymptotics of the Ground State Energy for Relativistic Atoms and Molecules

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Introduction

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1. To improve results of J. P. Solovej, T. Ø. Sørensen, W. L. Spitzer [SSS];
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The functional analytic arguments in these papers are the best (and way better than I could produce on my own), and I use them heavily on certain stages of my analysis.
On the other hand, the microlocal semiclassical arguments require improvements, which we provide.

The framework

Let us consider the following operator (quantum Hamiltonian)

$$\mathrm{H} = \mathrm{H}_N := \sum_{1\le j\le N} H_{V,x_j} + \sum_{1\le j<k\le N} \frac{\mathrm{e}^2}{|x_j - x_k|} \tag{1}$$

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

$$H_V = T - V(x) \tag{3}$$

describing N same type particles in the external field with the scalar potential $-V$ and repulsing one another according to the Coulomb law; e is a charge of the electron, T is an operator of the kinetic energy.

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

$$V(x) = \sum_{1\le m\le M} \frac{Z_m \mathrm{e}^2}{|x - \mathrm{y}_m|} \tag{4}$$

where $Z_m \mathrm{e} > 0$ and y_m are charges and locations of nuclei.

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The are two crucial questions: the quantum statistics and what is T?

Quantum statistics

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 $(x_1, \varsigma_1), \dots, (x_N, \varsigma_N)$ where $\varsigma_j \in \{1, \dots, q\}$, $q = 2$, are spin variables.

Kinetic energy operator

Non-magnertic, non-relativistic theory

In this the most basic case

$$T = \frac{1}{2\mathrm{m}}(-i\hbar\nabla)^2, \tag{5}$$

where m is the mass of electron, $\hbar$ is Planck constant.

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In the the relativistic case

$$T = \bigl(c^2(-i\hbar\nabla)^2 + \mathrm{m}^2c^4\bigr)^{\frac{1}{2}} - \mathrm{m}c^2, \tag{6}$$

where c is the speed of light.

Scaling

Using the scaling by the spatial variables and by the energy we can make $\mathsf{m} = \frac{1}{2}$, $\mathsf{e} = \hbar = 1$; then Z_m do not change, in the relativistic theory $\beta := \mathsf{e}^2/\hbar c$ also does not change.

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Remark

However, if $M\geq 2$ there is another parameter

$$d=\min_{1\leq m<m'\leq M}|\mathrm{y}_m-\mathrm{y}_{m'}|:\hbar^2/\mathrm{m}\mathrm{e}^2. \tag{7}$$

and in relativistic settings $\hbar^2/\mathrm{m}\mathrm{e}^2\cdot\beta=\hbar/\mathrm{m}c$ is called Compton wavelength.

Ground state energy

We are looking for the ground state energy, which is

$$\inf \mathrm{Spec}(\mathsf{H}_N) := \inf_{\Psi\in\mathfrak{H},\|\Psi\|=1} (\mathsf{H}_N\Psi, \Psi) \tag{8}$$

with $\mathsf{H}_N = \mathsf{H}_{N,V}$ (so operator is understood if necessary in the sense of forms).

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Remark

While non-relativistic operator is always semi-bounded from below, its relativistic cousin is semi-bounded from below if and only if

$$\beta Z_m \le \frac{2}{\pi} \qquad \text{for}\quad m = 1, \dots, M; \tag{9}$$

see [Herbst, Lieb-Yau]; we assume that $d \ge Z^{-1}$.

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 $H = T - W(x)$.

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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

$$\rho_\Psi(x) \approx P'(W+\nu) := q(2\pi)^{-3}\int_{\{\xi:T(\xi)-W(x)\le\nu\}} d\xi, \tag{10}$$

where $\nu=\lambda_N$.

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where $\nu = \lambda_N$.

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:

$$V - W^{\mathsf{TF}} = |x|^{-1} * \rho^{\mathsf{TF}}, \tag{11}$$

$$\rho^{\mathsf{TF}} = P'(W + \nu), \tag{12}$$

$$\int \rho^{\mathsf{TF}}\, dx = \min(N, Z), \tag{13}$$

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

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$$P'(W + \nu) = \frac{q}{6\pi^2}(W + \nu)_+^{\frac{3}{2}}, \tag{14}$$

and in the relativistic case we have

$$P'_*(W + \nu) = \frac{q}{6\pi^2}(W + \nu)_+^{\frac{3}{2}}(1 + c^{-2}(W + \nu))^{\frac{3}{2}} \tag{15}$$

We need also to know its primitive which in non-relativistic case is simple

$$P(W+\nu)=\frac{q}{15\pi^2}(W+\nu)_+^{\frac{5}{2}}; \tag{16}$$

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1. It looks strange because even $\int P'_*(W+\nu)\,dx$ logarithmically diverges at y_m but in the zones $\{x\colon |x-\mathsf{y}_m| \le Z^{-1}\}$ effective semiclassical parameter is $\gtrsim 1$, so Weyl approximation is wrong here anyway, and we will estimate nicely the contribution of these zones.

