Asymptotics of the ground state energy in the relativistic settings

Victor Ivrii

June 19, 2018

Abstract

The purpose of this paper is to derive sharp asymptotics of the ground state energy for the heavy atoms and molecules in the relativistic settings, and, in particular, to derive relativistic Scott correction term and also Dirac, Schwinger and relativistic correction terms. Also we will prove that Thomas-Fermi density approximates the actual density of the ground state, which opens the way to estimate the excessive negative and positive charges and the ionization energy.

1 Introduction

The purpose of this paper is to derive sharp asymptotics of the ground state energy for the heavy atoms and molecules in the relativistic settings, and, in particular, to derive relativistic Scott correction term and also Dirac, Schwinger and relativistic correction terms. The relativistic Scott correction term was first derived in [SSS] which both inspired our paper and provided necessary functional analytic tools; our improvement is achieved due to more refined microlocal semiclassical technique.

Also we will prove that Thomas-Fermi density approximates the actual density of the ground state, which opens the way to estimate the excessive negative and positive charges and the ionization energy.

In the next article we plan to introduce a self-generated magnetic field and improve results of [EFS2].
Multielectron Hamiltonian is given by

\[ H = H_N := \sum_{1 \leq j \leq N} H_{V,x_j} + \sum_{1 \leq j < k \leq N} \frac{e^2}{|x_j - x_k|} \]

on

\[ \mathcal{H} = \bigwedge_{1 \leq n \leq N} \mathcal{H}, \quad \mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}^q) \simeq L^2(\mathbb{R}^3 \times \{1, \ldots, q\}, \mathbb{C}) \]

with

\[ H_V = T - eV(x), \]

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.

In the non-relativistic framework this operator is defined as

\[ T = \frac{1}{2\mu} (-i\hbar \nabla)^2. \]

In the relativistic framework this operator is defined as

\[ T = \left( c^2 (-i\hbar \nabla)^2 + \mu^2 c^4 \right)^{\frac{1}{2}} - \mu^2 c^4, \]

in the non-magnetic, magnetic (Schrödinger) and magnetic (Schrödinger-Pauli) settings respectively.

Here

\[ V(x) = \sum_{1 \leq m \leq M} \frac{Z_m e}{|x - y_m|} \]

and

\[ d = \min_{1 \leq m < m' \leq M} |y_m - y_{m'}| > 0. \]

where \( Z_m e > 0 \) and \( y_m \) are charges and locations of nuclei.

It is well-known that the non-relativistic operator is always semibounded from below. On the other hand, it is also well-known [IH, LY] that

\[ Z_m \beta \leq \frac{2}{\pi} \quad \forall m = 1, \ldots, M; \quad \beta := \frac{e^2}{\hbar c}. \]
We will assume (1.9), sometimes replacing it by a strict inequality:

\[(1.10) \quad Z_m \beta \leq \frac{2}{\pi} - \epsilon \quad \forall m = 1, \ldots, M; \quad \beta := \frac{e^2}{\hbar c}.\]

We also assume that \(d \geq CZ^{-1}\). Then we are interested in \(E := \inf \text{Spec}(H)\).

**Remark 1.1.** (i) In the non-relativistic theory by scaling with respect to the spatial and energy variables we can make \(h = e = \mu = 1\) while \(Z_m\) are preserved.

(ii) In the relativistic theory by scaling with respect to the spatial and energy variables we can make \(h = e = \mu = 1\) while \(\beta\) and \(Z_m\) are preserved.

From now on we assume that such rescaling was done and we are free to use letters \(h, \mu\) and \(c\) for other notations.

## 2 Functional analytic arguments

### 2.1 Estimate from below

In contrast to [SSS] we will start from the more traditional approach. We estimate \(\sum_{1 \leq j < k \leq N} \langle x_j - x_k \rangle^{-1} \Psi, \Psi \rangle\) from below using Lieb’s electrostatic inequality by \(\frac{1}{2} D(\rho_\Psi, \Psi) - C \int \rho_\Psi^{4/3} dx\) where where \(\langle \cdot, \cdot \rangle\) means the inner product in \(\mathcal{H}\), \(\rho_\Psi(x)\) is a one particle density, and we use notations of Chapter 25 of [Ivr].

The the standard estimate (25.2.2) from [Ivr] from below holds:

\[(2.1) \quad \langle H_N \Psi, \Psi \rangle \geq \sum_{1 \leq j \leq N} \langle H_{V,x_j} \Psi, \Psi \rangle + \frac{1}{2} D(\rho_\Psi, \rho_\Psi) - C \int \rho_\Psi^{4/3}(x) dx =\]

\[\sum_{1 \leq j \leq N} \langle H_{W,x_j} \Psi, \Psi \rangle + \frac{1}{2} D(\rho_\Psi - \rho, \rho_\Psi - \rho) - \frac{1}{2} D(\rho, \rho) - C \int \rho_\Psi^{4/3}(x) dx\]

where \(H_W\) is one-particle Schrödinger (etc) operator with the potential

\[(2.2) \quad \mathcal{W} = V - |x|^{-1} * \rho,\]
where $\rho$ is an arbitrary chosen real-valued non-negative function. Then again we get

\begin{equation}
E_N \geq \text{Tr}(H_{W+\lambda}) + \lambda N + \frac{1}{2}D(\rho_\psi - \rho, \rho_\psi - \rho) - \frac{1}{2}D(\rho, \rho) - C \int \hat{\rho}_\psi^\frac{3}{2}(x) \, dx
\end{equation}

with arbitrary $\lambda$.

**Remark 2.1.** As usual, we will need to improve these estimates to recover remainder estimate better than $O(Z^{\frac{5}{3}})$.

