Asymptotics of the ground state energy of heavy molecules and related topics. II

Victor Ivrii

May 3, 2014

Abstract

We consider asymptotics of the ground state energy of heavy atoms and molecules in the strong external magnetic field and derive it including Schwinger and Dirac corrections (if magnetic field is not too strong). We also consider related topics: an excessive negative charge, ionization energy and excessive positive charge when atoms can still bind into molecules.

Contents

Contents

0 Introduction 3
  0.1 Framework 3
  0.2 Problems to consider 4
  0.3 Magnetic Thomas-Fermi theory 5
  0.4 Main results sketched and plan of the chapter 7

1 Magnetic Thomas-Fermi theory 8
  1.1 Framework and existence 8
  1.2 Properties 11
  1.3 Positive ions 16
2 Applying semiclassical methods: $M = 1$
  2.1 Heuristics .............................................. 20
  2.2 Smooth approximation ................................. 27
  2.3 Rough approximation ................................. 33

3 Applying semiclassical methods: $M \geq 2$
  3.1 Scaling functions in zone $\mathcal{X}_2$ ................ 47
  3.2 Zone $\mathcal{X}_2$: Semiclassical N-term ............... 51
  3.3 Zone $\mathcal{X}_2$: Semiclassical D-term ............... 56
  3.4 Semiclassical T-term ............................... 59
  3.5 Zone $\mathcal{X}_3$ ....................................... 64

4 Semiclassical analysis in the boundary strip as $M \geq 2$
  4.1 Properties of $W_{\mathcal{B}}^{\mathcal{Y}}$ as $N = Z$ ........... 65
  4.2 Analysis in the boundary strip $\mathcal{Y}$ for $N \geq Z$ .... 69
  4.3 Analysis in the boundary strip $\mathcal{Y}$ for $N < Z$ ....... 73
  4.4 Summary ................................................. 78

5 Ground state energy ..................................... 80
  5.1 Lower estimates ....................................... 80
  5.2 Upper estimate: general scheme ....................... 81
  5.3 Upper estimate as $M = 1$ ............................ 82
  5.4 Upper estimate as $M \geq 2$ ......................... 85

6 Negatively charged systems ................................... 95
  6.1 Estimates of the correlation function ................. 96
  6.2 Excessive negative charge .......................... 97
  6.3 Estimate for ionization energy ....................... 102

7 Positively charged systems .................................. 107
  7.1 Upper estimate for ionization energy: $M = 1$ .......... 108
  7.2 Lower estimate for ionization energy: $M = 1$ .......... 112
  7.3 Estimates for ionization energy: $M \geq 2$ ............ 121
  7.4 Free nuclei model ..................................... 122

8 Appendices ................................................ 128
  8.A Electrostatic inequalities ............................ 128
  8.B Very strong magnetic field case ....................... 134
  8.C Riemann sums and integrals .......................... 135
0 Introduction

In this Chapter we repeat analysis of the previous Chapter 24 but in the case of the constant external magnetic field\(^1\).

0.1 Framework

Let us consider the following operator (quantum Hamiltonian)

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

on

\[
\mathcal{S}_N = \bigwedge_{1 \leq n \leq N} \mathcal{H}, \quad \mathcal{H} = L^2(\mathbb{R}^d, \mathbb{C}^q)
\]

with

\[
H_{V, A} = \left( (i \nabla - A) \cdot \sigma \right)^2 - V(x)
\]

describing \(N\) same type particles in the external field with the scalar potential \(-V\) and vector potential \(A(x)\), and repulsing one another according to the Coulomb law.

Here \(x_j \in \mathbb{R}^d\) and \((x_1, ..., x_N) \in \mathbb{R}^{dN}\), potentials \(V(x)\) and \(A(x)\) are assumed to be real-valued. Except when specifically mentioned we assume that

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

where \(Z_m > 0\) and \(y_m\) are charges and locations of nuclei. Here \(\sigma = (\sigma_1, \sigma_2, ..., \sigma_d)\), \(\sigma_k\) are \(q \times q\)-Pauli matrices.

\(^1\) Actually we need a magnetic field either sufficiently weak or close to a constant on the very small scale.
So far in comparison with the previous Chapter 24 we only changed (24.1.3) to (0.1.3) introducing magnetic field. Now spin enters not only in the definition of the space but also into operator through matrices $\sigma_k$. Since we need $d = 3$ Pauli matrices it is sufficient to consider $q = 2$ but we will consider more general case as well (but $q$ should be even).

**Remark 0.1.1.** In the case of the the constant magnetic field $\nabla \times A$

\begin{equation}
H_{A,V} = (-i\nabla - A(x))^2 + \sigma \cdot (\nabla \times A) - V(x)
\end{equation}

In the case $d = 2$ this operator downgrades to

\begin{equation}
H_{A,V} = (-i\nabla - A(x))^2 + \sigma_3(\nabla \times A) - V(x)
\end{equation}

Again, let us assume that

\begin{equation}
\text{Operator } \mathcal{H} \text{ is self-adjoint on } \mathcal{H}.
\end{equation}

As usual we will never discuss this assumption.

## 0.2 Problems to consider

As in the previous Chapter we are interested in the *ground state energy* $E = E_N$ of our system i.e. in the lowest eigenvalue of the operator $H = H_N$ on $\mathcal{H}$:

\begin{equation}
E := \inf \operatorname{Spec} H \quad \text{on } \mathcal{H};
\end{equation}

more precisely we are interested in the asymptotics of $E_N = E(y; Z; N)$ as $V$ is defined by (0.1.4) and $N \asymp Z := Z_1 + Z_2 + \ldots + Z_M \to \infty$ and we are going to prove that\(^2\) $E$ is equal to *Magnetic Thomas-Fermi energy* $E_{TF}^B$, possibly with the Scott and Dirac-Schwinger corrections and with an appropriate error.

We are also interested in the asymptotics for the *ionization energy*

\begin{equation}
I_N := E_{N-1} - E_N
\end{equation}

---

\(^2\) Under reasonable assumption to the minimal distance between nuclei.
and we also would like to estimate maximal excessive negative charge

\[
\max_{N: l_N > 0} (N - Z).
\]

All these questions so far were considered in the framework of the fixed positions \(y_1, ..., y_M\) but we can also consider

\[
\hat{E} := \hat{E}_N = \hat{E}(y; Z; N) = E + U(y; Z)
\]

with

\[
U(y; Z) := \sum_{1 \leq m < m' \leq M} \frac{Z_{m}Z_{m'}}{|y_{m} - y_{m'}|}
\]

and

\[
\hat{E}(Z; N) = \inf_{y_1, ..., y_M} \hat{E}(y; Z; N)
\]

and replace \(l_N\) by \(\hat{l}_N = \hat{E}_{N-1} - \hat{E}_N\) and modify all our questions accordingly. We call these frameworks fixed nuclei model and free nuclei model respectively.

In the free nuclei model we can consider two other problems:

- Estimate from below minimal distance between nuclei i.e.

\[
\min_{1 \leq m < m' \leq M} |y_{m} - y_{m'}|
\]

for which such minimum is achieved;

- Estimate maximal excessive positive charge

\[
\max_{N} \{ (Z - N) : \hat{E} < \min_{N_1, ..., N_M: N_1 + ... + N_M = N} \sum_{1 \leq m \leq M} E(Z_m; N_m) \}
\]

for which molecule does not disintegrates into atoms.

### 0.3 Magnetic Thomas-Fermi theory

As in the previous Chapter the first approximation is the Hartree-Fock (or Thomas-Fermi) theory. Let us introduce the spacial density of the particle with the state \(\Psi \in \mathcal{F}\):

\[
\rho(x) = \rho_{\Psi}(x) = N \int |\Psi(x, x_2, ..., x_N)|^2 \, dx_2 \cdots dx_N.
\]
Let us write the Hamiltonian, describing the corresponding "quantum liquid":

\[ \mathcal{E}_B(\rho) = \int \tau_B(\rho(x)) \, dx - \int V(x)\rho(x) \, dx + \frac{1}{2} D(\rho, \rho), \]

with

\[ D(\rho, \rho) = \int \int |x - y|^{-1} \rho(x)\rho(y) \, dxdy \]

where \( \tau_B \) is the energy density of a gas of noninteracting electrons:

\[ \tau_B(\rho) = \sup_{w \geq 0} (\rho w - P_B(w)) \]

is the Legendre transform of the pressure \( P_B(w) \) given by the formula

\[ P_B(w) = \kappa_1 B \left( \frac{1}{2} w_\frac{d}{2} + \sum_{j \geq 1} (w - 2jB)_\frac{d}{2} \right) \]

with \( \kappa_1 = (2\pi)^{-1} q, (3\pi^2)^{-1} q \) for \( d = 2, 3 \) respectively.

The classical sense of the second and the third terms in the right-hand expression of (0.3.2) is clear and the density of the kinetic energy is given by \( \tau_B(\rho) \) in the semiclassical approximation (see remark 0.3.1). So, the problem is

(0.3.6) Minimize functional \( \mathcal{E}_B(\rho) \) defined by (0.3.2) under restrictions:

(0.3.7) \[ \rho \geq 0, \quad \int \rho \, dx \leq N. \]

The solution if exists is unique because functional \( \mathcal{E}_B(\rho) \) is strictly convex (see below). The existence and the property of this solution denoted further by \( \rho_{B}^{\text{TF}} \) is known in the series of physically important cases.

Remark 0.3.1. If \( w \) is the negative potential then

(0.3.8) \[ \text{tr} \, e(x, x, 0) \approx P'_B(w) \]

defines the density of all non-interacting particles with negative energies at point \( x \) and

(0.3.9) \[ \int_{-\infty}^{0} \tau \, d\tau \, \text{tr} \, e(x, x, \tau) \, dx \approx -\int P_B(w) \, dx \]

is the total energy of these particles; here \( \approx \) means “in the semiclassical approximation”.
We consider in the case of \( d = 3 \) a large (heavy) molecule with potential (24.1.4). It is well-known\(^3\) that

**Proposition 0.3.2.** (i) For \( V(x) \) given by (0.1.4) minimization problem (0.3.6) has a unique solution \( \rho = \rho_{B}^{\text{TF}} \); then denote \( \mathcal{E}_{B}^{\text{TF}} := \mathcal{E}_{B}(\rho_{B}^{\text{TF}}) \);

(ii) Equality in (0.3.7) holds if and only if \( N \leq Z := \sum_{m} Z_{m} \);

(iii) Further, \( \rho_{B}^{\text{TF}} \) does not depend on \( N \) as \( N \geq Z \);

(iv) Thus

\[
\int \rho_{B}^{\text{TF}} \, dx = \min(N, Z), \quad Z := \sum_{1 \leq m \leq M} Z_{m}.
\]

### 0.4 Main results sketched and plan of the chapter

In the first half of this Chapter we derive asymptotics for ground state energy and justify Thomas-Fermi theory. As construction of Section 24.2 works with minimal modifications (see Section 5) in the magnetic case as well we start immediately from magnetic Thomas-Fermi theory in Section 1.

We discover that there are three different cases: a *moderate magnetic field* case \( B \ll Z^{\frac{1}{4}} \) when \( \mathcal{E}_{B}^{\text{TF}} \simeq Z^{\frac{1}{2}} \) and \( \mathcal{E}_{B}^{\text{TF}} = \mathcal{E}_{B}^{\text{TF}}(1 + o(1)) \), a *strong magnetic field* case \( B \gg Z^{\frac{1}{4}} \) when \( \mathcal{E}_{B}^{\text{TF}} \simeq B^{\frac{1}{2}} Z^{\frac{1}{2}} \) and \( \mathcal{E}_{B}^{\text{TF}} = \mathcal{E}_{B}^{\text{TF}}(1 + o(1)) \) where \( \mathcal{E}_{B}^{\text{TF}} \) is Thomas-Fermi potential derived as \( P_{B}(w) = \frac{1}{2} \kappa_{1} w^{\frac{4}{3}} \) (cf. (0.3.5)), and an *intermediate case* \( B \sim Z^{\frac{1}{4}} \).

Then we apply semiclassical methods (like in Section 24.4) albeit now analysis is way more complicated due to two factors: the semiclassical theory of magnetic Schrödinger operator is more difficult than the corresponding theory for non-magnetic Schrödinger operator and also Thomas-Fermi potential \( W^{\text{TF}} \) is not very smooth in the magnetic case, so we need to approximate it by a smooth one (on a microscale).

We discover that both semiclassical methods and Thomas-fermi theory are relevant only as \( B \ll Z^{3} \). Case of the superstrong magnetic field \( B \gg Z^{3} \) was considered in E. H. Lieb, J. P. Solovej and J. Yngvarsson [LSY1] and we hope to cover it in the Chapter 27\(^1\).

\(^{1}\) Pending

\(^{3}\) Section IV of E. H. Lieb, J. P. Solovej and J. Yngvarsson [LSY2].
First of all, in Section 2 we consider the case $M = 1$; then Thomas-Fermi potential $W_B^{TF}$ is non-degenerate and in this case we derive sharp spectral asymptotics.

Next, in Section 3 we consider the case $M \geq 2$ but we analyze only zone $\{W_B^{TF} + \nu \gtrsim B\}$ where $\nu$ is a chemical potential and $B$ is an intensity of the magnetic field. A certain weaker non-degeneracy condition is satisfied due to Thomas-Fermi equation and we derive almost sharp spectral asymptotics.

Furthermore, in Section 4 analyze the boundary strip $\{W^{TF} + \nu \lesssim B\}$ containing the boundary of $\text{supp} \rho_B^{TF}$; this is the most difficult case to analyze and our remainder estimates are not sharp unless $N \geq Z - CZ^2$.

Finally, in Section 5 we derive asymptotics of the ground state energy. Their precision (or lack of it) follows from the precision of the corresponding semiclassical results; so our results in the case $M = 1$ are sharp, but results in the case $M \geq 2$ (especially if $N \leq Z - CZ^2$) are not.

In the second half of this Chapter we consider related problems. In Section 6 (cf. Section 24.5) we consider negatively charged systems ($N \geq Z$) and estimate both ionization energy $I_N$ and excessive negative charge $(N - Z)_+$.

In Section 7 (cf. Section 24.6) we consider positively charged systems ($N \leq Z$) and estimate the remainder $|I_N + \nu|$ in the formula $I_N \approx -\nu$; as $M \geq 2$ we also consider a free nuclei model and estimate from below the distance between nuclei and an excessive positive charge $(Z - N)_+$ when atoms can be bound into molecule.

Appendices contain some auxiliary material, most notably, electrostatic inequalities in Appendix 8.A and also Zhislin’s theorem (that system can bind at least $Z$ electrons) in Appendix 8.D—all in the case of magnetic field.

## 1 Magnetic Thomas-Fermi theory

### 1.1 Framework and existence

The Thomas-Fermi theory is well developed in the magnetic case as well albeit in the lesser degree than in the non-magnetic one. The most important source now is Section IV of E. H. Lieb, J. P. Solovej and J. Yngvarsson [LSY2].

---

4) In (magnetic) Thomas-Fermi theory both answers are 0.
Again as in the previous Chapter 24 to get the best lower estimate for the ground state energy (neglecting semiclassical errors) one needs to maximize functional $\Phi_{B,*}(W + \nu)$ defined by (24.3.1) albeit with the pressure $P_B(w)$ given for $d = 2, 3$ by (0.3.5). Formulae (24.3.2) and (24.3.3) also remain valid.

Further, to get the best upper estimate (neglecting semiclassical errors) one needs to minimize functional $\Phi_{B,*}^\ast(W, \nu)$ defined by (24.3.4) where (24.3.4) remains valid with $P$ replaced by $P_B$ and respectively $\tau(\rho')$ replaced by $\tau_B(\rho')$ which is Legendre transformation of $P_B$ (see (0.3.4)).

Since $P_B$ is given by much more complicated expression (0.3.5) rather than (24.3.6), and respectively

\[(1.1.1) \quad P_B'(w) = \frac{d}{2} \kappa_1 B \left( \frac{1}{2} w_+^{d-1} + \sum_{j \geq 1} (w - 2jB)_+^{d-1} \right) \]

(cf. (24.3.6)$_2$), there is no explicit expression for $\tau_B$ similar to (24.3.7).

**Remark 1.1.1.** (i) $B(x) = |\nabla \times A(x)|$;

(ii) From now on we will assume that $d = 3$;

(iii) $P_B$ is a strictly convex function and therefore $\tau_B$ is also a strictly convex function$^5$;

(iv) $P_B(w) \to P_0(w)$, $P_B'(w) \to P_0'(w)$ and $\tau_B(\rho) \to \tau_0(\rho)$ as $B \to 0$ where (without subscript ‘0’) the limit functions have been defined by (24.3.6)$_{1,2}$ and (24.3.7) respectively.

**Remark 1.1.2.** (i) Alternatively we minimize $\mathcal{E}_B(\rho) = \Phi_B^*(\rho, 0)$ under assumptions

\[(1.1.2)_{1,2} \quad \rho \geq 0, \quad \int \rho dx \leq N; \]

(ii) So far in comparison with the previous Chapter 24 we changed only definition of $P_B(w)$ and $\tau_B(\rho)$ respectively. Note that $P_B(w)$ belongs to $C^{\frac{d}{2}+1}$ (as $d = 2, 3$) as function of $w$; this statement will be quantified later;

$^5$ As $d = 2$, $P_B$ is a convex and piecewise linear function and therefore $\tau_B$ is also a convex function.
(iii) While not affecting existence (with equality in (1.1.2), if \( N \leq Z \)) and uniqueness of solution, it affects other properties, especially as \( B \geq Z^{\frac{2}{3}} \).

**Proposition 1.1.3.** In our assumptions for any fixed \( \nu \leq 0 \) statements (i)–(vii) of proposition 24.3.1 hold.

**Proof.** The proof is the same as of proposition 24.3.1. The proof that threshold \( \nu = 0 \) matches to \( N = Z \) are theorems 4.9 and 4.10 of Section IV of E. H. Lieb, J. P. Solovej and J. Yngvarsson [LSY2]. \( \square \)

Note that (24.3.8)–(24.3.9) and (24.3.10) become

\[
\begin{align*}
\rho &= \frac{1}{4\pi} \Delta (W - V) = P_B'(W + \nu), \\
W &= \mathcal{O}(1) \quad \text{as} \quad |x| \to \infty
\end{align*}
\]

and

\[
\mathcal{N}(\nu) = \int P_B'(W + \nu) \, dx
\]

respectively.

Similarly, proposition 24.3.2 remains true:

**Proposition 1.1.4.** For arbitrary \( W \) the following estimates hold with absolute constants \( \epsilon_0 > 0 \) and \( C_0 \):

\[
\begin{align*}
\epsilon_0 D(\rho - \rho^{TF}, \rho - \rho^{TF}) &\leq \Phi_B^*(W^{TF} + \nu) - \Phi_B^*(W + \nu) \leq C_0 D(\rho - \rho', \rho - \rho') \quad (1.1.6) \\
D(\rho' - \rho^{TF}, \rho' - \rho^{TF}) &\leq \Phi_B^*(\rho, \nu) - \Phi_B^*(\rho^{TF}, \nu) \leq C_0 D(\rho - \rho', \rho - \rho') \quad (1.1.7)
\end{align*}
\]

with \( \rho = \frac{1}{4\pi} \Delta (W - V), \rho' = P_B'(W + \nu) \).

**Proof.** This proof is rather obvious as well. \( \square \)
1.2 Properties

Proposition 1.2.1. The solution of the magnetic Thomas-Fermi problem has the following scaling properties

\begin{align}
W^{\text{TF}}(x; \mathbf{Z}; y; B; N; q) &= q^3 N^2 W^{\text{TF}}(q^3 N^2 x; N^{-1} \mathbf{Z}; q^3 N^2 y; q^{-3} N^{-4} B; 1; 1), \\
\rho^{\text{TF}}(x; \mathbf{Z}; y; B; N; q) &= q^2 N^2 \rho^{\text{TF}}(q^3 N^2 x; N^{-1} \mathbf{Z}; q^3 N^2 y; q^{-3} N^{-4} B; 1; 1), \\
\mathcal{E}^{\text{TF}}(\mathbf{Z}; y; B; N; q) &= q^3 N^2 \mathcal{E}^{\text{TF}}(N^{-1} \mathbf{Z}; q^3 N^2 y; q^{-3} N^{-4} B; 1; 1), \\
\nu^{\text{TF}}(\mathbf{Z}; y; B; N; q) &= q^3 N^2 \nu^{\text{TF}}(N^{-1} \mathbf{Z}; q^3 N^2 y; q^{-3} N^{-4} B; 1; 1),
\end{align}

where \( \nu^{\text{TF}} = \nu \) is the chemical potential; recall that \( \mathbf{Z} = (Z_1, \ldots, Z_M) \) and \( \mathbf{y} = (y_1, \ldots, y_M) \) are arrays and parameter \( q \) also enters into Thomas-Fermi theory.

In particular, \( \nu^{\text{TF}} \) and \( B \) scale the same way.

Proof. Proof is trivial by scaling. \( \square \)

Now one can guess that there are two cases \( B \ll Z^{4 \over 3} \) and \( B \gg Z^{4 \over 3} \) (recall that \( N \sim Z \)) in which magnetic Thomas-Fermi theory looks very different (and also an intermediate case \( B \sim Z^{4 \over 3} \)). To explain this difference let us consider one atom case:

First of all recall that if \( B = 0 \) and \( N = Z \) theory (as \( M = 1 \)) has just one parameter and we can get rid off it by rescaling; \( W^{\text{TF}} \sim Z \ell^{-1} \) as \( \ell \lesssim Z^{-1 \over 3} \) and \( W^{\text{TF}} \sim \ell^{-4} \) as \( \ell \gtrsim Z^{-1 \over 3} \). Then

\[
W^{\frac{1}{3}} \ell^{3} \sim Z^{2 \over 3} \ell^{2 \over 3}, \quad W^{\frac{1}{3}} \ell^{3} \sim Z^{5 \over 3} \ell^{5 \over 3}
\]

and

\[
W^{\frac{1}{3}} \ell^{3} \sim \ell^{-3}, \quad W^{\frac{1}{3}} \ell^{3} \sim \ell^{-7}
\]
respectively where the first factors are spacial densities of the charge and (negative) Thomas-Fermi energy respectively and therefore zone $\ell \simeq Z^{-\frac{1}{3}}$ provides the main contributions into both.

Therefore, if in this main zone $B \ll W^{TF} \simeq \frac{Z^2}{\ell}$ we guess that the magnetic theory is similar to non-magnetic one, and actually it is true.

However, let us study an atomic case rigorously. Let $M = 1$, $y_m = 0$ and $N \leq Z$. Then

(1.2.5) $W^{TF}_B$ is a spherically symmetric, and it is monotone non-increasing function of $|x|$; $W^{TF}_B \to +0$ as $|x| \to \infty$;

(1.2.6) $W^{TF}_B(x) \leq -\nu \implies W^{TF}_B = |x|^{-1}(Z - N)$.

Really, (1.2.5) is obvious and (1.2.6) follows from it and Newton screening theorem.

Two propositions below treat cases $B \lesssim Z^{\frac{4}{3}}$ and $B \gtrsim Z^{\frac{4}{3}}$ respectively; in the former case there is another fork: $B \lesssim (Z - N)^{\frac{4}{3}}$ and $B \gtrsim (Z - N)^{\frac{4}{3}}$.

**Proposition 1.2.2.** Let $M = 1$, $y_m = 0$, $N \simeq Z_m$ and $B \leq Z^{\frac{4}{3}}$.

(i) Then

(1.2.7) $W^{TF}_B \leq \min(Z|x|^{-1}, C|x|^{-4})$

and

(1.2.8) $\rho^{TF}_B \leq C \min(Z^{\frac{3}{2}}|x|^{-\frac{3}{2}} + BZ^{\frac{1}{2}}|x|^{-\frac{1}{2}}, |x|^{-6} + B|x|^{-2})$;

(ii) There exists

(1.2.9) $\bar{r}_m \simeq \min(B^{-\frac{1}{3}}, (Z - N)^{-\frac{1}{3}})$

such that $W^{TF}_B \gtrsim -\nu$ as $|x| \leq \bar{r}_m$ and then $\rho^{TF}_B = 0$ iff $x \geq \bar{r}_m$;

(iii) (1.2.7) and (1.2.8) become equivalencies ($\simeq$) as $|x| \leq (1 - \epsilon)\bar{r}_m$;

(iv) $B \leq (Z - N)^{\frac{4}{3}}_+$ implies $\bar{r}_m \simeq (Z - N)^{-\frac{1}{3}}_+$, $\nu \simeq (Z - N)^{\frac{4}{3}}_+$ and

(1.2.10) $W^{TF} + \nu \simeq (Z - N)^{\frac{5}{3}}_+(\bar{r}_m - |x|)$,

$-\partial |x| W^{TF} \simeq (Z - N)^{\frac{5}{3}}_+$ as $(1 - \epsilon)\bar{r}_m \leq |x| \leq \bar{r}_m$;
\( B \geq (Z - N)^\frac{4}{5} \) implies \( \bar{r}_m \asymp B^{-\frac{1}{5}} \), \( \nu \asymp (Z - N)_+ B^\frac{1}{2} \lesssim B \) and

\( W^{TF} + \nu \asymp B^2 (\bar{r}_m - |x|)^4 + B^{\frac{3}{2}} (Z - N)_+ (\bar{r}_m - |x|) \)
\(- \partial_{|x|} W^{TF} \asymp B^2 (\bar{r}_m - |x|)^3 + B^{\frac{3}{2}} (Z - N)_+ \)
as \( (1 - \epsilon) \bar{r}_m \leq |x| \leq \bar{r}_m \).

**Proposition 1.2.3.** Let \( M = 1, y_m = 0, N \asymp Z_m \) and \( B \geq Z^\frac{4}{5} \).

(i) Then

\[ W^{TF}_B \leq Z |x|^{-1} \]

and

\[ \rho^{TF}_B \leq C Z^{\frac{1}{2}} |x|^{\frac{1}{2}} + CBZ^{\frac{1}{2}} |x|^{-\frac{1}{2}} ; \]

(ii) There exist \( \bar{r}_m \) and \( \bar{r}'_m \),

\[ \bar{r}_m \asymp B^{-\frac{1}{5}} Z^{\frac{1}{5}}, \quad \bar{r}'_m \asymp B^{-1} Z_m. \]
such that \( W^{TF}_B \asymp B \) as \( |x| \leq \bar{r}_m \), \( W^{TF}_B \asymp -\nu \) as \( |x| \leq \bar{r}'_m \) and then \( \rho^{TF}_B = 0 \) iff \( x \geq \bar{r}'_m \);

(iii) \( (1.2.12) - (1.2.13) \) become equivalencies \( (\asymp) \) as \( |x| \leq (1 - \epsilon) \bar{r}_m \);

(iv) \( \nu \asymp (Z - N)_+ B^\frac{2}{5} Z^{-\frac{1}{5}} \lesssim B \) and

\[ W^{TF} + \nu \asymp B^2 (\bar{r}_m - |x|)^4 + \bar{r}_m^{-2} (Z - N)_+ (\bar{r}_m - |x|) \]
and

\[ - \partial_{|x|} W^{TF} \asymp B^2 (\bar{r}_m - |x|)^3 + \bar{r}_m^{-2} (Z - N)_+ \]
as \( (1 - \epsilon) \bar{r}_m \leq |x| \leq \bar{r}_m \).

**Proofs of propositions 1.2.2 and 1.2.3.** Proofs easily follow from equation and “boundary conditions” satisfied by \( w(r) \) where \( r = |x| \):

\[ w'' + 2r^{-1}w = P'_B (w + \nu), \]
\[ w = r^{-1} Z_m + O(1) \quad \text{as} \quad r \to 0, \]
\[ w(\bar{r}_m) = -\nu, \quad w'(\bar{r}_m) = \nu \bar{r}_m^{-1} \]
where \( \nu = -(Z_m - N)_+ \bar{r}_m^{-1} \). \( \square \)
Corollary 1.2.4. Let $M = 1, y_m = 0$ and $N \asymp Z_m$. Then

(i) $W_B^{TF} \lesssim B$ if $|x| \geq \bar{r}'_m$ where $\bar{r}'_m \asymp B^{-\frac{1}{2}}Z_m$ as $B \geq Z_m^\frac{2}{3}$ and $\bar{r}'_m \asymp B^{-\frac{1}{2}}$ as $B \leq cZ_m^\frac{3}{4};$

(ii) As $B \lesssim Z_m^\frac{4}{3}$ the main contribution to both the charge and the Thomas-Fermi energy is delivered by zone $\{x : |x| \asymp r^*_m\}$ with $r^*_m = Z_m^{-\frac{1}{3}}$; in particular, then $\mathcal{E}_B^{TF} \asymp \mathcal{E}^{TF} \asymp Z_m^\frac{7}{3};$ further, in this case $W_B^{TF} \asymp W^{TF}$ in the zone $\{x : |x| \lesssim \epsilon\bar{r}_m\};$

(iii) Further, $\mathcal{E}_B^{TF} \asymp \mathcal{E}^{TF}$ as $B \ll Z_m^\frac{4}{3};$ furthermore, in this case $W_B^{TF} \asymp W^{TF}$ in the zone $\{x : |x| \ll \bar{r}_m\};$

(iv) On the other hand, as $B \geq Z_m^\frac{4}{3}$, the main contributions to the total charge and energy are delivered by $\{x : |x| \asymp r_m\}$ and in particular $\rho_m \asymp BZ_m^\frac{1}{3}r_m^*,$ and

\begin{equation}
\mathcal{E}_B^{TF} \asymp BZ_m^\frac{3}{2}r_m^* \asymp B^\frac{3}{2}Z_m^\frac{3}{2};
\end{equation}

Recall that $\bar{r}_m \asymp B^{-\frac{1}{2}}$ as $B \leq Z_m^\frac{4}{3}$ and $\bar{r}_m \asymp B^{-\frac{3}{2}}Z_M^\frac{1}{2}$ as $B \geq Z_M^\frac{4}{3}.$ Note that proposition 24.3.5 (comparing $W^{TF}$ for molecule with the sum of those for single atoms) still holds. Therefore we conclude that

Corollary 1.2.5. (i) Assume that

\begin{equation}
Z_m \asymp Z
\end{equation}

for all $m = 1, \ldots, M$. Then all statements of corollary 1.2.4 remain true for $M \geq 2$ with $|x|$ and $Z_m$ replaced by $\ell(x)$ and $Z$ and $\bar{r}_m, \bar{r}'_m, r^*_m$ by $\bar{r}, \bar{r}', r^*$ respectively;

(ii) In the general case global statements remain true, pointwise statements remain true without modification only as $\ell(x) = \ell_m(x) := |x - y_m|$ with $Z_m \asymp Z.$

Remark 1.2.6. (i) Also holds proposition 24.3.12 as it uses only super-additivity of $\tau_*(\rho)$ and $\tau_B(\rho)$ is also super-additive (this follows from convexity of $\tau_B(\rho)$ and equality $\tau_B(0) = 0$).
(ii) However there is a significant difference: if there is no magnetic field atoms really repulse one another on any distances and we can attribute it to either excessive positive charge as \( N < Z \) or their infinite spatial size as \( N = Z \). However with magnetic field atoms have a finite size even as \( N = Z \) and they do not repulse one another on the large distances. In particular, Proposition 1.2.7 below holds.

\textbf{Proposition 1.2.7.} Let \( N = Z \) and

\[ |y_m - y_{m'}| \geq \bar{r}_m + \bar{r}_{m'} \quad \forall m: 1 \leq m < m' \leq M. \tag{1.2.22} \]

Then

\[ \mathcal{E}^{TF}_B(Z,y,B,Z) = \sum_{1 \leq m \leq M} \mathcal{E}^{TF}_B(Z_m,y_m,B,Z_m) \tag{1.2.23} \]

and

\[ \rho^{TF}_B(x,Z,y,B,Z) = \sum_{1 \leq m \leq M} \rho^{TF}_B(x,Z_m,y_m,B,Z_m). \tag{1.2.24} \]

\textbf{Proposition 1.2.8.} (i) \( \nu \) is monotone increasing function of \( N \);

(ii) \( W_B(x) \) is monotone non-increasing function of \( N \);

(iii) \( W_B(x) + \nu \) is monotone non-decreasing function of \( N \); in particular \( \rho_B \) can only increase as \( N \) increases;

(iv) \( \nu \) is monotone non-increasing function of \( Z_m \);

(v) \( W_B(x) \) is monotone non-decreasing function of \( Z_m \).

\textit{Proof.} (i) Statement (i) follows from strict convexity of \( \mathcal{E}(\rho) \): consider two solutions with corresponding subscripts. Then \( \mathcal{E}(\rho) - \mathcal{E}(\rho_j) > \nu_j(N - N_j) \) for any non-negative \( \rho \neq \rho_j \) and \( N = \int \rho \, dx \).

In particular, \( \mathcal{E}(\rho_1) - \mathcal{E}(\rho_2) > \nu_2(N_1 - N_2) \) and \( \mathcal{E}(\rho_2) - \mathcal{E}(\rho_1) > \nu_1(N_2 - N_1) \) and then \( (\nu_1 - \nu_2)(N_1 - N_2) > 0 \).

(ii) Really, consider \( N_1 < N_2 \) and in the definition of \( W_B \) slightly decrease \( Z_1, \ldots, Z_M \) thus replacing them by \( Z'_1, \ldots, Z'_M \). Then \( W_1 > W_2 \) for large \( |x| \), \( W_1 - W_2 \to +\infty \) as \( x \to y_m \) and therefore if (ii) fails \( W_1 - W_2 \) reaches non-positive minimum at some regular point \( \bar{x} \); at this point \( W_1 \leq W_2 \) and

\[ 0 \leq \frac{1}{4\pi} \Delta(W_1 - W_2) = P'(W_1 + \nu_1) - P'(W_2 + \nu_2). \]
This is possible only if at this point \( W_2 + \nu_2 \leq 0 \) and \( W_1 + \nu_1 < 0 \). Then in the small vicinity \( \Delta(W_1 - W_2) \leq 0 \) and \( \bar{x} \) cannot be a point of minimum unless \( W_1 - W_2 = \text{const} \) there. Then any point of this vicinity is also a point of minimum and then due to standard analytic arguments \( W_1 - W_2 = \text{const} \) everywhere which is impossible.

So, \( W_1(x; Z_1, \ldots, Z_M) > W_2(x; Z'_1, \ldots, Z'_M) \). Taking limit as \( Z'_m \to Z_m \) we arrive to \( W_1(x; Z_1, \ldots, Z_M) \geq W_2(x; Z_1, \ldots, Z_M) \).

(iii) Proof of (iii) is similar but roles of \( W_1 \) and \( W_2 \) are played by \( W_1 + \nu_1 \) and \( W_2 + \nu_2 \) respectively;

(iv) Let \( Z_{m,2} > Z_{m,1} \) for all \( m \). Assume that \( \nu_2 > \nu_1 \). Then similar arguments prove that \( W_2 + \nu_2 \geq W_1 + \nu_1 \) and thus \( \rho_2 \geq \rho_1 \) everywhere which is impossible unless there are just identical equalities as \( W_2 + \nu_2 > 0 \), which is impossible.

(v) Finally, after (iv) was established, the same arguments prove (v). \( \square \)

As far as we know Theorem 1 of R. Benguria [Be] (see Theorem 24.3.8) has not been proven in the case of magnetic field; however one can see easily that arguments of of R. Benguria’s proof remain valid and we arrive to

**Theorem 1.2.9.** All statements (i)–(iv) of Theorem 24.3.8 hold in the case of the constant magnetic field.

**Problem 1.2.10.** (i) Investigate how \( \psi_B^2 \rho_B \) depends on \( B \) and on \( Z \) in the atomic case \( M = 1 \);

(ii) More generally, investigate how \( \psi_B^2 \rho_B \) depends on \( B \) and on \( Z \) in the case \( M \geq 2 \).