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2. Meanwhile, $\int P_*(W+\nu)\,dx$ diverges at 0 in more malicious way but we will need to regularize both it and $\int P(W+\nu)\,dx$ by subtracting $\int P_*(V_m)\,dx$ and $\int P(V_m)\,dx$ respectively, $V_m=Z_m|x-y_m|^{-1}$.

Reduction to one-particle problem. I

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Reduction to one-particle problem. I

The original problem can be reduced to one-particle problem. Actually, there are two different reductions: in the estimate from below and in the estimate from above. We start from the the estimate from below.
In the non-relativistic case one uses Lieb's electrostatic inequality

$$(\sum_{1\le j<k\le N} |x_j - x_k|^{-1}\Psi, \Psi) \ge \frac{1}{2}\mathsf{D}(\rho_\Psi, \rho_\Psi) - C\int \rho_\Psi^{\frac{4}{3}}\,dx \tag{17}$$

with

$$\mathsf{D}(f,g) := \int |x-y|^{-1} f(x)g(y)\,dxdy \tag{18}$$

and

$$\rho_\Psi(x) = N\int |\Psi(x, x_2, \ldots, x_N)|^2\,dx_2\cdots dx_N \tag{19}$$

which is a spatial density of the system in the state Ψ.

Heuristically the first term in the right-hand expression of (17) is a potential energy of the electron cloud.

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$$\int \rho_\Psi^{\frac{4}{3}}\, dx \le CZ^{\frac{5}{3}}. \tag{20}$$

Then

$$(\mathrm{H}_N\Psi, \Psi) \ge \sum_k (H_{V,k}\Psi, \Psi) + \frac{1}{2}\mathrm{D}(\rho_\Psi, \rho_\Psi) - CZ^{\frac{5}{3}} \tag{21}$$

and the first two terms in the right-hand expression could be rewritten as

$$\sum_k (H_{W,k}\Psi, \Psi) - \frac{1}{2}\mathrm{D}(\rho, \rho) + \frac{1}{2}\mathrm{D}(\rho_\Psi - \rho, \rho_\Psi - \rho) \tag{22}$$

with arbitrary ρ and $W = V - |x|^{-1} * \rho$.

Since operators $H_{W,k}$ act by different variables

$$\sum_k (H_{W,k}\Psi, \Psi) \geq \sum_{1\leq j\leq N'} \lambda_j \tag{23}$$

where N' is either N or the number of negative eigenvalues of H_W, whatever is less (we take ρ such that the negative spectrum of H_W is discrete).

Since operators $H_{W,k}$ act by different variables

$$\sum_k (H_{W,k}\Psi,\Psi) \geq \sum_{1\leq j\leq N'} \lambda_j \geq \operatorname{Tr}((H_W-\nu)^-) + \nu N \tag{23}$$

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$$\mathsf{E}_N \geq \operatorname{Tr}((H_{W+\nu})^-) + \nu N - \frac{1}{2}\mathsf{D}(\rho, \rho) - CZ^{\frac{5}{3}}. \tag{24}$$

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Remark

Actually, in the right-hand expression is also a "bonus term" $\frac{1}{2}\mathsf{D}(\rho_\Psi-\rho,\rho_\Psi-\rho)$; we call it so because we do not need it but we estimate it also as a bonus.

Consider the semiclassical approximation to the trace term

$$\mathrm{Tr}((H_{W+\nu})^{-}) \approx -\int P(W+\nu)\,dx \tag{25}$$

and we arrive to

$$\mathsf{E}_N \gtrapprox -\int P(W+\nu)\,dx - \frac{1}{2}\mathsf{D}(\rho,\rho) + \nu N, \tag{26}$$

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and the right-hand expression should be maximized by the choice of ρ, $W = V - |x|^{-1} * \rho$ and $\nu \le 0$.