Now we need to prove estimate

\begin{equation}
\int \hat{\rho}_\psi^\frac{3}{2}(x) \, dx \leq CZ^\frac{5}{3}
\end{equation}

for the ground state energy. In follows from

\begin{equation}
\int \rho_\psi^\frac{3}{2}(x) \, dx \leq CZ^\frac{5}{3},
\end{equation}

equality $\int \rho_\psi \, dx = N$ and assumption $N \lesssim Z$. To prove (2.5) we apply classical arguments of Lieb–Thirring, but replacing the Lieb–Thirring inequality by some relativistic inequalities (see Appendix A). Namely, let $b := T - KU$ with $U = \hat{\rho}_\psi^\frac{3}{2}\phi_\psi + \beta^{-1}\rho_\psi^\frac{3}{2}\phi_\psi$ where $\phi_\psi$ is a characteristic function of $\{x: \rho_\psi \gtrless \beta^{-3}\}$.

Consider multiparticle operator $B = \sum b_j$ and its lowest eigenvalue $E_0$. Obviously,

\begin{equation}
E_0 \leq \langle B\Psi, \Psi \rangle = \sum_j \langle T_j \psi, \psi \rangle - K \int (\rho_\psi^\frac{3}{2}\phi_\psi + \beta^{-1}\rho_\psi^\frac{3}{2}\phi_\psi) \, dx.
\end{equation}

On the other hand, $E_0$ does not exceed the sum the sum of negative eigenvalues of $b$, and due to Daubechies inequality (A.1) the absolute value of this sum does not exceed

\begin{equation}
C_0 \int \text{max}(U^\frac{5}{2}, \beta^3 U^4) \, dx \leq C_0 K^\frac{5}{2} \int (\rho_\psi^\frac{3}{2}\phi_\psi + \beta^{-1}\rho_\psi^\frac{3}{2}\phi_\psi) \, dx.
\end{equation}

Therefore, assuming that $E_0 \leq 0$ we conclude that

$$\sum_j \langle T_j \psi, \psi \rangle - K \int \text{min}(\rho_\psi^\frac{3}{2}, \beta^{-1}\rho_\psi^\frac{3}{2}) + C_0 K^\frac{5}{2} \int (\rho_\psi^\frac{3}{2}\phi_\psi + \beta^{-1}\rho_\psi^\frac{3}{2}\phi_\psi) \, dx \geq 0.$$
and therefore for small positive constant $K$ we conclude that

\begin{equation}
\sum_j \langle T_j \Psi, \Psi \rangle \geq 2\epsilon_0 \int \left( \rho_{\Psi}^{\frac{5}{3}} \varphi_+ + \beta^{-1} \rho_{\Psi}^{\frac{4}{3}} \varphi_+ \right) dx.
\end{equation}

Thus, we proved that for any $\Psi \in \mathcal{H}$ (2.8) holds. Then

\begin{equation}
\sum_j \langle H_j \Psi, \Psi \rangle = \sum_j \langle T_j \Psi, \Psi \rangle - \int V(x)\rho_{\Psi}(x) dx \geq
\int (2\epsilon_0 \rho_{\Psi}^{\frac{5}{3}} - V(x)\rho_{\Psi}) \varphi_+ dx + \int (2\epsilon_0 \beta^{-1} \rho_{\Psi}^{\frac{4}{3}} - V(x)\rho_{\Psi}) \varphi_+ dx.
\end{equation}

We know, that this must be less than $-c_0 Z^\frac{7}{3}$ (it will follow, f.e. from the estimate from above). Observe that for $\ell(x) \geq aZ^{-\frac{1}{3}}$ we have $V(x) < a^{-1} Z^\frac{4}{3}$ and integral over this zone from $-V\rho_{\Psi}$ is greater than $-c_0 a^{-1} Z^\frac{7}{3}$. Let us fix $a$ a large enough constant.

Next,

\[ \int \chi_{\ell(x) \leq aZ^{-\frac{1}{3}}} \left( \epsilon_0 \rho_{\Psi}^{\frac{5}{3}} - V(x)\rho_{\Psi} \right) \varphi_+ dx \geq -C \int \chi_{\ell(x) \leq aZ^{-\frac{1}{3}}} V^{\frac{5}{3}} dx \geq -C_1 Z^\frac{7}{3} \]

and $(\epsilon_0 \beta^{-1} \rho_{\Psi}^{\frac{4}{3}} - V) \varphi_+$ is positive unless $\rho_{\Psi} > \beta^{-3}$ and $V \geq \epsilon_1 \beta^{-1} \rho_{\Psi}^{\frac{4}{3}} \geq \epsilon_1 \beta^{-2}$ (and then $\ell(x) \leq c_0 \beta$).

Therefore we estimate $\int \left( \rho_{\Psi}^{\frac{5}{3}} \varphi_+ + \beta^{-1} \rho_{\Psi}^{\frac{4}{3}} \varphi_+ \right) dx$ from above by $CZ^{7/3}$ plus $\int_{\chi_{\ell(x) \leq c_0 \beta}} V\rho_{\Psi} dx$ and to get (2.4) it is sufficient to estimate this term. Further, it is sufficient to replace $V$ by $V_m$ (since $V = V_m + O(\beta^2)$ provided distance between nuclei is $\geq c_0 \beta$). Also we can replace $V_m$ by $V_m + C\beta^{-2}$.