### 1.3 Positive ions

In view of Remark 1.2.6 we need to consider repulsion of positive ions in more details. Our purpose is to prove

**Theorem 1.3.1.** Let condition (1.2.21) be fulfilled. Then the energy excess is estimated from below

\[
Q := \hat{\epsilon}_B^{TF} - \sum_{1 \leq m \leq M} \epsilon_{B,m}^{TF} \geq \epsilon(Z - N)^2 a^{-1}.
\]
Note first that

\[(1.3.2) \quad D(\rho_{B(0)}^{TF} - \rho_{B,0}^{TF}, \rho_{B(\nu)}^{TF} - \rho_{B(0)}^{TF}) + \int (P_B^{TF}(W_{B(\nu)}^{TF} + \nu) - P_B^{TF}(W_{B(0)}^{TF})) (W_{B(\nu)}^{TF} + \nu - W_{B(0)}^{TF}) \, dx = \]

\[\nu \int (P_B^{TF}(W_{B(\nu)}^{TF} + \nu) - P_B^{TF}(W_{B(0)}^{TF} + 0)) \, dx\]

with the right-hand expression equal \(\nu(N - Z) \sim (Z - N)^{2\overline{r}-1}\) and due to monotonicity \(P_B^{TF}(w)\) we conclude that

**Proposition 1.3.2.** Let condition (1.2.21) be fulfilled. Then

\[(1.3.3) \quad D(\rho_{B(\nu)}^{TF} - \rho_{B,\nu}^{TF}, \rho_{B(0)}^{TF} - \rho_{B(0)}^{TF}) \leq C(Z - N)^{2\overline{r}-1}.\]

**Proof of Theorem 1.3.1. Step 1.** Note first that due to non-negativity of the expression

\[(1.3.4) \quad \hat{\mathcal{E}}_B^{TF}(Z, y, N) - \min_{N_1 + N_2 = N} (\mathcal{E}_B^{TF}(Z, N_1) - \hat{\mathcal{E}}_B^{TF}(Z', y', N'))\]

(see proof of Proposition 24.3.12 which persists even if there is constant magnetic field, see Remark 1.2.6) it is sufficient to prove theorem only for \(M = 2\). From now on we assume that \(M = 2\).

**Step 2.** According to Proposition 24.3.12

\[(1.3.5) \quad D(\rho_B^{TF} - \rho_{B,1}^{TF} - \rho_{B,2}^{TF}) \leq CQ.\]

Therefore due to superadditivity \(\tau_B\)

\[(1.3.6) \quad Q \geq - \int V_1 \rho_{B,2}^{TF} \, dx - \int V_2 \rho_{B,1}^{TF} \, dx + D(\rho_{B,2}^{TF}, \rho_{B,1}^{TF}) + Z_1Z_2a^{-1} - CQ\]

and it is sufficient to prove the same estimate from below for the right-hand expression without the last term. However this is easy if \(a \geq \overline{r}_1 + \overline{r}_2\) since \(V_m = |x - y_m|^{-1}Z_m\) and \(\rho_{B,m}^{TF} = \rho_{B,m}^{TF}(|x - y_m|)\) are spherically symmetric functions.

---

6) However this is not true in general as \(a < \overline{r}_1 + \overline{r}_2\). Really, consider \(N_m = Z_m\) and uniformly charged spheres. Then the right-hand expression of (1.3.6) is 0 as \(a \geq \overline{r}_1 + \overline{r}_2\) and is negative and decays as \(a\) decays from \(\overline{r}_1 + \overline{r}_2\) to \(\max(\overline{r}_1, \overline{r}_2)\) and it increases again as \(a\) decays from \(\max(\overline{r}_1, \overline{r}_2)\) to 0.
Therefore for $a \geq \bar{r}_1 + \bar{r}_2$ inequality (1.3.1) has been proven and in what follows we can assume that $a \leq \bar{r}_1 + \bar{r}_2$. Further, applying Theorem 1.2.9 we conclude then that

(1.3.7) Inequality (1.3.1) holds for $a \geq \epsilon \bar{r}$.

**Step 3.** Recall that the bulk of electrons are in the zone $\{\ell(x) \approx r^*\}$. Based on this one can prove easily that as $a \leq \epsilon \bar{r}$ the right-hand hand expression of (1.3.6) is greater than $(\epsilon - \epsilon_1)a^{-1}Z_1Z_2$ and therefore

(1.3.8) As $B \geq Z^\frac{3}{2}$ and $a \leq \epsilon r^*$ we have $Q \geq (1 - \epsilon_1)a^{-1}Z_1Z_2$ and combining with (1.3.7) we conclude that (1.3.1) holds for $B \geq Z^\frac{3}{2}$ and for $B \lessgtr Z^\frac{3}{2}$ we need to consider the case $\epsilon_0 r^* \leq a \leq \epsilon \bar{r}$ with arbitrarily small constant $\epsilon$.

Replacing then $P_B$ by $P_0$ and noting that an error will not exceed $C_0 \bar{r}B^2 \leq C_1 \epsilon a^{-7}$ while $Q \geq \epsilon_0 a^{-7}$ for $B = 0$ we conclude that (1.3.1) holds as $\epsilon_0 r^* \leq a \leq c \bar{r}$ and $(Z - N) \leq C_2 a^{-3}$.

Finally, as $(Z - N) \geq C_2 a^{-3}$ we see that $\bar{r} \leq C_0(Z - N)^{-\frac{1}{2}} \leq \epsilon a$ and (1.3.1) holds again.

Finally, even if we do not need it for our purposes we want to consider the repulsion of too close neutral atoms:

**Theorem 1.3.3.** Let condition (1.2.21) be fulfilled and $N = Z$. Then as $a \geq \epsilon \bar{r}$ the energy excess is estimated from below

(1.3.9) \[ Q \geq \epsilon G^2 \bar{r} \sum_{1 \leq m < m' \leq M} (\bar{r}_m + \bar{r}_n - |y_m - y_{m'}|)^{12} \bar{r}^{-12} \]

where

(1.3.10) \[ G := \begin{cases} B & \text{as } B \leq Z^\frac{3}{2}, \\ Z^\frac{3}{2}B^\frac{7}{3} & \text{as } B \geq Z^\frac{3}{2}. \end{cases} \]

and correspondingly $G^2 \bar{r} = \begin{cases} B^\frac{7}{3} & \text{as } B \leq Z^\frac{3}{2}, \\ Z^\frac{3}{2}B^\frac{1}{3} & \text{as } B \geq Z^\frac{3}{2}. \end{cases}$

---

7) I.e. zone $\{c(e)^{-1}r^* \leq \ell(x) \leq c(e)r^*\}$ contains at least $(1 - \epsilon)N$ electrons.
Proof. Again we need to consider case $M = 2$. Since

\begin{equation}
\frac{1}{4\pi} \Delta W_B = \rho_B - \sum_{m=1,2} Z_m \delta(x-y_m)
\end{equation}

and $W_{B,1}$, $W_{B,2}$ satisfy similar equations, (1.3.5) implies that

\begin{equation}
\|\nabla(W_B - W_{B,1} - W_{B,2})\| \leq cQ^{\frac{1}{2}}.
\end{equation}

This inequality and the fact that $W_B = 0$ as $\ell(x) \geq c\bar{r}$, and $W_{B,m} = 0$ as $|x-y_m| \geq \bar{r}_m$ imply that

\begin{equation}
\|(W_B - W_{B,1} - W_{B,2})\| \leq c\bar{r} Q^{\frac{1}{2}}.
\end{equation}

Note that $\int (-\rho_B + \rho_{B,1} + \rho_{B,2}) \, dx = 0$ implies that

\begin{equation}
\int ((W_{B,1} + W_{B,2})^{\frac{1}{2}} - W_{B,1}^{\frac{1}{2}} - W_{B,2}^{\frac{1}{2}}) \, dx \leq \int |W_B^{\frac{1}{2}} - (W_{B,1} + W_{B,2})^{\frac{1}{2}}| \, dx.
\end{equation}

One can calculate easily that the left-hand expression has a magnitude $(G\eta^4)^{\frac{1}{2}} \cdot \eta \bar{r} \cdot (\eta^{\frac{1}{2}}\bar{r})^2 \propto G^{\frac{1}{2}} \bar{r}^3 \eta^4$ where the first factor is a magnitude of an integrand as $W_{B,1} \approx W_{B,2} \approx G\eta^4$, $\eta \bar{r}$ is a depth, and $\eta^{\frac{1}{2}}\bar{r}$ the width of this zone.

On the other hand, consider the right hand expression. It consists of contributions of several zones:

(a) Zone $\mathcal{Y}_t$ where $W_{B,1} + W_{B,2} \leq Gt^4$, $W_B \leq 2Gt^4$. This contribution does not exceed $CG^{\frac{3}{2}}t^2 \text{mes}(\mathcal{Y}_t) \approx CG^{\frac{3}{2}} \bar{r}^3 t^3$; 

(b) Zone $\mathcal{Z}_t$ where $W_{B,1} + W_{B,2} \leq Gt^4$, $W_B \geq 2Gt^4$. Its contribution does not exceed

\begin{equation}
C \int_{\mathcal{Z}_t} W_B^{\frac{1}{2}} \, dx \leq C \|W_B\|_{L^2}^{\frac{1}{2}} (\text{mes}(\mathcal{Z}_t))^{\frac{1}{2}} \leq C \bar{r}^{\frac{11}{4}} Q^{\frac{1}{2}} t^{\frac{3}{2}}
\end{equation}

since due to (1.3.13) $\|W_B\|_{L^2} \leq c\bar{r} Q^{\frac{1}{2}}$;

\footnote{8) Obviously $\text{mes}(\mathcal{Y}_t \cup \mathcal{Z}_t) \approx \bar{r}^3 t$ and similarly $\text{mes}(\mathcal{X}_t) \approx \bar{r}^3 t$.}
(c) Zone where $W_{B,1} + W_{B,2} \asymp G \tau^4$. This contribution does not exceed

\begin{equation}
CG^{-\frac{1}{2}} \tau^{-2} \int |W_B - W_{B,1} - W_{B,2}| \, dx \leq
CG^{-\frac{1}{2}} \tau^{-2} \times \|W_B - W_{B,1} - W_{B,2}\| \times (\text{mes}(\mathcal{X}_\tau))^\frac{1}{2} \asymp CG^{-\frac{1}{2}} Q^\frac{1}{2} r^\frac{3}{2} \tau^{-\frac{3}{2}}.
\end{equation}

Integrating by $\tau^{-1} \, d\tau$ from $t$ we get (1.3.15) calculated as $\tau = t$ (and capped by the same expression as $\tau = \eta$).

So, the right-hand expression of (1.3.14) does not exceed

$$CG^\frac{1}{2} r^3 t^3 + C Q^\frac{1}{2} r^\frac{11}{4} t^\frac{3}{4} + CG^{-\frac{1}{2}} Q^\frac{1}{2} r^\frac{3}{2} t^{-\frac{3}{2}};$$

optimizing with respect to $t = G^{-\frac{1}{3}} Q^\frac{1}{3} r^{-\frac{1}{3}}$ we get all three terms equal to $CG^{-\frac{1}{6}} Q^\frac{1}{3} r^\frac{3}{2}$ comparing with $CG^\frac{1}{2} r^3 \eta^4$ we arrive to (1.3.9). \hfill $\square$

2 Applying semiclassical methods: $M = 1$

2.1 Heuristics

Let us consider first a mock proof of our main results; we deal here as if $W_B^{TF}$ was very smooth which it is not the case; however later we will show that its smoothness is sufficient to employ arguments of Chapter 18 rather than those of Chapter 13. We also will deal as if non-degeneracy conditions were satisfied leaving them also to more rigorous arguments below.

It will allow us to establish our target remainder estimates which we will be able to prove rigorously for $M = 1$ (in this section) while for $M \geq 2$ (in the next two sections) our results will be not that good.

2.1.1 Total charge

Consider

\begin{equation}
\int e(x, x, \nu) \psi(x) \, dx
\end{equation}

first with $\gamma$-admissible $\psi(x)$, where $\gamma \leq \epsilon \ell$. 

20
General arguments.

The main part of the semiclassical expression for (2.1.1) is of magnitude $\hbar' - \frac{\pi}{\zeta} + \mu' \hbar' - \frac{\pi}{\zeta}$ with $\hbar' = 1/(\zeta \gamma)$ and $\mu' = B\gamma/\zeta$.

Really, let us rescale $x \mapsto x/\gamma$ and $\tau \mapsto \tau/\zeta^2$ which leads to $h = 1 \mapsto \hbar'$ and $B \mapsto \mu'$. In particular, as $\gamma \approx \ell$ we get

\begin{equation}
\zeta^3 \ell^3 + B\zeta \ell^3.
\end{equation}

Meanwhile the remainder in the semiclassical expression for (2.1.1) does not exceed $C \hbar' + C\mu' \hbar' - \frac{\pi}{\zeta}$ (gaining factor $\hbar'$ in comparison to the main part; here we need smoothness and as $\mu' \geq \hbar'^{-1}$ we also need non-degeneracy); as $\gamma \approx \ell$ we get

\begin{equation}
\zeta^2 \ell^2 + B\ell^2.
\end{equation}

Sure, we ignored the fact that $\hbar' \leq 1$ does not necessarily hold even if $\gamma \approx \ell$ but we believe that the contributions to the main part and the remainder of these zones will be less than of zone where this inequality holds, provided $B \ll Z^3$.

Finally let us sum expressions (2.1.2) and (2.1.3) with respect to $\ell$-partition.

Moderate magnetic field.

Consider case $B \leq Z^\frac{3}{2}$ first. Then for $\ell \leq Z^{-\frac{1}{2}}$ we plug $\zeta = Z^\frac{1}{2} \ell^{-\frac{1}{2}}$ into (2.1.2) and (2.1.3) resulting in

\begin{equation}
(2.1.4)_{0,1} \quad Z^\frac{1}{2} \ell^\frac{3}{2} + BZ^\frac{1}{2} \ell^\frac{5}{2} \quad \text{and} \quad Z\ell + B\ell^2
\end{equation}

in the main part and in the remainder respectively and the summation over zone $\{\ell \leq Z^{-\frac{1}{2}}\}$ results in the same expressions as $\ell = Z^{-\frac{1}{2}}$ i. e. in $Z + BZ^{-\frac{1}{2}} \asymp Z$ and $Z^\frac{1}{2} + BZ^{-\frac{1}{2}} \asymp Z^\frac{3}{2}$ respectively.

On the other hand, for $\ell \geq Z^{-\frac{1}{2}}$ we plug $\zeta = \ell^{-2}$ into (2.1.2) and (2.1.3) resulting in

\begin{equation}
(2.1.5)_{0,1} \quad \ell^{-3} + B\ell \quad \text{and} \quad \ell^{-2} + B\ell^2;
\end{equation}

then summation over zone $\{Z^{-\frac{1}{2}} \leq \ell \leq \bar{r} = B^{-\frac{1}{2}}\}$ results in $Z + B^\frac{3}{2} \asymp Z$ and $Z^\frac{1}{2} + B^\frac{3}{2} \asymp Z^\frac{3}{2}$ respectively.
Strong magnetic field.

Consider case $B \geq Z^{\frac{1}{3}}$ now. Then threshold $Z^{-\frac{1}{3}}$ disappears and we sum expressions (2.1.4)$_{0,1}$ over $\ell \leq \bar{r} := Z^{\frac{1}{2}} B^{-\frac{1}{2}}$ resulting in $Z^{\frac{1}{2}} B^{-\frac{1}{2}} + Z \propto Z$ and $Z^{\frac{2}{5}} B^{-\frac{2}{5}} + Z^{\frac{2}{5}} B^{\frac{1}{5}} \propto Z^{\frac{2}{5}} B^{\frac{1}{5}}$.

Therefore,

(2.1.6) The total charge is $\min(N, Z)$ (due to the choice of $\nu$) with the remainder estimate $O(\max(Z^{\frac{2}{5}}, Z^{\frac{2}{5}} B^{\frac{1}{5}}))$ which is $O(Z^{\frac{2}{5}})$ as $B \leq Z^{\frac{1}{3}}$ and $O(Z^{\frac{2}{5}} B^{\frac{1}{5}})$ as $Z^{\frac{1}{4}} \leq B \leq Z^{\frac{3}{4}}$.

Remark 2.1.1. Remainder is less than the main part as $Z^{\frac{2}{5}} B^{\frac{1}{5}} \lesssim Z$ i.e. $B \leq Z^{\frac{3}{4}}$. It means exactly that $\zeta \ell \geq 1$ as $\ell = \bar{r}$ (as $B \geq Z^{\frac{1}{2}}$). The same is true for all other semiclassical asymptotics below.

As $B \ll Z^{\frac{3}{2}}$ we arrive to asymptotics, as $B \lesssim Z^{\frac{1}{2}}$ we have estimates and in the case of superstrong magnetic field $B \gg Z^{\frac{3}{4}}$ Thomas-Fermi theory is not valid for our main model.

2.1.2 Semiclassical D-term

Consider now the semiclassical D-term

(2.1.7) 
$$D(e(x, x, \nu) - \rho_{B}^{\text{TF}}(x), e(x, x, \nu) - \rho_{B}^{\text{TF}}(x)).$$

General arguments.

We do not have appropriate asymptotics for $e(x, x, \nu)$ in the case of magnetic field\(^9\) but we apply Fefferman–de Llave decomposition (16.3.1):

(2.1.8) 
$$|x - y|^{-1}(x, y) := |x - y| \varphi(\gamma^{-1}|x - y|) = \gamma^{-4} \int \psi_{1, \gamma}(x, z) \psi_{2, \gamma}(y, z) dz$$

where $\varphi \in C^{\infty}([1, 2])$.

Therefore contribution of $B(z, \gamma) \times B(z', \gamma)$ with $3\gamma \leq |z - z'| \leq 4\gamma$, $\gamma \leq \epsilon(z)$ to such term does not exceed $C(\zeta^2 \gamma^2 + B \gamma^2)^2 \gamma^{-1}$. There are

\(^9\) Unless we really assume that $W$ is smooth and apply results sections 16.5–16.8.
\( \asymp \ell^3 \gamma^{-3} \) of such pairs with \( \ell(x) \asymp \ell \) and their total contribution does not exceed \( C(c^2 + B)^2 \ell^3 \).

Now we need to sum over \( \gamma^{-1} d\gamma \) which does not look good as it leads to the logarithmic divergency but there is a simple remedy: we treat this way only pairs \( t\ell \leq |z - z'| \leq \ell \) and apply for pairs with \( |z - z'| \leq t\ell \) pointwise asymptotics; then we get

\[
(2.1.9) \quad C(c^2 + B)^2 \ell^3 \left( 1 + \log \frac{B\ell}{\zeta} \right);
\]

to get rid off this logarithmic factor we apply more delicate arguments similar to those of Subsection 16.9.3.

Thus, ignoring this logarithmic factor we conclude that the contribution of all pairs \( (z, z') \) with \( \ell(z) \asymp \ell(z') \asymp \ell \) does not exceed \( C(c^2 + B)^2 \ell^3 \) while contribution of all pairs \( (z, z') \) with \( \ell(z) \asymp \ell_1 \neq \ell(z') \asymp \ell_2 \) does not exceed \( C(c_1^2 + B)(c_2^2 + B)\ell_1^2 \ell_2^2 (\ell_1 + \ell_2)^{-1} \).

Finally let us sum these expressions over partitions of unity.

**Moderate magnetic field.**

Consider case \( B \leq Z \frac{1}{4} \). Then summation over zone \( \{ \ell_1 \leq Z^{-\frac{1}{4}}, \ell_2 \leq Z^{-\frac{1}{4}} \} \) results in \( CZ \frac{1}{4} \) and the same is true for summation over zone \( \{ Z^{-\frac{1}{4}} \leq \ell_1 \leq B^{-\frac{1}{4}}, Z^{-\frac{1}{4}} \leq \ell_2 \leq B^{-\frac{1}{4}} \} \).

Obviously, in such estimates, if there is a fixed number of zones, we do not need to sum over “mixed” pairs when \( z \) and \( z' \) belong to different zones.

**Strong magnetic field.**

Consider case \( B \geq Z \frac{3}{4} \). Then summation over zone \( \{ \ell_1 \leq Z^{\frac{1}{4}}B^{-\frac{3}{4}}, \ell_2 \leq Z^{\frac{1}{4}}B^{-\frac{3}{4}} \} \) results in \( CZ^\frac{1}{2}B^\frac{3}{2} \).

Therefore

\[
(2.1.10) \quad \text{Term (2.1.7) does not exceed } C \max(Z^\frac{1}{4}, Z^\frac{3}{4}B^\frac{1}{2}) \text{ which is } CZ^\frac{1}{3} \text{ as } B \leq Z^\frac{1}{4} \text{ and } CZ^\frac{3}{2}B^\frac{1}{2} \text{ as } Z^\frac{1}{4} \leq B \leq Z^3.\]

**2.1.3 \( |\lambda_N - \nu| \) and another D-term**

Consider two other non-trace terms in the upper estimate.
Moderate magnetic field.

As $B \leq Z^\frac{2}{3}$ we established the remainder in the total charge $O(Z^\frac{2}{3})$. Then using our standard arguments we conclude easily that $|\lambda_N - \nu| = O(Z)$ and then

$$|\lambda_N - \nu| \cdot |N(\nu) - N| \leq CZ^\frac{2}{3} \tag{2.1.11}$$

and

$$D(P'_B(W^TF_B(x) + \lambda_N) - P'_B(W^TF_B(x) + \nu), P'_B(W^TF_B(x) + \lambda_N) - P'_B(W^TF_B(x) + \nu)) \leq CZ^\frac{2}{3}; \tag{2.1.12}$$

combining with the estimate of the previous subsubsection we conclude that

$$D(\rho_B - \rho^TF_B, \rho_B - \rho^TF_B) \leq CQ = O(Z^\frac{2}{3}) \tag{2.1.13}$$

as in (24.4.55).

Strong magnetic field.

Let now $Z^\frac{2}{3} \leq B \leq Z^3$. Then we established the remainder in the total charge $O(Z^\frac{2}{3}B^\frac{1}{3})$ and for the semiclassical D-term we established estimate $O(Z^\frac{2}{3}B^\frac{1}{3})$ and therefore to estimate

$$|\lambda_N - \nu| \cdot |N(\nu) - N| \leq CZ^\frac{2}{3}B^\frac{1}{3} \tag{2.1.14}$$

as well we want to prove that

$$|\lambda_N - \nu| = O(Z^\frac{1}{3}B^\frac{1}{3}) \tag{2.1.15}.$$

Note that $|\nu| \lesssim Z^{-1} \approx Z^\frac{2}{3}B^\frac{2}{3} \leq CB$. Therefore if $|\lambda_N - \nu| \leq \frac{1}{2} |\nu|$ we conclude that

$$\int (P'_B(W^TF_B(x) + \lambda_N) - P'_B(W^TF_B(x) + \nu)) \, dx \geq \epsilon |\lambda_N - \nu|B \int (W + \nu)_{+}^{-\frac{1}{2}} \, dx \tag{2.1.16}$$

with integral taken over zone $\{x : W(x) + \nu \geq |\lambda_N - \nu|\}$.  

24
One can see easily that as \(|\lambda - N| \leq \epsilon |\nu|\) the right-hand expression of (2.1.16) is larger than \(\epsilon |\lambda - N| \cdot Z^{\frac{1}{2}} B^{-\frac{1}{2}}\) and it must be less than \(CZ^{\frac{1}{2}} B^{\frac{1}{2}}\): \(\lambda - N |Z^{\frac{1}{2}} B^{-\frac{1}{2}} \leq CZ^{\frac{1}{2}} B^{\frac{1}{2}}\) which implies (2.1.15).

Let us estimate the left-hand expression of (2.1.12). For this, however, estimate (2.1.15) is insufficient. We consider here only atomic case. Then using (1.2.15)–(1.2.16) one can prove easily that the right-hand expression of (2.1.16) is of magnitude
\[
|\lambda - N| \cdot B^{\frac{1}{2}} \times (|\nu|^{-1})^{-\frac{1}{2}} B^{-\frac{1}{2}} \approx |\lambda - N| \cdot |\nu|^{-\frac{1}{2}} Z^{\frac{1}{2}} B^{-\frac{1}{2}}
\]
preserved \(|\lambda - N| \leq \epsilon \nu\), where the selected factor is just \(\int (B^{2}z^{4} + |\nu|^{-1})^{-\frac{1}{2}} dz\) (appearing due to (1.2.15)–(1.2.16)). Comparing with \(Z^{\frac{1}{2}} B^{\frac{1}{2}}\) we conclude that

(a) If \(|\nu| \geq C_{1}Z^{-\frac{1}{2}} B^{\frac{1}{2}}\) (i.e. \(C_{1}Z^{\frac{1}{2}} B^{\frac{1}{2}} \times Z^{-\frac{1}{2}} B^{\frac{1}{2}}\)) then

(2.1.17) \(|\lambda - N| \leq C|\nu|^{\frac{1}{2}} Z^{-\frac{1}{2}} B^{\frac{1}{2}}\)

which is less than \(\epsilon |\nu|\) and coincides with (2.1.15) as \((Z - N)_{+} \approx Z\); (b) If \(|\nu| \geq C_{1}Z^{-\frac{1}{2}} B^{\frac{1}{2}}\) then \(|\lambda - N| \leq C_{2}Z^{-\frac{1}{2}} B^{\frac{1}{2}}\).

In the former case one can prove easily that the left-hand expression of (2.1.12) does not exceed \(CZ^{\frac{1}{2}} B^{\frac{1}{2}}\).

In the latter case (as in Subsection 24.4.2) we consider Thomas-Fermi theory with \(\nu = 0\) i.e. \(N = Z\) and also prove that that

(2.1.18) The left-hand expression of (2.1.15) does not exceed \(Q = CZ^{\frac{1}{2}} B^{\frac{1}{2}}\).

In particular we slightly improve estimate (2.1.14) to \(|\nu|^{\frac{1}{2}} Z^{\frac{1}{2}} B^{\frac{1}{2}}\) as well (if \((Z - N) \ll Z\)).

Therefore in our framework we estimated all non-trace terms in the upper estimate by \(CZ^{\frac{1}{2}} B^{\frac{1}{2}}\) and therefore “proved” estimate

(2.1.19) \(D(\rho_{\psi} - \rho_{B}^{\text{TF}}, \rho_{\psi} - \rho_{B}^{\text{TF}}) \leq CQ = O(Z^{\frac{1}{2}} B^{\frac{1}{2}})\).
2.1.4 Trace

Consider now $\text{Tr}^{-}(H_{A,W} - \nu)$. This term is of magnitude $\int (\zeta^5 + B\zeta^3) \, dx$ and one can see easily that it is $\sim Z^\frac{5}{2}$ as $B \leq Z^\frac{5}{4}$ and $\sim B^\frac{5}{2}Z^\frac{3}{2}$ as $Z^\frac{3}{4} \leq B \leq Z^3$.

Meanwhile consider the remainder. Again for simplicity consider only atomic case. As $B \leq Z$ contribution of zone $\{x : \ell(x) \leq Z^{-\frac{1}{4}}\}$ is $O(Z^\frac{5}{2})$ (we need to include Scott correction term in the main part) while contribution of zone $\{x : \ell(x) \geq Z^{-\frac{1}{4}}\}$ does not exceed

\[(2.1.20) \quad C \int (\zeta^3 + B\zeta) \ell^{-2} \, dx\]

taken over this zone and it is $\sim Z^\frac{5}{2}$ as well.

As $Z \leq B \leq B^2$ contribution of zone $\{x : \ell(x) \leq b := B^{-\frac{3}{4}}Z^{\frac{1}{4}}\}$ is $O(b^\frac{5}{2}Z^\frac{3}{2}) = O(Z^\frac{5}{2}B^{\frac{5}{4}})$ and we need to include Scott correction term. Meanwhile contribution of zone $\{x : \ell(x) \geq b\}$ does not exceed integral (2.1.20) taken over this zone which is $\sim Z^\frac{5}{2}B^{\frac{5}{4}} + Z^\frac{3}{2}B^{\frac{3}{4}}$ where the last term coincides with estimate for (2.1.7) as $B \geq Z^\frac{3}{4}$ and does not exceed $CZ^\frac{5}{2}$ as $B \leq Z^\frac{3}{4}$.

Finally, as $Z^2 \leq B \leq B^3$ we need to reset $b = Z^{-1}$ as $h = 1/(\zeta\ell)$ becomes $\geq 1$ inside; then we do not need Scott correction term and contributions of zone $\{x : \ell(x) \leq b\}$ to both main part and remainder do not exceed $C \int (\zeta^5 + B\zeta^3) \, dx \sim Z^\frac{5}{2} + B \propto B$ and contribution of zone $\{x : \ell(x) \geq b\}$ to the remainder does not exceed integral (2.1.20) taken over this zone which results in $CB + CZ^\frac{5}{2}B^{\frac{3}{4}}$ and the second term dominates due to assumption $B \ll Z^3$. Thus we arrive to

\[(2.1.21) \quad \text{The main term in } \text{Tr}^{-}(H_{A,W} - \nu) \text{ is of magnitude } Z^\frac{5}{2} \text{ as } B \leq Z^\frac{3}{4} \text{ and } B^\frac{5}{2}Z^\frac{3}{2} \text{ as } Z^\frac{3}{4} \leq B \leq Z^3 \text{ while remainder estimate is } O(Z^\frac{5}{2}) \text{ as } B \leq Z, O(Z^\frac{5}{2}B^{\frac{5}{4}}) \text{ as } Z \leq B \leq Z^\frac{5}{4}, O(Z^\frac{5}{2}B^{\frac{5}{4}} + Z^\frac{3}{2}B^{\frac{3}{4}}) \text{ as } Z^\frac{3}{4} \leq B \leq Z^3.\]

As $B \leq Z^\frac{2}{3}$ we need to include into main part Scott correction term.

2.1.5 Discussion

Now let us formulate our expectations:

*Remark 2.1.2.* We expect

(i) Estimate (2.1.13) as $B \leq Z^\frac{3}{4}$ and (2.1.19) as $Z^\frac{3}{4} \leq B \leq Z^3$;
(ii) Furthermore as for $B \leq Z^{\frac{3}{2}}$ the main contribution to all terms needed to derive this estimate is delivered by zone $\{x : \ell(x) \approx Z^{-\frac{3}{2}}\}$ and effective magnetic field is $\mu = B\ell/\zeta \approx BZ^{-1}$ we expect improved to “o” (or better) estimate (2.1.13) as $B \ll Z$ and $a \gg Z^{-\frac{1}{2}}$\(^{10}\);

(iii) Statement (ii) should be also true for the trace term; however then we need to include Schwinger term;

(iv) The remainder estimate for the ground state energy is maximum of the remainder estimate for non-trace and trace terms; therefore we expect the same remainder estimate as in (2.1.21); statement (ii) should be also correct for the ground state energy; however then we need to include both Schwinger and Dirac terms;

(v) We expect the described remainder estimate of the trace term and the ground state energy if $a$ is large enough; otherwise it should contain term $O(a^{-\frac{3}{2}}Z^\frac{1}{2})$ as $B \leq Z^\frac{3}{2}$ and $a \geq Z^{-1}$ (and in this case we include Scott correction term).

Remark 2.1.3. The other difference between cases $B \leq Z^{\frac{3}{2}}$ and $B \geq Z^{\frac{3}{2}}$ is that $\mu \hbar = B\zeta^{-2} \lesssim 1$ in the former case as $\ell(x) \leq \tilde{r}$; however in the latter case it happens only as $\ell(x) \leq B^{-1}Z$ but in the zone $\{B^{-1}Z \leq \ell(x) \leq B^{-\frac{3}{2}}Z^\frac{1}{2}\}$ an opposite inequality holds.

### 2.2 Smooth approximation

An approach described in Subsection 2.1 hits two obstacles: non-smoothness of $W_{TF}^B$ and its possible degeneration i.e. $\nabla W_{TF}^B$ is not disjoint from 0. However non-smoothness of $W_{TF}^B$ is due to the non-smoothness of $P_B$. So we want to consider first the zone where we can just replace $P_B(W + \nu)$ by $P(W + \nu)$ and therefore $W_{TF}^B$ by some smooth function $W$ which does not necessary coincides with $W_{TF}^B$.

#### 2.2.1 Trivial arguments

Obviously we can do this as an effective magnetic field $\mu = B\ell/\zeta \lesssim 1$. In this case we do not need assumption $W + \nu \asymp \zeta^2$ and therefore we can

\(^{10}\) Recall that $a = \min_{1 \leq m < m' \leq M} |y_m - y_{m'}|$ is the minimal distance between nuclei.
take \( \zeta = \ell^{-4} \) as \( B \lesssim Z^{\frac{4}{3}} \) and \( \ell \gtrsim Z^{-\frac{1}{3}} \) and \( \zeta = Z^{\frac{1}{2}} \ell^{-\frac{1}{2}} \) in all other cases. Therefore zone in question is

(2.2.1) \( \mathcal{X}_1 := \{ x : \ell(x) \leq r_1 \} \)

with \( r_1 = \begin{cases} B^{-\frac{1}{3}} & \text{as } 1 \leq B \lesssim Z, \\ B^{-\frac{1}{3}} Z^{\frac{1}{3}} & \text{as } Z \lesssim B \lesssim Z^2. \end{cases} \)

In this zone \( \mathcal{X}_1 \) for such modified \( W \) we can unleash the full power of the same smooth theory as in section 24.4 and prove easily the following

**Proposition 2.2.1.** Let \( 1 \leq B \leq Z^2 \). Then

(i) Contribution of zone \( \mathcal{X}_1 \) defined by (2.2.1) to

(2.2.2) \[ \int \left( e(x, x, \nu) - P'(W(x) + \nu) \right) dx \]

does not exceed \( CZ^{\frac{3}{10}} \), its contribution to

(2.2.3) \[ D \left( e(x, x, \nu) - P'(W(x) + \nu), e(x, x, \nu) - P'(W(x) + \nu) \right) \]

does not exceed \( CZ^{\frac{5}{10}} \) and its contribution to

(2.2.4) \[ \int \left( e_1(x, x, \nu) + P(W(x) + \nu) \right) dx - \text{Scott} \]

does not exceed \( CZ^{\frac{3}{10}} + Ca^{-\frac{1}{2}} Z^{\frac{1}{3}} + CB^{-\frac{1}{2}} Z^{\frac{1}{3}} \) \( 10 \), \( 11 \)

(ii) Further, as \( B \ll Z \) and \( a \gg Z^{-\frac{1}{3}} \) we can recover for these contributions estimates \( CZ^{\frac{3}{10}} \), \( CZ^{\frac{5}{10}} v \) and \( CZ^{\frac{5}{10}} v \) with

(2.2.5) \[ v := Z^{\delta} + (aZ^{\frac{1}{2}})^{-\delta} + (BZ^{-1})^{\delta} \]

respectively where expression (2.2.4) should be modified to

(2.2.6) \[ \int \left( e_1(x, x, \nu) - P(W(x) + \nu) \right) dx - \text{Scott} - \text{Schwinger}; \]

\( \text{11) As } a \lesssim Z^{-1} \text{ we skip Scott and reset } a = Z^{-1} \text{ in the remainder estimate which become } CZ^2. \)
Furthermore in this case contribution of $X_1$ to

$$\frac{1}{2} \int \text{tr} e^\dagger(x, y, \nu)e(x, y, \nu)\, dxdy - \text{Dirac} \tag{2.2.7}$$

does not exceed $CZ^{\frac{5}{2} - \delta}$.