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It turns out that the optimal choice are Thomas-Fermi potential W^{TF} and density ρ^{TF} and a chemical potential ν i.e. solutions of (11)–(13)

$$V - W^{\mathsf{TF}} = |x|^{-1} * \rho^{\mathsf{TF}}, \tag{11}$$

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It turns out that the optimal choice are Thomas-Fermi potential W^{TF} and density ρ^{TF} and a chemical potential ν i.e. solutions of (11)–(13) and we call the result Thomas-Fermi energy and denote by $\mathcal{E}^{\mathsf{TF}}$.

It has a magnitude $Z^{\frac{7}{3}}$ and the error here consist of two parts: semiclassical error in the trace term and $\asymp Z^{\frac{5}{3}}$ from electrostatic inequality.

Currently semiclassical error is $\asymp Z^2$ but we will improve it with Scott correction term; still ρ^{TF} etc will remain our choice.

Reduction to one-particle problem. II

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

Reduction to one-particle problem. II

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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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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 $\mathsf{N}^-(H_W)$.
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 $\nu < \lambda_N < 0$

Note that

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

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 $\nu<\lambda_N<0$ and

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

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$$\mathsf{E}_N \lessapprox -\int P(W(x)+\nu)\,dx - \frac{1}{2}\mathsf{D}(\rho,\rho) + \nu N \\ + \mathsf{D}(P'(W+\nu)-\rho, P'(W+\nu)-\rho)$$

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.

So in the non-relativistic case both estimates we got the same answer

$$\operatorname{Tr}(H^-_{W+\nu}) + \nu N - \frac{1}{2}\mathsf{D}(\rho,\rho) \approx \\ -\int P(W+\nu)\,dx + \nu N - \frac{1}{2}\mathsf{D}(\rho,\rho) \tag{27}$$

with $W = W^{\mathsf{TF}}$ etc except

1. there is a term $-CZ^{\frac{5}{3}}$ in the estimate from below,
2. in the estimate from above there are some semiclassical errors,
3. and the transition from the trace term on the left to its semiclassical expression on the right will be reexamined.

Reduction to one-particle problem. III

But what about relativistic case?

Reduction to one-particle problem. III

But what about relativistic case?

1. It turns out that under assumption

$$\beta Z_m \le \frac{2}{\pi} - \epsilon \qquad \text{for} \quad m = 1, \dots, M \tag{9}^*$$

   inequality (20) $\int \rho_\Psi^{\frac{4}{3}}\, dx \le CZ^{\frac{5}{3}}$ holds for the ground state;
2. But we dont't know it is the case under (9);
3. And the semiclassical errors are not purely semiclassical anymore because while operator is relativistic, we write Weyl expressions for non-relativistic one.

To remedy the first issue we will use the correlation inequality [SSS]

$$\sum_{1\le j<k\le N} |x_j - x_k|^{-1} \ge \sum_{j=1}^{N} (|x|^{-1} * \rho * \phi_\varepsilon)(x_j) - \frac{1}{2}\mathsf{D}(\rho,\rho) - CN\varepsilon^{-1}, \qquad (28)$$

where $\rho \ge 0$ is any function, $\phi \ge 0$ is spherically symmetric, with $\int \phi\, dx = 1$, $\phi_\varepsilon(x) = \varepsilon^{-3}\phi(x/\varepsilon)$.

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Then in operator $W = V - |x|^{-1} * \rho$ is replaced by $W_\varepsilon = V - |x|^{-1} * \rho * \phi_\varepsilon$,

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Then in operator $W = V - |x|^{-1} * \rho$ is replaced by $W_\varepsilon = V - |x|^{-1} * \rho * \phi_\varepsilon$, which leads to a relative error $\min(\varepsilon^2 \ell(x)^{-2}, 1)$ ($\ell_m(x) = \min |x - \mathsf{y}_m|$ is the distance to the nearest nucleus) in pointwise Weyl expressions,

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And we do not have "bonus term" $\frac{1}{2}\mathsf{D}(\rho_\Psi - \rho, \rho_\Psi - \rho)$, which is a bad news for some applications.

Semiclassics: singular zone

First, we need to do something in the singular zone $\{x\colon \ell(x)\le Z^{-1}\}$ where $P'_*(W+\mu)\asymp \ell(x)^{-3}$, $P_*(W+\mu)\asymp \ell(x)^{-4}$ and all integrals in the semiclassical expressions are diverging.