If $Z_m \beta \leq \frac{2}{\pi} - \epsilon$, then we can decompose $H = \eta(H - V^1) + (1 - \eta)(H - V^0)$ where $(1 - \eta)V^0$ coincides with $V$ in $\beta$-vicinity of $y_m$ and equals 0 outside of $2\beta$-vicinity of it and $V^1 = \eta^{-1}(V - (1 - \eta)V^0)$ and apply all above arguments for operator with $V = V^1$ while simply observing that $H - V^0$ is positive operator for $\eta$ sufficiently small. So we have proven that

**Proposition 2.2.** Under assumption (1.10) for the ground state

\begin{equation}
\int \min(\beta^{-1} \rho_{\Psi}^{\frac{4}{3}}, \rho_{\Psi}^{\frac{5}{3}}) dx \leq CZ^\frac{7}{3}
\end{equation}

and (2.4) holds.
Then we immediately arrive to Statement (i) below, and Statement (ii)
follows from [Bach] and [GS]:

**Corollary 2.3.** Under assumption (1.10)

(i) The following estimate hold:

\[
E_N \geq \text{Tr}(H^{-}_{W+\lambda}) - \frac{1}{2}D(\rho, \rho) - CZ^\frac{1}{2} + \frac{1}{2}D(\rho - \rho_\Psi, \rho - \rho_\Psi)
\]

where \(\rho, \lambda\) are arbitrary and \(W = V - |x|^{-1} * \rho\).

(ii) Further,

\[
E_N \geq \text{Tr}(H^{-}_{W+\lambda}) - \frac{1}{2}D(\rho, \rho) - \\
\frac{1}{2} \int |x - y|^{-1} \text{tr}(e_N^i(x, y)e_N(x, y)) \, dx \, dy - CZ^\frac{1}{2} - \frac{1}{2}D(\rho - \rho_\Psi, \rho - \rho_\Psi)
\]

where \(e_N(x, y)\) is the Schwartz kernel of the projector to \(N\) lower eigestaes of \(H_\mathcal{W}\).

To cover\(^{1}\) the critical case\(^{2}\) we will use (2.21) from [SSS]

\[
\sum_{1 \leq i < j \leq N} |x_i - x_j|^{-1} \geq \sum_{j=1}^{N} (\rho * |x|^{-1} * \Phi_\epsilon)(x_j) - \frac{1}{2}D(\rho, \rho) - CN\epsilon^{-1},
\]

where again \(\rho \geq 0\) is arbitrary \(\lambda\) is arbitrary, \(\Phi \geq 0\) is spherically symmetric with \(\int \Phi \, dx = 1, \Phi_\epsilon(x) = \epsilon^{-3}\Phi(x/\epsilon)\). Here \(\frac{1}{2}\) is due to the difference in notations and also now

\[
W := W_\epsilon = V - |x|^{-1} * \rho * \Phi_\epsilon,
\]

instead of (2.2) and \(-CNs^{-1}\) instead of the last term in (2.3):

**Proposition 2.4.** Under assumption (1.9)

\[
E_N \geq \text{Tr}(H^{-}_{W+\lambda}) + \lambda N - \frac{1}{2}D(\rho, \rho) - CN\epsilon^{-1}.
\]

\(^{1}\) Unfortunately, only partially.

\(^{2}\) I.e. with the non-strict inequality (1.9) instead of (1.10).
Remark 2.5. (i) Later we set \( \varepsilon = Z^{-\frac{2}{3}} \). This would lead to \( O(Z^{\frac{2}{3}}) \) remainder estimate.

(ii) Proposition 2.4 falls short in two instances: there is no improved version of corollary 2.3(ii) and also there is no “bonus term” \( \frac{1}{2}D(\rho - \rho_\Psi, \rho - \rho_\Psi) \) in the right-hand expression.

2.2 Estimate from above

Estimate from above is straight-forward: we simply take \( \Psi \) as a Slater determinant of \( N \) lower eigenfunctions of \( H_W \). If there are only \( N' < N \) negative eigenvalues then we take only \( N' \) such eigenvalues, because \( E_N \leq E_{N'} \). Then we arrive to

Proposition 2.6.

\[
(2.16) \quad E_N \leq \text{Tr}(H_{W+\lambda}) - \frac{1}{2}D(\rho, \rho) + |\lambda - \nu| \cdot |N_{W+\nu} - N| + D(\text{tr} e_N(x, x) - \rho, \text{tr} e_N(x, x, \nu) - \rho) - \frac{1}{2} \int |x - y|^{-1} \text{tr}(e_N^1(x, y)e_N(x, y)) \, dx dy
\]

with arbitrary \( \rho \) and \( \nu \leq 0 \), \( W = V - |x|^{-1} \rho \).

3 Semiclassical methods

We will need the following semiclassical expressions:

\[
(3.1) \quad P'(w) = (2\pi)^{-3} q \int \frac{d\xi}{\{\xi : b(\xi) \leq w\}}
\]

and its integral

\[
(3.2) \quad P(w) = (2\pi)^{-3} q \int \frac{b(\xi) \, d\xi}{\{\xi : b(\xi) \leq w\}}
\]
where in the non-relativistic case \( b(\xi) = \frac{\hbar^2}{2\mu} |\xi|^2 \) and respectively for \( \mu = \hbar = 1 \)

\[
\begin{align*}
(3.3) \quad P^{TF}(w) &= \frac{q}{6\pi^2} w_+^3, \\
(3.4) \quad P^{TF}(w) &= \frac{q}{15\pi^2} w_+^{\frac{5}{3}},
\end{align*}
\]

and in the relativistic case we have \( b(\xi) = (c^2\hbar^2 |\xi|^2 + \mu^2 c^4)^{\frac{1}{2}} - \mu c^2 \) and respectively for \( \mu = \hbar = 1 \)

\[
(3.5) \quad P^{RTF}(w) = \frac{q}{6\pi^2} w_+^{\frac{3}{2}} (1 + \beta^2 w_+)^{\frac{1}{2}}
\]

in the relativistic case \( P^{RTF}(w) \) is an elementary function as well and a sadistic Calculus instructor can give it on the test. However it turns out that we really do not need any separate relativistic Thomas-Fermi theory.