**Remark 2.2.2.**

(i) So far we should use $P(.)$ instead of $P_B(.)$ but we will prove that the same results would hold for $P_B$ as well;

(ii) In the next subsubsections we expand this zone to one defined by $\mu \leq h^{-\frac{1}{2}}$ but for trace term we still need a separate analysis as $\mu \lesssim 1$;

(iii) The same estimates hold as we replace in all expressions (2.2.2)–(2.2.6) $P$ by $P_B$;

(iv) We assumed that $B \leq Z^2$ as otherwise $h \gtrsim 1$ not only in $X_1$ but even in $\{x : W^{TF} \geq B\}$;

(v) Note that as $r_1 \gtrsim (Z - N)^{\frac{1}{2}}$ this zone (and the whole analysis) could be cut short as outside zone in question $W + \nu \geq 0$. From Chapter 24 we already know how to deal with such irregularities;

(vi) We need to assume that $a \geq Z^{-\frac{1}{2}}$ and to include the second term $(aZ^{\frac{1}{2}})^{-\delta}$ in the definition of $\nu$ only as we estimate the trace term (2.2.4).

### 2.2.2 Formal expansion

Now we want to expand zone $X_1$. Note first that

$$P_B'(W + \nu) - P'(W + \nu) = O(B^2) \tag{2.2.8}$$

and

$$P_B(W + \nu) - P(W + \nu) - \kappa_1 B^2(W + \nu)^{\frac{1}{2}} = O(B^\frac{5}{2}). \tag{2.2.9}$$

Really, one can consider $P_B'(w)$ and $P_B(w)$ as Riemann sums for integrals $P'(w)$ and $P(w)$ respectively; see Appendix 8.C for details.

However under non-degeneracy assumption $|\nabla W| \asymp \zeta^2 \ell^{-1}$ we can do better with the integrated expressions.

---

12) Or even to $\mu \leq h^{-\frac{1}{2}}$ under non-degeneracy assumption (2.2.11) with $\gamma = \ell$, in particular, in the atomic case.
Proposition 2.2.3. Assume that in \( B(z, \gamma) \)

\[
|\nabla^\alpha W| \leq C_\alpha \zeta^2 \gamma^{-|\alpha|} \quad \forall \alpha : |\alpha| \leq n, \tag{2.2.10}
\]

\[
|\nabla W| \geq \epsilon \zeta \gamma^{-1}, \tag{2.2.11}
\]

and

\[
B \leq \zeta^2. \tag{2.2.12}
\]

Then

\[
\int \phi(x) \left( P_B'(W(x) + \nu) - \tilde{P}_B'(W(x) + \nu) \right) \, dx = O(B^2 \zeta^{-1} \gamma^3), \tag{2.2.13}
\]

\[
\int \phi(x) \left( P_B(W(x) + \nu) - \tilde{P}_B(W(x) + \nu) \right) \, dx = O(B^5 \zeta^{-5} \gamma^3) \tag{2.2.14}
\]

and

\[
D \left( \phi(x)(P_B'(W(x) + \nu) - \tilde{P}_B'(W(x) + \nu)) \right), \quad \phi(x)(P_B'(W(x) + \nu) - \tilde{P}_B'(W(x) + \nu)) = O(B^5 \zeta^{-4} \gamma^5) \tag{2.2.15}
\]

with

\[
\tilde{P}_B(w) := P(w) + (\kappa_1 P''(w)B^2 + \kappa_2 P^{IV}B^4) \cdot (1 - \varphi(w/B)) \tag{2.2.16}
\]

where \( \varphi \in \mathcal{C}^\infty([-2, 2]), \ \varphi = 1 \) on \([-1, 1]\).

Proof. Rescaling \( x \mapsto x \gamma^{-1}, \ w \mapsto w \zeta^{-2} \) and therefore \( B \mapsto \beta = B \zeta^{-2} \)

one can reduce the case to \( \gamma = \zeta = 1, \ \beta \leq 1 \). Then estimates (2.2.13) and (2.2.14) are trivially proven by (multiple) integration by parts which integrates \( P_\beta \) on each step increasing its smoothness\(^\text{13}\).

To prove estimate (2.2.15) we apply decomposition (2.1.8). Integration by parts shows that (2.2.13) with \( t \)-admissible function \( \phi \) is \( O(\beta^3 t^{3}) \) as \( t \geq \beta \)

and therefore contribution of zone \( \{(x, y) : |x - y| \asymp t\} \) is \( O(\beta^6 t^3 \times t^{-4}) \)

and therefore the total contribution of zone \( \{(x, y) : |x - y| \geq \beta\} \) is \( O(\beta^5) \). Meanwhile a total contribution of the zone \( \{(x, y) : |x - y| \leq \beta\} \) is \( O(\beta^3 \times \beta^2) \).

\(^{13}\) In fact one can prove then estimates \( O(\beta^3) \) but adding correction terms \( \sum \kappa_k \beta^{2k} \). However this improvement is not carried on to (2.2.15) in full.
Therefore we expect that the zone \( \mathcal{X}_1 \) defined by \( \mu \lesssim 1 \) could be expanded to the zone \( \mathcal{X}_1' \) defined by \( \mu \lesssim h^{-\frac{5}{12}} \) or even larger\(^{14}\); furthermore, under assumption \( |\nabla W| \asymp \zeta^2 \ell^{-1} \) we can define \( \mathcal{X}_1' \) by \( \mu \lesssim h^{-\frac{3}{8}} \) or even larger\(^{14}\).

### 2.2.3 Expansion: justification

Now however we need to deal with \( e(x, x, \nu) \) rather than \( P'_B(W(x) + \nu) \) (etc).

**Proposition 2.2.4.** Assume that in \( B(z, \gamma) \) conditions (2.2.10), \( \zeta \gamma \geq 1 \) and

\[
(2.2.17) \quad B \leq c \zeta^2 (\zeta \gamma)^{-\delta}
\]

are fulfilled. Then for \( \gamma \)-admissible \( \phi \)

\[
(2.2.18) \quad \int \phi(x) \left( e(x, x, \nu) - \tilde{P}'_B(W(x) + \nu) \right) dx = O(\zeta^2 \gamma^2),
\]

\[
(2.2.19) \quad \int \phi(x) \left( e_1(x, x, \tau) - \tilde{P}_B(W(x) + \nu) \right) dx = O(\zeta^3 \gamma)
\]

and

\[
(2.2.20) \quad D \left( \phi(x) \left( e(x, x, \nu) - \tilde{P}'_B(W(x) + \nu) \right) \right) \phi(x) \left( e(x, x, \nu) - \tilde{P}'_B(W(x) + \nu) \right) = O(\zeta^4 \gamma^3).
\]

**Proof.** Estimates (2.2.18) and (2.2.19) are due to Chapter 13. Really, rescale \( x \mapsto x \gamma^{-1}, \tau \mapsto \tau \zeta^{-2} \) and \( h = 1 \mapsto h = \gamma^{-1} \zeta^{-1}, B \mapsto \mu = B \gamma \zeta^{-1} \).

To prove (2.2.20) let us apply decomposition (2.1.8); then according to (2.2.18) \( J(t) \) (defined as expression (2.2.18) with \( t \gamma \)-admissible \( \phi_t \)) does not exceed \( C \zeta^2 \gamma^2 t^2 \) as long as \( t \zeta \gamma \geq 1 \); therefore contribution of zone \( \{(x, y) : |x - y| \approx t\} \) into the left-hand expression of (2.2.20) does not exceed \( C(\zeta^2 \gamma^2 t^2)^2 \times t^{-4} \gamma^{-1} \approx C \zeta^4 \gamma^3 \).

Then summation over \( t \geq \mu^{-1} = B^{-1} \gamma^{-1} \zeta \) returns \( C \zeta^4 \gamma^3 \int t^{-1} dt \approx C \zeta^4 \gamma^3 \log \mu \) (we assume that \( \mu \geq 2 \); case \( \mu \lesssim 2 \) has been covered already).

So, the total contribution of zone \( \{(x, y) : |x - y| \geq \mu^{-1}\} \) does not exceed \( C \zeta^4 \gamma^3 \log \mu \).

\(^{14}\) We do not need for each \( \ell \) have a sharp remainder estimates but need only them to sum to a sharp estimate.
Let us get rid off the logarithmic factor. Returning back to $B(z, t)$ stretched to $B(0, 1)$ one can see easily that conditions of proposition 13.6.25 are fulfilled as well with $T = \min(t^{-\delta}, h^{-\delta}t^{\delta})$ and thus $|J(t)| \leq C(h^{-1})^{-2}T^{-1} \leq Ch^{-2}t^2(t^{\delta} + h^{\delta}t^{-\delta})$. Plugging into (2.1.8) we get

$$Ch^{-4}\gamma^{-1}\int_{\mu^{-1}}^{1} t^{-1}(t^{\delta} + h^{\delta}t^{-\delta}) dt \sim Ch^{-4}\gamma^{-1} = C\zeta^{4}\gamma^{3}.$$ 

On the other hand, in zone $t \leq \mu^{-1}$ we use the trivial estimate

$$e(x, x, \nu) - P'(W(x) + \nu) = O(\mu\zeta^{2}\gamma^{2})$$

(due to simple rescaling $x \mapsto \mu x$) and its contribution to the left-hand expression of (2.2.20) does not exceed $C(\mu\zeta^{2}\gamma^{2}) \times \mu^{-2}\gamma^{-1} \sim C\zeta^{4}\gamma^{3}$. □

Combining with estimates (2.2.8) and (2.2.9) we arrive to the statement (i) below; combining with Proposition 2.1.7 to the statement (ii):

**Corollary 2.2.5.** Assume that in $B(z, \gamma)$ conditions (2.2.10) and $\zeta\gamma \geq 1$ are fulfilled. Let $\phi$ be $\gamma$-admissible function.

(i) Let

$$(2.2.21) \quad B \leq c\zeta^{\frac{4}{3}}\gamma^{-\frac{2}{3}};$$

then

$$(2.2.22) \quad \int \phi(x)(e(x, x, \nu) - \tilde{P}'(W(x) + \nu)) \, dx = O(\zeta^{2}\gamma^{2}),$$

$$(2.2.23) \quad \int \phi(x)(e_{1}(x, x, \tau) - \tilde{P}(W(x) + \nu)) \, dx = O(\zeta^{3}\gamma)$$

and

$$(2.2.24) \quad D\left(\phi(x)(e(x, x, \nu) - \tilde{P}'(W(x) + \nu)), \right.$$ 

$$\left.\phi(x)(e(x, x, \nu) - \tilde{P}'(W(x) + \nu))\right) = O(\zeta^{4}\gamma^{3});$$

(ii) Let assumption (2.2.11) be fulfilled and

$$(2.2.25) \quad B \leq c\zeta^{\frac{8}{3}}\gamma^{-\frac{2}{3}}.$$ 

Then (2.2.22)–(2.2.24) hold.
2.3 Rough approximation

Unless our analysis has been cut short with $r_1 \gtrsim (Z - N)^{-\frac{1}{2}}$, we need to consider zone \( \{ x : \ell(x) \geq r_1 \} \) with redefined $r_1$, so that this zone is described by $\mu \gtrsim \hbar^{-\frac{1}{2}}$ or $\mu \gtrsim \hbar^{-\frac{3}{2}}$ in the general or non-degenerate (i.e. satisfying assumption (2.2.11)) cases respectively.

In this zone we consider $\varepsilon\ell$-mollification with $\varepsilon \ll 1$. In contrast to potentials considered in Chapter 18 function $W_\theta^{TF}$ is more regular.

2.3.1 Properties of mollification

First, recall regularity properties of $W_\theta^{TF}$:

**Proposition 2.3.1.** $W_\theta^{TF}$ have the following properties:

\begin{align}
|\nabla^\alpha W_\theta^{TF}(x)| &\leq c_\alpha \zeta(x)^2 \ell(x)^{-|\alpha|} \quad \forall \alpha : |\alpha| \leq 2, \\
|\nabla^\alpha (W_\theta^{TF}(x) - W_\theta^{TF}(y))| &\leq c_0 B \ell(x)^{-\frac{3}{2}} |x - y|^\frac{1}{2} + c_0 \zeta(x)^2 \ell(x)^{-3} |x - y| \\
&\quad \forall |\alpha| = 2 \quad \forall x, y : |x - y| \leq \varepsilon \ell(x)
\end{align}

where we recall

\begin{align}
\zeta(x) &= \min(Z^{\frac{1}{2}} \ell(x)^{-\frac{1}{2}}, \ell(x)^{-2}) \quad \text{as} \quad B \leq Z^{\frac{1}{2}}; \\
\zeta(x) &= Z^{\frac{1}{2}} \ell(x)^{-\frac{1}{2}} \quad \text{as} \quad B \geq Z^{\frac{1}{2}};
\end{align}

**Proof.** This proof is rather obvious corollary of the Thomas-Fermi equation (1.1.3). See also arguments below. \(\square\)

Let us consider $B(z, \ell(z))$ with $\zeta^2 \gtrsim B$ and rescale $x \mapsto x \ell^{-1}$, $W \mapsto w = \zeta^{-2}(W + \nu)$ (where we included $\nu$ for a convenience). After such rescaling $w \in C^{\frac{1}{2}}$ uniformly, but there is more: Thomas-Fermi equation (1.1.3) translates into

\begin{align}
\frac{1}{4\pi} \Delta w = \ell^2 P_\beta'(w) = \ell^2 \zeta P'(w) + \ell^2 \zeta (P_\beta'(w) - P'(w))
\end{align}
with \( \beta = B \zeta^{-2} \); observe that \( P'_\beta(W) \) is positively homogeneous of degree \( 3 \) with respect to \((W, B)\).

Note that parameter \( \eta := \zeta \ell^2 \lesssim 1 \) and \( \eta \asymp 1 \) if and only if \( B \lesssim Z^{\frac{3}{2}} \) and \( \ell \gtrsim Z^{-\frac{1}{4}} \) (in which case \( \zeta \asymp \ell^{-2} \)).

Also note that the first term and the second terms in the right-hand expression of (2.3.5) belong to \( C^{\frac{3}{2}} \) and \( \beta \eta C^{\frac{3}{2}} \) respectively uniformly\(^{15}\) and

\[
\beta \eta = \beta \zeta \ell^2 = B \zeta^{-1} \ell^2, \quad \eta := \zeta \ell^2 \quad \text{as} \quad \beta \lesssim 1
\]

Because of this \( w \in C^{\frac{3}{2}} \oplus \beta \eta C^{\frac{3}{2}} \) again uniformly. Iterating we conclude that \( w \in C^n \oplus \beta \eta C^{\frac{3}{2}} \) with arbitrarily large exponent \( n \).

On the other hand, if \( B \gtrsim \zeta^2 \) (i.e. \( \beta \gtrsim 1 \)) without invoking \( P'_\beta \) one can prove easily that \( w \in \eta C^{\frac{3}{2}} \) with \( \eta := \beta \zeta \ell^2 = B \zeta^{-1} \ell^2 \) as \( \beta \gtrsim 1 \)

Therefore

\[
(2.3.6)' \quad \eta := \beta \zeta \ell^2 = B \zeta^{-1} \ell^2 \quad \text{as} \quad \beta \gtrsim 1
\]

and one can see easily that

\[
(2.3.7) \quad w \in C^n \oplus \beta \eta C^{\frac{3}{2}} \quad \text{with arbitrarily large exponent} \quad n \quad \text{as} \quad \beta \lesssim 1 \quad \text{and} \quad w \in \eta C^{\frac{3}{2}} \quad \text{as} \quad \beta \gtrsim 1
\]

Remark 2.3.2. It may seem strange to define \( \eta \) differently as \( \beta \lesssim 1 \) and \( \beta \gtrsim 1 \) but there is a good reason for this as we consider \( M \geq 2 \). Anyway, \( \eta \) is the magnitude of the right-hand expression of (2.3.5).

Proposition 2.3.3. (i) Let \( w_\varepsilon \) be a \( \varepsilon \)-mollification of \( w \) with \( \varepsilon \lesssim \min(\beta, h^4) \) (recall that \( h = 1/(\zeta \ell) \)). Then as \( \beta \lesssim 1 \)

\[
(2.3.9) \quad |\nabla^\alpha (w - w_\varepsilon)| \leq c_{\alpha, \beta} \eta \varepsilon^{\frac{5}{2} - |\alpha|} \quad \forall \alpha : |\alpha| \leq 2,
\]

\[
(2.3.10) \quad |P_\beta(w) - P_\beta(w_\varepsilon)| \leq c \beta \eta \varepsilon^{\frac{5}{2}}
\]

and

\[
(2.3.11) \quad |P'_\beta(w) - P'_\beta(w_\varepsilon)| \leq c \beta^2 \eta \varepsilon^{\frac{3}{2}} + c \beta \eta \varepsilon^{\frac{5}{2}};
\]

\(^{15}\) I.e. norms do not depend on any parameters.
(ii) On the other hand as $\beta \gtrsim 1$ the right-hand expressions of (2.3.9)–(2.3.11) should be replaced by similar expressions albeit without $\beta$:

$$(2.3.9)' \quad |\nabla^\alpha (w - w_\epsilon)| \leq c_\alpha \eta \varepsilon^{\frac{5}{2} - |\alpha|}, \quad \forall \alpha : |\alpha| \leq 2,$$

$$(2.3.10)' \quad |P_\beta (w) - P_\beta (w_\epsilon)| \leq c \eta \varepsilon^{\frac{5}{2}},$$

and

$$(2.3.11)' \quad |P_\beta' (w) - P_\beta' (w_\epsilon)| \leq c \eta \varepsilon^{\frac{5}{2}}.$$

(iii) Further, under assumption $|\nabla w| \asymp 1$ in both cases

$$(2.3.12) \quad |\int \phi(x)(P_\beta (w) - P_\beta (w_\epsilon)) \, dx| \leq c \eta \varepsilon^{\frac{7}{2}},$$

$$(2.3.13) \quad |\int \phi(x)(P_\beta' (w) - P_\beta' (w_\epsilon)) \, dx| \leq c \eta \varepsilon^{\frac{7}{2}}$$

and

$$(2.3.14) \quad D(\phi(P_\beta' (w) - P_\beta' (w_\epsilon)), \phi(P_\beta' (w) - P_\beta' (w_\epsilon))) \leq c \eta^2 \varepsilon^{\frac{9}{2}}.$$

Proof. Proof of (i) is trivial; in particular we note that $\eta \varepsilon^{\frac{3}{2}} \lesssim \beta$.

Proof of (iii) is also easy as then $w_\epsilon$ is different from $w$ on the set of measure $\asymp \beta^{-1} \varepsilon$ as $\beta \leq C_0$ and on the set of measure $\asymp \varepsilon$ as $\beta \geq C_0$. Actually $w$ is uniformly smooth as $\beta \gtrsim 1$ and $\ell(x) \leq \epsilon \bar{r}$ and we do not need any mollification here.

One definitely can improve estimates (2.3.12)–(2.3.14) but we do not need it.

Consider now the analytical expressions and estimate the semiclassical errors. From now on until the end of this Subsection we assume that $M = 1$ to avoid possible degenerations.

Remark 2.3.4. Note that we can reduce operator to a canonical form as $\varepsilon \geq C(\mu^{-1} \hbar)^{\frac{3}{2}} |\log \mu|$ (see Section 18.7) but here we will have a much better estimate as we will take $\varepsilon \geq \hbar^{\frac{3}{2} - \delta}$.

2.3.2 Charge term

Let us consider the charge term i.e. expression $\int e(x, x, \nu) \, dx = (\text{Tr} \theta (\nu - H))$. 

35
Regular zone.

Then the results of Section 18.9 implies that as

\[(2.3.15) \quad W + \nu \asymp \zeta^2\]

and

\[(2.3.16) \quad |\nabla W| \asymp \zeta^2\ell^{-1}\]

corresponds to the ball \(B(x, \ell(x))\) to expression (2.2.2) does not exceed

\[C(1 + \mu h)h^{-2} \asymp C\zeta^2\ell^2 + CB\ell^2\]

exactly as in the mock proof.

Then summation with respect to \(\ell\)-partition in this zone results in \(CB\) as \(B \leq Z, CZ\) as \(Z \leq B \leq Z^\frac{3}{2}\), and \(CBZ\) as \(Z^\frac{3}{2} \leq B \leq Z^3\).

**Remark 2.3.5.** (i) Condition (2.3.15) is fulfilled as \(\ell(x) \leq \epsilon r\).

(ii) Further, as \(M = 1\) both conditions (2.3.15) and (2.3.16) are fulfilled as \(|x| \leq (1 - \epsilon)\bar{r}_m\) (we pick up \(y_m = 0\) and \(\bar{r}_m\) exact radii of \(\text{supp } \rho_B\)).

Border strip.

Now we need to consider the contribution of the border strip \(Y := \{x: \gamma(x) \leq \epsilon\}\) with \(\gamma(x) = \epsilon(\bar{r} - |x|)\bar{r}^{-1}\) and \(\bar{r} := \bar{r}_m\). Here \(\ell \asymp \bar{r}, \zeta \asymp \bar{\zeta}\) with

\[(2.3.17) \quad \bar{r} \asymp \begin{cases} (Z - N)^{\frac{1}{3}}_+ & \text{as } B \leq (Z - N)^{\frac{4}{3}}_+, \\ B^{-\frac{2}{3}} & \text{as } (Z - N)^{\frac{4}{3}}_+ \leq B \leq Z^\frac{2}{3}, \\ Z^\frac{3}{2}B^{-\frac{2}{3}} & \text{as } Z^\frac{3}{2} \leq B \leq CZ^3 \end{cases}\]

and

\[(2.3.18) \quad \bar{\zeta} \asymp \begin{cases} (Z - N)^{\frac{2}{3}}_+ & \text{as } B \leq (Z - N)^{\frac{4}{3}}_+, \\ B^{\frac{1}{3}} & \text{as } (Z - N)^{\frac{4}{3}}_+ \leq B \leq Z^{\frac{4}{3}}, \\ Z^\frac{3}{2}B^{\frac{1}{3}} & \text{as } Z^\frac{3}{2} \leq B \leq CZ^3 \end{cases}\]

and scaling we get \(\mu = B\bar{r}\bar{\zeta}^{-1}\) and \(h = \bar{\zeta}^{-1}\bar{r}^{-1}\) here.

Let us consider first the case \(\nu = 0\). Then both conditions (2.3.15) and (2.3.16) are fulfilled albeit with \(\ell_1 = \gamma(x)\bar{r}\) and \(\zeta(x) = \bar{\zeta}\gamma(x)^2\) instead of \(\ell\) and \(\zeta\).
Thus as \( \zeta \ell_1 \geq 1 \) (i.e. \( \gamma \geq \bar{\gamma} := \hbar^{\frac{3}{2}} \)) the contribution of the ball \( B(x, \gamma(x)\bar{r}) \) to the remainder does not exceed \( C\mu h^{-1}\gamma^2 \) and therefore the total contribution of zone \( \mathcal{Y}_1 := \{ x : \bar{\gamma} \leq \gamma(x) \leq \epsilon \} \) to the remainder does not exceed

\[
(2.3.19) \quad C\mu h^{-1} \int \gamma(x)^{-1} dx \asymp C\mu h^{-1}|\log h| = CB\bar{r}^2|\log h|
\]

which is \( O(Z^{\frac{3}{2}}) \) as long as \( B \leq Z^{\frac{1}{2}}(\log Z)^{-2} \).

Further, the same approach works as \( |\nu| \lesssim \bar{\zeta}^2\bar{\gamma}^3 \asymp \bar{\zeta}^2 \hbar \asymp \bar{\zeta} \bar{r}^{-1} \) which is equivalent to \( (Z - N)_+ \leq \bar{\zeta} \) (then \( |\nabla W| \asymp \bar{\zeta}^2 \ell_1^{-1} \) as \( \gamma(x) \geq \bar{\gamma} \)) and also if this condition is violated but \( |\nu| \leq \bar{\zeta}^2 \); in the latter case we need to pick up \( \bar{\gamma} = \bar{\gamma}_1 := |\nu|^{\frac{1}{3}}\bar{\zeta}^{-\frac{2}{3}} \).

To get rid off the logarithmic factor let us consider propagation. Recall that it goes along magnetic lines i.e. as \( (x_1, x_2) \) remain constant. Let us consider propagation in the direction in which \( |x_3| \) increases (i.e. \( \gamma(x) \) decays); we do not need to consider zone \( \mathcal{Y}_1 \cap \{ |x_3| \leq Z^{-\delta}\bar{r} \} \) as contribution of this zone \( (2.3.19) \) is \( o(B\bar{r}^2) \).

One can see easily that we can follow dynamics which does not return for a time \( T_1(x) := T_1(x)(\gamma(x)/\bar{\gamma})^\delta \) where \( T(x) \asymp \ell_1^{-1} - \bar{r} = \bar{r}\bar{\zeta}^{-1} \) is a time required for this dynamics to pass through \( B(x, \ell_1(x)) \). Therefore one can replace \( (2.3.19) \) by

\[
(3.2.20) \quad C\mu h^{-1} \int_{\{ x : \gamma(x) \geq \bar{\gamma} \}} \bar{\gamma}^\delta \gamma(x)^{-1-\delta} dx \asymp C\mu h^{-1} = CB\bar{r}^2.
\]

Further, as \( |\nu| \geq B\bar{r} \) we need also to consider zone \( \mathcal{Y}_0 := \{ x : \gamma(x) \leq \bar{\gamma} \} \).

In this zone we take \( \ell_1 = \bar{\ell}_1 = \bar{\gamma}\bar{r} \) and \( \zeta = \bar{\zeta} = (|\nu|\bar{\gamma})^{\frac{1}{2}} \) with \( \ell_1\zeta \geq 1 \) and since \( |\nabla W| \asymp \zeta\ell_1^{-1} \), contribution of \( B(x, \ell_1(x)) \) to the remainder does not exceed \( CB\bar{r}^2 \) and the total contribution of \( \mathcal{Y}_2 \) does not exceed \( CB\bar{r}^2 \) which what exactly we achieved for zone \( \mathcal{Y}_1 \) after we got rid off logarithm. We take mollification parameter \( \varepsilon = \bar{\gamma}^{\frac{1}{3}}Z^{\delta} \).

Furthermore, zone \( \mathcal{Y}_3 = \{ x : |x| \geq \bar{r} + \bar{\ell}_1 \} \) is classically forbidden. So we can take here

\[
(3.2.21) \quad \ell_1(x) = \epsilon(|x| - \bar{r}), \quad \zeta(x) = \min(\bar{\zeta}\ell_1^{\frac{1}{2}}\ell_1(x)^{\frac{1}{2}}, |\nu|^{\frac{1}{2}})
\]

\[\text{\footnotesize 16} \) Really, after additional rescaling \( x \mapsto x\gamma^{-1}, w \mapsto w\gamma^{-2} \) we have \( \mu_1 = \mu_\gamma^{-1}, h_1 = \hbar\gamma^{-3} \) and \( \mu_1 h_1^{-2} = \mu\hbar^{-1}\gamma^{-2} \).

\[\text{\footnotesize 17} \) One can see easily that the resulting errors in the expressions \( (2.2.2) \) and \( (2.2.3) - (2.2.4) \) will not violate our claims.
and prove easily that its contribution also does not exceed \( CB\bar{r}^2 \).

Returning to the case \(|\nu| \lesssim \zeta\) we see that the contribution of zone \( \mathcal{Y}_2 \) to the remainder does not exceed \( CB\bar{r}^2 \) because effective semiclassical parameter here is \( \hbar_1 = 1 \) and non-degeneracy condition is of no concern for us. We take mollification parameter \( \varepsilon = \zeta^{-1}Z^{\delta} \).

Moreover, we can modify \( W \) in \( \mathcal{Y}_2 \) (make it negative there) so that this zone would be classically forbidden with \( \ell_1, \varsigma \) defined by (2.3.21) with \(|\nu| \) replaced by \( \zeta \).

Finally in the case \( B \leq |\nu| \) (i.e. \( B \leq C(Z - N)^{\frac{4}{3}} \)) we can apply the above arguments with \( \bar{\gamma} = 1 \) and arrive to the same result. Therefore we proved in all cases:

\[
\text{(2.3.22) As } M = 1 \text{ the total contribution of the border strip } \mathcal{Y} \text{ to the remainder in the charge term is } O(B\bar{r}^2) \text{ which does not exceed } CB\bar{r}^2 \text{ as } B \leq Z^{\frac{1}{3}} \text{ and } CB^{\frac{1}{3}}Z^{\frac{2}{3}} \text{ as } Z^{\frac{1}{3}} \leq B \leq Z.
\]

**Conclusion.**

As \( Z^{\frac{2}{3}} \leq B \leq Z \) we need to estimate also contribution of the *inner core* \( \mathcal{X}_0 := \{x: \ell(x) \leq CZ^{-1}\} \). By means of variational methods we will prove (see Corollary 8.B.2)

\[
\text{(2.3.23) As } Z^{\frac{2}{3}} \leq B \leq Z \text{ the contributions of } \mathcal{X}_0 \text{ to both } \int e(x, x, \nu) \, dx \text{ and } \int P_B(W(x) + \nu) \, dx \text{ do not exceed } CBZ^{-2}.
\]

Then we arrive to the following

**Proposition 2.3.6.** Let \( M = 1 \). Then

(i) For constructed above potential \( W \) expression (2.2.2) does not exceed \( CZ^{\frac{2}{3}} + CB^{\frac{1}{3}}Z^{\frac{2}{3}} \);

(ii) As \( B \leq Z \) expression (2.2.2) does not exceed \( C(B + 1)^{\delta}Z^{\frac{2}{3} - \delta} \).

### 2.3.3 Trace term

Let us consider the *trace term* i.e. expression \( \int e_t(x, x, \nu) \, dx = \text{Tr}((H - \nu)^{-}) \).
Regular zone.
Here again let us consider first zone where \(|x| \leq (1 - \epsilon)\bar{r}\). Then the contribution of \(B(x, \ell(x))\) to the Tauberian remainder\(^{18}\) does not exceed \(C\zeta^2(h^{-1} + \mu) \simeq C\zeta^3 \ell + CB\zeta \ell\) as in the mock proof and the summation over zone results in \(CZ^{\frac{3}{2}} + CB\zeta Z^{\frac{3}{2}} + CZ^{\frac{3}{2}} B^{\frac{3}{2}}\).

Border strip.
Again in zone \(\mathcal{Y}_1\) contribution of \(B(x, \gamma(x))\) does not exceed \(CB\zeta \ell_1\) and the summation over this zone returns
\[
(2.3.24) \quad CB \int \zeta \ell_1^{-2} dx
\]
and plugging \(\ell_1 = \bar{r}\gamma\) and \(\zeta = \bar{\zeta}\gamma^2\) results in \(CB\zeta\) as \(B \lesssim Z^{\frac{1}{2}}\) and \(CB\zeta Z^{\frac{1}{2}}\) otherwise. The analysis of zone \(\mathcal{Y}_0\) if there \(\mathcal{Y}_2 = \emptyset\) is also easy.

Consider zones \(\mathcal{Y}_2\) and \(\mathcal{Y}_0\). The same arguments as before imply that their contributions to the remainder do not exceed \(CB\bar{r}\zeta \ell_1^{-1}\) which is what we got before.

Justification: from Tauberian to magnetic Weyl expression.

Case \(\mu h \leq C_0\). We need to prove that with the announced error we can replace the Tauberian expression by magnetic Weyl one. Note that the canonical form of \(\zeta^{-2} H_{A,W}\) as described in Sections 13.2 and 18.7 is
\[
(2.3.25) \quad \mathcal{H} = \mathcal{H}_0 + \\
m^{-2}\omega_1(x_1, \mu^{-1}hD_1, x_3) + m^{-2}\omega_2(x_1, \mu^{-1}hD_1, x_3)(x_2^2 + \mu^2h^2D_2^2) \\
\quad + m^{-1}h\omega_3(x_1, \mu^{-1}hD_1, x_3) + O(m^{-3}h(\gamma + \mu^{-1})^{-\frac{3}{2}} + m^{-4})
\]
with
\[
(2.3.26) \quad \mathcal{H}_0 = h^2D_3^2 - (x_2^2 + \mu^2h^2D_2^2 \pm \mu h) + w(x_1, \mu^{-1}hD_1, x_3)
\]
and
\[
(2.3.27) \quad \gamma = \epsilon \min_j |w - 2j\mu h|
\]
\(^{18}\) We will consider a bit later transition from the Tauberian to magnetic Weyl expression.
where we used the fact that $w \in \mu h\mathcal{C}^{\frac{3}{2}} + \mathcal{C}^{n}, \mu^{-3}h = \mu^{-4} \cdot \mu h$. Here we have signs “+” and “−” on $a/2$ of the diagonal elements equally.

Then the Tauberian expression is

$$
(2.3.28) \quad \text{const} \cdot \mu h^{-2} \int \sum_{j \geq 0} (w - 2j\mu h - \mu^{-2}\omega_1 - 2j\mu^{-1}h\omega_2) \frac{3}{4} \times

(\psi + \mu^{-2}\psi_1 + 2j\mu^{-1}h\psi_2) \, dx
$$

where term with $j = 0$ enters with the weight $\frac{1}{2}$ and an error does not exceed

$$
C h^{-3} \left( \mu^{-4} + \mu^{-3}h \int (\gamma + \mu^{-1})^{-\frac{3}{2}} \, dx \right) \lesssim C \mu^{-\frac{7}{2}} h^{-3}
$$

because an integral does not exceed $C \mu^{\frac{1}{2}}(\mu h)^{-1}$; since $\mu \geq h^{-\frac{3}{5}}$ this error does not exceed $C h^{-\frac{9}{5}}$ which is better than $O(h^{-1})$.

On the other hand, if we consider the difference between (2.3.28) and the same expression with $\omega_1 = \omega_2 = \psi_1 = \psi_2 = 0$ and consider it as a Riemannian sum and replace it by an integral we get $G \mu^{-2}h^{-3}$ with an error not exceeding $C \mu^{-4}(\mu h)\frac{3}{4}h^{-3}$ which is even less. Therefore (2.3.28) becomes

$$
\int P_{\mu h}(w) \psi \, dx + G \mu^{-2}h^{-3}
$$

and comparing with the result as $\mu \asymp h^{-\frac{3}{5}}$ when we get the same answer albeit with $G = 0$ we conclude that $G$ must be 0. This concludes the justification in $\mathcal{X}_2$.

**Case** $\mu h \geq C_0$. In this case we need a simplified version of (2.3.25) $\mathcal{H} = \mathcal{H}_0 + O(\mu^{-1}h)$ and we need to consider only $j = 0$ and replacing $\mathcal{H}$ by $\mathcal{H}_0$ brings and error $C \mu h^{-2} \times \mu^{-1}h = O(h^{-1})$. This takes care of $\mathcal{X}_2$ and after scaling of $\mathcal{Y}$.

**Conclusion.**

As $Z^2 \leq B \leq Z^3$ we need to estimate also contribution of $\mathcal{X}_0 = \{x : \ell(x) \leq CZ^{-1}\}$. By means of variational methods we will prove (see Corollary 8.B.2)

$$
(2.3.29) \quad \text{As } Z^2 \leq B \leq Z^3 \text{ the contributions of } \mathcal{X}_0 \text{ to both } \int e_1(x, x, \nu) \, dx \text{ and } \int P'_B(W(x) + \nu) \, dx \text{ do not exceed } CB.
$$
Then we arrive to the following

**Proposition 2.3.7.** Let $M = 1$. Then

(i) For constructed above potential $W$ expression (2.2.4) does not exceed $CZ^\frac{5}{2} + CB\frac{1}{2}Z^\frac{3}{2} + CZ\frac{1}{2}B\frac{1}{2}$;

(ii) As $B \leq Z$ expression (2.2.4) does not exceed $C(B + 1)^{\delta}Z^{\frac{5}{2} - \delta}$ (but one should subtract a Schwinger term from the trace).