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But effective semiclassical parameter is $\gtrsim 1$ here anyway, so semiclassics is wrong, and we need to estimate properly $e(x,x,\tau)$ here where $e(x,y,\tau)$ is the Schwartz kernel of the spectral projector of H_W.

Using Lieb-Yau inequality [Lieb-Yau]

$$\sqrt{\Delta} - \frac{2}{\pi|x|} \geq A_s \Delta^s - B_s \tag{29}$$

for any $s \in [0, 1/2)$ and $A_s, B_s > 0$ (recall that $\Delta = (-i\nabla)^2$ is a positive Laplacian),

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$$e(x, x, \tau) \le CZ^{1-\delta}\ell(x)^{\delta-2} \qquad \text{for } \ \ell(x) \le Z^{-1},\ \tau \le C_0Z^2 \tag{30}$$

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Then contributions of the singular zone to $\int e(x, x, \tau)\, dx$, $\mathsf{D}(e(x, x, \tau),\, e(x, x, \tau))$ and $\int\int^{\tau} e(x, x, \tau')\, d\tau' dx$ do not exceed C, CZ and CZ^2 respectively, exactly as in non-relativistic case.

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Two former are too small to care and the latter will be dealt properly later.

Semiclassics: regular zone

In the regular zone $\{x\colon \ell(x)\ge Z^{-1}\}$ semiclassical errors are exactly as in the non-relativistic case and the contributions of the regular zone to $\int e(x,x,\tau)\,dx$, $\mathsf{D}(e(x,x,\tau),\, e(x,x,\tau))$ and $\int\int^{\tau} e(x,x,\tau')\,d\tau' dx$ do not exceed $CZ^{\frac{2}{3}}$, $CZ^{\frac{5}{3}}$ and CZ^{2} respectively.

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Trace term and Scott correction term

To get an error better than $O(Z^2)$ we need to consider

$$\operatorname{Tr}(H^-_{W+\nu}) + \int P(W+\nu)\,dx = \int \Bigl(\int_{-\infty}^0 \operatorname{tr} e(x,x,\tau)\,d\tau + P(W+\nu)\Bigr)\,dx. \tag{31}$$

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Let $d\ge Z^{-1}$ be a minimal distance between nuclei, or $Z^{-\frac{1}{3}}$, whatever is smaller, and $1=\sum_{0\le m\le 1}\psi_m$ where ψ_m are supported in $d/2$-vicinities of y_m, and ψ_0 is supported in $\{x\colon \ell(x)\ge d/4\}$.

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On the other hand, using the same technique as in the non-relativistic case, see V. Ivrii, [Ivr1], Chapter 25, one can prove that for $m = 1, \ldots, M$ the difference between (31) with ψ_m cut-off, and the same expression but with and $W + \nu$ replaced by $V_m = Z_m|x - \mathsf{y}_m|^{-1}$, both in the definition of operator and Weyl expression, also is $O(Z^{\frac{3}{2}}d^{-\frac{1}{2}})$.

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Further, in the same way in the right-hand expressions of (31) for such operators we can drop ψ_m with the same error, thus arriving to the sum of

$$\int \Bigl(\int_{-\infty}^{0} \operatorname{tr} e_m(x, x, \tau)\, d\tau + P(V_m) \Bigr)\, dx. \tag{32$_m$}$$

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In each such expression we can take $\mathsf{y}_m = 0$. Then scaling $x \mapsto Z_m x$ we get $qZ_m^2 S(\beta Z_m)$ where $S(k)$ is delivered by $(32)_m$ with $\beta := \beta Z_m$, $Z_m := 1$, and $q := 1$.

The rest is no different from non-relativistic case and we arrive to

Theorem 1

Let $\mathrm{m} = \frac{1}{2}$, $\mathrm{e} = \hbar = 1$, $\beta := \mathrm{e}^2/\hbar c$. *Assume that* (9) *holds and* $d \ge Z^{-1}$. *Then*

1. $$\mathsf{E}_N = \mathcal{E}^{\mathsf{TF}} + \sum_{1\le m\le M} qZ_m^2 S(\beta Z_m) + O(Z^{\frac{3}{2}} d^{-\frac{1}{2}} + Z^{\frac{5}{3}}). \tag{33}$$

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2. *In particular, for* $d \ge Z^{-\frac{1}{3}}$
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3. *Further, under condition* $(9)^*$
$$\mathrm{D}(\rho_\Psi - \rho^{\mathsf{TF}}, \rho_\Psi - \rho^{\mathsf{TF}}) \le CZ^{\frac{5}{3}}. \tag{35}$$

Sharper estimate

Can we do better than (34)?