After scalings we have a semiclassical zone \( \mathcal{X}_{\text{scl}} := \{ x : \ell(x) \geq cZ^{-1} \} \), where the effective semiclassical parameter \( h = 1/\ell \) and the operator is very similar to the non-relativistic one. There is also a singular zone \( \mathcal{X}_{\text{sing}} := \{ x : \ell(x) \leq cZ^{-1} \} \) and it covers the relativistic zone \( \mathcal{X}_{\text{rel}} := \{ x : \ell(x) \leq c\beta \} \).

Important is that

\[
\begin{align*}
(3.6) \quad 0 &\leq V(x) - W(x) \leq C\zeta^2 := \min(Z^\frac{4}{3}, Z\ell^{-1}), \\
(3.7) \quad |\partial^\gamma (W - V)| &\leq C\zeta^2 \ell(x)^{-|\gamma|} \quad \forall \gamma : |\gamma| \leq 2.
\end{align*}
\]

### 3.1 Trace term

Now the rescaling methods of [Ivr] allow us to prove the following:

**Proposition 3.1.** Let condition (1.9) be fulfilled and let \( W \) satisfy (3.6) and (3.7).

(i) Let \( \psi_0(x) \) be \( \ell \)-admissible function, equal 1 in \( \{ x : \ell(x) \geq 2a \} \) and supported in \( \{ x : \ell(x) \geq a \} \). Then for \( W = W^{TF} \)

\[
(3.8) \quad |\text{Tr}(H_{W,\lambda}^{-} \psi_0) - \int P^{RTF}(W + \lambda) \psi_0(x) \, dx| \leq C \left\{ \begin{array}{ll} 
Z^\frac{1}{3} a^{-\frac{1}{2}} & a \leq Z^{-\frac{1}{2}}, \\
Z^\frac{5}{3} (aZ^{\frac{1}{2}})^{-\delta} & a \geq Z^{-\frac{1}{2}}.
\end{array} \right.
\]
(ii) Let $\psi_m(x)$ be $\ell$-admissible, equal 1 in $\{x: |x - y_m| \leq a\}$ and supported in $\{x: |x - y_m| \leq 2a\}$. Then for $W = V_m = Z_m |x - y_m|^{-1}$

$$\int |\text{tr}(e^1(x,x,0)) - P^{RTF}(V_m))(1 - \psi_m(x))| dx \leq Z^3 d^{-\frac{1}{2}}$$

where $e^1(.,.,\tau) = \int_{-\infty}^{\tau} e(x,x,\tau') d\tau'$.

**Proof.** Indeed, the contribution of the $\ell$-element of the partition to the remainder is $O(\zeta^3 \ell)$ exactly as in the non-relativistic case. Summation by partition elements results in the right-hand expression.

Next, we need to consider vicinities of the singularities. Then the methods of Chapter 25 of [Ivr] allow us to prove the following:

**Proposition 3.2.** In the framework of Proposition 3.1 let $\phi_m$ be equal 1 in $\{x: |x - y_m| \leq Z_m^{-1}\}$ and supported in $\{x: |x - y_m| \leq 2Z_m^{-1}\}$. Let $|\lambda| \leq C_0 Zd^{-1}$. Then

$$\int (P^{RTF}(W + \lambda) - P^{RTF}(V_m)) \psi_m(x)(1 - \phi_m(x)) dx \leq C \begin{cases} Z^3 d^{-\frac{1}{2}} & d \leq Z^{-\frac{1}{2}}, \\ Z^3 & d \geq Z^{-\frac{1}{2}} \end{cases}$$

where $d \geq cZ^{-1}$ is the minimal distance between nuclei.

**Proof.** Indeed, exactly as in the non-relativistic case, using methods of Sections 12.5 and 25.4 of [Ivr] we estimate the contribution of $\ell$-element to the remainder by $O(\zeta^3 \ell)$ provided $Z^{-1+\delta} \lesssim \ell \lesssim d$ and by $O(\zeta^2 \ell^2 \zeta^2)$ provided $Z^{-1} \lesssim \ell \lesssim Z^{-1+\delta}$. This proves the required remainder estimate. For $d \leq Z^{-1+\delta}$ we use a rescaling.

Summation by partition elements results in the right-hand expression.

**Remark 3.3.** We need to put cut-off $(1 - \phi_m(x))$ because not only integrals of $P^{RTF}(W + \lambda)$ and $P^{RTF}(V_m)$ (of magnitude $\beta^3 Z^4 \ell^{-4}$) and $P^{RTF'}(W + \lambda)$ are diverging at $y_m$, but even integral of their difference is logarithmically diverging.
Now we need to consider $CZ^{-1}$ vicinities of $y_m$ and we will use the following Proposition:

**Proposition 3.4.** In the framework of Proposition 3.1

(i) $H_W \geq -C_0Z^2$.

(ii) Further

\[(3.11) \quad e(x,x,\lambda) \leq CZ^{1-\delta}\ell(x)^{\delta-2} \quad \text{for} \quad |\lambda| \leq c_0Z^2.\]

**Proof.** (a) Assume first that $Z \asymp \beta^{-1}$ (i.e. $Z \geq \epsilon_0\beta^{-1}$); then Statement (i) follows immediately from Lieb-Yau inequality (Theorem A.2): in the operator sense $H \geq \beta^{-1}\sqrt{\Delta} - \beta^{-2} - Zr^{-1} \geq -\beta^{-2}$, $r = |x - y_m|$.