### 2.3.4 Semiclassical D-term: local theory

Unfortunately, we do not have non-smooth theory (cf. Section 16.7) here but actually we almost do not need it as singularities are rather rare. Let us introduce a scaling function (2.3.27) and consider

\[(2.3.30) \quad J_\lambda(z) = \int \phi_{z,\lambda}(x)(e(x, x, \tau) - P_\beta(w(x) + \tau)) \, dx\]

with $\phi_{z,\lambda}(x) = \phi(\lambda^{-1}(x - z))$ and $\lambda \leq \gamma(z)$. Scaling $x \mapsto \lambda^{-1}(x - z)$ we have $\mu \mapsto \mu' = \lambda\mu$ and $\hbar \mapsto \hbar' = \lambda^{-1}\hbar$.

Then, according to Section 13.4

\[(2.3.31) \quad |J_\lambda(z)| \leq C\hbar'^{-2}(1 + \mu'h') \precsim C\lambda^2\hbar^{-2}(1 + \mu\hbar)\]

as long as $\lambda \geq \hbar$.

Really, transition from the Tauberian decomposition to magnetic Weyl one in this case is easy: skipping all perturbation terms $O(\mu^{-2} + \mu^{-1}\hbar)$ in (2.3.25) and also setting $\psi_1 = \psi_2 = 0$ results in error $O(\mu^{-2}\hbar^{-3} + \hbar^{-1})$ in (2.3.28)-like expression albeit with the power $\frac{1}{2}$ rather than $\frac{3}{2}$ and without integration:

\[(2.3.32) \quad \text{const} \cdot \mu\hbar^{-2} \sum_{j \geq 0} \left( w - 2j\mu\hbar - \mu^{-2}\omega_1 - 2j\mu^{-1}\hbar\omega_2 \right)^{\frac{1}{2}} \times \]

\[\left( \psi + \mu^{-2}\psi_1 + 2j\mu^{-1}\hbar\psi_2 \right); \]

scaling produces expression smaller than (2.3.31).

Let us apply this estimate (2.3.31) to the Fefferman–de Llave decomposition (2.1.8).
Case $\mu \leq C_0 h^{-1}$.

(i) Consider first a pair $(z, z')$ such that $|z' - z''| \leq \epsilon_0 \gamma(z')$; then also $|z' - z''| \leq \epsilon_0 \gamma(z'')$ and we take $\lambda = \epsilon|z' - z''|$. Then in the virtue of (2.3.31) the total contribution to D-term of all such pairs belonging to $B(z, \gamma(z))$, and with $|z' - z''| \approx \lambda$ does not exceed

$$C \gamma^3 \lambda^{-3} \times \lambda^{-1} \times \lambda^2 h^{-4}(1 + \mu h)^2 \approx C \gamma^3 h^{-4}(1 + \mu h)^2$$

where $C \gamma^3 \lambda^{-3}$ estimate the number of such pairs, $\lambda^{-1}$ the inverse distance between them, and $C \lambda^2 h^{-2}(1 + \mu h)$ is the right-hand expression of (2.3.31).

Then summation over $\lambda \in (\mu^{-1}, \gamma)$ results in $C \gamma^3(1 + \mu h)^2 h^{-4} |\log(\mu \gamma)|$.

Further, summation over all balls $B(z, \gamma) \subset B(0,1)$ with $\gamma(z) \asymp \gamma$ results in $C(\mu h)^{-1} \gamma |\log(\mu \gamma)|$ as there are $\asymp (\mu h)^{-1} \gamma^{-2}$ such balls due to non-degeneracy assumption $|\nabla w| \asymp 1$. Summation over $\gamma \in (\mu^{-1}, \mu h)$ results in $C h^{-4} |\log(\mu h)|$.

As $\lambda \leq \mu^{-1}$ we can apply standard non-magnetic methods without Fefferman–de Llave decomposition (2.1.8). Coefficients are smooth after scaling as long as $\epsilon \geq \mu^{-1}$.

(ii) Consider disjoint pairs $(z', z'')$ with $|z' - z''| \geq \max(\gamma(z'), \gamma(z''))$. Here estimate (2.3.31) is not sufficient and it should be replaced by

$$|J_{\gamma}(z)| \leq C \lambda^2 h^{-2}(1 + \mu h)$$

as

$$\gamma \geq h^{\frac{3}{2} - \delta}.$$

Really, the shift for time $T$ with respect to $\xi_3$ is $\asymp T$ provided $|\nabla x_i w| \asymp 1$ and this shift is observable if $T \times \gamma \gtrsim h^{1-\delta}$. Similarly, in the canonical form the shift for time $T$ with respect to $\mu^{-1} \xi_i$ is $\asymp \mu^{-1} T$ provided $|\nabla x_i w| \asymp 1$ and this shift is observable if $\mu^{-1} T \times \gamma \gtrsim \mu^{-1} h^{1-\delta}$. In both cases shift with $T \in (\gamma^{\frac{3}{2}}, \epsilon_0)$ is observable under assumption (2.3.35) and therefore we can extend $T \asymp \gamma^{\frac{3}{2}}$ to $T \asymp 1$.

Note that for $\epsilon \geq h^{\frac{3}{2} - \delta}$ assumption (2.3.35) is fulfilled automatically. Then contribution of each disjoint pair to D-term does not exceed

$$C h^{-4}(1 + \mu h)^2 \gamma(z')^3 \gamma(z'')^3 |z' - z''|^{-1}$$
and the total contribution does not exceed

$$Ch^{-4}(1 + \mu h)^2 \int \int |z' - z''|^{-1} dz' dz'' \leq Ch^{-4}(1 + \mu h)^2.$$ 

(iii) To shed off logarithm in (i) we need a slightly better estimate than (2.3.31). The same arguments as in (ii) result in

$$(2.3.36) \quad |J_\lambda(z)| \leq C\lambda^2 h^{-2}(1 + \mu h) \cdot (1 + \lambda \gamma/h)^{-\delta}.$$ 

Really, we just advance from time $T \asymp \lambda$ to $T \asymp \lambda(1 + \lambda \gamma/h)^\delta$.

Then the same factor is acquired by the right-hand expression of (2.3.33) and the summation with respect to $\lambda \in (h \gamma^{-1}, \gamma)$ results in $C\gamma^3(1 + \mu h)^2 h^{-4}$ but summation with respect to $\lambda \in (\mu^{-1}, h \gamma^{-1})$ results in $C\gamma^3(1 + \mu h)^2 h^{-4}(1 + |\log(\mu h \gamma^{-1})|)$.

Further, summation over all balls $B(z, \gamma) \subset B(0, 1)$ with $\gamma(z) \asymp \gamma$ results in $C(\mu \lambda)^{-1}\gamma(1 + \mu h)^2 h^{-4}(1 + |\log(\mu h \gamma^{-1})|)$ and, finally, summation over $\gamma \lesssim \mu h$ results in $Ch^{-4}(1 + \mu h)^2$.

Note that in all cases perturbation terms in (2.3.25) and (2.3.32) result in the error not exceeding the announced one.

**Case** $\mu \geq C_0 h^{-1}$. So far factor $(1 + \mu h)$ was for compatibility only. Now it is important.

Exactly the same arguments work as $\mu \geq C_0 h^{-1}$ with a minor modifications:

(a) $\gamma(x)$ now is defined by (2.3.27) with $j = 0$ and its upper bound is 1 rather than $\mu h$;

(b) Also the number of $\gamma$-balls is $\asymp \gamma^{-2}$ rather than $\asymp (\mu h)^{-1}\gamma^{-2}$;

(c) $\lambda$ now runs from $h$ to $\gamma$ in (i), (iii).

(d) We need to estimate contribution of pairs $(z', z'')$ with $|z' - z''| \leq h$. One can see easily that $e(x, x, \tau) \leq \mu h^{-2}$ and therefore the total contribution of these pairs does not exceed $C\mu^2 h^{-4} \int \int |z' - z''|^{-1} dz' dz'' \asymp C\mu^2 h^{-4} \times h^2 \asymp C\mu^2 h^{-2}$.
Therefore we have the following

**Proposition 2.3.8.** As \(|\nabla w| \asymp 1\) and \(\varepsilon \geq h^{2-\delta}\) in \(B(0,1)\) and \(\phi \in C^\infty(B(0,\frac{1}{2}))\)

\[
(2.3.37) \quad D\left(\phi(e(x,x,\tau) - P_\beta^r(w(x) + \tau)), \phi(e(x,x,\nu) - P_\beta^r(w(x) + \tau)\right) \leq C(1 + \mu h)h^{-4}.
\]

**Remark 2.3.9.** One can see easily that one can select \(\varepsilon \geq h^{2-\delta}\) such that expressions (2.3.12), (2.3.13) and (2.3.13) will be respectively \(O(h^{2+\delta})\), \(O(h^{1+\delta})\) and \(O(h^{2+\delta})\).

### 2.3.5 Semiclassical \(\mathcal{D}\)-term: global theory

**Regular zone.**

The above results allow us to consider a total contribution of zone \(X_2\) into semiclassical \(\mathcal{D}\)-term. As before let us consider \(\ell\)-admissible partition of unity there and apply it to Fefferman–de Llave decomposition (2.1.8). Then the total contribution of the elements which are not disjoint does not exceed

\[
(2.3.38) \quad \sum_n \ell_n^{-1}(1 + B\zeta_n^{-2})^2 \ell_n^4 \zeta_n^4 \asymp \int (\tilde{\zeta}^4 + B^2)\ell^3 \ell^{-1} d\ell
\]

where \((1 + B\zeta_n^{-2})^2\) and \(\ell_n^4 \zeta_n^4\) are \((1 + \mu h)\) and \(h^{-4}\) respectively and \(\ell_n^{-1}\) is a scaling factor.

Then as \(\zeta^2 = Z\ell^{-1}\) an integral equals to the value of the selected expression as \(\ell\) reaches its maximum, i.e. as \(\ell = Z^{-\frac{1}{2}}\) for \(B \leq Z^\frac{1}{2}\) and \(\ell = Z\frac{1}{2}B^{-\frac{1}{2}}\) for \(Z^\frac{1}{2} \leq B \leq Z^3\) and we arrive to \(CZ^\frac{3}{2}\) and \(CZ^\frac{3}{2}B^\frac{1}{2}\) respectively.

On the other hand, as \(\zeta^2 = \ell^{-4}\) an integral equals to the value of the selected expression as \(\ell\) reaches its minimum, i.e. \(\ell = Z^{-\frac{1}{2}}\) and only in the case \(B \leq Z^\frac{3}{2}\) and we arrive to \(CZ^\frac{3}{2}\) again.

Furthermore, the total contribution of the disjoint elements does not exceed

\[
(2.3.39) \quad \sum_{n,p} |z_n - z_p|^{-1}(1 + B\zeta_n^{-2})(1 + B\zeta_p^{-2})\ell_n^2 \ell_p^2 \zeta_n^2 \zeta_p^2 \asymp \int \int (\ell + \ell')^{-1}(\zeta^2 + B)\ell^2 (\zeta'^2 + B)\ell'^2 \ell^{-1} d\ell \ell^{-1} d\ell'.
\]
Then as $\zeta^2 = Z\ell^{-1}$ and $\zeta'^2 = Z\ell'^{-1}$ an integral equals to the value of the selected expression as both $\ell$ and $\ell'$ reach their maxima, and we arrive to $CZ^\frac{3}{4}$ and $C\frac{1}{2}Z^\frac{3}{4}B^\frac{1}{2}$ respectively.

On the other hand, as $\zeta^2 = \ell^{-4}$ and $\zeta'^2 = \ell'^{-4}$ (we do not need to consider mixed pair) an integral equals to the value of the selected expression as both $\ell$ and $\ell'$ reach their minima, and we arrive to $CZ^\frac{1}{4}$.

Therefore (combining with proposition 8.B.2 as $Z^2 \leq B \leq Z^3$) we arrive to

**Proposition 2.3.10.** Let $M = 1$. Then

(i) The total contribution of the zone $\{ x : \ell(x) \leq (1 - \epsilon)\bar{r} \}$ to the semiclassical D-term does not exceed $CZ^\frac{3}{4}$ and $C\frac{1}{2}Z^\frac{1}{4}B^\frac{1}{2}$ as $B \leq Z^\frac{3}{4}$ and $Z^\frac{1}{4} \leq B \leq Z^3$ respectively;

(ii) As $B \leq Z$ this contribution does not exceed $C(B + 1)^{\frac{1}{2}}Z^{3 - \frac{1}{2}}$.

**Border strip.**

Border strip $\mathcal{Y} = \{ x : (1 - \epsilon)\bar{r} \leq \ell(x) \leq (1 + \epsilon)\bar{r} \}$ is more subtle. Here we need to use the same $\ell_1(x) = \epsilon_0(\bar{r} - |x|)$ partition as before.

**Remark 2.3.11.** $\mathcal{Y}$ is already covered by our arguments if $\bar{r} \asymp (Z - N)^{-\frac{3}{4}}$.

**Close elements.** Consider first contribution of elements which are not disjoint. It is given by the left-hand expression of (2.3.38) with $\ell$, $\zeta$ replaced by $\ell_1(x) = \bar{\gamma}(x)$ and $\zeta(x) = \bar{\zeta} \gamma(x)^2$ respectively. However since the layer $\{ x : \gamma(x) \asymp \gamma \}$ contains $\asymp \gamma^{-2}$ elements the right-hand expression should be replaced by

$$\int B^2\bar{\gamma}^3 \gamma^{-1}d\gamma \asymp B^2\bar{r}^3$$

since $\zeta^2 \leq B$; so we arrive to $O(\max(B^\frac{3}{2}, Z^\frac{1}{2}B^\frac{1}{2})).$

Meanwhile for $\mathcal{Y}_2$ we have $\gamma(x) = \bar{\gamma} \leq 1$ and $\zeta(x) = \bar{\zeta} = \bar{\zeta} \gamma^2$ and its contribution does not exceed what we got for $\mathcal{Y}_1$.

**Disjoint elements.** Consider contribution of the disjoint elements. It is given by the left-hand expression of (2.3.39) with $\ell$, $\zeta$ replaced by $\gamma$ and $\varsigma$ respectively. Note that $\sum_{n,p} |z_n - z_p|^{-1} \asymp \bar{r}^{-1}\gamma^{-2}\gamma'^{-2}$ where we sum with
respect to all pairs with \( \gamma_n \approx \gamma \) and \( \gamma_p \approx \gamma' \). Therefore the right-hand expression should be replaced by

\[
\int \tilde{r}^3 B^2 \gamma^{-1} d\gamma \gamma'^{-1} d\gamma'
\]

which leads to \( C\tilde{r}^3 B^2 |\log(\tilde{r}^{-1}\tilde{x})|^2 \) which differs from what we got before by a logarithmic factor. To get rid off it we will use exactly the same trick as in paragraph “Border strip” proving proposition 2.3.6 because considering disjoint pairs we consider the same objects as there. Then instead of (2.3.40) we arrive to

\[
\int \tilde{r}^3 B^2 \gamma^{-\delta} \gamma'^{-\delta} \gamma^\delta \gamma'^\delta \gamma^{-1} d\gamma \gamma'^{-1} d\gamma'
\]

which results in \( C\tilde{r}^3 B^2 \).

Meanwhile for \( \mathcal{Y}_2 \) we have \( \gamma(x) = \tilde{\gamma} \leq \tilde{r} \) and \( \zeta(x) = \tilde{\zeta} = \tilde{\zeta}^2 \) and its contribution does not exceed what we got for \( \mathcal{Y}_1 \).

**Conclusion.** Finally, analysis in the outer zone is trivial. Therefore we arrive

**Proposition 2.3.12.** Let \( M = 1 \). Then for constructed above potential \( W \)

(i) Expression (2.2.3) does not exceed \( CZ^\frac{5}{4} + CZ^\frac{1}{2} B^\frac{3}{4} \);

(ii) As \( B \leq Z \) expression (2.2.3) does not exceed \( C(B + 1)^{\delta} Z^\frac{5}{4} - \delta \).

3 Applying semiclassical methods: \( M \geq 2 \)

Let us consider now the molecular case (\( M \geq 2 \)). The major problem is that non-degeneracy condition \( |\nabla w| \approx 1 \) is not necessarily fulfilled. Therefore we need to find an alternative approach to the zone where \( \mu \geq h^{-\frac{1}{3}} \). Recall that it consists of three zones: zone \( \mathcal{X}_2 := \{\mu h \leq C_0, \ W_{B}^{\text{TF}} \geq \epsilon_0 \zeta^2\} \), zone \( \mathcal{X}_3 := \{\mu h \geq C_0, \ W_{B}^{\text{TF}} \geq \epsilon_0 \zeta^2\} \), and the (most difficult) boundary strip \( \mathcal{Y} = \{W_{B}^{\text{TF}} \leq \epsilon_0 \zeta^2\} \), which we leave for the next Section 4.

19) Only as \( B \leq C_1 Z^2 \); this zone disappears for \( C_1 Z^2 \leq B \lesssim Z^3 \).
20) Only as \( Z^\frac{3}{4} \lesssim B \lesssim Z^3 \); this zone disappears for \( B \lesssim Z^\frac{7}{4} \).
3.1 Scaling functions in zone $X_2$

Step 1.

We will use the scaling method here; the good news is that $W_B^{\text{TF}}$ is sufficiently regular for a proper rescaling. Recall that after we rescale $x \mapsto \tilde{\ell}^{-1}(x - \tilde{x})$, $\tau \mapsto \tilde{\zeta}^{-2}\tau$ in the ball $B(\tilde{x}, \frac{1}{2}\tilde{\ell})$ with $\tilde{\ell} = \ell(\tilde{x})$, $\tilde{\zeta} = Z^2 \tilde{\ell}^{-1}$, the rescaled potential $w = \tilde{\zeta}^{-2} W_B^{\text{TF}}$ satisfies in $B(0, 2)$ equation

$$\frac{1}{4\pi} \Delta w = \eta P'_\beta(w)$$

with $\eta = \tilde{\zeta}^2 \leq 1$, $\beta = \mu \hbar = B \tilde{\zeta}^{-2} \leq 1$ and therefore in $B(0, 1)$

$$w = -\frac{1}{4\pi} \int |x - z|^{-1} \eta P'_\beta(w(z)) \phi(z) \, dz + w'$$

with $\phi \in \mathcal{C}_0^\infty B(0, \frac{5}{6})$ and $w' \in \mathcal{C}_0^\infty B(0, \frac{2}{3})$.

Let us introduce a function

$$\gamma_0(x) = \left( \min_j |w - 2j\beta|^3 + |\nabla w|^4 + |\nabla^2 w|^6 + |\nabla^3 w'|^{12} \right)^{\frac{1}{12}}.$$

Note that we cannot replace $w'$ by $w$ in the last term because $w \in \mathcal{C}^2$ only.

**Proposition 3.1.1.** $\gamma_0(x)$ is a scaling function i.e. $|x - y| \leq c \gamma_0(x) \implies \gamma_0(y) \leq \gamma_0(x)$.

**Proof.** (i) If $w$ belonged to $\mathcal{C}^4$ (and we would put $w$ instead of $w'$ in the last term of (3.1.3)) then we would just prove that $|\nabla \gamma_0| \leq c$. Here we should be more subtle. We need to prove that if

$$\min_j |w - 2j\beta| \leq \gamma_0^4, \quad |\nabla w| \leq \gamma_0^3,$$

$$|\nabla^2 w| \leq \gamma_0^2, \quad |\nabla^3 w'| \leq \gamma_0$$

at point $x$, then at point $y$ the same inequalities hold with $\gamma_0$ replaced by $c \gamma_0^{21)}$. Definitely this is true for (3.1.4) since $w'$ is smooth.

---

21) We need to prove a bit of reverse as well; see (iii).
Consider $|\nabla^2 w|$. Consider $|\Lambda_\alpha w(y) - \Lambda_\alpha w(x)|$ with $\Lambda_\alpha = \nabla^\alpha - \frac{1}{3}\delta_\alpha \Delta$, $\alpha = (i,j)$. Then due to (3.1.2)

$\nabla^2$}

where the last term estimates $|\Lambda_{\alpha,y}w'(y) - \Lambda_{\alpha,x}w'(x)|$ and we used (3.1.4). Integrals are understood in the sense of the principal value ($\text{vrai}$) and $\epsilon_1 = \epsilon_1(\epsilon) \to +0$ as $\epsilon \to +0$.

Note that the integral in expression (3.1.5) does not change if we add to $P_\beta'(w)$ any constant with respect to $z$.

Let us consider first this integral over $\{z: |x - z| \geq 2\gamma_0\}$, as $\gamma_0 \geq |x - y|$, and note that this integral does not exceed

$$\eta \int |x - z|^{-4}|x - y| \times$$

$$\left(|\nabla w(x)| \cdot |x - z| + |\nabla^2 w(x)| \cdot |x - z|^2 + |x - z|^{\frac{3}{2}}\right) dz \leq C\epsilon_1 \eta.$$
Furthermore, combining this inequality with (3.1.4) we conclude that
\[ \left| \nabla w(x) - \nabla w(y) \right| \leq \epsilon_1 \gamma_0^3 \text{ in } B(x, \gamma_0); \]
finally, combining with (3.1.4) we conclude that \[ \left| w(x) - w(y) \right| \leq \epsilon_1 \gamma_0^4 \text{ in } B(x, \gamma_0). \]

(iii) Therefore (3.1.4) are fulfilled in \( y \in B(x, \epsilon \gamma_0) \) with \( \gamma_0 \) replaced by \( \gamma_0(1 + C \epsilon_1) \). Further, if we redefine \( \gamma_0 \) as the minimal scale such that inequalities (3.1.4) are fulfilled in \( x \), then (3.1.4) fail in \( y \in B(x, \epsilon \gamma_0) \) with \( \gamma_0 \) replaced by \( \gamma_0(1 - C \epsilon_1) \). Therefore with appropriate \( \epsilon > 0 \) we conclude that \( \frac{1}{2} \leq \frac{\gamma_0(x)}{\gamma_0(y)} \leq 2. \)

Obviously \( \gamma_0 \asymp \gamma_{\text{old}} \) where \( \gamma_{\text{old}} \) was defined by (3.1.3) and therefore the same conclusion also holds for \( \gamma_{\text{old}}. \)

Now let us reintroduce the scaling function

\[ (3.1.3)^* \quad \gamma_0(x) = \epsilon \left( \min_j |w - 2j\beta|^3 + |\nabla w|^4 + |\nabla^2 w|^6 + |\nabla^3 w'|^2 \right)^{\frac{1}{12}} + C_0 \eta^\frac{3}{2} + C_0 \eta^\frac{3}{2}. \]

Then

\[ (3.1.6) \quad |x - y| \leq 2 \gamma_0(x) \implies \gamma_0(y) \asymp \gamma_0(x) \text{ and } (3.1.4)_{1-4} \text{ hold (with some constant factor in the right-hand expression).} \]

Consider \( B(\bar{x}, \bar{\gamma}_0) \), \( \bar{\gamma}_0 = \gamma_0(\bar{x}) \), and scale again \( x \mapsto \bar{\gamma}_0^{-1}(x - \bar{x}), \tau \mapsto \bar{\gamma}_0^{-4} \tau \) and respectively \( w \mapsto w_1 = \bar{\gamma}_0^{-4}(w - 2j\beta) \), \( h \mapsto h_1 = h \bar{\gamma}_0^{-3}. \)

If \( \bar{\gamma}_0 \asymp h^{\frac{1}{3}} \) then \( h_1 \asymp 1 \) and we are done. If \( \bar{\gamma}_0 \asymp \eta^{\frac{1}{3}} \) then go to Step 3.

**Step 2.**

So, let \( \eta_1 \ll 1 \). Let us introduce scaling function in \( B(0, 1) \) obtained after the previous rescaling

\[ (3.1.7) \quad \gamma_1(x) = \epsilon \left( \min_j |w_1 + 2(j - j)\beta\bar{\gamma}_0^{-4}|^2 + |\nabla w_1|^3 + |\nabla^2 w_1|^6 \right)^{\frac{1}{6}}. \]

Then

\[ (3.1.8)_{1-2} \quad \min_j |w_1 + 2(j - j)\beta\bar{\gamma}_0^{-4}| \leq C_0 \gamma_1^3, \quad |\nabla w_1| \leq C_0 \gamma_1^2. \]

\[ (3.1.8)_{3} \quad |\nabla^2 w_1| \leq C_0 \gamma_1. \]
Proposition 3.1.2. (i) $\gamma_1(x)$ is a scaling function: $|x - y| \leq 2\gamma_1(x) \implies \gamma_1(y) \asymp \gamma_1(x)$;

(ii) If $\eta_1 \leq \epsilon_0$ then

(3.1.9) $|\nabla^2 w_1(x) - \nabla^2 w'_1(x)| \leq \epsilon_2 \gamma_1$, \quad $w'_1 = (w' - j\beta)\gamma_0^{-4}$.

Proof. Proof is similar but simpler than one of Proposition 3.1.1; it is based on the rescaled version of (3.1.1)–(3.1.2):

(3.1.10) \quad $\frac{1}{4\pi} \Delta w_1 = \eta_1 P_{\beta}(w_1\gamma_0^4 + 2j\beta)$, \quad $\eta_1 = \epsilon_0^{-2} \leq 1$

and therefore in $B(0,1)$

(3.1.11) \quad $w_1 = -\frac{1}{4\pi} \int |x - z|^{-1} \eta_1 P'_\beta(w_1(z)\gamma_0^4 + 2j\beta) \phi(z) \, dz + w'_1$.

$\square$

Now let us reintroduce scaling function

(3.1.7)* \quad $\gamma_1(x) = \epsilon \left( \min_j |w_1 + 2(j - j_0)\beta\gamma_0^{-4}|^2 + |\nabla w_1|^3 + |\nabla^2 w_1|^6 \right)^{\frac{1}{6}} + C_0 h_1^{\frac{2}{3}}$

Then

(3.1.12) \quad $|x - y| \leq 2\gamma_0(x) \implies \gamma_0(y) \asymp \gamma_0(x)$ and (3.1.8)$_{1-3}$ hold (with some constant factor in the right-hand expression).

Let us consider $\bar{x} \in B(0,1)$ (it is a new point), $B(\bar{x}, \gamma_1)$, $\overline{\gamma}_1 = \gamma_1(\bar{x})$, and scale again $x \mapsto \overline{\gamma}^{-1}_1(x - \bar{x})$, $\tau \mapsto \overline{\gamma}^{-3}_1 \tau$ and respectively $w_1 \mapsto w_2 = \overline{\gamma}^{-3}_1 w_1$, $h_1 \mapsto h_2 = h_1 \overline{\gamma}^{-\frac{5}{2}}_1$.

If $\overline{\gamma}_1 \asymp h_1^{\frac{2}{3}}$ then $h_2 \asymp 1$ and we are done. If $|\nabla w_2| \asymp 1$ we are done as well.

50
Step 3.

So, consider the remaining case $|\nabla^2 w_2| \asymp 1$. Then we introduce scaling function

$$
\gamma_2(x) = \epsilon \left( \min_j |w_2 + 2(j - j)\beta \bar{\gamma}_0^{-4}\bar{\gamma}_1^{-3}| + |\nabla w_2|^2 \right)^{\frac{1}{2}} + C_0 h_2^{\frac{1}{2}}.
$$

Let us consider $\bar{x} \in B(0, 1)$ (it is a new point), $B(\bar{x}, \bar{\gamma}_2)$, $\bar{\gamma}_2 = \gamma_2(\bar{x})$, and scale again $x \mapsto \bar{\gamma}_2^{-1}(x - \bar{x})$, $\tau \mapsto \bar{\gamma}_2^{-2}\tau$ and respectively $w_2 \mapsto w_3 = \bar{\gamma}_2^{-2}w_2$, $h_2 \mapsto h_3 = h_2\bar{\gamma}_2^{-2}$.

If $\bar{\gamma}_2 \asymp h_1^{\frac{1}{3}}$ then $h_3 \asymp 1$ and we are done. If $|\nabla w_3| \asymp 1$ we are done as well.

Step 4.

Finally, introduce

$$
\gamma_3(x) = \epsilon \min_j |w_3 + 2(j - j)\beta \bar{\gamma}_0^{-4}\bar{\gamma}_1^{-3}\bar{\gamma}_2^{-2}| + Ch_3^{\frac{3}{2}}.
$$

3.2 Zone $\mathcal{X}_2$: Semiclassical N-term

Now we apply scaling arguments using scaling functions constructed above.

We revert our steps. While we call $\gamma_{1-3}$ relative scaling functions let us introduce absolute scaling functions $\alpha_0(x) = \gamma_0(x)$, $\alpha_1(x) = \gamma_0(x)\gamma_1(x)$, $\alpha_2(x) = \gamma_0(x)\gamma_1(x)\gamma_2(x)$, and $\alpha_3(x) = \gamma_0(x)\gamma_1(x)\gamma_2(x)\gamma_3(x)$\footnote{So far we ignore the first scaling $x \mapsto (x - \bar{x})\ell^{-1}$.}.

We need first

**Proposition 3.2.1.** Consider $B(0, 1)$ and assume that in it

$$
|\nabla w| \asymp \theta, \\
|\nabla^2 w| \leq c\theta.
$$

Let

$$
\gamma(x) := \epsilon \min_j |w - 2\mu hj|\theta^{-1} + h_3^{\frac{3}{2}}.
$$
and
\( \varepsilon \geq (h_*)^{\frac{7}{10} - \delta}, \quad h_* = h\theta^{-\frac{1}{2}}. \)

Let \( \varphi \in C_0^\infty([-\epsilon_0, \epsilon_0]) \). Then for \( \alpha \leq \tilde{\gamma} := \gamma(\bar{x}), \)

\[
(3.2.5) \quad |\int \phi_\alpha(x) \left( e_\varphi(x, x, \tau) - P'_{\mu, \varphi} (w(x) + \tau) \right) dx| \leq C \mu h^{-1} \alpha^3 + C \mu h^{-1} \alpha^3 \tilde{\gamma}^{-1} (h_* \tilde{\gamma}^{-\frac{1}{2}} \alpha^{-1})^s
\]

with

\[
(3.2.6) \quad e_\varphi(x, y, \tau) := \varphi(h^2 D_x D_y (\mu h)^{-1}) e(x, y, \tau)
\]

and Weyl expression

\[
(3.2.7) \quad P'_{\beta, \varphi}(w + \tau) = \text{const} \sum_j \beta(w + \tau - 2j \mu h)^{\frac{3}{2}} \varphi(w + \tau - 2j \mu h)
\]

with the standard constant where for each \( x \) only one term is present in this sum. Here we take large \( s > 0 \) as \( h_* \leq \tilde{\gamma} \alpha \) and \( s = 0 \) otherwise.

**Proof.** The proof is standard and based on the standard reduction to the canonical form, standard estimates for \( U(x, y, t) \) a Schwartz kernel of propagator \( e^{i h^{-1} a^{-1} t H}. \)

\[
(3.2.8) \quad |F_{t \to h_*^{-1} T} \int \bar{\chi}(t) \phi_\alpha(x) U_\varphi(x, x, t) dx| \leq C \mu h^{-1} \alpha^3
\]

as \( T \approx 1 \) and

\[
(3.2.9) \quad |F_{t \to h_*^{-1} T} \int \phi_\alpha(x)(\bar{\chi}(t) - \bar{\chi}(t)) U_\varphi(x, x, t) dx| \leq C \mu h^{-1} \alpha^3 (h_* \tilde{\gamma}^{-\frac{1}{2}} \alpha^{-1})^s
\]

with \( \bar{T} = \varepsilon \gamma^{\frac{1}{2}} \) where \( U_\varphi \) is defined similarly to (3.2.6).

Here obviously we can skip in (3.2.5) all perturbation terms in the argument and in \( \phi_\alpha \) transformed. \( \square \)
Then plugging into (3.2.5) \( \alpha = \gamma (= \bar{\gamma}) \), we have factor \((\hbar \gamma^{-\frac{1}{2}})^n\) in the second term.

There are two cases: \( \theta \leq \mu \hbar \) and \( \theta \geq \mu \hbar \).

In the former case taking the sum over \( \gamma \)-partition of 1-element we estimate the same expressions with \( \phi \) instead of \( \phi_{\gamma} \) by their right-hand expressions integrated over \( \gamma^{-3} d\gamma \) which returns \( C \mu \hbar^{-1} \).

On the other hand, in the latter case let \( \lambda = \mu \hbar \theta^{-1} \). Taking the sum over \( \gamma_3 \)-partition of \( \lambda \)-element \( \phi_{\lambda} \) by the right-hand expressions which returns \( C \mu \hbar_2^{-1} \lambda^2 \). In this case summation over \( \lambda \)-partition return \( C \theta \hbar^{-2} \).

In both cases we arrive to

\[
(3.2.10) \quad | \int \phi(x) \left( e_{\psi}(x, x, \tau) - P_{\mu h, \psi}(w(x) + \tau) \right) dx | \leq C \theta \hbar^{-2} + C \mu \hbar^{-1}.
\]

Applying this estimate after \( \alpha_2 \)-scaling we conclude that the left-hand expression with \( \phi = \phi_{\alpha_2} \) (in the non-scaled settings) does not exceed \( C \theta \hbar^{-2} \alpha_2^2 + C \mu \hbar^{-1} \alpha_2^2 \). Here the first term is \( O(h^{-2} \alpha_2^2) \) and the summation over 1-element returns \( O(h^{-2}) \).

Consider the second term \( C \mu h^{-1} \alpha_2^2 = C \mu h^{-1} \gamma_0 \gamma_1^2 \gamma_2^2 \). Then summation over \( \alpha_2 \)-partition of \( \alpha_1 \)-element returns

\[
C \mu h^{-1} \gamma_0^2 \gamma_1^2 \int \gamma_2^2 \times \gamma_3^{-1} dx \asymp C \mu h^{-1} \gamma_0^2 \gamma_1^2 (1 + | \log \gamma_2 |)
\]

where \( \gamma_k \) is a minimal value of \( \gamma_k \) over \( \gamma_{k-1} \)-element. However in fact there will be no logarithmic factor because in virtue of equation (3.1.1) there is a positive eigenvalue of \( \text{Hess} w_2 \) of the maximal size (cf. Section 5.1.1). Therefore, in fact we have \( C \mu h^{-1} \gamma_0^2 \gamma_1^2 \).

Now summation over \( \alpha_1 \)-partition of \( \alpha_0 \)-element returns

\[
C \mu h^{-1} \gamma_0^2 \gamma_1 \int \gamma_2^2 \times \gamma_3^{-1} dx \asymp C \mu h^{-1} \gamma_0^2 \gamma_1^2 (1 + | \log \gamma_1 |).
\]

Finally, summation over \( \alpha_0 \)-partition of 1-element returns

\[
C \mu h^{-1} \int \gamma_0^2 (1 + | \log \gamma_1 |) \times \gamma_3^{-3} dx \asymp C \mu h^{-1} \gamma_0^{-1} (1 + | \log \gamma_1 |).
\]

where \( \gamma_k \) is an absolute minimum of \( \gamma_k \). However \( \gamma_0^2 \geq \eta \) and \( \gamma_1 \geq \eta \) and therefore expression above does not exceed \( C \mu h^{-1} \gamma_0^{-\frac{1}{2}} (1 + | \log \eta |) \).
Remark 3.2.2. Recall that we estimated only cut-off expression. To calculate the full expression we need to calculate also the contribution of zone \(\{\xi_3 \geq \mu h\}\). However this is easy.

Really, instead of \(\varphi(\hbar^2 D_3^2 / (\mu h))\) consider \(\varphi'(\hbar^2 D_3^2 / \theta)\) with \(\varphi' \in C^\infty([1, 4])\) and \(\epsilon \mu h \leq \theta \leq 1\). Without any scaling one can prove easily that such modified expression (3.2.10) does not exceed \(C\theta h^{-2}\). We leave easy details to the reader.