Sharper estimate

Can we do better than (34)? In the non-relativistic case we could, provided $d \gg Z^{-\frac{1}{3}}$ (we do not reset it to $Z^{-\frac{1}{3}}$):

$$\mathsf{E}_N = \mathcal{E}^{\mathsf{TF}} + \sum_{1\le m\le M} qZ_m^2 S(\beta Z_m) + \mathsf{Dirac} + \mathsf{Schwinger} + O(Z^{\frac{5}{3}-\delta} + Z^{\frac{5}{3}+\frac{\delta}{3}} d^{-\delta}) \qquad (36)$$

with Dirac and Schwinger correction terms of magnitude $Z^{\frac{5}{3}}$ each:

$$\mathsf{Dirac} = -\frac{9}{2}(36\pi)^{\frac{2}{3}} q^{-\frac{1}{3}} \int (\rho^{\mathsf{TF}})^{\frac{4}{3}}\, dx, \qquad (37)$$

$$\mathsf{Schwinger} = (36\pi)^{\frac{2}{3}} q^{-\frac{1}{3}} \int (\rho^{\mathsf{TF}})^{\frac{4}{3}}\, dx \qquad (38)$$

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- The semiclassical errors are $O(Z^{\frac{2}{3}-\delta} + Z^{\frac{2}{3}+\frac{\delta}{3}} d^{-\delta})$ in $\int e(x,x,0)\,dx$ and $O(Z^{\frac{5}{3}-\delta} + Z^{\frac{5}{3}+\frac{\delta}{3}} d^{-\delta})$ in all other terms.

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- Schwinger, coming from the semiclassical expression from the trace term, and Dirac, coming from $-Z\iint |x-y|^{-1}|e(x,y,0)|^2\,dxdy$ in the estimate from above remain.
- Appears a new, relativistic correction term, again coming from the trace term, and equal to

$$\int \Bigl(-P_*(W+\nu)+P(W+\nu)+P_*(V)-P(V)\Bigr)\,dx \tag{39}$$

which equal modulo the same error to

$$\mathsf{RCT}:=\frac{q}{6\pi^2c^2}\int\Bigl(-(W+\nu)^{\frac{7}{2}}+V^{\frac{7}{2}}\Bigr)\,dx \tag{40}$$

of the magnitude $\beta^2Z^{\frac{11}{3}}$.

Theorem 2

In the framework of Theorem 1 let condition $(9)^*$ *be fulfilled and* $d \geq Z^{-\frac{1}{3}}$. *Then*

$$\mathsf{E}_N \leq \mathcal{E}^{\mathsf{TF}} + \sum_{1\leq m\leq M} qZ_m^2 S(\alpha Z_m) + \mathsf{Dirac} + \mathsf{Schwinger} + \mathsf{RCT} + O(Z^{\frac{5}{3}-\delta} + Z^{\frac{5}{3}+\frac{\delta}{3}} d^{-\delta}) \qquad (34)^*$$

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$$\mathsf{D}(\rho_\Psi - \rho^{\mathsf{TF}}, \rho_\Psi - \rho^{\mathsf{TF}}) = O(Z^{\frac{5}{3}-\delta} + Z^{\frac{5}{3}+\frac{\delta}{3}} d^{-\delta}). \qquad (35)^*$$

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Remark

We do not need $(9)^*$ for this estimate from above.

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Remark

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Discussion: corollaries

1. Like in non-relativistic case the same results hold in the free nuclei model when E_N is replaced by

$$\widehat{\mathsf{E}}_N = \mathsf{E}_N + \sum_{1\le m<m'\le M} \frac{Z_m Z_{m'} \mathsf{e}^2}{|\mathsf{y}_m - \mathsf{y}_{m'}|}, \tag{41}$$

which is minimized by y_m. Then the minimal distance between nuclei $d \gtrsim Z^{-\frac{5}{21}}$ (provided $Z_m \asymp Z$ for all $m = 1, \dots, M$), and under assumption $(9)^*$ and in the non-relativistic case $d \ge Z^{-\frac{5}{21}+\delta}$.

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2. Like in non-relativistic case all correction terms can be calculated for atoms, and if $(Z-N)_+ \ll Z$, for neutral atoms.