Then $e(x,x,\lambda) \leq C\ell(x)^{-3}\gamma^{-3}$ with the semiclassical parameter $\gamma$, which is $\asymp 1$ for $\ell \lesssim Z^{-1}$, $\lambda \lesssim Z^2$. Then

\[(3.12) \quad e(x,x,\lambda) \leq C\ell(x)^{-3} \quad \text{for} \quad \lambda \leq C_0Z^2, \quad \ell(x) \lesssim Z^{-1}.\]

Unfortunately it falls short for our needs. Let us shift $y_m \mapsto 0$, and scale $x \mapsto Zx$, $\tau \mapsto Z^{-2}\tau$. Then we arrive to operator which modulo $O(1)$ is $\sqrt{\Delta} - Zr^{-1}$. Due to

\[(3.13) \quad \sqrt{\Delta} - \frac{2}{\pi|x|} \geq A_s(\Delta)^s - B_s\]

for any $s \in [0, 1/2)$ and $A_s, B_s > 0$ we can “trade” (due to Sobolev embedding theorem) $\ell^{-1+\delta}$ by 1 in the scaled inequality (3.12) and by $Z^{1-\delta}$ in the original one, thus arriving to (3.11).

(b) Let us consider $Z \leq \epsilon_0\beta^{-1}$. Observe that in the operator sense

\[H \geq (14\beta^{-2}r^{-2} + \beta^{-4})^{1/2} - Zr^{-1} - C\beta^{-2} \geq CZ^{-2};\]

the latter inequality is proven separately for $r \lesssim \beta$ and for $r \gtrsim \beta$.

Moreover, we get $H \geq \epsilon_1 \min(r^{-2}, \beta^{-1}r^{-1})$ for $r \leq \epsilon_1Z^{-1}$ and then we can trade $\ell^{-3}$ to $CZ^3$ arriving even to the stronger version of (3.12): namely,

\[(3.14) \quad e(x,x,\lambda) \leq CZ^3.\]

Actually (3.14) holds as $Z_m\beta \leq 2\pi^{-1} - \sigma$ and could by quantified even for a parameter, rather than constant $\sigma > 0$. $\square$
Then we immediately conclude that

**Corollary 3.5.** *In the framework of Proposition 3.1 for $|\lambda| \leq C_0 Z d^{-1}$*

\[
\text{(3.15)} \quad |\text{Tr}(H_{\tilde{W}+\lambda}\phi_m) - \text{Tr}(H_{\tilde{V}_m}\phi_m)| \leq CZd^{-1}.
\]

Now we can assemble all these results. However before doing this we replace $P^{\text{RTF}}$ by $P^{\text{TF}}$:

**Proposition 3.6.** (i) Estimates (3.8), (3.9) and (3.10) hold with $P^{\text{RTF}}$ replaced by $P^{\text{TF}}$.

(ii) Estimate (3.10) with $P^{\text{RTF}}$ replaced by $P^{\text{TF}}$ also holds with $\phi_m = 0$.

**Proof.** Statement (i) follows immediately from

\[
\text{(3.16)}_{1.2} \quad P^{\text{RTF}}(w) - P^{\text{TF}}(w) \asymp \beta^2 w^{\frac{7}{2}}, \quad P^{\text{RTF}}(w) - P^{\text{TF}}(w) \asymp \beta^2 w^{\frac{5}{2}}
\]

for $\beta^2 w \lesssim 1$ due to (3.5). Statement (ii) follows immediately from $P^{\text{TF}}(w) \asymp w^3$, $P^{\text{TF}}(w) \asymp w^2$. \hfill \Box

**Remark 3.7.** Meanwhile,

\[
\text{(3.17)} \quad \int (P^{\text{RTF}}(V + \lambda) - P^{\text{TF}}(V + \lambda)) \psi(x) \, dx \asymp \beta^2 Z^4
\]

which could be as large as $Z^2$.

Due to the scaling properties of $e(x, x, 0)$ for $H = H_V$ and $P^{\text{TF}}(V)$ for $V = V_m$ we conclude that

\[
\text{(3.18)} \quad \int (\text{tr}(e^1(x, x, 0)) - P^{\text{RTF}}(V_m)) \, dx = qZ_m^2 S(Z_m \beta)
\]

with unknown function $S(Z_m \beta)$. Indeed, if $y_m = 0$ then $x \mapsto x/k$ transforms operator with parameters $Z_m, \beta$ into operator with parameters $Z_m k, \beta k^{-1}$ multiplied by $k^{-2}$.

**Remark 3.8.** Obviously, $S(Z_m \beta)$ monotone decreases as $\beta \to 0^+$ and tends to $S(0)$ for the Schrödinger operator.
Then due to (3.9) for $V = V_m$

\[(3.19) \quad | \int \left( \text{tr} (e^1(x, x, 0)) - P_{TF}(V_m) \right) \psi_m(x) \; dx - qZ_m^2 \Sigma(Z_m \beta) | \leq Z^{\frac{3}{2}} d^{-\frac{1}{2}} \]

and we arrive to

**Proposition 3.9.** Let (1.9) be fulfilled. Then for $W = W_{TF}$

\[(3.20) \quad | \text{Tr}(H_{W+\lambda}) + \int P_{TF}(W + \lambda) \; dx - \sum_{1 \leq m \leq M} qZ_m^2 \Sigma(Z_m \beta) | \leq C \begin{cases} \frac{Z^{\frac{3}{2}} d^{-\frac{1}{2}}}{d \leq Z^{-\frac{1}{2}}}, \\ \frac{Z^{\frac{3}{2}}}{d \geq Z^{-\frac{1}{2}}}. \end{cases} \]

### 3.2 Trace term. II

Let improve the above results for $d \gg Z^{-\frac{1}{2}}$. Observe first that the in this case the error in (3.8) can be made $O(Z^{\frac{3}{2}}(dZ^{\frac{1}{2}})^{-\delta} + Z^{\frac{3}{2}}\delta)$ provided we include the relativistic Schwinger correction term. Since this term has a magnitude $Z^{\frac{3}{2}}$ and the contributions of the zones \{\(x: \ell(x) \leq Z^{-\frac{1}{2}+\delta}\}\} and \{\(x: \ell(x) \geq Z^{-\frac{1}{2}+\delta}\}\} in this term are $O(Z^{\frac{3}{2}}\delta)$, the difference between relativistic and the standard non-relativistic Schwinger terms is $O(Z^{\frac{3}{2}-\delta})$ and we can use the latter

\[(3.21) \quad \text{Schwinger} = (36\pi)^{\frac{3}{2}} q^{\frac{3}{2}} \int (\rho_{TF})^{\frac{3}{2}} \; dx. \]