Therefore plugging \(\theta = 2^n \mu h\) and taking a sum over \(n = 0, \ldots, \lceil \log_2 \mu h \rceil \) we get required expressions. Also note that in such expressions we need to consider perturbed argument \(w + \mu^{-2} \omega_1 + j \mu^{-1} \hbar \omega_2\) (all other terms which are \(O(\mu^{-4} + \mu^{-\frac{1}{2}} h)\) could be skipped and also a perturbed function transformed).

Remark 3.2.3. (i) However we need to get rid off these perturbations for \(\theta \leq \mu h^{1-\delta}\) only. Really, for \(\theta \geq \mu h^{1-\delta}\) we need canonical form only to study propagation and calculations could be performed without it. But then getting rid of perturbation is trivial provided perturbation does not exceed \(C\mu h^{1+\delta}\) which is the case if

\[
(3.2.11) \quad \mu \geq h^{-\frac{1}{2} - \delta}.
\]

(ii) Note that in the smooth approximation contributions of \(X_1\) is always less than \(CZ^{\frac{3}{2} - \delta_1}, C \max(Z^{\frac{5}{4}}, Z^{\frac{1}{2}} B^{\frac{1}{2}})Z^{-\delta_1}\) or \(C \max(Z^{\frac{5}{4}}, Z^{\frac{1}{2}} B^{\frac{1}{2}})Z^{-\delta_1} + CB^{\frac{1}{2}} Z^{\frac{1}{2} - \delta_1}\) respectively with an exception of the first two and only in the case of the threshold value between \(\geq Z^{-\frac{1}{2} - \delta_2}\). However in this case \(\eta \geq Z^{-\delta_3}\) and the errors of the smooth approximation approach in fact are less than \(CZ^{\frac{3}{4} - \delta_4}, CZ^{\frac{3}{2} - \delta_4}\) as well. Therefore there are in fact no exception.

(iii) It is important to have \(\varepsilon \leq \mu h^\ast\) and with \(\varepsilon = h^{\frac{2}{3} - \delta}\) we need \(\mu \geq h^{-\frac{1}{2} - \theta^{\frac{1}{2} - \frac{1}{2}\delta}}\) which is due to (3.2.11).

Therefore we conclude that in the completely non-scaled settings with \(\phi = \phi_t(x)\)

\[
(3.2.12) \quad |\int \phi(x)(e(x, x, \tau) - P_{B_\ell}(W(x) + \tau))| \leq C\zeta^2 \ell^2 + CB\ell \zeta^{-\frac{1}{2}}(1 + |\log \ell^2 \zeta|)
\]

54
where the first term is $C \hbar^{-2}$ and the second term is $C \mu \hbar^{-1} \eta^{-\frac{1}{2}}(1 + |\log \eta|)$; recall that $\hbar^{-1} \approx \ell \zeta$, $\mu \approx B \zeta^{-1}$ and $\eta \approx \ell^2 \zeta$. In comparison with the non-degenerate case $|\nabla W^p_B| \approx \zeta^2 \ell^{-1}$ we acquired the last term.

Assume first that condition (1.2.21) is fulfilled. Then

(i) As $B \leq Z^\frac{4}{3}$, $\ell \leq Z^{-\frac{1}{3}}$ we have $\zeta = Z^{\frac{1}{3}} \ell^{-\frac{1}{3}}$ and the right-hand expression of (3.2.12) returns $CZ \ell + CB \ell^2 Z^{-\frac{4}{3}}$ and the summation with respect to $\ell$ results in its value as $\ell = Z^{-\frac{1}{3}}$ i.e. $CZ^{\frac{1}{3}} + CBZ^{-\frac{4}{3}}$ with the dominating first term.

(ii) As $B \leq Z^\frac{4}{3}$, $\ell \geq Z^{-\frac{1}{3}}$ we have $\zeta = \ell^{-2}$ and the right-hand expression of (3.2.12) returns $C\ell^{-2} + CB\ell^2$. We need to sum as long as $\mu \eta \leq 1$ i.e. $Z^{-\frac{1}{3}} \leq \ell \leq B^{-\frac{1}{3}}$ and the summation returns $CZ^{\frac{2}{3}} + CB$ with the dominating first term.

(iii) As $Z^\frac{4}{3} \leq B \leq Z^2$, $\ell \leq B^{-1} Z$ we have $\zeta = Z^\frac{1}{3} \ell^{-\frac{1}{3}}$ and the right-hand expression of (3.2.12) returns $CZ \ell + CBZ^{-\frac{1}{3}} \ell^{\frac{1}{3}}$. Then summation results in $CZ^2 B^{-1} + CZ^2 B^{-\frac{4}{3}} Z \lesssim Z^{\frac{2}{3}}$.

If assumption (1.2.21) is not fulfilled we can estimate in the first term of the right-hand expression of (3.2.12) parameter $\zeta$ from above by $\min(Z^{\frac{1}{3}} \ell^{-\frac{1}{3}}, \ell^{-2})$ and in the second term from below by $\zeta_m = \min(Z_m^{\frac{1}{3}} \ell_m^{-\frac{1}{3}}, \ell_m^{-2})$ as $\ell = \ell_m := |x - y_m|$ and repeat all above arguments.

Therefore we arrive to the statement (i) of Proposition 3.2.4 below. Furthermore, as $B \leq Z$ zone $\mathcal{X}_2$ is contained in $\{x : \ell(x) \geq B^{-\frac{1}{3}} \geq Z^{-\frac{1}{3}}\}$ (really, $\mu \geq h^{-\frac{1}{3}}$ in $\mathcal{X}_2$) and we arrive to the statement (ii) below.

**Proposition 3.2.4.** (i) As $B \leq Z^2$ contribution of zone $\mathcal{X}_2$ to expression

$$\int (e(x, x, \nu) - P_B'(W(x) + \nu)) \, dx$$

(3.2.13) does not exceed $CZ^{\frac{3}{2}}$;

(ii) As $B \leq Z$ contribution of zone $\mathcal{X}_2$ to expression (3.2.13) does not exceed $CZ^{\frac{2}{3}-\delta}$.
3.3 Zone $\mathcal{X}_2$: Semiclassical D-term

Further, we need to estimate Semiclassical D-term

\begin{equation}
D(\phi_\alpha[e(x, x, \nu) - P'_B(W(x) + \nu)], \phi_\alpha[e(x, x, 0) - P'_B(W(x))])
\end{equation}

where $\phi_\alpha(x)$ is an $\alpha$-admissible function. Again we revert our steps.

Consider $B(x, \tilde{a}_3)$ and apply Fefferman–de Llave decomposition (2.1.8). Then in the framework of Proposition 3.2.1 contribution of pairs $B(x, \alpha)$ and $B(y, \alpha)$ with $3\alpha \leq |x - y| \leq 4\alpha$ does not exceed the right-hand expression of (3.2.5) squared and multiplied by $\alpha^{-4}$ where $C\alpha^{-3}$ estimates the number of the pairs and $\alpha^{-1}$ is the inverse distance. At this moment we discuss a cut-off version of (3.3.1) i.e. with $e_\varphi(\ldots)$ and $P'_{\mu h, \varphi}(\ldots)$. So, we have

$$C\mu^2h^{-2}(1 + \gamma_3^{-1}(h_2\gamma_3^{-1/2}\alpha^{-1})^s)^2\alpha^4.$$  

Then integrating this expression with respect to $\alpha^{-1}d\alpha$ with $\alpha \leq \gamma_3$ we arrive to $C\mu^2h^{-2}(\gamma_3^4 + h_2^2\gamma_3)$.

Therefore

\begin{equation}
A \text{ cut-off version of (3.3.1) with } \alpha = \alpha_3 \text{ does not exceed } C\mu^2h^{-2}(\gamma_3^4 + h_2^2\gamma_3)\alpha_3^3 \approx C\mu^2h^{-2}. 
\end{equation}

The first term here $C\mu^2h^{-2}\gamma_3\alpha_3^3$ does not exceed $C\mu^2h^{-2}\alpha_3^3$ (recall that $\alpha_j = \alpha_{j-1}\gamma_j$) and the summation over $\alpha_3$-partition of 1-element returns $C\mu^2h^{-2}$.

Consider the second term $C\mu^2h^{-2}\gamma_3\alpha_3^3$; its summation with respect to $\alpha_3$-partition of $\alpha_2$-element returns $C\mu^2h^{-2}\alpha_2^3\gamma_3\alpha_3^3$ (really, recall that according to (3.1.14) $\gamma_3 \geq \gamma_3^2$) and then the summation over $\alpha_2$-partition of 1-element returns $C\mu^2h^{-2}$.

Consider $B(x, \tilde{a}_2)$ and apply Fefferman–de Llave decomposition (2.1.8). There are two kinds of pairs:

(a) those with $|x - y| \geq \epsilon(\alpha_3(x) + \alpha_3(y))$ for all $(x, y)$ and

(b) those with $|x - y| \leq \min(\alpha_3(x), \alpha_3(y))$ for all $(x, y)$.

The total contribution of the pairs of the second type (i.e. summation is taken over all pairs of $\alpha_3$-elements in $B(0, 1)$) as we already know is
$O(\mu^2 h^{-2})$. Meanwhile according to the analysis in the previous Subsection 3.2 a contribution of one pair of kind (a) does not exceed

\[
C \left( \frac{h^{-2} + \mu h^{-1} \gamma_0^{-1} \gamma_1^{-1} \gamma_2^{-1} \gamma_3^{-1} \delta}{\gamma_3} \right) \alpha_3^3 \times \left( \frac{h^{-2} + \mu h^{-1} \gamma_0^{-1} \gamma_1^{-1} \gamma_2^{-1} \gamma_3^{-1} \delta}{\gamma_3} \right) \alpha_3^3 \times |x - y|^{-1}
\]

where each of two first factors is just an estimate of the integral (3.2.10) calculated over corresponding argument. If we take the first term in the first factor and sum over $\alpha_3$-partition of $1$-element we get only the second factor multiplied by $\mu h^{-1}$ and then summation was done in the previous subsection. Similarly we can deal with the first term in the second factor.

On the other hand, if we take only second factors and sum over pairs of $\alpha_2$-subelements of the same $\alpha_3$-element we get

\[
C \mu^2 h^{-2} \gamma_0^{-2} \gamma_1^{-2} \gamma_2^{-2} \alpha_2^5 \approx C \mu^2 h^{-2} \alpha_2^3.
\]

Then summation with respect to $\alpha_2$-partition of $1$-element returns $C \mu^2 h^{-2}$.

Consider now $B(\tilde{x}, \tilde{\alpha}_1)$ and apply here Fefferman-de Llave decomposition (2.1.8). There are two kinds of pairs:

(a) those with $|x - y| \geq \epsilon(\alpha_2(x) + \alpha_2(y))$ for all $(x, y)$ and

(b) those with $|x - y| \leq \min(\alpha_2(x), \alpha_2(y))$ for all $(x, y)$.

According to the above analysis the total contribution of the pairs of the second type (i.e. the summation is taken over all pairs of $\alpha_2$-elements in $B(0, 1)$) as we already know is $O(\mu^2 h^{-2})$. Meanwhile according to the analysis in the previous Subsection 3.2 a contribution of one pair of kind (a) does not exceed

\[
C \left( \frac{h^{-2} + \mu h^{-1} \gamma_0^{-1} \gamma_1^{-1} \gamma_2^{-1}}{\gamma_3} \right) \alpha_3^3 \times \left( \frac{h^{-2} + \mu h^{-1} \gamma_0^{-1} \gamma_1^{-1} \gamma_2^{-1}}{\gamma_3} \right) \alpha_3^3 \times |x - y|^{-1}
\]

and here again we can “forget” about the first terms in each factor. Then the summation with respect to pairs of $\alpha_2$-subelements of the same $\alpha_1$-element results in $C \mu^2 h^{-2} \gamma_0^{-2} \gamma_1^{-2} \alpha_2^5 \approx C \mu^2 h^{-2} \alpha_2^3$ where we avoid logarithmic factor in virtue of the same positive eigenvalue of Hess $w$. Summation with respect to $\alpha_1$-admissible partition of $1$-element returns $C \mu^2 h^{-2}$.
Consider now \( B(\bar{x}, \alpha_0) \) and apply here Fefferman–de Llave decomposition. Again there are two kinds of pairs and the total contributions of the pairs of the second kind we already calculated and contribution of the pairs of \( \alpha_1 \)-subelements of the same \( \alpha \)-element does not exceed
\[
C \mu^2 h^{-2} \gamma_0^{-2} (1 + |\log \hat{\gamma}_1|)^2 \alpha_0^5 \lesssim C \mu^2 h^{-2} (1 + |\log \eta|)^2 \alpha_0^3
\]
and the summation with respect to \( \alpha_0 \)-partition of \( 1 \)-element returns
\[
C \mu^2 h^{-2} (1 + |\log \eta|)^2.
\]

Finally, consider \( B(\bar{x}, 1) \) and apply here Fefferman-de Llave decomposition. Again there are two kinds of pairs and the total contributions of the pairs of kind (b) we already estimated while the total contribution of the pairs of kind (a) does not exceed
\[
C \mu^2 h^{-2} \eta^{-1} (1 + |\log \eta|)^2 \gamma_0^{-2}
\]
where we recalled the forgotten terms.

Again, this is estimate for cut-off expression. Going to uncut expression we repeat the same trick as before but as we deal with \( \psi \)-term we need to consider “mixed” pairs when one “factor” comes with \( \theta \) and another with \( \theta' \) but then contribution of such pair does not exceed
\[
C (\nu h^{-4})^{\frac{3}{2}} (\nu'h^{-4})^{\frac{3}{2}}.
\]
Easy details are left to the reader.

Therefore returning to the original scale we conclude that the contribution of \( \ell \)-layer to (3.3.1) does not exceed
\[
(3.3.3) \quad C \zeta^4 \ell^3 + CB^2 \ell \zeta^{-1} (1 + |\log \ell^2 \zeta|)^2
\]
which is exactly the right-hand expression of (3.2.12) squared and multiplied by \( \ell^{-1} \) due to scaling. In comparison with the non-degenerate case \( |\nabla W^\text{tr}_B| \asymp \zeta^2 \ell^{-1} \) we acquired the last term.

Assume first that condition (1.2.21) is fulfilled. Then

(i) As \( B \leq Z^4, \ell \leq Z^{-\frac{1}{2}} \) we have \( \zeta = Z^{\frac{1}{2}} \ell^{-\frac{1}{2}} \) and expression (2.2.18) returns
\[
CZ^2 \ell + CB^2 \ell \frac{1}{2} Z^{-\frac{1}{2}}
\]
and the summation with respect to \( \ell \) results in its value as \( \ell = Z^{-\frac{1}{2}} \) i.e. \( CZ^{\frac{3}{2}} + CB^2 Z^{-1} \) with the dominating first term.

(ii) As \( B \leq Z^4, \ell \geq Z^{-\frac{1}{2}} \) we have \( \zeta = \ell^{-2} \) and expression (2.2.18) returns
\[
C \ell^{-5} + CB^2 \ell^3.
\]
We need to sum as long as \( \mu h \leq 1 \) i.e. \( Z^{-\frac{1}{2}} \leq \ell \leq B^{-\frac{1}{2}} \) and the summation returns \( CZ^3 + CB^2 Z \ell \) with the dominating first term.

(iii) As \( Z^4 \leq B \leq Z^2, \ell \leq B^{-1} Z \) we have \( \zeta = Z^{\frac{1}{2}} \ell^{-\frac{1}{2}} \) and expression (2.2.18) returns
\[
CZ^2 \ell + CB^2 Z^{-\frac{1}{2}} \ell^2.
\]
Then summation results in \( CZ^3 B^{-1} + CB^2 Z \lesssim Z^{\frac{3}{2}} B^2 \).

58
Sure, we need to consider also mixed pairs of the layers and their contributions are
\[ C(\zeta^2\ell^2 + CB\zeta^{-\frac{1}{2}}(1+|\log \ell^2\zeta|)) \times (\zeta'^2\ell'^2 + CB\zeta'^{-\frac{1}{2}}(1+|\log \ell'^2\zeta'|)) \times (\ell + \ell')^{-1} \]
and the summation with respect to \(\ell\) and \(\ell'\) returns the same expression as above.

If assumption (1.2.21) is not fulfilled we use the same trick as in the previous subsubsection. Therefore we arrive to the statement (i) of Proposition 3.3.1 below. Applying the same arguments as in the proof of Proposition 3.2.4 we arrive to the statement (ii):

**Proposition 3.3.1.**

(i) As \(B \leq Z^2\) contribution of zone \(\mathcal{X}_2 \times \mathcal{X}_2\) to expression (3.3.1) does not exceed \(C\max(Z\frac{4}{3}, Z\frac{5}{3}B^{\frac{1}{2}})\);

(ii) As \(B \leq Z\) contribution of zone \(\mathcal{X}_2\) to expression (3.3.1) does not exceed \(CZ^{\frac{5}{3} - \delta}\).

### 3.4 Semiclassical T-term

#### 3.4.1 Semiclassical T-term: zone \(\mathcal{X}_1\) extended

First let us cover zone \(\mathcal{X}_1\) extended.

**What is \(\mathcal{X}_1\) extended?**

First, let us analyze the precise extension in the framework of D- and N-terms. For these terms we have errors \(C(\mu\ell)^2\eta^{-\frac{1}{2}}h^{-3} = CB^2\zeta^{-\frac{1}{2}}\ell^2\) and this expression squared and multiplied by \(\ell^{-1}\) i.e. \(CB^4\zeta^{-3}\ell^3\) respectively, and both sum to their values as \(\ell = r\).

(i) As \(B \leq Z\frac{4}{3}\) and \(r \geq Z^{-\frac{1}{2}}\) we have \(CB^2r^5\) and \(CB^4r^9\) and we want them to be less than \(CZ\frac{4}{3}\) and \(CZ\frac{5}{3}\) respectively. As \(B < Z\frac{7}{6}\) the first requirement is more restrictive and we set \(CB^2r^5 = Z\frac{4}{3}\) i.e. \(r = B^{-\frac{5}{9}}Z^{\frac{4}{9}}\) and then \(\mu = Br^3 = B^{-\frac{5}{9}}Z^{\frac{5}{3}} \geq Z\frac{4}{3}\) and \(h = B^{-\frac{7}{9}}Z^{\frac{3}{9}} \geq Z^{-\frac{1}{3}}\) so \(\mu \geq h^{-\frac{1}{3}}\).

(ii) As \(Z\frac{7}{6} \leq B \leq Z\frac{4}{3}\) the second requirement is more restrictive and we set \(B^4Z^{-\frac{1}{2}}r^2 = Z\frac{4}{3}\), i.e. \(r = B^{-\frac{5}{9}}Z^{\frac{4}{9}}\) and \(\mu = B^{-\frac{1}{9}}Z^{\frac{5}{9}}\) and \(h = Z^{-\frac{1}{9}}r^{-\frac{1}{2}} = B^{\frac{5}{9}}Z^{-\frac{3}{9}}\) and \(\mu \geq h^{-\frac{1}{3}}\) (better than \(h^{-\frac{1}{3}}\)).
But $\mu \hbar \leq \eta$ iff $r \geq B^2Z^{-3}$ i.e. $B \leq Z^{\frac{90}{59}}$ and this is less than $Z^{\frac{3}{5}}$ so we test $\mu$ and $\hbar$ in this case: $\mu = Z^{\frac{3}{5}}$ and $\hbar = Z^{\frac{11}{5}}$ and $\mu \geq h^{-\frac{1}{11}}$. As $B \geq Z^{\frac{59}{58}}$ we have error $(\mu h)^3 \hbar^{-6} r^{-1} = B^3 r^5$ and we want it to be $\leq Z^{\frac{3}{5}}$, so $r = Z^{\frac{3}{5}} B^{-\frac{1}{5}}$ and $\mu = B^\frac{3}{5}$ and $h = B^\frac{11}{5} Z^{-\frac{3}{5}}$ and we test it as $B = Z^{\frac{3}{5}}$ when $\mu = B^\frac{3}{5}$ and $h = B^{-\frac{1}{5}}$, so exponent $-\frac{5}{11}$ fits.

As $B \leq Z^{\frac{3}{5}}$ we consider $B^3 r^5 = B^\frac{3}{5} Z^\frac{3}{5}$ i.e. $r = B^{-\frac{11}{5}} Z^\frac{3}{5}$, $\mu = B^\frac{17}{5} Z^{-\frac{3}{5}}$, $h = B^\frac{11}{5} Z^{-\frac{13}{5}}$ and exponent $-\frac{5}{11}$ fits as well.

When we can use the same method for $T$-term?

As far as semiclassical $T$-expression is concerned an error of such approach in the localized and scaled settings would be $C(\mu h)^{\frac{3}{2}} h^{-\frac{3}{2}}$ which is $O(h^{-1})$ only as $\mu \geq h^{-\frac{1}{2}}$. One can extend it to $\mu \geq h^{-\frac{1}{2}}$ using the same trick as in Remark 3.2.3 but we need to do better than this.

Note first that in fact an error does not exceed $C(\mu h)^{3/2} h^{-3} = CB^3 r^5 \zeta^{-\frac{3}{2}}$ in the localized scaled settings (we skip $Ch^{-1}$ as the result here is already taken into account). The simple proof is left to the reader. This is translated into $CB^3 r^5 \zeta^{-\frac{3}{2}}$ into unscaled settings. Summation with respect to $\ell \leq r$ returns its value as $\ell = r$.

So we get $CB^3 r^5$ as $B \leq Z^\frac{3}{5}$ and $r \geq Z^{-\frac{3}{5}}$. Let $B \leq Z$. Then we want $CB^3 r^5 \leq CZ^\frac{3}{5}$ i.e. $r = B^{-\frac{3}{5}} Z$, which is greater than $Z^{-\frac{3}{5}}$ as $B \leq Z^{\frac{90}{59}}$. Then $\mu = Br^3 = B^{-\frac{3}{5}} Z \geq Z^\frac{3}{5}$ and $h = r = B^{-\frac{3}{5}} Z \geq Z^{-\frac{3}{5}}$ and $\mu \geq h^{-\frac{3}{5}}$.

As $Z \leq B \leq Z^\frac{3}{5}$ but $r \geq Z^{-\frac{3}{5}}$ still we want $CB^3 r^5 \leq CB^\frac{5}{5} Z^\frac{3}{5}$ i.e. $r = B^{-\frac{5}{5}} Z^\frac{5}{5}$ and we want it to be $\geq Z^{-\frac{3}{5}}$ i.e. $B \leq Z^\frac{5}{5}$. Then $\mu = Br^3 = B^{-\frac{5}{5}} Z^\frac{5}{5} \geq Z^\frac{3}{5}$ and $h = B^{-\frac{3}{5}} Z^\frac{5}{5} \geq B^{-\frac{3}{5}}$ and $\mu \geq h^{-\frac{3}{5}}$. It is not as good as $\mu \geq h^{-\frac{3}{5}}$.

Then we use the smooth canonical form. In the operator perturbation terms have factors $\mu^{-2}$, $\mu^{-4}$ etc and we can use the standard approach to get rid off $\mu^{-4} \leq \mu h$, so we need to consider only $\mu^{-2}$.

However let before scaling the second derivative of $W$ be of magnitude $\theta$; then after scaling it becomes of magnitude $\theta' = \gamma_0^2 \gamma_1^2 \theta$ and then the perturbation is of magnitude $\theta \mu^{-2}$ but contribution of the error will be (after we compare the true Riemann sum and the corresponding integral and their difference $Ch^{-3} \nu \mu^{-2} (\mu h)^2 (\theta')^{-\frac{1}{2}} \times Q^2 \leq C\theta^2 h^{-1} \gamma_0^{-1} \mu^{-1} \mu_0^2 \leq C h^{-1} \gamma_1^{-\frac{1}{2}} \mu_0^3$ where we used that $\theta \leq C \gamma_0^2 \gamma_1$. Then summation over $\alpha_1$-partition of $\alpha_0$ element returns $Ch^{-1} \alpha_0^3$ and the summation over $\gamma_0$-partition returns $Ch^{-1}$ as desired. Therefore we covered zone $X_1$ for $T$-term.
3.4.2 Semiclassical T-term: zone $\mathcal{X}_2$

Tauberian estimate.

Tauberian estimate for cut-off expression is rather simple:

$$C\mu h^{-1}\gamma_0^{-1}\gamma_1^{-1}\gamma_2^{-1} \times h^{-3}\gamma_1^{-3}\gamma_1^{-2} \times \gamma_0^3\gamma_1^2\alpha_2^3 \approx C\mu\gamma_1^{-1}\gamma_2^{-1}\alpha_2^3$$

which nicely sums to $C\mu$ without logarithm due to the same positive eigenvalue arguments as before; for $\theta$-cut-off with $\theta \geq \mu h$ we get the same albeit with $\gamma_j$ defined by the same formula albeit with $(w_j - 2j\mu h s_j^{-1})$ replaced by $\theta s_j^{-1}$ where $s_j^{-1}$ means the scale; and this should be multiplied by $\theta/\mu h$.

The result nicely sums to $C h^{-1}$. This is what was required.

Magnetic Weyl expression.

Now we will get the same answer albeit $C\mu^{-4}$ term will be supplemented by $C\mu^{-3}h$ which in cut-off sum adds $C\mu^{-3}h \times \mu h^{-2} \leq Ch^{-1}$.

We can use the standard approach, with an error $C\mu^{-3}h \times \theta/(\mu h) \times \mu h^{-2} \approx C\theta\mu^{-3}h^{-2}$ which means that we can take $\theta = \mu^{3/2}h$ which is sufficient to deal with with $\theta \geq C\mu^{3/2}h$; in particular, for $\mu \geq h^{3/2}$ we are done. But for $\theta \geq \mu h^{3-\delta}$ we can apply the weak magnetic field approach, which is sufficient. So we arrive to inequality

$$(3.4.1) \quad \left| \int_{-\infty}^{\tau} \int \phi(x) \left( e_{\phi}(x, x, \tau) - P_{\beta,\phi}(w(x) + \tau) \right) dx d\tau \right| \leq Ch^{-1}$$

and therefore we arrive to

**Proposition 3.4.1.** (i) As $B \leq Z^2$ contribution of zone $\mathcal{X}_2$ to expression

$$(3.4.2) \quad \int_{-\infty}^{\tau} \int \phi(x) \left( e_{\phi}(x, x, \tau) - P_{\beta,\phi}(W(x) + \tau) \right) dx d\tau$$

does not exceed $C \max((Z + B)^{3/2}Z^{3/2}, Z^{5/2}B^{3/2})$.

(ii) As $B \leq Z$ contribution of zone $\mathcal{X}_2$ to expression (3.4.2) does not exceed $CZ^{5/2-\delta}$.
Mollification errors.

Further, we need to estimate

\[ \int \phi(x) \left( P_B'(W(x) + \tau) - P_B(W_B^{TF}(x) + \tau) \right) \, dx, \tag{3.4.3} \]

\[ \int \phi(x) \left( P_B(W(x) + \tau) - P_B(W_B^{TF}(x) + \tau) \right) \, dx, \tag{3.4.4} \]

\[ D \left( \phi(x) \left( P_B'(W(x) + \tau) - P_B'(W_B^{TF}(x) + \tau) \right) \right), \]
\[ \phi(x) \left( P_B'(W(x) + \tau) - P_B'(W_B^{TF}(x) + \tau) \right) \right) \]

and

\[ \| \phi(x) \nabla (W(x) - W_B^{TF}(x)) \|^2. \tag{3.4.6} \]

We start from local versions (so in fact we dealing with \( w \) and \( W_B^{TF} \)).

Obviously after all rescalings \( h_* = h_{\gamma_0^{-3} \gamma_1^{-\frac{1}{2}} \gamma_2^{-2}} \) and therefore \( \varepsilon = h_*^\frac{3}{2} = h^\frac{3}{2} \left( \gamma_0^{-3} \gamma_1^{-\frac{1}{2}} \gamma_2^{-2} \right)^{-\frac{1}{2}} \) where we set \( \delta = 0 \) but we will show that we have a reserve to set it as \( \delta > 0 \) if we want to estimate (3.4.3) by \( h \) and (3.4.4)–(3.4.6) by \( h^2 \).

We claim that

\[ |w - W_B^{TF}| \leq C_\varepsilon \alpha_2 \beta \gamma_0^{-3} \gamma_1^{-\frac{1}{2}} \gamma_2^{-2} \]  \( \tag{3.4.7} \)
and

\[ |\nabla (w - W_B^{TF})| \leq C_\varepsilon \alpha_2 \beta \gamma_0^{-3} \gamma_1^{-\frac{1}{2}} \gamma_2^{-2} \]  \( \tag{3.4.8} \)

Really it follows from equation (3.1.2).

Then the contribution of \( \alpha_2 \)-element to (3.4.4) does not exceed \( C_\varepsilon \alpha_2^3 \) as measure of zone of \( \alpha_2 \)-element where \( w \neq W_B^{TF} \) is \( O(\varepsilon \alpha_2^3) \). One can see easily that \( \varepsilon \alpha_2 \) \( O(h^\frac{3}{2}) \) and therefore \( C_\varepsilon \alpha_2^3 \) \( O(h^\frac{3}{2} \alpha_2^3) \) and the summation over \( \alpha_2 \)-partition of 1-element returns \( O(h^\frac{3}{2}) \).

Modulo above calculations the contribution of \( \alpha_2 \)-element to (3.4.3) does not exceed \( C_\varepsilon \alpha_2^3 \). One can check easily that \( \varepsilon \alpha_2^3 \) \( O(h^\frac{3}{2} \gamma_2^{-\frac{1}{2}}) \) and therefore \( C_\varepsilon \alpha_2^3 \) \( O(h^\frac{3}{2} \alpha_1^3 \gamma_2^{-\frac{1}{2}}) \) and the summation over \( \alpha_2 \)-partition of \( \alpha_1 \)-element returns \( O(h^\frac{3}{2} \alpha_1^3) \) and then the summation over \( \alpha_1 \)-partition of 1-element returns \( O(h^\frac{3}{2}) \).
Similarly, expression (3.4.5) with $\phi = \phi_\alpha$ does not exceed $C\zeta_\varepsilon_2\alpha_2^{\frac{5}{2}} \leq Ch^3\alpha_2^2$ and the summation over $\alpha_2$-partition of 1-element returns $O(h^3)$. However we need to consider disjoint pairs of $\alpha_2$-elements belonging to given $\alpha_1$-element and their contribution does not exceed

$$Ch^3 \int \frac{1}{\gamma_2^* \gamma_2} |x - y|^{-1} \, dx dy \leq C h^2 \alpha_1^5$$

and then summation over $\alpha_1$-partition of 1-element returns $O(h^\frac{3}{2})$. We need also to consider disjoint pairs of $\alpha_1$-elements belonging to given 1-element and their contribution does not exceed $Ch^3 \int |x - y|^{-1} \, dx dy = O(h^3)$.

Finally, contribution of $\alpha_2$-element to (3.4.6) does not exceed $C\zeta_\varepsilon \zeta_\varepsilon \alpha_2^\frac{5}{2}$ and one can check easily that this does not exceed $C\alpha_1^2 \gamma_1^\frac{5}{2} h^\frac{3}{2}$ and the summation over $\alpha_2$-partition of $\alpha_1$-element returns $C\alpha_1^3 h^\frac{5}{2}$; then summation over 1-element returns $O(h^\frac{5}{2})$.

So, the scaled versions of (3.4.3) and (3.4.4)–(3.4.6) do not exceed $Ch$ and $Ch^2$ respectively. Then the original versions of (3.4.3), (3.4.4), (3.4.4), and (3.4.6) do not exceed respectively $C\zeta_\varepsilon \zeta_\varepsilon \alpha_2^\frac{5}{2} h^\frac{3}{2}$, $C\zeta_\varepsilon \zeta_\varepsilon \alpha_2^\frac{5}{2} h^\frac{3}{2}$, $C\zeta_\varepsilon \zeta_\varepsilon \alpha_2^\frac{5}{2} h^\frac{3}{2}$, and $C\zeta_\varepsilon \zeta_\varepsilon \alpha_2^\frac{5}{2} h^\frac{3}{2}$.

Leaving easy details to the reader we arrive to

**Proposition 3.4.2.** (i) Contribution of zone $X_2$ to the mollification error (3.4.3) does not exceed $CZ^\frac{3}{2}$;

(ii) Contribution of zone $X_2$ to the mollification error (3.4.4) does not exceed $C \max(Z^\frac{3}{2}, B^\frac{1}{2} Z^\frac{1}{2})$;

(iii) Contributions of zone $X_2$ to the mollification errors s(3.4.5) and (3.4.5) do not exceed $CZ^\frac{5}{2}$.

and

**Proposition 3.4.3.** Let $B \leq Z$. Then

(i) Contribution of zone $X_2$ to the mollification error (3.4.3) does not exceed $CB^\delta Z^\frac{3}{2} - \delta$;

(ii) Contributions of zone $X_2$ to the mollification errors (3.4.5)–(3.4.5) do not exceed $CB^\delta Z^\frac{3}{2} - \delta$.

**Remark 3.4.4.** Obviously scaled $\varepsilon = \gamma_0 \gamma_1 \gamma_2 \gamma(h/\gamma_0^\frac{5}{2} \gamma_1^\frac{5}{2} \gamma_2^\frac{5}{2})^\frac{3}{2} - \delta \geq \frac{h^\frac{3}{2} - \delta}{(\mu^{-1}h)^\frac{3}{2} - \delta}$ which makes reduction possible.
3.5 Zone $\mathcal{X}_3$

Zone $\mathcal{X}_3$ defined by $\mu h \geq C_0$, $h \leq 1$, $\{x : \ell(x) \leq \epsilon_0 \bar{r}\}$ appears only as $Z_3^{\frac{1}{4}} \leq B \leq Z_3^{\frac{1}{2}}$; here $W_b^{\text{TF}}$ is smooth and no mollification is necessary. Further here the canonical form contains only one number $j = 0$ and $|D^\alpha W| \leq C_\alpha \zeta^{2 \ell_{-|\alpha|}}$ and $W \asymp \zeta^2$.

Therefore we have non-degeneracy condition fulfilled and applying the standard theory we conclude that in the scaled version contribution of $B(0,1)$ to the semiclassical errors in $\mathcal{N}$- and $\mathcal{T}$-terms and into $\mathcal{D}$-term are $C\mu h^{-1}$, $C\mu$ and $C\mu^2 h^{-2}$ respectively.

In the unscaled version they become $CB\ell^2$, $CB\ell\zeta \leq CBZ_3^{\frac{1}{2}}\ell^{\frac{1}{2}}$ and $CB_2^2\ell^3$ and after summation (where for $\mathcal{D}$-term we need to consider mixed contribution of different layers) we arrive to the same expressions calculated as $\ell = \bar{r} = B^{-\frac{1}{2}}Z_3^{\frac{1}{2}}$ i.e. $CB_2^2Z_3^{\frac{1}{2}}$, $CB_2^2Z_3^{\frac{1}{2}}$ and $CB_2^2Z_3^{\frac{1}{2}}$ respectively. Thus we have proven

**Proposition 3.5.1.** Let $Z_3^{\frac{1}{4}} \leq B \leq Z_3^{3}$. Then

(i) Contribution of zone $\mathcal{X}_3$ to the $\mathcal{N}$-error does not exceed $CZ_3^{\frac{3}{2}}B_3^{\frac{1}{2}}$;

(ii) Contributions of zone $\mathcal{X}_3$ to the $\mathcal{T}$-error and $\mathcal{D}$-term do not exceed $CZ_3^{3}B_3^{\frac{1}{2}}$.