3. Under assumption $(9)^*$ we have estimates (35) and even $(35)^*$ for $\mathsf{D}(\rho_\Psi - \rho, \rho_\Psi - \rho)$, and we can estimate excessive negative charge, or excessive positive charge in the molecule in the free nuclei model, or estimate the difference between ν and ionization energy.

Self generated magnetic field:set-up

Consider now operator with a magnetic field i. e. with non-relativistic one-particle kinetic energy operator

$$T = \frac{1}{2\mathrm{m}} P^2 \tag{42}$$

and relativistic one-particle kinetic energy operator

$$T = (c^2 P^2 + \mathrm{m}^2 c^4)^{\frac{1}{2}} - \mathrm{m}c^2 \tag{43}$$

where

$$P = \bigl((i\nabla - \mathrm{e}A)\cdot \boldsymbol{\sigma}\bigr) \tag{44}$$

and $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$, σ_j are Pauli matrices.

Non-relativistic case

In the non-relativistic case self-generated magnetic field A was considered, i.e. to E is added the energy of the magnetic field

$$\mathsf{E}(A) = \inf \operatorname{Spec}(\mathsf{H}_N) + \underbrace{\frac{1}{\alpha}\int |\nabla \times A|^2\, dx} \tag{45}$$

with $\mathsf{H}_N = \mathsf{H}_{N,A,V}$, and the result is minimized by A:

$$\mathsf{E}^* := \inf_{A\in \mathscr{H}^1_0} \mathsf{E}(A). \tag{46}$$

In [EFS1] it was proven that for $\alpha Z_m < \kappa$ (some unknown constant $\kappa > 0$, may be even ∞) $\mathcal{E}^{\mathsf{TF}}$, while Scott correction term is $q\sum_m Z_m^2 S(\alpha Z_m)$.

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The crucial step was the proof that the minimizer exists (but we do not know if it is unique) and satisfies after rescaling equation

$$\frac{2}{\kappa h^2}\Delta A_j(x) = \Phi_j := \\ -\operatorname{Re}\operatorname{tr}\Bigl[\upsigma_j\Bigl((hD-A)_x\cdot\boldsymbol{\upsigma}\, e(x,y,\tau) + e(x,y,\tau)\,{}^t(hD-A)_y\cdot\boldsymbol{\upsigma}\Bigr)\Bigr]\Bigr|_{y=x}, \tag{47}$$

where $e(x,y,\tau)$ is the Schwartz kernel of the spectral projector $\uptheta(-H)$ of $H=H_{A,V}$ and tr is a matrix trace.

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where $e(x,y,\tau)$ is the Schwartz kernel of the spectral projector $\theta(-H)$ of $H=H_{A,V}$ and tr is a matrix trace.
Then, using newly developed methods of semiclassical microlocal analysis, certain estimates to A and $e(.,.,\tau)$ where proven, which led to estimates of the trace.

Relativistic case

Consider the same problem in the relativistic case, assuming (9)* and

$$\alpha Z_m \le \kappa(\frac{2}{\pi} - \beta Z_m)^{3/2} \qquad \forall m = 1, \dots, M. \tag{48}$$

Again, we prove that the minimizer exists (but we do not know if it is unique) and satisfies after rescaling equation

$$\begin{aligned} \frac{2}{\kappa h^2}\Delta A_j(x) = \Phi_j := \\ & -\operatorname{Re}\operatorname{tr}\Bigl[\int_0^\infty \sigma_j((hD-A)_x\cdot\boldsymbol{\sigma})e^{-\lambda S}e(.,.,0)e^{-\lambda S}\,d\lambda\Bigr]\Bigr|_{x=y} \\ & -\operatorname{Re}\operatorname{tr}\Bigl[\int_0^\infty \sigma_j e^{-\lambda S}e(.,.,0)e^{-\lambda S}\,{}^t((hD-A)_y\cdot\boldsymbol{\sigma})\,d\lambda\Bigr]\Bigr|_{x=y} \end{aligned} \tag{49}$$

where

$$S = \beta^2(T+\beta^{-2}) = \bigl((\beta^2(hD-A)\cdot\boldsymbol{\sigma})^2+1\bigr)^{\frac{1}{2}}. \tag{50}$$

Then, using the same methods of semiclassical microlocal analysis, we prove the similar estimates to A and $e(.,.,\tau)$, which lead to the same trace estimates.

Discussion

1. The Scott correction term is now $q\sum_m Z_m^2 S(\beta Z_m, \alpha Z_m)$.

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7. See results and more references in [Ivr3].

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Thank you!