Next, consider relativistic correction term

\[(3.22) \quad \int (-P_{RTF}(W + \lambda) + P_{RTF}(V_m) + P_{TF}(W + \lambda) - P_{TF}(V_m)) \psi_m(1 - \phi_m) \; dx. \]

Again, one can see easily that the contributions of these two zones \{\(x: \ell(x) \leq Z^{-\frac{1}{2}+\delta}\}\} and \{\(x: \ell(x) \geq Z^{-\frac{1}{2}+\delta}\}\} in this term are $O(Z^{\frac{3}{2}-\delta})$, so we need to consider the contribution of the zone \{\(x: Z^{-\frac{1}{2}+\delta} \leq \ell(x) \leq Z^{-\frac{1}{2}+\delta}\}\}, where due to (3.5) $P_{RTF}(w) - P_{TF}(w) = \frac{q}{14\pi^2 \beta} w^2 + O(Z^{\frac{3}{2}-\delta})$ (for both $w = W_{TF} + \lambda$ and $w = V_m$) and therefore modulo the same error expression (3.22) coincides with

\[(3.23) \quad \text{RCT} := \frac{q}{14\pi^2 \beta^2} \int (- (W_{TF} + \lambda)^{\frac{7}{2}} + V_{\frac{3}{2}}) \; dx. \]
with the integral taken over this zone or $\mathbb{R}^3$ (does not matter). Then we arrive to

**Proposition 3.10.** Let (1.9) be fulfilled and $d \geq Z^{-\frac{1}{2}}$. Then for $W = W^{TF}$

$$
(3.24) \quad |\text{Tr}(H_{W+\lambda}) + \int P^{TF}(W + \lambda) \, dx - \sum_{1 \leq m \leq M} qZ_m^2 S(Z_m^\beta) - \text{Schwinger} - \text{RCT}| \leq C(Z^\frac{5}{2}(dZ) - Z^\frac{5}{2} - \delta).
$$

### 3.3 Trace term. III

Obviously, all these results hold for $W = W_\varepsilon$ defined by (2.14) with $\rho = \rho^{TF}$. However we need to estimate an error when we replace $W_\varepsilon$ by $W^{TF}$. One can prove easily that

$$
(3.25) \quad |W_\varepsilon - W^{TF}| \leq C_s(Z\varepsilon^{-1})^\frac{3}{2} \varepsilon^2 (\varepsilon \ell - 1)^s
$$

with arbitrary $s$ for $\ell \leq \varepsilon_0 Z^{-\frac{1}{2}}$ and with $s = \frac{1}{2} \ell \leq \varepsilon_0 Z^{-\frac{1}{2}}$ and therefore

$$
(3.26) \quad |\int (P^{TF}(W_\varepsilon + \lambda) - P^{TF}(W^{TF} + \lambda)) \, dx| \leq CZ^\frac{5}{2} \varepsilon^2;
$$

adding error $CZ^\varepsilon^{-1}$ in (2.15) we get $C(Z^3 \varepsilon^2 + Z^\varepsilon^{-1})$. It reaches minimum $CZ^\frac{5}{2}$ as $\varepsilon \approx Z^{-\frac{1}{2}}$ and we arrive to

**Proposition 3.11.** Let (1.9) be fulfilled. Then for $W = W_\varepsilon$ with $\varepsilon = Z^{-\frac{1}{2}}$ (3.20) holds and the left-hand expression of (3.26) is $O(Z^\frac{5}{2})$.

### 3.4 N- and D-terms

For these terms (needed for the estimate from above) arguments are simpler; let $\phi_0 = 1 - \phi_1 - \ldots - \phi_M$.

**Proposition 3.12.** In the framework of Proposition 3.1

(i) The following estimates hold

$$
(3.27) \quad |\int (e(x, x, \lambda) - P^{RTF}(W + \lambda)) \phi_0(x) \, dx| \leq CZ^\frac{5}{2}
$$
and for $d \geq Z^{-\frac{1}{2}}$

(3.28) $|\int (e(x, x, \lambda) - P^{RTF}(W + \lambda))\phi_0(x) \, dx| \leq C(Z^{\frac{5}{2}}(dZ^{\frac{1}{2}})^{-\delta} + Z^{\frac{3}{2} - \delta})$.

(ii) Further,

(3.29) $|\int e(x, x)\phi_m(x) \, dx| \leq C$.

(iii) Finally,

(3.30) $|\int (P^{RTF}(W + \lambda) - P^{TF'}(W + \lambda))\phi_0(x) \, dx| \leq CZ^\frac{5}{2}$.

**Proposition 3.13.** In the framework of Proposition 3.1

(i) The following estimates hold

(3.31) $D((e(x, x, \lambda) - P^{RTF}(W + \lambda))\phi_0, (e(x, x, \lambda) - P^{RTF}(W + \lambda))\phi_0) \leq CZ^\frac{5}{2}$

and for $d \geq Z^{-\frac{1}{2}}$

(3.32) $D((e(x, x, \lambda) - P^{RTF}(W + \lambda))\phi_0, (e(x, x, \lambda) - P^{RTF}(W + \lambda))\phi_0) \leq CZ^\frac{5}{2}(dZ^{\frac{1}{2}})^{-\delta} + CZ^{\frac{3}{2} - \delta}$.

(ii) Further,

(3.33) $D(e(x, x, \lambda)\phi_m(x) e(x, x, \lambda)\phi_m(x)) \leq CZ$.