4 Semiclassical analysis in the boundary strip as $M \geq 2$

To finish our analysis we need to get the same estimates as before in the boundary strip

(4.0.1) $\mathcal{Y} := \{x : W(x) + \nu \leq \epsilon G, \epsilon \bar{r} \leq \ell(x) \leq c \bar{r}\}$

with

(4.0.2) $G := \left\{ \begin{array}{ll}
(Z - N)_+^{\frac{3}{4}} & \text{as } B \leq (Z - N)_+^{\frac{3}{4}}, \\
B & \text{as } (Z - N)_+^{\frac{3}{4}} \leq B \leq Z_3^{\frac{3}{4}}, \\
Z_3^{\frac{3}{4}}B_3^{\frac{1}{2}} & \text{as } B \geq Z_3^{\frac{3}{4}}.
\end{array} \right.$

64
which coincides with (1.3.10) as $B \geq (Z - N)^{\frac{4}{5}}$. Analysis of external zone $X_{4} := \{ x : \ell(x) \geq C_{1}\bar{r} \}$ will be easy and inner zone $\{ x : W(x) + \nu \geq \varepsilon G \}$ has been covered already.

4.1 Properties of $W_{B}^{\text{TF}}$ as $N = Z$

Let us rescale $x \mapsto x' = x\bar{r}^{-1}$, $W \mapsto w = G^{-1}W$ and define $h = G^{-\frac{1}{2}}\bar{r}^{-1}$, $\mu = G^{-\frac{1}{2}}B\bar{r}$. Then

(a) In the case $B \leq Z^{\frac{2}{5}}$ we need to rescale $w(x') = \bar{r}Z^{-1}W_{B}^{\text{TF}}(x'\bar{r})$ and take $h = B^{-\frac{1}{2}} \leq 1$, $\mu = B^{\frac{1}{2}} \geq 1$, $\mu h = 1$;

(b) On the other hand, for $B \geq Z^{\frac{2}{5}}$ one should set $w(x') = \bar{r}Z^{-1}W_{B}^{\text{TF}}(x'\bar{r})$ and $h = (Z\bar{r})^{-\frac{1}{2}} = (BZ^{-3})^{\frac{1}{2}} \leq 1$, $\mu = BZ^{-\frac{1}{2}}\bar{r}^{-1} = B^{\frac{3}{2}}Z^{-\frac{1}{2}} \geq 1$, $\mu h = B^{\frac{3}{2}}Z^{-\frac{3}{2}} \geq 1$ ($\mu h \asymp 1$ if $B \lesssim Z^{\frac{2}{3}}$, $h \asymp 1$ if $B \asymp Z^{3}$).

We will use now only rescaled coordinates unless the opposite is specified.

Then in our zone

\[ \Delta w = \kappa w_{x}^{\frac{2}{3}}, \quad \kappa = 12, \quad w \to \theta = \nu \bar{\zeta}^{-2} \quad \text{as} \quad |x| \to \infty, \]

with $\bar{\zeta} := G^{\frac{1}{2}}$ where one can always get $\kappa = 12$ after rescaling $w \mapsto 144\kappa^{-2}w$.

**Proposition 4.1.1.** Let $Z = N$. Then in $\mathcal{V}$ after rescaling

\[ |D^{\alpha}w| \leq C_\alpha w\gamma^{-|\alpha|} \quad \forall \alpha \]

with the scaling function $\gamma = w^{\frac{1}{3}}$ and

\[ |\nabla w_{x}^{\frac{2}{3}}| \leq 1 + Cw^{t} \]

with some constant $C$ and exponent $t > 0$.

**Proof.** Rescaling $x \mapsto x\bar{r}^{-1}$ we get an equations (4.1.1)$_{0} = (4.1.1)$ with $\theta = 0$. We know that $W = 0$ for $\ell(x) \geq c\bar{r}$; so after rescaling $w = 0$ for $\ell(x) \geq c$.

On the other hand, $w \asymp 1$ as $\ell(x) \leq \epsilon$ (uniformly with respect to all the parameters).

Let us consider solution of the equation

\[ \Delta w_{s} = 12w_{x}^{s} \]

65
Then with \( \gamma \)

Then the lowest eigenvalue we need more subtle arguments.

Further, the standard maximum principle arguments show that \( w_s \nabla \gamma \) as \( s \nabla \frac{23}{2} \). Obviously \( w_s \nabla w \) and \( w_s \to w \) in \( \mathcal{C}^\infty \) in \( \{ x : w(x) > 0 \} \) as \( s \nabla \frac{1}{2} \).

We claim that

\[
(4.1.5) \quad w_s \in \mathcal{C}^{4s + 2}.
\]

To prove (4.1.5) note first that \( w \in \mathcal{C}^{2-\delta} \) uniformly with respect to all the parameters for any \( \delta > 0 \). Then \( w_s \in \mathcal{C}^{s-\delta} \) and then (4.1.4) yields that \( w_s \in \mathcal{C}^{2+s-\delta} \) as soon as \( s - \delta \notin \mathbb{Z} \). Then since \( w_s \geq 0 \) we get \( |\nabla w_s| \leq Cw_s^{\frac{1}{2}} \) and so \( w_s \in \mathcal{C}^{s-\frac{1}{2}} \). Then equation (4.1.4) again yields that \( w_s \in \mathcal{C}^{s+\frac{2}{3}} \). Now we need more subtle arguments.

First, for \( |y| = 1 \)

\[
(4.1.6) \quad w_s(x + ty) = w_s(x) + t(\nabla w_s)_x \cdot y + \frac{1}{2}(\nabla^2 w_s)_x(y)t^2 + O(t^3).
\]

Then the lowest eigenvalue \( \zeta \) of \( \nabla^2 w_s \) at \( x \) should be greater than \( -Cw_s^{\frac{1}{2}} \). Really, otherwise we can take \( y \) as the corresponding eigenvector and \( t \) with \( |t| = \zeta \) and with a sign making second term non-positive and get \( w_s(x + ty) < 0 \).

This lower estimate for eigenvalues of \( \nabla^2 w_s \) and equation (4.1.4) yield that \( |\nabla^2 w_s| \leq Cw_s^{\frac{1}{2}} \). But then \( |\nabla w_s| \leq Cw_s^{\frac{2}{3}} \). Really, otherwise picking \( y = |\nabla w_s|^{-1} \nabla w_s \) with \( |t| = \epsilon|\nabla w_s|^{\frac{1}{2}} \) and an appropriate sign we would get \( w_s(x + ty) < 0 \).

These estimates yield that \( w_s(x') \approx w_s(x) \) in \( B(x, \gamma(x)) \) with \( \gamma(x) = \epsilon w_s^{\frac{1}{2}} \).

Then \( w_s \in \mathcal{C}^{\frac{2}{3}} \). In fact, let us consider \( f = w_s^{\frac{1}{2}} \nabla w \) and \( |f(x) - f(x')| \). Let us consider first \( |x - x'| \geq \frac{1}{\epsilon}(\gamma(x) + \gamma(x')) \); since \( |f(x)| \leq \gamma(x)^{\frac{1}{2}} \) at each point we get that \( |f(x) - f(x')| \leq |x - x'|^{\frac{1}{2}} \).

On the other hand, for \( |x - x'| \leq \frac{1}{\epsilon}(\gamma(x) + \gamma(x')) \) we conclude that \( \gamma(x) \approx \gamma(x') \) and \( |f(x) - f(x')| \leq |\nabla f| \cdot |x - x'| \leq |x - x'|^{\frac{1}{2}} \) because \( |\nabla f| \leq |\nabla^2 w_s| w_s^{\frac{1}{2}} + |\nabla w_s|^2 w_s^{-\frac{1}{2}} \leq C\gamma^{\frac{1}{2}} \).

\[\text{23)}\text{ If } \Delta w_1 = f_1(w) \text{ in } \Omega, f_1(w) \nabla \text{ as } w \nabla \text{ and } f_1(w) \geq f_2(w) \text{ then } \Delta(w_1 - w_2) > 0 \text{ as } w_1 > w_2 \text{ and then } w_1 - w_2 \text{ does not reach maximum inside } \Omega.\]
Therefore \( w_s^2 \in C^{s+1} \) and equation (4.1.4) yields that \( w_s \in C^{3+s} \).

In the next round we assume that \( w \in C^{4+s-\delta} \) with some \( \delta \in (0, 1) \). Then

\[
(4.1.7) \quad w_s(x + ty) \leq w_s(x) + t(\nabla w_s)_x \cdot y + \frac{1}{2} (\nabla^2 w_s)_x(y)t^2 + \frac{1}{6} (\nabla^3 w_s)_x(y)t^3 + C|t|^p
\]

with \( p = \min(4, 4 + s - \delta) \).

We claim now that the lowest possible eigenvalue \( \zeta \) of \( (\nabla^2 w_s)_x \) is greater than \(-Cw_s^{(p-2)/p}\). Really, otherwise let us pick up \( y \) as the corresponding eigenvector, \( t \) with \( |t| = \epsilon|\zeta|^{1/(p-2)} \) and with a sign making expression

\[
t(\nabla w_s)_x \cdot y + \frac{1}{6} t^3 (\nabla^3 w_s)_x(y)
\]

non-positive and get \( w_s(x + ty) < 0 \) again. Now equation (4.1.4) yields that inequality

\[
(4.1.8)_k \quad |\nabla^k w_s| \leq Cw_s^{(p-k)/p}
\]

holds with \( k = 2 \).

Further, we claim that this inequality holds with \( k = 1, 3 \). Indeed, if one or both of these inequalities are violated then let us take corresponding \( y \) and \( t \) with

\[
|t| = \epsilon \left( |\nabla w_s|^{1/(p-1)} + |\nabla^3 w_s(y)|^{1/(p-3)} \right)
\]

(calculated on \( y \)); replacing \( \epsilon \) by \( 2\epsilon \) if necessary we get

\[
|t(\nabla w_s)_x \cdot y + \frac{1}{6} t^3 (\nabla^3 w_s)_x(y)| \geq \epsilon_0 |t(\nabla w_s)_x \cdot y| + \frac{1}{6} t^3 (\nabla^3 w_s)_x(y)|
\]

and choosing an appropriate sign of \( t \) we get \( w(x + ty) < 0 \).

Therefore inequalities (4.1.8) hold. The same arguments as above with \( \gamma = w_s^{1/p} \) lead us to \( w^2 \in C^{ps} \) and then equation (4.1.4) yields that \( w_s \in C^{ps+2} \). So, now we came back with \( \delta \) replaced by \( \delta' = 2 + s - ps \) and one can see easily that if \( \delta > s \) then \( \delta' = s + (2 - 4s) + (\delta - s)s \) and after few repeats \( \delta < s \). Then we get (4.1.5). Unfortunately, constants depend on \( s \) due to the fact that \( \Delta w \in C^2 \) fails to yield \( w \in C^4 \).
Now we are going to finish the proof of (4.1.2). Let us consider \( w_s \) again and let \( \gamma = \gamma_{s,\delta} = w_s^{1/(4-\delta)} \). Due to the previous inequalities \( \gamma \in C^1 \). We claim that \( |\nabla \gamma| \) is bounded uniformly with respect to \( s, \delta \). Note first that \( \Delta \gamma^{4-\delta} = \gamma^{(4-\delta)s} \) implies that

\[
(4.1.9) \quad a|\nabla \gamma|^2 + b\gamma \Delta \gamma = \gamma^\sigma
\]

with \( a = \frac{1}{12}(4 - \delta)(3 - \delta) \), \( b = \frac{1}{12}(4 - \delta) \), and \( \sigma = 4s - 2 + (1 - s)\delta \). Let \( \psi = |\nabla \gamma|^2 \); obviously \( \psi \) is uniformly bounded at \( \partial \Omega \). Let us consider maximum of \( \psi \) reached inside \( \Omega \). At the point of maximum

\[
(4.1.10) \quad \sum_i \gamma_{x_ix_j}\gamma_{x_i} = 0
\]

and

\[
\frac{1}{2}\Delta \psi = \sum_{i,j} \gamma_{x_ix_j}^2 + \sum_i \gamma_{x_i}(\Delta \gamma)_{x_i} = \sum_{i,j} \gamma_{x_ix_j}^2 + b^{-1} \sum_i \gamma_{x_i} \left( \gamma^{-1}(\gamma^\sigma - a|\nabla \gamma|^2) \right)_{x_i}
\]

due to (4.1.9) and due to (4.1.10) this expression is equal to

\[
\sum_{i,j} \gamma_{x_ix_j}^2 - b^{-1}\gamma^{-2}|\nabla \gamma|^2 \left( \gamma^\sigma - a|\nabla \gamma|^2 \right) + b^{-1}\sigma \gamma^{-2}|\nabla \gamma|^2
\]

and therefore at an inner point of minimum \( a|\nabla \gamma|^2 \leq \gamma^\sigma \). So, \( |\nabla \gamma| \leq C \) is proven and for \( s \searrow \frac{1}{2}, \delta \searrow 0 \) we get that \( |\nabla w^t| \leq C \).

Let us pick \( \gamma(x) = \epsilon' w^t(x) \); then \( |\nabla w| \leq \frac{1}{2} \) and \( w(x) \asymp w(x) \) in \( B(x, \gamma(x)) \). This and equation (4.1.4) easily yield (4.1.2).

To prove inequality (4.1.3) let us consider \( w_s \) again and let us take now \( \psi = |\nabla \gamma|^2 - Ft^{2t} \gamma^2 \) with \( t > 0 \); obviously \( \psi \) is non-positive at \( \partial \Omega \) for sufficiently large \( F \). Let us consider maximum of \( \psi \) reached inside \( \Omega \). At the point of maximum

\[
(4.1.10)' \quad \sum_i \gamma_{x_ix_j}\gamma_{x_j} - Ft\gamma^{2t-2}\gamma_{x_j} = 0
\]

and the same arguments as before (plus inequality \( |\nabla \gamma| \leq C_0 \) show that at an inner point of maximum \( a|\nabla \gamma|^2 \leq \gamma^\sigma + CtF\gamma^{2t} \) where \( C \) does not depend on \( F \) and small \( t > 0 \). Then at this point \( \psi \leq 1 \) for small enough \( t > 0 \) and as \( s \to \frac{1}{2} \) and \( \delta \to 0 \) we get (4.1.3). \( \Box \)
The following statement heavily uses estimate (4.1.3):

**Proposition 4.1.2.** The following estimate holds

\[(4.1.11) \quad D(\gamma^{-1+s}, \gamma^{-1+s}) \leq Cs^{-2}\]

with some constant $C$ which does not depend on $s \in (0, 1)$ where we set $\gamma^{-1+s} := w_{1}^{\frac{1}{s}(-1+s)}$ (i.e. it is 0 as $w \leq 0$).

**Proof.** As in the notations of the proof of proposition 4.1.1 $\delta = 0$ and $s = \frac{1}{2}$ we have (4.1.9) with $a = 1$, $b = 3$ and $\sigma = 0$:

\[(4.1.12) \quad \frac{1}{3} \gamma \Delta \gamma + |\nabla \gamma|^2 = 1.\]

Then

\[\gamma^{-1+s} = \gamma^{-1+s}|\nabla \gamma|^2 + \frac{1}{3} \gamma^2 \Delta \gamma = (1 - \frac{s}{3}) \gamma^{-1+s}|\nabla \gamma|^2 + \frac{1}{3(1+s)} \Delta \gamma^{1+s}\]

and

\[D(\gamma^{-1+s}, \gamma^{-1+s}) \leq (1 - \frac{s}{3})D(\gamma^{-1+s}|\nabla \gamma|^2, \gamma^{-1+s}) + C \leq (1 - \frac{s}{3})D(\gamma^{-1+s}, \gamma^{-1+s}) + CD(\gamma^{-1+s+t+s}, \gamma^{-1+s}) + C\]

due to (4.1.3) and this yields

\[D(\gamma^{-1+s}, \gamma^{-1+s}) \leq Cs^{-2}D(\gamma^{-1+s+t+s}, \gamma^{-1+s}) + Cs^{-1}.\]

Substituting $s + mt$ instead of $s$, $0 \leq m \leq Ct^{-1}$ we recover (4.1.11). \qed

### 4.2 Analysis in the boundary strip $\mathcal{Y}$ for $N \geq Z$

It is really easy to construct the proper potential in this case: we just take

\[(4.2.1) \quad w_{\epsilon} = w\phi_{\epsilon}, \quad \phi_{\epsilon} = f(w\epsilon^{-4})\]

with $f \in C_{0}^{\infty}(\left(\frac{1}{2}, \infty\right))$, $0 \leq f \leq 1$, $f(t) = 1$ for $t > 1$. Note that due to (4.1.1)

\[D(\gamma^{-1} \phi_{\epsilon}, \gamma^{-1} \phi_{\epsilon}) \leq C\epsilon^{-2s}D(\gamma^{s-1}, \gamma^{s-1}) \leq Cs^{-2}\epsilon^{-2s},\]

\[D(1 - \phi_{\epsilon}, 1 - \phi_{\epsilon}) \leq C\epsilon^{2-2s}D(\gamma^{s-1}, \gamma^{s-1}) \leq Cs^{-2}\epsilon^{2-2s};\]
then minimizing with respect to \( s = |\log \varepsilon|^{-1} \) the right-hand expression we conclude that

\[
D(\gamma^{-1}\phi_{\varepsilon}, \gamma^{-1}\varphi_{\varepsilon}) + \varepsilon^{-2}D(1 - \phi_{\varepsilon}, 1 - \varphi_{\varepsilon}) \leq C(1 + |\log \varepsilon|)^2
\]

and therefore

\[
\int \gamma^{-1}\phi_{\varepsilon} \, dx + \varepsilon^{-1} \int (1 - \phi_{\varepsilon}) \, dx \leq C(1 + |\log \varepsilon|).
\]

**Remark 4.2.1.**

(i) Recall that all these integrals are taken over domain \( \{ x : w(x) > 0 \} \). To avoid possible troubles we pick \( \varepsilon = h^{\frac{1}{2}} \) and set in the zone \( \{ x : w(x) \leq C_0 h^{\frac{3}{2}} \} \)

\[
\gamma(x) = \text{dist}(x, \{ w \geq 2C_0 h^{\frac{3}{2}} \}),
\]

\[
(4.2.1)'
\]

\[
w_{\varepsilon} = \begin{cases} -\gamma^{4} \phi'_{\varepsilon} & \text{for } \gamma \leq \varepsilon, \\ -\varepsilon^{4} & \text{for } \gamma \geq \varepsilon \end{cases}
\]

with \( \phi'_{\varepsilon} = f(\gamma\varepsilon^{-1}) \) and then in the complementary domain \( \{ x : w(x) \leq -\varepsilon^{2} \} \) with \( \varepsilon = \varepsilon^{2} \) and \( \varepsilon^{3} = \gamma^{3} \geq h \);

(ii) Further, for \( \varepsilon = h^{\frac{1}{2}-\delta} \) with sufficiently small exponent \( \delta > 0 \) it does not break estimate for mollification error in \( T \)-term;

(iii) Furthermore, for \( t > \varepsilon \)

\[
\text{mes}(\{ x : \gamma(x) \leq t \}) \leq Ct^3 \varepsilon^{-3} \text{mes}(\{ x : \gamma(x) \leq \varepsilon \varepsilon \})
\]

and therefore

\[
h^s \int \gamma^{-1-s}\varsigma^{-s} \, dx \leq C\varepsilon^{-1} \text{mes}(\{ x : \gamma(x) \leq \varepsilon \varepsilon \}) \leq CL := C(1 + |\log h|)
\]

for sufficiently large \( s \).

Using these estimates and the last remark we can prove easily

**Proposition 4.2.2.** Let \( N \geq Z \). Then
(i) Contribution of $\mathcal{Y} \cup \mathcal{X}_4$ with $\mathcal{X}_4 := \{x : w(x) = 0\}$ to mollification and approximation errors in $N$-term do not exceed $CT_0\varepsilon^3(1 + |\log \varepsilon|)$ and $R_0(1 + |\log \varepsilon|)$ respectively with

\begin{equation}
(4.2.4)_1 \quad T_0 = B^{\frac{3}{2}}, \quad R_0 = B^{\frac{1}{2}}, \quad T = B^{\frac{5}{2}}, \quad R = B^{\frac{3}{2}}
\end{equation}

as $B \leq Z^{\frac{3}{4}}$

and

\begin{equation}
(4.2.4)_2 \quad T_0 = Z, \quad R_0 = B^{\frac{3}{2}}Z^{\frac{5}{2}}, \quad T = Z^{\frac{3}{2}}B^{\frac{5}{2}}, \quad R = Z^{\frac{3}{2}}B^{\frac{5}{2}}
\end{equation}

as $Z^{\frac{3}{4}} \leq B \leq Z^3$.

(ii) Contribution of $\mathcal{Y} \cup \mathcal{X}_4$ to mollification and semiclassical $D$-terms do not exceed $CT \varepsilon^5(1 + |\log \varepsilon|)^2$ and $R(1 + |\log \varepsilon|)^2$ respectively;

(iii) Contribution of $\mathcal{Y} \cup \mathcal{X}_4$ to both mollification and approximation errors in $T$-term do not exceed $CT \varepsilon^7(1 + |\log \varepsilon|)$ and $CR$ respectively.

Proof. Really, estimates for mollification errors and terms immediately follow from the inequality

\begin{equation}
(4.2.5) \quad \text{mes}(\{x : w(x) \leq \varepsilon^4\}) \leq C\varepsilon(1 + |\log \varepsilon|)
\end{equation}

which is due to (4.2.3).

Let us consider semiclassical errors and terms.

(i) Let us consider $N$-term first. Let us consider all possible balls and their contributions: the contribution of each ball $B(x, \gamma(x))$ to the semiclassical error does not exceed $C\mu h^{-1} \gamma^2 \geq CB\tau^2 \gamma^2$ and the total contribution does not exceed $CR_0 \int \gamma(x)^{-1} dx \leq CR_0(1 + |\log \varepsilon|)$ where $R_0 = B\tau^2$; recall that $\gamma(x) \geq \varepsilon$;

(ii) Consider semiclassical $D$-term. Let us consider all possible balls and their contributions: the similar arguments with the analysis of disjoint balls of different types and with analysis of the intersecting balls (of the same type) lead us to the proper estimate of the contribution of $\mathcal{Y}_4 \cup \mathcal{X}_4$ to semiclassical $D$-term: namely, it does not exceed $CR_0^2 \tau^{-1}(1 + |\log \varepsilon|)^2$ where $R_0^2 \tau^{-1} \asymp R$;
(iii) Consider T-term. Let us consider all possible balls and their contributions. The contribution of each ball $B(x, \gamma(x))$ to the semiclassical error does not exceed $C\zeta^2 \mu \epsilon^2 \gamma \approx CB\zeta^2 \tau \epsilon \gamma^2$ and the total contribution does not exceed $CR \int \zeta(x)\gamma(x)^{-2} dx \approx CR$ where $R = B\zeta^2 \tau$ and $\zeta(x) \approx \gamma(x)^2$. \hfill $\Box$

Then picking appropriate $\epsilon = \hbar^{\frac{1}{3}}$ we arrive to

**Corollary 4.2.3.** Let $N \geq Z$. Then

(i) Contributions of $\mathcal{Y} \cup \mathcal{X}_4$ to all errors in $N$-terms do not exceed $CR_9 L$ with $L = (1 + |\log BZ^{-3}|)$;

(ii) Contribution of $\mathcal{Y} \cup \mathcal{X}_4$ to all $D$-terms do not exceed $CRL^2$;

(iii) Contribution of $\mathcal{Y} \cup \mathcal{X}_4$ to all errors in $T$-terms do not exceed $CR$.

We will sum contributions of all zones to errors in Propositions 4.3.6 and 4.4.2 below.

**Remark 4.2.4.** Could we get rid off logarithmic factors i.e. make $L = 1$ as in the case $M = 1$?

(i) With the mollification errors we need to replace (4.2.5) by

$$
(4.2.6) \quad \text{mes}(\{x : w(x) \leq \epsilon^4\}) \leq C \epsilon;
$$

(ii) With the semiclassical terms our arguments here are insufficient even if we established (4.2.6); we need extra propagation arguments in the direction of decaying $w$ along magnetic lines–exactly as in the case $M = 1$. Surely there could be points where such arguments do not work; e.g. consider $M = 2$ and nuclei so that $|\gamma_1 - \gamma_2|$ is slightly less than $\tau_1 + \tau_2$ where $\tau_{1,2}$ are precise radii of support. Then $w$ reaches its minimum at $\mathcal{Y}$.

So, we need to prove that the measure of such points is sufficiently small (f.e. less than $C|\log BZ^{-3}|^{-1}$).

Unfortunately I do not know how to make the above remark work and I suggest

**Problem 4.2.5.** Follow through the discussed plan. For $M = 2$ it could be easier due to rotational symmetry.
4.3 Analysis in the boundary strip $\mathcal{Y}$ for $N < Z$

Now let us consider $N < Z$.

4.3.1 Case $B \geq (Z - N)^{\frac{4}{3}}$

We start from the case $B \geq (Z - N)^{\frac{4}{3}}$ when $\tilde{r} = \min(B^{-\frac{4}{3}}, Z^{\frac{1}{3}}B^{-\frac{4}{3}})$.

**Remark 4.3.1.** (i) The results of the previous Subsubsection remain true as long as $|\nu|G^{-1} \leq C_0 h^\frac{4}{3}$; in other words, as $(Z - N)_+ \leq C_0 \tilde{r} h^\frac{4}{3}$. Plugging $\tilde{r}$, $G$ and $h$, we rewrite it as

\[
(Z - N)_+ \leq C_0 \min\left(B^\frac{5}{3}, Z^\frac{1}{3}B^\frac{4}{3}\right)
\]

matching cases $B \lesssim Z^\frac{4}{3}$ and $Z^\frac{1}{3} \lesssim B \lesssim Z^3$.

(ii) Therefore in what follows we assume that (4.3.1) fails. Let $\tilde{r} = |\nu|G^{-1} \times (Z - N)_+ \cdot \max(B^{-\frac{1}{3}}, Z^{-1})$ also matching cases $B \lesssim Z^\frac{4}{3}$ and $Z^\frac{1}{3} \lesssim B \lesssim Z^3$.

**Proposition 4.3.2.** Consider dependence of $W_B^{TF} = W_{B(\nu)}^{TF}(x)$ on $\nu$. Then

(i) $W_B^{TF}(x) + \nu$ is non-decreasing with respect to $\nu$ at each point $x$;

(ii) $W_B^{TF}(x)$ is non-increasing with respect to $\nu$ at each point $x$;

(iii) In particular, $W_B^{TF}(x) + \nu \nearrow W_{B(\nu)}^{TF}(x)$ and $W_B^{TF}(x) \searrow W_{B(\nu)}^{TF}(x)$ at each point $x$ as $\nu \to -0$.

**Proof.** (i) Consider $W_j = W_{B(\nu)}^{TF} + \nu_j$ with $0 > \nu_1 > \nu_2$. One can prove easily that $W_B^{TF} - V$ is a continuous function and since $W_1 - W_2 = \nu_1 - \nu_2 > 0$ as $\ell(x) \geq C$ we conclude that $W_1 \geq W_2$ at each point $x$ (which is exactly our statement (i)) unless $W_1 - W_2$ achieves a negative minimum at some point $x^*$.

(a) Let $x^* \neq y_m$; then $\Delta(W_1 - W_2)(x^*) = P_B'(W_1) - P_B'(W_2) \leq 0$ because $W_1 < W_2$ at $x^*$ and $x^*$ cannot be such point.
(b) Let $x^* = y_m$. From Thomas-Fermi equations for $W_{1,2}$ one can prove easily that

$$(W_1 - W_2)(x) = (W_1 - W_2)(y_m) + L_m(x - y_m) + \kappa_m|x - y_m|^\frac{3}{2}(W_1 - W_2)(y_m) + O(|x - y_m|^2)$$

near $y_m$ where $L_m(x)$ is a linear function and $\kappa_m > 0$ and therefore if $(W_1 - W_2)(y_m) < 0$, $y_m$ cannot be a minimum point either.

(ii) So, $W_1 \geq W_2$ and therefore $W_1 - W_2$ is a subharmonic function and since $W_1 - W_2 = \nu_1 - \nu_2$ as $\ell(x) \geq C$ we conclude that $W_1 - W_2 \leq \nu_1 - \nu_2$

i.e. $W_{B(\nu)}^{TF} \leq W_{B(\nu_2)}^{TF}$ at each point.

(iii) Statement (iii) follows from (i), (ii).

Therefore in the zone $\{x : W_{B(\nu)}^{TF} \geq (1 + \epsilon)|\nu|\}$ we can apply the same $(\gamma, \varsigma)$ scaling with $\varsigma = \gamma^2$ defined for $\nu = 0$. Really, we know that there $W_{B(\nu)}^{TF} + \nu \simeq W_{B(\nu_2)}^{TF} \simeq \varsigma^2$ and $\varsigma = \gamma^2$.

Then Thomas-Fermi equation (1.1.3) implies that

$$|\nabla^\alpha W_{B(\nu)}^{TF}| \leq C_{\alpha} \varsigma^2 \gamma^{-|\alpha|} \quad \forall \alpha$$

and then we arrive to the statement (i) in Proposition 4.3.3 below. On the other hand, in the zone $\{x : W_{B(\nu)}^{TF} \leq (1 - \epsilon)|\nu|\}$ we can apply the same arguments but this zone is classically forbidden and we arrive to to the statement (ii) below. In both cases $\gamma \geq \hbar$ (where in the latter case $\gamma$ is the distance from $x$ to $W_{B(\nu_2)}^{TF}$ (scaled) and $\varsigma = |\theta|^{\frac{3}{2}}$ in virtue of Remark 4.3.1.

Then we arrive to the statement (ii) in Proposition 4.3.3 below.

**Proposition 4.3.3.** Let either $B \leq Z^\frac{4}{3}$ and $|\nu|^{\frac{3}{2}} \geq Z^\frac{3}{5}$ or $Z^\frac{4}{3} \leq B \leq Z^3$ and $|\nu|^{\frac{3}{2}} \geq B^\frac{3}{2}$. Then

(i) Contributions of zone $\{x : W_{B(\nu)}^{TF}(x) \geq (1 + \epsilon_0)|\nu|\}$ to semiclassical errors in $N$- and $T$-terms and into semiclassical $D$-term do not exceed $CR_0L$, $CR$ and $CRL^2$ respectively;

(ii) Contributions of zone $\{x : W_{B(\nu)}^{TF}(x) \leq (1 - \epsilon_0)|\nu|\}$ to semiclassical errors in $N$- and $T$-terms and into semiclassical $D$-term do not exceed $CR_0L$, $CR$ and $CRL^2$ respectively.
Remark 4.3.4. Here actually we can replace \( L \) by \( L_\ast = 1 + |\log \theta| \) with 

\[
\theta = |\nu| G^{-1} \asymp \begin{cases} 
(Z - N)_+ B^{-\frac{1}{2}} & \text{as } (Z - N)_+ \frac{1}{4} \leq B \leq Z^\frac{1}{4}, \\
(Z - N)_+ Z^{-1} & \text{as } Z^\frac{1}{4} \leq B \leq Z^3.
\end{cases}
\]

Therefore we need to explore zone 

\[
\mathcal{Y}^\ast := \{ x : (\nu - \epsilon) |\nu| \leq W_B^{TF}(x) \leq (1 + \epsilon) |\nu| \}
\]

in the framework of Proposition 4.3.3. in virtue of Remark 4.3.1 \( h_\ast \leq 1 \) where 

\[
h_\ast = h\theta^{-\frac{1}{2}} \asymp \begin{cases} 
(Z - N)^{-\frac{3}{2}} B^\frac{5}{16} & \text{as } B \leq Z^\frac{4}{5}, \\
(Z - N)^{-\frac{3}{2}} Z^\frac{3}{2} B^\frac{5}{16} & \text{as } Z^\frac{4}{5} \leq B \leq Z^3.
\end{cases}
\]

Let us rescale \( B(., \alpha) \) to \( B(., 1) \) by \( x \mapsto x\alpha^{-1} \) with \( \alpha = \theta^\frac{1}{2} \) (after we rescaled \( x \mapsto x\tilde{r}^{-1} \)). After this let us introduce scaling function \( \gamma_0 \) by (3.1.3). Then let us introduce consequently scaling functions \( \gamma_1 \) by (3.1.7), \( \gamma_2 \) by (3.1.13) and \( \gamma_3 \) by (3.1.14) \(^{24}\)

Consider contributions of different balls in this hierarchy into semiclassical and approximation errors in \( N \)- and \( T \)-terms and into \( D \) semiclassical and approximation \( D \)-terms.

(i) Due to Chapter 18 contribution of \( \phi_\ast \) into the semiclassical error in \( N \)-term does not exceed \( C B \gamma_2^2 \alpha_j^2 \gamma_3^2 \) as \( j = 2, 3 \) where \( \alpha_j = \gamma_0 \cdots \gamma_j \).

Then for \( j = 2 \) we have \( C B \gamma_2^2 \alpha_2^2 = C B \gamma^2 \alpha_2^2 \gamma_1^2 \) and therefore we estimate contribution of \( \gamma_1 \) element by \( C B \gamma^2 \alpha_2^2 \int \gamma_1^{-1} dx \) \(^{25}\) which results in \( C B \gamma^2 \alpha_2^2 \) but with the logarithmic factor. However we can get rid off this factor due to a simple observation:

\[
(4.3.4) \quad \text{If } \gamma_2 \leq \epsilon \text{ then } \text{Hess}(w_1) \text{ has at least two eigenvalues of magnitude } 1 \text{ due to } |\Delta w_1| \leq \epsilon_1.
\]

Then contribution of \( \alpha_0 \)-element does not exceed \( C B \gamma^2 \alpha_0^2 \int \gamma_1^{-1} dx \); we claim that it is \( C B \gamma^2 \alpha_0^2 \). Really we need to consider only points with \( \gamma_1 \leq \epsilon \) and there we use a similar observation:

\(^{24}\) With \( j = \bar{j} = 0 \) and corrected as in (3.1.3)* and (3.1.7)*.

\(^{25}\) With integral calculated in the scaled coordinates.
(4.3.5) If $\gamma_1 \leq \epsilon$ then $|\nabla^3 w| \asymp 1$ and also $|\nabla^3 w - e \otimes e \otimes e| \geq c^{-1}$ for any $e \in \mathbb{R}^3$ due to $|\partial_i \Delta w_1| \leq \epsilon_1$; here $\nabla^3 w$ is a 3-tensor of third derivatives.

Further, contribution of $\alpha$-element does not exceed $CB\tau^2 \alpha^2 \int \gamma_0^{-1} dx^{25}$; since $\gamma \geq \bar{\gamma}_0 = \hbar_\star^{3}$ we estimate it by $CB\tau^2 \alpha^2 \hbar_\star^{-\frac{3}{2}}$.

Finally, since $\tau^{-1} \mathcal{Y}^*$ is covered by no more than $CL_\star \alpha^{-2}$ such elements we conclude that the total contribution of $\mathcal{Y}^*$ into semiclassical (and also approximation) errors in $N$-term does not exceed $CB\tau^2 \hbar_\star^{-\frac{3}{2}} L_\star$ where $L_\star := (1 + |\log \theta|)$. Plugging values of $\hbar$ and $\theta$ we arrive to expression (4.3.6) in Proposition 4.3.5(i) below.

(ii) Similarly, in virtue of Subsubsection 2.1.2.2 Semiclassical D-term we know that contribution of the non-disjoint pair $(\phi_\star, \phi_\star)$ of $\alpha_j$-elements to semiclassical D-term does not exceed $CB^2 \ell^3 = CB^2 \tau^3 \alpha_j^3$ as $j = 2, 3$; therefore contribution of all non-disjoint pairs of $\alpha_2$ subelements to the same expression for $\alpha_1$-element does not exceed $CB^2 \tau^3 \alpha_1^3$. Adding all disjoint pairs we get $CB^2 \tau^3 \alpha_1^3 \int \int |x - y|^{-1} \alpha_2(x)^{-1} \alpha_2(y)^{-1} dxdy^{25}$; using use the results of (i) together with observation (4.3.4) we get $CB^2 \tau^3 \alpha_1^3$.

Further, continuing in the same manner we estimate the contribution of the non-disjoint pair $(\phi_\star, \phi_\star)$ of $\alpha_0$-elements by $CB^2 \tau^3 \alpha_0^3$.

Furthermore, we estimate the contribution of the non-disjoint pair $(\phi_\star, \phi_\star)$ of $\alpha$-elements by $CB^2 \tau^3 \alpha^3 \hbar_\star^{-\frac{3}{2}}$.

Finally, we conclude that the total contribution of $\mathcal{Y}^* \times \mathcal{Y}^*$ into semiclassical (and also approximation) D-terms does not exceed $CB^2 \tau^3 \hbar_\star^{-\frac{3}{2}} L_\star^2$. Plugging values of $\hbar$ and $\theta$ we arrive to expression (4.3.7) in Proposition 4.3.5(ii) below.

(iii) Due to Chapter 18 contribution of $\phi_\star$ to semiclassical error in $T$-term does not exceed $CB \ell_\star \zeta_\star$ as $j = 3, 2$. Note that $\zeta = G^{\frac{1}{2}} \gamma_0^2 \gamma_1^2 \gamma_2^3$ and $\zeta = G^{\frac{1}{2}} \gamma_0^2 \gamma_1^2 \gamma_2$ for $j = 3, 2$. Here we took $\theta = \alpha = 1$ thus covering the whole zone $\mathcal{Y}$.

Then the contribution of $\alpha_2$-element does not exceed $CBG^{\frac{1}{2}} \tau^3 \gamma_0^3 \gamma_1^3 \gamma_2^2$; contribution of $\alpha_1$-element does not exceed $CBG^{\frac{1}{2}} \tau^3 \gamma_0^3 \gamma_1^3 \int \gamma_2^{-1} dx^{25}$ resulting in $CBG^{\frac{1}{2}} \tau^3 \gamma_0^3 \gamma_1^3$ in virtue of the same observation (4.3.4).

Further, contribution of $\alpha_0$-element does not exceed $CBG^{\frac{1}{2}} \tau^3 \gamma_0^3 \int \gamma_1^{-\frac{1}{2}}$ resulting in $CBG^{\frac{1}{2}} \tau^3 \gamma_0^3$ in virtue of the same observation (4.3.5).
Finally the total contribution of $\mathcal{Y}$ does not exceed $CBG^{\frac{1}{2}} \tau = CB^2 \tau^3 = \max(B^{\frac{1}{2}}, Z^{\frac{3}{2}} B^{\frac{3}{2}})$.

Therefore we arrive to

**Proposition 4.3.5.** In the framework of Proposition 4.3.5 there exists potential $W_\varepsilon$ such that

(i) Contributions of $\mathcal{Y}^*$ to both semiclassical and approximation errors for $\mathcal{N}$-term do not exceed

$$ (4.3.6) \quad (Z - N)^{\frac{3}{2}} L \times (B^{\frac{3}{2}}; Z^{\frac{3}{2}} B^{\frac{3}{2}}) $$

where we list different values for $(Z - N)^{\frac{3}{2}} \leq B \leq Z^{\frac{3}{2}}$ and $Z^{\frac{3}{2}} \leq B \leq Z^3$;

(ii) Contributions of $\mathcal{Y}^* \times \mathcal{Y}^*$ to both semiclassical and approximation $\mathcal{D}$-terms do not exceed

$$ (4.3.7) \quad (B^{\frac{3}{2}}; Z^{\frac{3}{2}} B^{\frac{3}{2}}) $$

(iii) Contributions of $\mathcal{Y}^*$ to both semiclassical and approximation errors for $\mathcal{T}$-term do not exceed

$$ (4.3.8) \quad B^{\frac{3}{2}}, Z^{\frac{3}{2}} B^{\frac{3}{2}}). $$

### 4.3.2 Case $B \leq (Z - N)^{\frac{4}{3}}$

Now let us consider case $B \leq (Z - N)^{\frac{4}{3}}$. In this case boundary strip

$$ (4.3.9) \quad \mathcal{Y} := \{ x : |W(x) + \nu| \leq \varepsilon |\nu| \} $$

consists of two subzones

$$ (4.3.10) \quad \mathcal{Y}_1 := \{ x : \varepsilon B \leq |W(x) + \nu| \leq \varepsilon |\nu| \} $$

and

$$ (4.3.11) \quad \mathcal{Y}^* := \{ x : |W(x) + \nu| \leq \varepsilon B \}. $$

Applying arguments of Section 3 (more precisely, analysis in zones $\mathcal{X}_1$, $\mathcal{X}_1$ extended and $\mathcal{X}_2$) one can prove easily that
Proposition 4.3.6. Let $B \leq (Z - N)^{\frac{4}{7}}$. Then

(i) Contributions of $\mathcal{Y}_1$ into semiclassical and approximation errors in $\mathsf{N}$-term do not exceed $C|\nu|^2 \tilde{r} \asymp C(Z - N)^{\frac{3}{4}}$;

(ii) Contributions of $\mathcal{Y}_1 \times \mathcal{Y}_1$ into semiclassical and approximation $\mathsf{D}$-terms do not exceed $C|\nu|^2 \tilde{r}^3 \asymp C(Z - N)^{\frac{5}{4}}$;

(iii) Contribution of $\mathcal{Y}_1$ into semiclassical and approximation errors in $\mathsf{T}$-term do not exceed $C|\nu|^\frac{3}{2} \tilde{r} \asymp C(Z - N)^{\frac{5}{4}}$.

Proof. We leave easy details to the reader. \qed

On the other hand, applying arguments of the previous Subsubsection 4.3.1 with $\theta = 1$, $\hbar_* = |\nu|^{-\frac{1}{2}} \tilde{r}^{-1} \asymp (Z - N)^{-\frac{1}{2}}$ one can prove easily that

Proposition 4.3.7. Let $B \leq (Z - N)^{\frac{4}{7}}$. Then

(i) Contributions of $\mathcal{Y}_2$ into semiclassical and approximation errors in $\mathsf{N}$-term do not exceed $C(Z - N)^{-\frac{5}{4}} B$;

(ii) Contributions of $\mathcal{Y}_2 \times \mathcal{Y}_2$ into semiclassical and approximation $\mathsf{D}$-terms do not exceed $C(Z - N)^{-\frac{7}{4}} B^2$;

(iii) Contribution of $\mathcal{Y}_2$ into semiclassical and approximation errors in $\mathsf{T}$-term do not exceed $C(Z - N)^{\frac{5}{4}}$.

Proof. We leave easy details to the reader.

4.4 Summary

Adding contributions of all other zones we arrive to

Proposition 4.4.1. Let $M \geq 2$. Then for the constructed potential $W$
(i) Total semiclassical and approximation errors in N-term do not exceed
\[ C \begin{cases} CZ^{\frac{5}{3}} + (Z - N)^{-\frac{3}{2}}B & \text{as } B \leq (Z - N)^{\frac{4}{3}}, \\ Z^\frac{3}{2} + B^\frac{1}{2}L + (Z - N)^{\frac{1}{2}}B^\frac{3}{2}L_\ast & \text{as } (Z - N)^{\frac{4}{3}} \leq B \leq Z^\frac{4}{3}, \\ Z^\frac{5}{2}B^\frac{1}{2}L + (Z - N)^{\frac{1}{2}}Z^\frac{7}{2}B^\frac{5}{2}L_\ast & \text{as } Z^\frac{4}{3} \leq B \leq Z^3, \end{cases} \]

where \( L_\ast = (1 + |\log \theta|) \) with \( \theta = |\nu|G^{-1} = (Z - N)_+ \cdot \max(B^{-\frac{3}{4}}, Z^{-1}) \) and \( L = (1 + |\log BZ^3|) \).

(ii) Both semiclassical and approximation D-terms do not exceed
\[ C \begin{cases} Z^\frac{3}{2} + (Z - N)^{\frac{7}{2}}B^2 & \text{as } B \leq (Z - N)^{\frac{4}{3}}, \\ Z^\frac{5}{2} + B^\frac{3}{2}L^2 + (Z - N)^{\frac{1}{2}}B^\frac{5}{2}L_\ast^2 & \text{as } (Z - N)^{\frac{4}{3}} \leq B \leq Z^\frac{4}{3}, \\ Z^\frac{5}{2}B^\frac{1}{2}L^2 + (Z - N)^{\frac{1}{2}}Z^\frac{7}{2}B^\frac{5}{2}L_\ast^2 & \text{as } Z^\frac{4}{3} \leq B \leq Z^3, \end{cases} \]

(iii) Total approximation error in T-term does not exceed
\[ CQ := C \max(Z^\frac{3}{2}, Z^\frac{5}{2}B^\frac{1}{2}) = C \begin{cases} Z^\frac{5}{2} & \text{as } B \leq Z^\frac{4}{3}, \\ Z^\frac{5}{2}B^\frac{1}{2} & \text{as } Z^\frac{4}{3} \leq B \leq Z^3. \end{cases} \]

(iv) Total semiclassical error in T-term does not exceed
\[ CQ + CZ^\frac{5}{2}B^\frac{1}{2} + CZ^\frac{3}{2}a^{-\frac{1}{2}} \]
provided \( a \geq Z^{-1} \); as \( a \leq Z^{-1} \) the last term should be replaced by \( CZ^2 \).

Also we arrive to

**Proposition 4.4.2.** Let \( M \geq 2, B \leq Z \) and \( a \geq Z^{-\frac{1}{2}} \). Then for the constructed potential \( W \)

(i) Total semiclassical and approximation errors in N-term do not exceed
\[ CZ^\frac{5}{3}((BZ^{-1})^\delta + (aZ^\frac{1}{2})^{-\delta} + Z^{-\delta}) ; \]

(ii) Both semiclassical and approximation D-terms and semiclassical and approximation errors in T-term do not exceed
\[ CZ^\frac{5}{3}((BZ^{-1})^\delta + (aZ^\frac{1}{2})^{-\delta} + Z^{-\delta}) . \]
5 Ground state energy

5.1 Lower estimates

Now the lower estimates are already proven: in virtue of the analysis given in Subsection 24.2.1

\begin{equation}
E_N \geq \Phi_s(W) + \left( \text{Tr}(H_{A,W} - \nu)^{-} + \int P_B(W + \nu) \, dx \right) - \nu N
\end{equation}

for arbitrary potential \( W \) and \( \nu \leq 0 \); picking Thomas-Fermi potential \( W = W_B^{\text{TF}} \) and chemical potential \( \nu \) we arrive to estimate (5.1.2) below with \( W = W_B^{\text{TF}} \) and \( Q = 0 \).

However we use slightly different potential \( W \) and arrive to estimate (5.1.2) below where \( CQ \) defined by (4.4.4) estimates an approximation error; replacing \( T \)-term by its semiclassical approximation and applying Proposition 4.4.1(iii) and 4.4.2(ii) we arrive to estimates (5.1.3)–(5.1.6):

**Proposition 5.1.1.** Let \( B \leq Z^3 \). Then

(i) The following estimate holds with an approximate potential \( W \) we constructed:

\begin{equation}
E^{\text{TF}} \geq \mathcal{E}^{\text{TF}} + \left( \text{Tr}(H_{A,W} - \nu)^{-} + \int P_B(W + \nu) \, dx \right) - CQ
\end{equation}

with \( Q \) defined by (4.4.3); further, for \( W = W_B^{\text{TF}} \) this estimate holds with \( Q = 0 \);

(ii) The following estimates hold for \( M = 1 \) and \( M \geq 2 \) respectively

\begin{equation}
E^{\text{TF}} \geq \mathcal{E}^{\text{TF}} + \text{Scott} - CQ - CZ^\frac{a}{2} B^{\frac{1}{2}}
\end{equation}

and

\begin{equation}
E^{\text{TF}} \geq \mathcal{E}^{\text{TF}} + \text{Scott} - CQ - CZ^\frac{1}{2} B^{\frac{1}{2}} - CZ^\frac{1}{2} a^{-\frac{1}{2}}
\end{equation}

provided \( a \geq Z^{-1} \) \(^{26}\) and \( B \leq Z^2 \); otherwise we can skip Scott and replace the last term by \( CZ^2 \);

\(^{26}\) Recall that \( a \) is the minimal distance between nuclei.
(iii) As \( B \leq Z \) the following estimates hold for \( M = 1 \) and \( M \geq 2 \), \( a \geq Z^{-\frac{1}{3}} \) respectively

\begin{equation}
E_{TF} \geq E_{TF} + \text{Scott} + \text{Dirac} + \text{Schwinger} - CZ^{\frac{5}{3}} (Z^{-\delta} + (BZ^{-1})^{\delta})
\end{equation}

and

\begin{equation}
E_{TF} \geq E_{TF} + \text{Scott} + \text{Dirac} + \text{Schwinger} - CZ^{\frac{5}{3}} (Z^{-\delta} + (BZ^{-1})^{\delta} + (aZ^{\frac{1}{3}})^{-\delta}).
\end{equation}

### 5.2 Upper estimate: general scheme

On the other hand, an upper estimate is more demanding. Recall that according to Subsection 24.2.2 for an upper estimate in addition to the trace we need to estimate also \( |\lambda_N - \nu| \) where \( \lambda_N < 0 \) is \( N \)-th eigenvalue of \( H_{A,W} \) and 0 as \( H_{A,W} \) has less than \( N \) negative eigenvalues, and

\begin{equation}
|\lambda_N - \nu| \cdot |N(H_{A,W}) - N|
\end{equation}

and also three \( D \)-terms: two of them are semiclassical:

\begin{equation}
D\left( e(x, x, \lambda) - P_B'(W(x) + \lambda), e(x, x, \lambda) - P_B'(W(x) + \lambda) \right)
\end{equation}

with \( \lambda = \nu \) and \( \lambda = \lambda_N \) and also

\begin{equation}
D\left( P_B'(W(x) + \lambda_N) - P_B'(W(x) + \nu), P_B'(W(x) + \lambda_N) - P_B'(W(x) + \nu) \right);
\end{equation}

our tool will be semiclassical estimates for two semiclassical \( N \)-terms

\begin{equation}
\int \left( e(x, x, \lambda) - P_B'(W(x) + \lambda) \right) dx
\end{equation}

with \( \lambda = \nu \) and \( \lambda = \lambda_N \) and also estimate from below for the third \( N \)-term

\begin{equation}
| \int \left( P_B'(W(x) + \lambda_N) - P_B'(W(x) + \nu) \right) dx |
\end{equation}

81
5.3 Upper estimate as $M = 1$

5.3.1 Estimate for $|\lambda_N - \nu|$

As in Subsection 24.2.2 we have two cases: in the first case $\nu$ is small enough so we construct $W^{TF}$ with $\nu = 0$ and estimate $|\lambda_N|$ and in the second case $\nu$ we prove that $\lambda_N \sim \nu$ and estimate $|\lambda_N - \nu|$.

Proposition 5.3.1. Let $M = 1, B \leq Z^3$.

(i) Let
\[(Z - N)_+ \leq K := C_0 \max(Z \frac{2}{3}, Z \frac{2}{3} B^{\frac{1}{3}})\]
and let us construct $W$ as if $\nu = 0$ i.e. $N = Z$. Then
\[|\lambda_N| \leq C_1 \max(Z \frac{8}{3}, B^{\frac{2}{3}});\]

(ii) Let
\[(Z - N)_+ \geq K = C_0 \max(Z \frac{2}{3}, Z \frac{2}{3} B^{\frac{1}{3}})\]
with sufficiently large $C_0$. Then $\lambda_N \sim \nu$ and
\[|\lambda_N - \nu| \leq C_1 \max(Z \frac{2}{3}, B^{\frac{1}{3}})|\nu|^{\frac{1}{3}}.\]

Proof. (i) One can see easily that
\[(5.3.5) \text{ In the framework of (i) as } B \geq (Z - N)^{\frac{4}{3}} \text{ expression (5.2.5) is}\]
\[\asymp B|\lambda_N|^{\frac{1}{3}} \times \left(\frac{|\lambda_N|}{G}\right)^{\frac{1}{3}} \asymp |\lambda_N|^{\frac{1}{3}} \min(1, B^{-\frac{3}{5}} Z^{\frac{2}{3}})\]
where $(|\lambda_N|/G)^{\frac{1}{3}}$ is a width of the zone where $W \leq -\lambda_N$ and the selected factor is the volume of this zone; this expression should be less than $C \max(Z \frac{2}{3}, Z \frac{2}{3} B^{\frac{1}{3}})$ which is exactly an error estimate in the semiclassical expression for $N$. Thus
\[|\lambda_N|^3 \min(1, Z \frac{2}{3} B^{-\frac{3}{5}}) \leq C \max(Z \frac{2}{3}, Z \frac{2}{3} B^{\frac{1}{3}})\]
where everywhere the first and the second cases are as $B \leq Z^{\frac{4}{3}}$ and $Z^{\frac{4}{3}} \leq B \leq Z^{3}$ respectively. The last inequality is equivalent to (5.3.2).

As $B \leq (Z - N)^{\frac{4}{3}}$ inequality (5.3.6) is replaced by $|\lambda_N|^2 \leq CZ^{\frac{4}{3}}$ which coincides with (5.3.6) with $B$ reset to $(Z - N)^{\frac{4}{3}}$ and also with the same inequality derived for $B = 0$ in the previous Chapter; therefore (5.3.2) holds in this case as well.

(ii) One can prove easily that

(5.3.7) If condition (5.3.3) is fulfilled, and expression (5.2.5) does not exceed a semiclassical error $C_0 \max(Z^{\frac{5}{3}}, Z^{\frac{5}{3}} B^{\frac{1}{2}})$ then $\lambda_N \varpropto \nu$ and, furthermore, expression (5.2.5) is

\begin{align*}
(5.3.8) \quad \Rightarrow B|\lambda_N - \nu| \int P_B^2(W + \nu)\, dx \lesssim B|\lambda_N - \nu| \int (W + \nu)^{-\frac{1}{2}}\, dx
\end{align*}

which for $B \geq (Z - N)^{\frac{4}{3}}$ is

\begin{align*}
(5.3.9) \quad \Rightarrow B^{-\frac{2}{3}}|\lambda_N - \nu| \cdot |\nu|^{-\frac{1}{2}} \left( \frac{|\nu|}{C} \right)^{\frac{1}{2}} \lesssim |\lambda_N - \nu| \cdot |\nu|^{\frac{1}{2}} \min(1, B^{-\frac{3}{3}} Z^{\frac{1}{3}})
\end{align*}

and this should be less than $C \max(Z^{\frac{5}{3}}, Z^{\frac{5}{3}} B^{\frac{1}{2}})$ which implies (5.3.4).

On the other hand, as $B \leq (Z - N)^{\frac{4}{3}}$ the right-hand expression of (5.3.8) is

\begin{align*}
\Rightarrow |\lambda_N - \nu| \tilde{\gamma} \approx |\lambda_N - \nu|(Z - N)^{-\frac{1}{3}} \text{ and this should be less than } CZ^{\frac{1}{3}} \text{ which implies (5.3.4) in this case as well.}
\end{align*}

Proposition 5.3.1 immediately implies

**Corollary 5.3.2.** In the framework of proposition (i), (ii),

\begin{align*}
(5.3.10) \quad |\lambda_N - \nu| \cdot N([\lambda_N, \nu]) \leq CQ
\end{align*}

where $N(\lambda_N, \nu)$ is the number of (non-zero) eigenvalues on interval $[\lambda_N, \nu]$ or $[\nu, \lambda_N]$. 

83
5.3.2 Estimate for D-terms

Proposition 5.3.3. In the framework of Proposition (i), (ii)

\( D(e(x, x, \lambda) - P'_B(W + \lambda), e(x, x, \lambda) - P'_B(W + \lambda)) \)

with \( \lambda = \nu, \lambda_N \) respectively and

\( D(P'_B(W + \nu) - P'_B(W + \lambda), P'_B(W + \nu) - P'_B(W + \lambda_N)) \)

with \( \lambda = \lambda_N \) do not exceed \( C \max(Z^\frac{5}{4}, Z^\frac{3}{4}B^\frac{3}{4}) \).

\textbf{Proof.} Term (5.3.11) with \( \lambda = \nu \) has been estimated this way and the same estimate for this term with \( \lambda = \lambda_N \) is proven in the same way; we leave easy details to the reader.

Term (5.3.12) is estimated using proposition 5.3.1; again we leave easy details to the reader. \( \square \)

Remark 5.3.4. Let \( B \leq Z \). Then in (5.3.1)–(5.3.4) and therefore also in (5.3.8) and in proposition 5.3.3 one can replace \( C_0 \) and \( C \) by \( C_0 \varepsilon \) and \( C \varepsilon \) respectively with the small parameter \( \varepsilon: \max(Z^{-\delta}, (BZ^{-1})^{\delta}) \leq \varepsilon \leq 1 \).

5.3.3 Summary

Then following the scheme of subsection 24.4.4 we arrive to upper estimates in Theorem 5.3.5 below (lower estimates have been proven in Proposition 5.1.1); we also arrive to Theorem 5.3.6 below:

\textbf{Theorem 5.3.5.} Let \( M = 1, B \leq Z^3 \). Then

(i) The following estimate holds:

\( E^{TF} \leq E^{TF} + \left( \text{Tr}(H_A,W - \nu)^- + \int P_B(W^{TF}(x) + \nu) dx \right) + CQ \)

with \( Q = \max(Z^\frac{5}{4}, Z^\frac{3}{4}B^\frac{3}{4}) \);

(ii) The following estimate holds:

\( E^{TF} \leq E^{TF} + \text{Scott} + CQ + CZ^\frac{4}{3}B^\frac{1}{3} \);

As \( Z^2 \leq B \leq Z^3 \) one can skip Scott;
As $B \leq Z$

\begin{equation}
E^{\text{TF}} \geq E^{\text{TF}} + \text{Scott} + \text{Dirac} + \text{Schwinger} + CZ^\frac{5}{2}(Z^{-\delta} + (BZ^{-1})^\delta).
\end{equation}

**Theorem 5.3.6.** Let $M = 1$, $B \leq Z^3$. Then

(i) The following estimate holds:

\begin{equation}
D(\rho_\psi - \rho_B^{\text{TF}}, \rho_\psi - \rho_B^{\text{TF}}) \leq CQ;
\end{equation}

(ii) As $B \leq Z$

\begin{equation}
D(\rho_\psi - \rho_B^{\text{TF}}, \rho_\psi - \rho_B^{\text{TF}}) \leq CZ^\frac{5}{2}(Z^{-\delta} + (BZ^{-1})^\delta).
\end{equation}

### 5.4 Upper estimate as $M \geq 2$

#### 5.4.1 Estimate for $|\lambda_N - \nu|$

Again we need to consider two cases: *almost neutral molecules* (systems) when $(Z - N)_+ \leq C_0K$ with $K$ slightly redefined below and we can set $\nu = 0$ in the definition of Thomas-Fermi potential and establish estimate for $|\lambda_N|$ (and for optimal $\nu$ we have the same estimate for both $|\nu|$ and $\lambda_N$) and *not almost neutral molecules* (systems) when $(Z - N)_+ \geq C_0K$ and we can prove that $|\lambda_N| \asymp |\nu|$ and estimate $|\lambda_N - \nu|$.

**Proposition 5.4.1.** *(cf. Proposition 5.3.1).* Let $M \geq 2$, $B \leq Z^3$ and condition (1.2.21) be fulfilled.

(i) Let

\begin{equation}
(Z - N)_+ \leq K := C_0 \begin{cases} 
Z^\frac{5}{2} + B^\frac{1}{2}L & \text{as } B \leq Z^\frac{5}{2}, \\
Z^\frac{1}{2}B^\frac{3}{4}L & \text{as } Z^\frac{5}{2} \leq B \leq Z^3.
\end{cases}
\end{equation}

and let us construct $W$ as if $\nu = 0$ i.e. $N = Z$. Then

\begin{equation}
|\lambda_N| \leq C_1 \begin{cases} 
Z^\frac{5}{2} + B^\frac{5}{4}L^\frac{5}{4} & \text{as } B \leq Z^\frac{5}{2}, \\
Z^\frac{1}{2}B^\frac{1}{4}L^\frac{3}{4} & \text{as } Z^\frac{5}{2} \leq B \leq Z^3.
\end{cases}
\end{equation}

recall that $L = |\log BZ^{-3}|$;
(ii) Let
\begin{equation}
(Z - N)_+ \geq K
\end{equation}
with sufficiently large \( C_0 \) in the definition of \( K \). Then \( \lambda_N \approx \nu \) and moreover
\begin{equation}
|\lambda_N - \nu| \leq C \max(Z^{\frac{2}{3}}, B^{\frac{2}{3}}l_1)|\nu|^{\frac{1}{3}};
\end{equation}
where
\begin{equation}
l_1 = \begin{cases}
1 & \text{as } B \leq (Z - N)^{\frac{4}{3}}, \\
|\log((Z - N)_+/B^{\frac{1}{3}})| & \text{as } (Z - N)^{\frac{4}{3}} \leq B \leq Z^{\frac{4}{3}}, \\
|\log(Z - N)_+/B^{\frac{1}{3}}Z^{\frac{2}{3}})| & \text{as } Z^{\frac{4}{3}} \leq B \leq Z^3.
\end{cases}
\end{equation}

**Proof.** We will apply arguments slightly more sophisticated than the obvious ones. These better arguments will allow us to derive slightly better estimates for \( |\lambda_N - \nu| \) as \( (Z - N)_+ \geq CK \).

Recall that estimates for \( |\lambda_N - \nu| \) are derived by comparison of expression (5.3.2) and the semiclassical errors for the number of eigenvalues below \( \lambda = \nu \) and \( \lambda = \lambda_N \): expression (5.3.2) should be less than the sum of these semiclassical errors.

Consider contribution of each ball
\begin{equation}
B(x, \ell(x)) \subset \mathcal{V} = \{x : \min_m |x - y_m| \geq \epsilon \}
\end{equation}
to semiclassical errors as \( \lambda = \nu \) and \( \lambda = \lambda_N \) and compare it with its contribution to (5.3.2):

(a) Each ball contributes no more than \( CB\ell^2 \) to the first error (with \( \lambda = \nu \)) where due to our choice \( \zeta \ell \geq 1 \);

(b) Further, each ball with \( \zeta \geq C_1|\lambda_N - \nu|^{\frac{1}{2}} \) contributes no more than \( CB\ell^2 \), but each ball with \( \zeta \leq C_1|\lambda_N - \nu|^{\frac{1}{2}} \) contributes no more than \( CB\ell^{3-\sigma}|\lambda_N - \nu|^{{\sigma}/2} \) to the second error (with \( \lambda = \lambda_N \)); here \( \sigma = \frac{1}{3} \) is due to rescaling;

(c) Meanwhile each ball with \( \zeta \geq C_1|\lambda_N - \nu|^{\frac{1}{2}} \) contributes no less than \( \epsilon_0B|\lambda_N - \nu|\zeta^{-1}\ell^3 \), and each ball with \( \zeta \geq C_1|\lambda_N - \nu|^{\frac{1}{2}} \) contributes no less than \( \epsilon_0|\lambda_N - \nu|\ell^3 \) to expression (5.3.2) and it is larger than the contributions of this ball to each of semiclassical errors (multiplied by \( C \)) as long as
\begin{equation}
(5.4.7)_{1,2} \quad \zeta^2 \geq |\lambda_N - \nu| \geq C_2\zeta \ell^{-1}, \quad |\lambda_N - \nu| \geq C_2\ell^{-2}.
\end{equation}
Obviously in (i), (ii) we can assume that

\[(5.4.8)\) (5.4.2) and (5.4.4) respectively (with \(C\) replaced by arbitrarily large \(C_3\)) are violated.

(i) (a) Assume first that \((Z - N) \frac{4}{5} \leq B \leq Z^3\). Then in the framework of \(\zeta = B^2 \ell^4\) with minimal \(\ell = B^{-\frac{3}{4}}\) and therefore \((5.4.7)_{1,2}\) are fulfilled for \(\ell \leq C_2 B^{-1}|\lambda_N|\). Therefore we need to account for the semiclassical errors contributed by an inner shell (not exceeding \(C \max(Z^\frac{3}{2}, B^\frac{1}{2})\)) and by zone \(Y \cap \{ \ell \geq C_2 B^{-1}|\lambda_N| \};\) there \(\zeta \geq C_1 |\lambda_N|^\frac{1}{2}\) and therefore its contribution does not exceed \(CB \int \ell(x)^{-1} dx\) with integral over this zone and it does not exceed \(CB \ell^2 L\).

So, these truncated semiclassical errors do not exceed \(C \max(Z^\frac{3}{2}, B^\frac{1}{2})\). Meanwhile expression \((5.3.2)\) is no less than \(CB \ell^2 |\lambda_N|^\frac{3}{2}\). Therefore comparing these two expressions as \(B \leq Z^3\) and as \(Z^\frac{4}{5} \leq B \leq Z^3\) we arrive to \((5.4.2)\).

(b) Consider remaining case \(B \leq (Z - N) \frac{4}{5}\). Semiclassical arguments remain valid while estimate of \((5.3.2)\) from below by \(\epsilon_0 |\lambda_N|^\frac{3}{2}\) also could be proven easily.

(ii) (a) Again, assume first that \((Z - N) \frac{4}{5} \leq B \leq Z^3\). Again, in the calculation of the truncated semiclassical errors we integrate over \(\ell \geq C_2 B^{-1}|\lambda_N - \nu|\) where \(\zeta \geq C_1 |\lambda_N|^\frac{3}{2}\) and therefore its contribution does not exceed \(CB \int \ell(x)^{-1} dx\) with integral over this zone and it does not exceed \(CB \ell^2 L\textsuperscript{27}\).

Again, expression \((5.3.10)\) is larger than the expressions afterwards and comparing with the semiclassical error estimate we arrive to \((5.4.4)\).

(b) Consider remaining case \(B \leq (Z - N) \frac{4}{5}\). Semiclassical arguments remain valid while estimate of \((5.3.2)\) from below by \(\epsilon_0 |\lambda_N - \nu|^{-\frac{3}{4}}\) also could be proven easily. \(\square\)

**Corollary 5.4.2.** In the framework of proposition 5.4.1 \(|\lambda_N - \nu| \cdot N([\lambda_N, \nu])\) does not exceed expression \((4.4.2)\).

\textsuperscript{27}In Statement (i) this leads only to insignificant improvement.
5.4.2 Estimate for D-terms for almost neutral systems

We need to estimate semiclassical error D-term (5.3.13) with \( \lambda = \lambda_N \) because for \( \lambda = \nu \) we already estimated it, and also we need to estimate a term (5.3.14). We start from the latter one. Recall that under assumption (5.4.1) we take \( \nu = 0 \). The trivial estimate is based on

\[
|P_B'(W) - P_B'(W + \lambda)| \leq CW^{\frac{1}{2}}|\lambda| + CBW^{-\frac{1}{2}}|\lambda|^{\frac{3}{2}},
\]

leading to

\[
J \leq CD(W^{\frac{1}{2}}, W^{\frac{1}{2}})|\lambda|^2 + CB^2|\lambda|^\frac{3}{2}D(W^{-\frac{1}{2}}\theta, W^{-\frac{1}{2}}\theta)
\]

where here and below \( J \) is expression (5.3.14), \( \theta \) is a characteristic function of domain \( \{ x : \gamma(x) \geq \hbar^{\frac{3}{2}} \} \) and we can ignore contribution of \( \{ x : \gamma(x) \leq \hbar^{\frac{3}{2}} \} \).

Really, contribution of this zone does not exceed a semiclassical error estimate \( R = C \max(Z^{\frac{3}{2}}, Z^{\frac{3}{2}}B^{\frac{3}{2}}L^2) \).

Note that even without assumption (5.4.1)

\[
D(W^{\frac{1}{2}}, W^{\frac{1}{2}}) \asymp (B^{-\frac{1}{4}}; B^{-\frac{3}{8}}Z^{\frac{3}{2}}) \quad \text{as} \quad B \leq Z^{\frac{3}{4}}, Z^{\frac{3}{4}} \leq B \leq Z^{3}
\]

respectively and (5.4.2) implies that the first term is much less than \( R \).

Meanwhile under assumption (5.4.1)

\[
D(W^{-\frac{1}{2}}\theta, W^{-\frac{1}{2}}\theta) \asymp B^{-1}D(\ell^{-1}\theta, \ell^{-1}\theta) \asymp B^{-1}\tau^3D(\gamma^{-1}\theta, \gamma^{-1}\theta)
\]

where in the right-hand expression \( D \) and \( \gamma, \theta \) are in the scale \( x \mapsto x\tau^{-1} \) and then \( D(\gamma^{-1}\theta, \gamma^{-1}\theta) \asymp L^2 \) so the second term in (5.4.10) does not exceed \( CB\tau^3|\lambda_N|^{\frac{3}{2}}L^2 \) which due to (5.4.2) does not exceed

\[
R := C \max(Z^{\frac{3}{2}}, Z^{\frac{3}{2}}B^{\frac{3}{2}}L^4).
\]

Consider now term (5.3.13) with \( \lambda = \lambda_N \). Let us consider zones \( \Omega_1 := \{ x : |\lambda - \nu| \lesssim \zeta\ell^{-1} \} \) and \( \Omega_2 := \{ x : |\lambda - \nu| \gtrsim \zeta\ell^{-1} \} \).

Note that contribution to the term in question of each couple of balls contained in \( \Omega_1 \times \Omega_1 \) does not exceed estimate for the same term with \( \lambda = \nu \); really, after rescaling \( x \mapsto x/\ell \) and \( \tau \mapsto \tau/\zeta^2 \) we conclude that the difference between energy levels does not exceed local semiclassical parameter \( C/(\zeta\ell) \).

Therefore the total contribution of \( \Omega_1 \times \Omega_1 \) to this term does not exceed \( C \max(Z^{\frac{3}{2}}, Z^{\frac{3}{2}}B^{\frac{3}{2}}L^2) \).
On the other hand, contribution to the term in question of each couple of balls contained in $\Omega_2 \times \Omega_2$ does not exceed its contribution to (5.3.14) and therefore the total contribution of $\Omega_2 \times \Omega_2$ to this term does not exceed expression (5.4.13). Thus, term (5.3.13) with $\lambda = \lambda_M$ does not exceed (5.4.13).

Therefore we arrive immediately to

**Theorem 5.4.3.** Let $M \geq 2$, $B \leq Z^3$ and condition (1.2.21) be fulfilled. Then under assumption (5.4.1)

(i) The following estimate holds:

$$E^{TF} \leq E^{TF} + \left(\text{Tr}(H_{A,W} - \nu)^- + \int P_B(W^{TF} + \nu) \, dx\right) + C \max(Z^{\frac{5}{3}}, Z^{\frac{3}{2}}B^{\frac{3}{2}}L^4);$$

(ii) As $a \geq Z^{-1}$ The following estimate holds:

$$E^{TF} \leq E^{TF} + \text{Scott} + C \max(Z^{\frac{5}{3}}, Z^{\frac{3}{2}}B^{\frac{3}{2}}L^4) + CZ^{\frac{5}{2}}B^{\frac{3}{2}} + Ca^{-\frac{1}{2}}Z^{\frac{5}{3}};$$

as $a \leq Z^{-1}$ one should replace the last term in the right-hand expression by $CZ^2$ and skip Scott;

(iii) As $B \leq Z$ and $a \geq Z^{-\frac{1}{3}}$

$$E^{TF} \leq E^{TF} + \text{Scott} + \text{Dirac + Schwinger} + CZ^{\frac{5}{3}}(Z^{-\delta} + (BZ^{-1})^\delta + (aZ^{\frac{1}{3}})^{-\delta}).$$

Here proof of (iii) is due to the same arguments as in the case $B = 0$. Combining with the estimate from below we also conclude that

**Theorem 5.4.4.** (i) In the framework of theorem 5.4.3 the following estimate holds:

$$D(\rho_\psi - \rho^{TF}, \rho_\psi - \rho^{TF}) \leq C \max(Z^{\frac{5}{3}}, Z^{\frac{3}{2}}B^{\frac{3}{2}}L^4);$$

(ii) In the framework of theorem 5.4.3(iii) the following estimate holds:

$$D(\rho_\psi - \rho^{TF}, \rho_\psi - \rho^{TF}) \leq CZ^{\frac{5}{3}}(Z^{-\delta} + (BZ^{-1})^\delta + (aZ^{\frac{1}{3}})^{-\delta}).$$
5.4.3 Estimate for D-terms for positively charged systems

Let assumption (5.4.3) be fulfilled. Let $W = W_\nu$ and $\ell = \ell_\nu$ be a potential and a scaling function (used to derive semiclassical remainder estimates) for this $\nu < 0$ (and $N < Z$) while $W_0$ and $\ell_0$ be a potential and a scaling function for $\nu = 0$ (and $N = Z$).