(iii) Finally,

(3.34) $D((P^{RTF}(W + \lambda) - P^{TF}(W + \lambda))\phi_0, (P^{RTF}(W + \lambda) - P^{TF'}(W + \lambda))\phi_0) \leq CZ$.

**Proof of Propositions 3.12 and 3.13.** Proof is straightforward:

Statements (i) are proven by the semiclassical scaling technique exactly as in [Ivr], Chapter 25.

Statements (ii) follow from Proposition 3.4. Statements (iii) follow from (3.5) and properties $W^{TF}$.
3.5 Dirac term

Finally, consider $-\frac{1}{2} \iint \text{tr}(e_N^\dagger(x,y)e_N(x,y)) \, dxdy$. The main contribution to it is delivered by the zone $\mathcal{Y} \times \mathcal{Y}$ with $\mathcal{Y} = \{ x : Z^{-\frac{1}{3}} - \delta \leq \ell(x) \leq Z^{-\frac{1}{3}} + \delta \}$ and in this zone non-magnetic approximation delivers correct the expression

$$\text{(3.35)} \quad \text{Dirac} = -\frac{9}{2}(36\pi)^{\frac{3}{2}} q^{\frac{3}{2}} \int (\rho^{\text{TF}})^{\frac{3}{2}} \, dx,$$

with an error $Z^{\frac{3}{2} - \delta}$.

4 Main theorems

Now repeating arguments of Section 25.4 of [Ivr] we arrive to our main results:

**Theorem 4.1** 3). Let assumption (1.9) be fulfilled. Then

(i) The following asymptotic holds

$$\text{(4.1)} \quad E_N = E_N^{\text{TF}} + \text{Scott} + O(Z^{\frac{5}{2}} + Z^{\frac{3}{2}} d^{-\frac{1}{2}}).$$

Recall that $\text{Scott} = q \sum Z_m^2 S(Z_m \beta)$ and $d$ is the minimal distance between nuclei.

(ii) Furthermore, let assumption (1.10) be fulfilled. Then for $d \geq Z^{-\frac{1}{3}}$

$$\text{(4.2)} \quad E_N = E_N^{\text{TF}} + \text{Scott} + \text{Dirac} + \text{Swinger} + \text{RCT} +
\quad O(Z^{\frac{5}{2}} (dZ^{\frac{1}{2}})^{-\delta} + Z^{\frac{5}{3} - \delta}).$$

**Remark 4.2.** (i) For the improved upper estimate in (4.2) we do not need assumption (1.10).

(ii) These theorems allow us to consider the free nuclei model and recover Theorem 25.4.14 of [Ivr], albeit without assumption (1.10) we get only $\delta = 0$.

3) Cf. Theorems 25.4.8 and 25.4.13 of [Ivr].
We also recover estimate

\[
\lambda_N - \nu = C \begin{cases} 
Z^\frac{d}{2} & (Z - N) \leq Z^\frac{\delta}{2}, \\
-Z^\frac{1}{2} & (Z - N) \geq Z^\frac{\delta}{2},
\end{cases}
\]

where \( \nu \) is a chemical potential and \( \lambda_N \) is the \( N \)-th lowest eigenvalue of \( H_{\text{WTF}} \) (reset to 0 if there are less than \( N \) negative eigenvalues). Furthermore, for \( d \geq Z^{-\frac{\delta}{2}} \) one can include the factor \( ((dZ^\frac{1}{2})^{-\delta} + Z^{-\delta}) \) into the right-hand expression.

**Theorem 4.3** \(^4\). Let assumption (1.10) be fulfilled. Then

(i) The following estimate holds:

\[
D(\rho_\Psi - \rho_{\text{TF}}, \rho_\Psi - \rho_{\text{TF}}) \leq CZ^\frac{\delta}{2}.
\]

(ii) Furthermore, for \( d \geq Z^{-\frac{\delta}{2}} \)

\[
D(\rho_\Psi - \rho_{\text{TF}}, \rho_\Psi - \rho_{\text{TF}}) \leq C(Z^\frac{1}{2}dZ^\frac{1}{2})^{-\delta} + Z^\frac{\delta}{2} - \delta).
\]

**Remark 4.4.** (i) Estimates (4.4) and (4.5) allow us to consider the excessive negative charge and ionization energy and, repeating arguments of Section 25.5 of [Ivr], to recover Theorems 25.5.2 and 25.5.3.

(ii) Further, these estimates allow us to consider the excessive positive charge in the free nuclei model and, repeating arguments of Section 25.6 of [Ivr], to recover 25.6.4.

**Remark 4.5.** We can even make a poor man version of (4.2) in the critical case, when only assumption (1.9) is fulfilled.

(i) Consider how our terms depend on \( q \). In the atomic case consider given \( Z, N \) and shift to \( y_1 = 0 \). Then

\[
\rho_{q}^{\text{TF}}(x) = q^2 \rho_1^{\text{TF}}(q^2x), \quad W_{q}^{TF}(x) = q^2 W_{1}^{TF}(q^2x)
\]

and \( E_{\text{TF}} \simeq q^2Z^\frac{3}{2} \), \( \text{Scott} \simeq qZ^2 \), \( \text{Dirac} \simeq \text{Schwinger} \simeq q^4Z^\frac{5}{4} \), while \( \text{RCT} \simeq q^2 \beta^2 Z^\frac{11}{4} \).

\(^4\) Cf. Theorem 25.4.15 of [Ivr].
(ii) Repeating corresponding arguments of [SSS], one can prove that in the correlation inequality (2.13) the constant is \( C(q) \leq C_0 q^{3/2} \). On the other hand, we use the estimate for \( |W - W_\varepsilon| \approx q e^{2Z_2^{-1} \varepsilon^{-1}} \) and then approximation error is \( C_0 Z^3 q^2 \varepsilon^{-2} \). Optimizing \( Z^3 q^2 \varepsilon^{-2} + Z q^2 \varepsilon^{-1} \) by \( \varepsilon \) we get \( C q^{1/2} Z \) and for large constant \( q \) it is less than \( q^{3/4} \). In the “real life” \( q = 2 \).

A Appendix: Some inequalities

We follow [SSS] with some modifications:

The following two inequalities we recall are crucial in many of our estimates. They serve as replacements for the Lieb-Thirring inequality [LT] used in the non-relativistic case.

**Theorem A.1 (Daubechies inequality).** *(i) One-body case:*

\[
\text{Tr} \left[ (\beta^2 \Delta + \beta^{-4})^{1/2} - \beta^{-2} - V(x) \right] \geq -C \int \left( V_+^{(n+2)/2} + \beta^n V_+^{n+1} \right) dx.
\]

where \( n \geq 3 \) is a dimension.

**(ii) Many-body case:** Let \( \Psi \in \bigwedge_{j=1}^N \mathcal{L}^2(\mathbb{R}^3; \mathbb{C}^q) \) and let \( \rho_\Psi \) be its one-particle density. Then for \( n = 3 \)

\[
\sum_{j=1}^N [(\beta^2 \Delta_j + \beta^{-4})^{1/2} - \beta^{-2}] \geq \int \min(\rho_\Psi^{1/3}, \beta^{-1} \rho_\Psi^{2/3}) dx.
\]

This theorem also holds in the non-relativistic limit \( \beta = 0 \) and operator \( (\beta^2 \Delta + \beta^{-4})^{1/2} - \beta^{-2} \) replaced by \( \frac{1}{2} \Delta \).

**Theorem A.2 (Lieb-Yau inequality).** Let \( n = 3 \). Let \( C > 0 \) and \( R > 0 \) and let

\[
H_{C,R} = \Delta^{1/2} - \frac{2}{\pi |x|} - C/R.
\]

Then, for any density matrix \( \gamma \) and any function \( \theta \) with support in \( B_R = \{x \mid |x| \leq R\} \)

\[
\text{Tr} [\bar{\theta} \gamma H_{C,R}] \geq -4.4827 C^4 R^{-1} \{3/(4\pi R^3) \int |\theta(x)|^2 dx\}.
\]
Note that when $\theta = 1$ on $B_R$ then the term inside the brackets $\{\}$ equals $1$.

**Theorem A.3 (Critical Hydrogen inequality).** Let $n = 3$. For any $s \in [0, 1/2)$ there exists constants $A_s, B_s > 0$ such that

\[(A.5) \quad \Delta^{\frac{1}{2}} - \frac{2}{\pi |x|} \geq A_s \Delta^s - B_s.\]

**Theorem A.4 (Hardy-Littlewood-Sobolev inequality).** There exists a constant $C$ such that

\[(A.6) \quad D(f) := \int_\mathbb{R} \int_\mathbb{R} |x - y|^{-1} f(x)f^\dagger(y) \, dx \, dy \leq C \|f\|_{L^{5/3}}^{\frac{2}{5}}.\]

**Bibliography**

[Bach] V. Bach. *Error bound for the Hartree-Fock energy of atoms and molecules.* Commun. Math. Phys. 147:527–548 (1992).

[Dau] I. Daubechies. *An uncertainty principle for fermions with generalized kinetic energy.* Commun. Math. Phys. 90(4):511–520 (1983).

[EFS1] L. Erdős, S. Fournais, J. P. Solovej. *Scott correction for large atoms and molecules in a self-generated magnetic field.* Commun. Math. Physics, 312(3):847–882 (2012).

[EFS2] L. Erdős, S. Fournais, J. P. Solovej. *Relativistic Scott correction in self-generated magnetic fields.* Journal of Mathematical Physics 53, 095202 (2012), 27pp.

[FLS] R. L. Frank, E. H. Lieb, R. Seiringer. *Hardy-Lieb-Thirring inequalities for fractional Schrödinger operators.* J. Amer. Math. Soc. 21(4), 925-950 (2008).

[FSW] R. L. Frank, H. Siedentop, S. Warzel. *The ground state energy of heavy atoms: relativistic lowering of the leading energy correction.* Comm. Math. Phys. 278(2):549-566 (2008).
[GS] G. M. Graf, J. P Solovej. A correlation estimate with applications to quantum systems with Coulomb interactions Rev. Math. Phys., 6(5a):977–997 (1994). Reprinted in The state of matter a volume dedicated to E. H. Lieb, Advanced series in mathematical physics, 20, M. Aizenman and H. Araki (Eds.), 142–166, World Scientific (1994). 6

[IH] I. W. Herbst. Spectral Theory of the operator \((p^2 + m^2)^{1/2} - Ze^2/r\), Commun. Math. Phys. 53(3):285–294 (1977). 2

[Ivr] V. Ivrii. Microlocal Analysis, Sharp Spectral Asymptotics and Applications. http://www.math.toronto.edu/ivrii/monsterbook.pdf 3, 8, 9, 14, 15, 16

[LT] E. H. Lieb, W. E. Thirring, Inequalities for the moments of the eigenvalues of the Schrödinger Hamiltonian and their relation to Sobolev inequalities, in Studies in Mathematical Physics (E. H. Lieb, B. Simon, and A. S. Wightman, eds.), Princeton Univ. Press, Princeton, New Jersey, 1976, pp. 269–303. 17

[LY] E. H. Lieb, H. T. Yau. The Stability and instability of relativistic matter. Commun. Math. Phys. 118(2): 177–213 (1988). 2

[SSS] J. P. Solovej, T. Ø. Sørensen, W. L. Spitzer. The relativistic Scott correction for atoms and molecules. Comm. Pure Appl. Math., 63:39–118 (2010). 1, 3, 6, 17