Let us start from rather trivial arguments. Note that

$$|(P_B'(W + \lambda) - P_B'(W + \nu))| \leq CW^{\frac{1}{2}}|\lambda - \nu|\theta_1 + CB|\lambda - \nu|^{\frac{1}{2}}\theta_2$$

where $\theta_1$ and $\theta_2$ are characteristic functions of $\mathcal{Y}_1 = \{x : W(x) + \nu \geq C_0|\nu|\}$ and $\mathcal{Y}_2 := \{x : 0 < W(x) + \nu \leq C_0|\nu|\}$ respectively. Let

$$J_k := D([P_B'(W + \lambda_N) - P_B'(W + \nu)]\theta_k, [P_B'(W + \lambda_N) - P_B'(W + \nu)]\theta_k).$$

Then in virtue of (5.4.19)

$$J_1 \leq CD(W^{\frac{1}{2}}\theta_1, W^{\frac{1}{2}}\theta_1)|\lambda_N - \nu|^2.$$ 

Note that $D(W^{\frac{1}{2}}\theta_1, W^{\frac{1}{2}}\theta_1) \prec ((Z - N)^{-\frac{1}{2}}; B^{-\frac{1}{2}}; Z^\frac{9}{8}B^{-\frac{5}{8}})^{28)}$ and using (5.4.4)

one can prove easily that $J_1 \leq CZ^\frac{3}{2}$.

However estimate for a contribution of $\mathcal{Y}_2$ is much worse:

$$J_2 \leq CB^2D(\theta_2, \theta_2)|\lambda_N - \nu| \leq CB^2\mathcal{P}^3(|\nu|/B^2)^{\frac{1}{2}}L_1^3|\lambda_N - \nu|,$$

where for $B \leq (Z - N)^{\frac{1}{4}}$ we should replace $(|\nu|/B^2)^{\frac{1}{2}}L_1^3$ by $\mathcal{P}^3$. Using (5.4.4)

we conclude that for $(Z - N)^{\frac{1}{4}} \lesssim B \lesssim Z^3$

$$J_2 \leq CB\mathcal{P}^3|\nu|^2L_1^3\max(Z^\frac{3}{2}, B^\frac{3}{2}) \asymp CB(Z - N)^{\frac{3}{4}}\mathcal{P}^\frac{5}{4}\max(Z^\frac{3}{2}, B^\frac{3}{2}L_1)L_1^2,$$

and therefore we arrive to the last two cases below; the first case is proven similarly:

$$J_2 \leq C \begin{cases} (Z - N)^{-\frac{4}{3}}Z^\frac{3}{2}B^2, \\ (Z - N)^{\frac{3}{4}}B^\frac{3}{2}\max(Z^\frac{3}{2}, B^\frac{3}{2}L_1)L_1^2, \\ (Z - N)^{\frac{3}{4}}Z^\frac{3}{2}B^\frac{3}{2}L_1^3 \end{cases}$$



\footnote{In our three cases $B \leq (Z - N)^{\frac{1}{4}}$, $(Z - N)^{\frac{4}{3}} \leq B \leq Z^\frac{3}{2}$, and $Z^\frac{3}{2} \leq B \leq Z^3$ respectively.}
in our three cases. This is really shabby estimate. To improve it let us note that

(5.4.22) If $|\lambda_N - \nu| \leq C \max(B^{\frac{3}{2}}, (Z - N)^{\frac{3}{2}})$ then $J_2$ does not exceed (4.4.2) and therefore we can assume that

(5.4.23) $|\lambda_N - \nu| \geq C \max((Z - N)^{\frac{3}{2}}; B^{\frac{3}{2}})$.

**Proposition 5.4.5.** (i) Let $(Z - N)^{\frac{4}{3}} \leq B \leq Z^3$ and

(5.4.24) $C_0 B^{\frac{3}{2}} \leq |\lambda_N - \nu| \leq C_1 B^{\frac{3}{2}} |\nu|^{\frac{1}{2}}$,

then the truncated semiclassical error does not exceed

(5.4.25) $F := CZ^{\frac{3}{2}} + CB^2 |\nu| B^{\frac{3}{2}} (|\nu|/B^2)^{\frac{3}{2}} \times (B^{-1}|\lambda_N - \nu|)^{-1}$;

(ii) Let $(Z - N)^{\frac{4}{3}} \leq B \leq Z^3$ and

(5.4.26) $C_1 B^{\frac{3}{2}} |\nu|^{\frac{1}{2}} \leq |\lambda_N - \nu| \leq C_1 B^{\frac{3}{2}} |\nu|^{\frac{1}{2}} L$,

then the truncated semiclassical error does not exceed

(5.4.27) $F := CZ^{\frac{3}{2}} + CB^2 L$;

(iii) Let $B \leq (Z - N)^{\frac{4}{3}}$ and

(5.4.28) $(Z - N)^{\frac{8}{3}} \leq |\lambda_N - \nu| \leq C_1 (Z - N)^{\frac{8}{3}}$,

then the truncated semiclassical error does not exceed

(5.4.29) $F := CZ^{\frac{3}{2}} + C(Z - N)^{\frac{5}{3}} |\lambda_N - \nu|^{-1}$;

(iv) Let $B \leq (Z - N)^{\frac{4}{3}}$ and

(5.4.30) $C_0 (Z - N)^{\frac{8}{3}} \leq |\lambda_N - \nu| \leq C_1 Z^{\frac{4}{3}} (Z - N)^{\frac{4}{3}}$,

then the truncated semiclassical error does not exceed $F := CZ^{\frac{3}{2}}$. 

91
Proof. Easy proof using arguments of the proof of proposition 5.4.1 is left to the reader. □

**Proposition 5.4.6.** In the framework of proposition (i)–(iv) term (5.3.14) does not exceed \( CF^{\frac{3}{5}}(B|\lambda_N - \nu|^{\frac{1}{3}})^{\frac{1}{5}} + (4.4.2) \) with \( F \) defined defined in the corresponding cases in Proposition 5.4.5.

Proof. Using proposition 5.4.1 one can prove easily that

\[
(5.4.31) \text{The contribution of } \{x : \ell(x) := \min_m |x - y_m| \leq \epsilon \} \text{ to (5.3.14) does not exceed } CZ^{\frac{3}{5}}.
\]

Now we need to estimate excess of expression (5.3.14) over semiclassical \( \mathcal{D} \)-term (with \( \lambda = \nu \)) which has been estimated by (4.4.2). To do so we need to estimate

\[
(5.4.32) \quad \mathcal{D}([P_B(W + \nu) - P_B(W + \lambda)]\theta, [P_B(W + \nu) - P_B(W + \lambda)]\theta_0)
\]

which is the contribution of the domain \( \Omega' := \{x : \ell(x) \leq CB^{-1}|\lambda - \nu|\} \) where \( \theta \) is the characteristic function of \( \Omega' \). Recall that on the complimentary domain \( |P_B(W + \nu) - P_B(W + \lambda)| \leq C\ell^{-1} \). Let us consider

\[
(5.4.33) \quad \mathcal{D}([P_B(W + \nu) - P_B(W + \lambda)]\theta_0, [P_B(W + \nu) - P_B(W + \lambda)]\theta_0)
\]

and

\[
(5.4.34) \quad \mathcal{D}([P_B(W + \nu) - P_B(W + \lambda)]\theta_t, [P_B(W + \nu) - P_B(W + \lambda)]\theta_{t'})
\]

where \( \theta_0 \) is a characteristic function of

\[
\Omega'_0 := \{x : \ell(x) \leq t_0 := (|\lambda_N - \nu|B^{-2})^{\frac{1}{2}}\}
\]

and \( \theta_t \) is a characteristic function of \( \Omega'_t := \{x : \ell(x) \leq 2t\} \) with \( t \geq t' \geq t_0 \).

When calculating (5.3.2) the contribution of \( \Omega'_0 \) is \( \asymp B|\lambda_N - \nu|^{\frac{1}{3}} \text{mes}(\Omega'_0) \) and therefore due to proposition 5.4.5

\[
(5.4.35) \quad \text{mes}(\Omega'_0) \leq CF(B|\lambda_N - \nu|^{\frac{1}{3}})^{-1}
\]

while term (5.4.33) is

\[
\asymp B^2|\lambda_N - \nu|D(\theta_0, \theta_0) \leq CB^2|\lambda_N - \nu|(\text{mes}(\Omega_0))^{\frac{1}{3}} \leq CF^{\frac{3}{5}}(B|\lambda_N - \nu|^{\frac{1}{3}})^{\frac{3}{5}}
\]
where the middle inequality

\[
D(\chi_G, \chi_G) \leq C(\text{mes}(G))^{\frac{3}{2}}
\]

is well known\(^{29}\) and the last one is due to (5.4.35); \(\chi_G\) denotes characteristic function of \(G\).

Similarly, when calculating expression (5.3.2) one can see easily that the contribution of \(\Omega'_t\) is \(\asymp B|\lambda_N - \nu|^{-1}t^2\) and therefore

\[
\text{mes}(\Omega'_t) \leq CF|\lambda_N - \nu|^{-1}t^2
\]

while term (5.4.34) is \(\asymp |\lambda_N - \nu|^2t^{-2}t'^{-2}D(\theta_t, \theta_{t'})\) which does not exceed

\[
C|\lambda_N - \nu|^2t^{-2}t'^{-2}\text{mes}(\Omega_t)\text{mes}(\Omega_{t'})[\max(\text{mes}(\Omega_t), \text{mes}(\Omega_{t'}))]|^{-\frac{1}{2}}
\]

due to inequality

\[
D(\chi_G, \chi_{G'}) \leq C\text{mes}(G)\text{mes}(G')[\max(\text{mes}(G), \text{mes}(G'))]^{-\frac{1}{2}}
\]

which trivially follows from the obvious inequality \(D(\chi_G, \delta_x) \leq C(\text{mes}(G))^{\frac{3}{2}}\), where \(\delta_x(x) = \delta(x - z)\).

Due to (5.4.37) expression (5.4.38) does not exceed \(CF^{\frac{3}{2}}t^{-\frac{3}{2}}\); recall that \(t \geq t'\). Since summation with respect to \(t \geq t'\) and then with respect to \(t' \geq t_0\) returns \(CF^{\frac{3}{2}}t_0^{-\frac{3}{2}}\) we conclude that term (5.4.33) with \(\theta_0\) replaced by \(\theta''\) (the characteristic function of \(\{x : \ell(x) \geq t_0\}\)) also does not exceed \(CF^{\frac{3}{2}}(B|\lambda_N - \nu|^{\frac{1}{2}})^{\frac{1}{2}}\). \(\square\)

So, we have now two estimates for an excess of expression (5.3.14) over (4.4.2): one estimate is

\[
(5.4.40) \quad CF^{\frac{3}{2}}(B|\lambda_N - \nu|^{\frac{1}{2}})^{\frac{1}{2}}
\]

with \(F = F(|\lambda_N - \nu|)\) derived in Proposition 5.4.5 and another one is due to (5.4.20). Let us consider the best of them. Note that estimate (5.4.40) consists of two terms each due to the corresponding term in the definition of \(F\). The second term in the framework of proposition 5.4.5(i) is

\[
C(B^{\frac{3}{2}}t^2|\nu|^{\frac{1}{2}}L|\lambda_N - \nu|^{-1})^{\frac{3}{2}}(B|\lambda_N - \nu|^{\frac{1}{2}})^{\frac{1}{2}} \asymp B^{\frac{12}{5}}t^{\frac{4}{5}}|\nu|^{\frac{2}{5}}L^{\frac{3}{5}}|\lambda_N - \nu|^{-\frac{3}{2}}
\]

\(^{29}\) Really, among uniform solids of equal mass and density the ball has the least potential energy; then \(C = \frac{1}{5}(12\pi)^{\frac{1}{2}}\).
and taking minimum of this expression and $CB\bar{r}^3|\nu|^{1/2}L^2|\lambda_N - \nu|$ we see that this minimum does not exceed

$$C\left( B^{\frac{17}{20}} \bar{r}^{\frac{13}{20}} |\nu|^{\frac{3}{20}} L^{\frac{1}{10}} \right)^{\frac{8}{5}} \left( B^{\frac{3}{2}} |\nu|^{\frac{1}{2}} L^2 \right)^{\frac{8}{5}} \approx CB^{\frac{3}{5}} \bar{r}^{\frac{3}{5}} (Z - N)^{\frac{3}{4}} L^{\frac{28}{10}} \approx$$

$$C \begin{cases} (Z - N)^{\frac{3}{4}} B L^{\frac{28}{10}} & \text{as } (Z - N)^{\frac{3}{4}} \leq B \leq Z^{\frac{4}{3}}, \\ (Z - N)^{\frac{3}{4}} Z^{\frac{28}{10}} B^{\frac{1}{2}} L^{\frac{28}{10}} & \text{as } Z^{\frac{4}{3}} \leq B \leq Z^{3}. \end{cases}$$

which is achieved as $|\lambda_N - \nu| \approx B^{\frac{11}{15}} \bar{r}^{\frac{13}{15}} |\nu|^{-\frac{1}{15}} L^{-\frac{2}{15}}$ and one can see easily that it does not exceed (4.4.2).

Therefore in the framework of Proposition 5.4.5(i,ii) we can select $F = (Z^{\frac{2}{3}} + B\bar{r}^2 L)$ according to (5.4.27) arriving to

$$C(Z^{\frac{2}{3}} + B\bar{r}^2 L)^{\frac{5}{3}} B^{\frac{1}{2}} |\lambda_N - \nu|^{\frac{1}{3}} \leq C(Z^{\frac{2}{3}} + B\bar{r}^2 L)^{\frac{5}{3}} B^{\frac{1}{2}} (Z^{\frac{3}{4}} + B^{\frac{1}{2}} L_1)^{\frac{5}{3}} |\nu|^{\frac{1}{3}} \approx$$

which we can rewrite (slightly increasing powers of logarithms) as two last cases in expression

$$\begin{array}{ll}
\text{(5.4.41)} & C \begin{cases} (Z - N)^{\frac{1}{4}} Z^{\frac{3}{4}} B^{\frac{1}{2}} & \text{as } B \leq (Z - N)^{\frac{3}{4}}, \\ (Z - N)^{\frac{1}{4}} (Z^{\frac{3}{4}} + B^{\frac{1}{10}} L^4) B^{\frac{1}{2}} & \text{as } (Z - N)^{\frac{3}{4}} \leq B \leq Z^{\frac{4}{3}}, \\ (Z - N)^{\frac{1}{4}} Z^{\frac{28}{10}} B^{\frac{1}{2}} & \text{as } Z^{\frac{4}{3}} \leq B \leq Z^{3}. \end{cases} \\
\end{array}$$

In the framework of proposition 5.4.5(iii) one should replace $(\nu/B^2)^{\frac{1}{2}}$ by $\bar{r}$ and $L$ by 1, so $B^{\frac{1}{2}} \bar{r}^2 |\nu|^{\frac{1}{2}} L|\lambda_N - \nu|^{-1} \approx B^2 \bar{r}^2 |\lambda_N - \nu|^{-1}$; further, one should preserve $B|\lambda_N - \nu|^{\frac{1}{2}}$ and therefore the second term becomes

$$(B^2 \bar{r}^3|\lambda_N - \nu|^{-1})^{\frac{3}{4}} (B|\lambda_N - \nu|^{\frac{1}{2}})^{\frac{1}{4}} \approx B^{\frac{11}{15}} \bar{r}^5 |\lambda_N - \nu|^{-\frac{3}{4}}$$

and taking minimum of it and (5.4.20) we again get a term lesser than (4.4.2).

Meanwhile the first term becomes $Z^{\frac{28}{10}} B^{\frac{1}{2}} |\lambda_N - \nu|^{\frac{1}{3}} \leq (Z - N)^{\frac{1}{4}} Z^{\frac{28}{10}} B^{\frac{1}{2}}$ occupying the first line in (5.4.41).

Therefore we have proven

**Proposition 5.4.7.** As $M \geq 2$, $B \leq Z^3$ all three D-terms do not exceed (4.4.2) + (5.4.41).
5.4.4 Summary

Therefore all error terms in the upper estimate do not exceed \((4.4.2)\) and we arrive to

**Theorem 5.4.8.** Let \(M \geq 2, B \leq Z^3\). Then

(i) The following estimate holds:

\[
E^{\text{TF}} \leq \mathcal{E}^{\text{TF}} + \left(\text{Tr}(H_{A,W} - \nu)^- + \int P_B(W^{\text{TF}} + \nu) \, dx\right) + (4.4.2) + (5.4.41);
\]

(ii) The following estimate holds as \(a \geq Z^{-1}\):

\[
E^{\text{TF}} \leq \mathcal{E}^{\text{TF}} + \text{Scott} + CZ^\frac{1}{3} B^\frac{1}{3} + a^{-\frac{1}{3}} Z^\frac{1}{3} + (4.4.2) + (5.4.41);
\]

as \(a \leq Z^{-1}\) one should replace selected terms by \(CZ^2\);

(iii) As \(B \leq Z\) and \(a \geq Z^{-\frac{1}{3}}\)

\[
E^{\text{TF}} \geq \mathcal{E}^{\text{TF}} + \text{Scott} + \text{Dirac} + \text{Schwinger} + CZ^\frac{5}{3} (Z^{-\delta} + (BZ^{-1})^\delta + (aZ^\frac{1}{3})^{-\delta})
\]

**Theorem 5.4.9.** (i) In the framework of Theorem 5.4.8(i) the following estimate holds:

\[
D(\rho_\psi - \rho^{\text{TF}}, \rho_\psi - \rho^{\text{TF}}) \leq (4.4.2) + (5.4.41);
\]

(ii) In the framework of Theorem 5.4.8(iii) (albeit without assumption \(a \geq Z^{-\frac{1}{3}}\)) the following estimate holds:

\[
D(\rho_\psi - \rho^{\text{TF}}, \rho_\psi - \rho^{\text{TF}}) \leq C Q := CZ^\frac{5}{3} (Z^{-\delta} + (BZ^{-1})^\delta).
\]

**Remark 5.4.10.** Unfortunately there are gaps in the proofs of V. Ivrii [Ivr2] in the case of \(M \geq 2\) and large \(Z - N > 0\) and I was unable to fill them.

6 Negatively charged systems

In this section we following Section 24.5 consider the case \(N \geq Z\) and provide upper estimates for excessive negative charge \((N - Z)\) as \(l_N > 0\) and for ionization energy \(l_N\).
6.1 Estimates of the correlation function

First of all we provide some estimates which will be used for both negatively and positively charged systems. Let us consider the ground-state function \( \Psi(x_1, s_1; \ldots; x_N, s_N) \) and the corresponding density \( \rho_\Psi(x) \). Again the crucial role play estimates\(^{30}\)

\[
(6.1.1) \quad D(\rho_\Psi - \rho_{TF}, \rho_\Psi - \rho_{TF}) \leq \tilde{Q}
\]

where \( \tilde{Q} \geq Q \) is just the right-hand expression of the corresponding estimate; as \( B \leq Z \) we can slightly decrease \( Q = \tilde{Q} \).

The same estimate holds also for difference between upper and lower bounds for \( E_N \) (with \( N_k(H_{W} - \nu) + \nu N \) not replaced by its semiclassical approximation).

Remark 6.1.1. All arguments and conclusions of Subsection 24.5.1 up to but excluding estimate (24.5.28) are not related to the Schrödinger operator and remain true.

So we need to calculate both semiclassical errors and the principal parts. Note that all semiclassical errors for \( W_\varepsilon \) do not exceed those obtained for \( W \) we selected. Consider approximations errors in the principal part, namely

\[
(6.1.2) \quad D(P'(W_\varepsilon + \nu) - P'(W + \nu), P'(W_\varepsilon + \nu) - P'(W + \nu))
\]

and

\[
(6.1.3) \quad D(\rho_\varepsilon - \rho, \rho_\varepsilon - \rho)
\]

as we already estimated terms \( D(P'(W + \nu) - \rho_{TF}^B, P'(W + \nu) - \rho_{TF}^B) \) and \( D(\rho - \rho_{TF}^B, \rho - \rho_{TF}^B) \) by \( \tilde{Q} \).

Note that

\[
(6.1.4) \quad |W - W_\varepsilon| \leq C(1 + \ell \varepsilon^{-1})^{-2} \zeta^2
\]

and

\[
(6.1.5) \quad |P'(W_\varepsilon + \nu) - P'(W + \nu)| \leq C(1 + \ell \varepsilon^{-1})^{-2} \zeta^3 + C(1 + \ell \varepsilon^{-1})^{-1} \zeta B
\]

\(^{30}\) Namely estimates (5.3.16) and (5.3.17) of theorem 5.3.6 as \( M = 1 \), and similar estimates (5.4.17) of theorem 5.4.4 and (5.4.45) of theorem 5.4.9 as \( M \geq 2 \). As \( B \leq Z \) we use estimate (5.4.46) in all cases.
and therefore expression (6.1.2) does not exceed \( C(Z^3\varepsilon^2 + ZB^2\varepsilon^2r^2) \) and it does not exceed \( C \max(Z^{\frac{1}{2}}, B^{\frac{1}{2}}Z^{\frac{3}{2}}) \) for \( \varepsilon = \min(Z^{-\frac{1}{2}}, Z^{\frac{3}{2}}B^{-\frac{1}{2}}) \) and this does not exceed \( CQ \).

Further, consider expression (6.1.3); it is equal to \( 4\pi|W_\varepsilon - W, \rho_\varepsilon - \rho| \) and one can prove easily the same estimate for it.

Furthermore, under this restriction an error in the principal part of asymptotics of \( \int e(x, x, \lambda) \, dx \), namely \( |\int (P'(W_\varepsilon + \nu) - P'(W + \nu)) \, dx| \), namely \( |\int (P'(W_\varepsilon + \nu) - P'(W + \nu)) \, dx| \), does not exceed \( C(Z^{\frac{1}{2}}\varepsilon^{\frac{3}{2}} + Z^{\frac{3}{2}}B\varepsilon^{\frac{1}{2}}) \) which is less than the semiclassical error. Then \( S \leq CQ \) with \( S \) defined by (24.5.22).

So, the following proposition is proven:

**Proposition 6.1.2.** (cf. Proposition 24.5.1) If \( \theta, \chi \) are as in Subsection 24.5.2 then estimate (24.5.29) holds, namely,

\[
\mathcal{J} = |\int \left( \rho_\psi^{(2)}(x, y) - \rho(y) \rho_\psi(x) \right) \theta(x) \chi(x, y) \, dx \, dy | \leq 
\]

\[
C \sup_x \| \nabla_y \chi_x \|_{L^2(\mathbb{R}^3)} \left( (Q + \varepsilon^{-1}N + T)^{\frac{1}{2}} \Theta + P^{\frac{1}{2}} \Theta^{\frac{1}{2}} \right) + C \varepsilon N \| \nabla_y \chi \|_{L^\infty} \Theta
\]

with \( \Theta = \Theta_\psi \) defined by (24.5.15) and \( T, P \) defined by (24.5.23), (24.5.25) and arbitrary \( \varepsilon \leq \min(Z^{-\frac{1}{2}}, Z^{\frac{3}{2}}b^{-\frac{1}{2}}) \).

### 6.2 Excessive negative charge

Let us select \( \theta = \theta_b \) according to (24.5.30):

\[
(24.5.30) \quad \text{supp} \theta \subset \{ x : \ell(x) \geq b \}.
\]

Note that \( H_N \psi = E_N \psi \) yields identity (24.5.31) and isolating the contribution of \( j \)-th electron in \( j \)-th term we get inequality (24.5.32)

\[
(24.5.32) \quad -I_N \int \rho_\psi(x) \ell(x) \theta \, dx \geq 
\]

\[
\sum_j \langle \psi, \ell(x_j) \theta(x_j) \left( -V(x_j) + \sum_{k: k \neq j} |x_j - x_k|^{-1} \right) \psi \rangle - \sum_j \| \nabla (\theta^{\frac{1}{2}}(x_j) \ell(x_j)^{\frac{1}{2}}) \psi \|^2
\]

due to non-negativity of operator \( ((D_x - A(x)) \cdot \sigma)^2 \).
Now let us select $b$ to be able to calculate the magnitude of $\Theta$. Note that inequality (24.5.33) holds. Also (24.5.34) holds as long as

\[(6.2.1) \quad Z^{-\frac{1}{2}} \leq b \leq \epsilon \min\left((Z - N)^{-\frac{1}{2}}, B^{-\frac{1}{2}}\right)\]

Using inequalities

\[|\nabla (\theta_b(x)^{\frac{1}{2}} \ell^{\frac{1}{2}})| \leq cb^{-1}\theta_{(1-\epsilon)b}(x)\]

and

\[\int \rho(x)\ell(x) \theta_b(x) \, dx \geq b\Theta_b\]

(i.e. (24.5.39)) we conclude that

\[(6.2.2) \quad b lN\Theta_b \leq \theta_b(x)V(x)\ell(x)\rho(x) \, dx - \int \varphi^{(2)}(x,y)\ell(x)|x-y|^{-1}\theta_b(x) \, dx \, dy + Cb^{-1}\Theta_b(1-\epsilon) = \]

\[= \int \theta_b(x)V(x)\ell(x)\rho(x) \, dx - \int \varphi^{(2)}(x,y)\ell(x)|x-y|^{-1}(1-\theta_b(y))\theta_b(x) \, dx \, dy - \int \varphi^{(2)}(x,y)\ell(x)|x-y|^{-1}\theta_b(y)\theta_b(x) \, dx \, dy + Cb^{-1}\Theta_b(1-\epsilon)\]

(cf. (24.5.40)). Denote by $I_1$, $I_2$, and $I_3$ the first, second and third terms in the right-hand expression of (6.2.2) respectively. Symmetrizing $I_3$ with respect to $x$ and $y$

\[I_3 = -\frac{1}{2} \int \varphi^{(2)}(x,y)(\ell(x) + \ell(y))|x-y|^{-1}\theta(y)\theta(x) \, dx \, dy\]

and using inequality $\ell(x) + \ell(y) \geq \min_j(|x - y_j| + |y - y_j|) \geq |x - y|$ we conclude that this term does not exceed

\[(6.2.3) \quad -\frac{1}{2} \int \varphi^{(2)}(x,y)\theta_b(y)\theta_b(x) \, dx \, dy = \]

\[-\frac{1}{2}(N-1) \int \rho(x)\theta_b(x) \, dx + \frac{1}{2} \int \varphi^{(2)}(x,y)(1 - \theta_b(y))\theta_b(x) \, dx \, dy\]

98
Here the first term is exactly $-\frac{1}{2}(N - 1)\Theta_b$; replacing $\varrho_\psi^{(2)}(x,y)$ by $\rho(y)\varrho_\psi(x)$ we get

\begin{equation}
\frac{1}{2} \int (1 - \theta_b(y)) \rho(y) \, dy \times \Theta_b
\end{equation}

with an error

\begin{equation}
\frac{1}{2} \int (\varrho_\psi^{(2)}(x,y) - \rho(y)\varrho_\psi(x)) (1 - \theta_b(y)) \theta_b(x) \, dxdy
\end{equation}

(cf. (24.5.42), (24.5.43)). We estimate it using proposition 6.1.2 with $\chi(x,y) = 1 - \theta_b(y)$. Then $\|\nabla_y \chi\|_{L^2} \approx b^{\frac{1}{2}}$, $\|\nabla_y \chi\|_{L^\infty} \approx b^{-1}$ and $P \approx b^{-1}\Theta_b$.\(^{31}\) While $T \lesssim b^{-4}$ as long as $B \leq Z^4$ and $b \leq B^{-\frac{1}{4}}$.

To estimate excessive negative charge we assume that $(N - Z) > 0$ with $1_N \geq 0$. In this case the left-hand expression in (6.2.2) should be positive.

**Remark 6.2.1.** Recall that in Subsection 24.5.2 we picked $b = Z^{2/3}$ and it makes sense here as well as long as $b \leq \bar{r} = B^{-\frac{1}{4}}$ i.e. as $B \leq Z^{2/3}$. However as $B \geq Z^{2/3}$ we just pick up $b = C_0 \bar{r}$ and then $T = 0$ in our framework.

Estimating (6.2.5) we conclude that

\begin{equation}
\mathcal{I}_3 \leq -\frac{1}{2} \left( N - 1 - \int (1 - \theta_b(y)) \rho(y) \, dy \right) \Theta_b + \mathcal{I}_0,
\end{equation}

with

\begin{equation}
\mathcal{I}_0 = Cb^{\frac{1}{2}} \left( S\Theta_b + Nb^{-2} \right)^{\frac{1}{2}} \Theta_b^{\frac{1}{2}} + C\varepsilon Nb^{-1}\Theta_b
\end{equation}

(cf. (24.5.44)).

On the other hand,

\begin{equation}
\mathcal{I}_2 \leq -\int \varrho_\psi^{(2)}(x,y) f(x) |x - y|^{-1} (1 - \theta_{b(1-\varepsilon)}(y)) \theta_b(x) \, dxdy
\end{equation}

\(^{31}\) Recall that $P = \int |\nabla \theta_b| \rho_\psi \, dx$ and $T = \sup_{\text{supp} \varrho} \theta \, W$. 

99
and replacing $\varphi^{(2)}(x, y)$ by $\rho(y)\rho(x)$ and estimating an error due to Proposition 6.1.2 we get

\( (6.2.9) \quad I_2 \leq - \int \rho(y)\rho(x)\ell(x)|x - y|^{-1}(1 - \theta_b(1-\epsilon)(y))\theta_b(x) \, dxdy + \)

\[
Cb^{-\frac{\epsilon}{2}}(S\Theta_b + Nb^{-2})^{\frac{1}{2}}\Theta_b^{\frac{1}{2}} + C\varepsilon Nb^{-1} = \\
- \int (V - W)(x)\ell(x)\theta_b(x) \, dx + \\
\int \rho(y)\rho(x)\ell(x)|x - y|^{-1}(1 - \theta_b(1-\epsilon)(y))\theta_b(x) \, dxdy + I_0.
\]

So, we pick up

\( (6.2.10) \quad b = C \min(Z^{-\frac{5}{2}}, r) = \begin{cases} 
\frac{Z^{\frac{5}{2}}}{Z^{32}} & \text{as } B \leq \frac{Z^{20}}{Z^{32}}, \\
\frac{B^{-\frac{1}{2}}}{Z^{32}} & \text{as } \frac{Z^{20}}{Z^{32}} \leq B \leq \frac{Z^{4}}{Z^{32}}, \\
\frac{B^{-\frac{5}{2}}Z^{\frac{1}{2}}}{Z^{32}} & \text{as } \frac{Z^{4}}{Z^{32}} \leq B \leq Z^{3}.
\end{cases} \)

and

\( (6.2.11) \quad \varepsilon = \min(Z^{-\frac{3}{2}}, B^{-\frac{4}{2}}Z^{\frac{2}{3}}) \)

and preserving all the estimates one can take $W = \rho = 0$ at $\text{supp} \theta_b^{32}$ and then

\( (6.2.12) \quad I_1 + I_2 = \int \theta_b(x)W(x)\ell(x)\rho(x) \, dx - \\
\int \left(\varphi^{(2)}(x, y) - \rho(x)\rho(y)\right)\ell(x)|x - y|^{-1}(1 - \theta_b(y))\theta_b(x) \, dxdy \leq I_0. \)

Further, since $\int (1 - \theta_b(y)) \rho(y) \, dy \leq Z^{33}$ we get from (6.2.2) and estimate (6.2.6) for $I_3$ that

\( (6.2.13) \quad (N - Z) \leq Cb^{\frac{1}{2}}S^{\frac{1}{2}} + C\Theta_b^{-\frac{1}{2}}N_b^{\frac{1}{2}}b^{-1} + Cb^{-1}\Theta_b(1-\epsilon)\Theta_b^{-1} \\
\)
because then $\varepsilon N^{\frac{1}{2}}b^{-1}$ does not exceed $Cb^{\frac{1}{2}}Q^{\frac{1}{2}}$.

---

32) For $B \geq Z^{\frac{20}{32}}$ this is fulfilled automatically.
33) Actually for $B \geq Z^{\frac{20}{32}}$ this is an equality.
Let us assume that estimate (6.2.14) below does not hold. Then \( \Theta_b = N - \int (1 - \theta_b(y)) \rho_b(y) \, dy \) and due to Theorem 5.4.9

\[
|\Theta_b - N - Z| \leq C_b \bar{Q}^\frac{1}{2} \leq \frac{1}{2} (N - Z)
\]

and the same is true for \( \Theta_{b(1-\epsilon)} \). Then (6.2.13) yields (6.2.14). So, (6.2.14) has been proven.

**Theorem 6.2.2.** Let condition (1.2.21) be fulfilled. In the fixed nuclei model let \( l_N > 0 \).

(i) Then

\[
(N - Z)_+ \leq C \begin{cases} 
  Z^{\frac{5}{2}} & \text{as } B \leq Z^{\frac{20}{\pi}}, \\
  Z^{\frac{5}{2}} B^{-\frac{1}{8}} + B^{\frac{1}{2}} L & \text{as } Z^{\frac{20}{\pi}} \leq B \leq Z^{\frac{4}{3}} L \\
  Z^{\frac{5}{2}} B^{\frac{1}{2}} & \text{as } Z^{\frac{4}{3}} \leq B \leq Z^{3}
\end{cases}
\]

where \( L = |\log(Z^{-3} B)| \).

(ii) As \( M = 1 \) the same estimate holds with \( L = 1 \):

\[
(N - Z)_+ \leq C \begin{cases} 
  Z^{\frac{7}{2}} & \text{as } B \leq Z^{\frac{20}{\pi}}, \\
  Z^{\frac{5}{2}} B^{-\frac{1}{8}} & \text{as } Z^{\frac{20}{\pi}} \leq B \leq Z^{\frac{4}{3}} L \\
  Z^{\frac{5}{2}} B^{\frac{1}{2}} & \text{as } Z^{\frac{4}{3}} \leq B \leq Z^{3}
\end{cases}
\]

Furthermore as \( B \leq Z \) one can use a slightly sharper estimate for \( \bar{Q} \):

**Theorem 6.2.3.** Let condition (1.2.21) be fulfilled. In the fixed nuclei model let \( l_N > 0 \). Then for a single atom and for molecule with \( B \leq Z \) and \( a \geq Z^{-\frac{1}{4} + \delta_1} \)

\[
(N - Z)_+ \leq C \begin{cases} 
  Z^{\frac{5}{2} - \delta} & \text{as } B \leq Z^{\frac{20}{\pi}}, \\
  Z^{\frac{5}{2} - \delta} B^{-\frac{1}{8} + \delta} & \text{as } Z^{\frac{20}{\pi}} \leq B \leq Z
\end{cases}
\]

Results for a free nuclei model follow from the above results and an estimate of \( a \) from below (see Subsubsection 7.4.4.4.)
Theorem 6.2.4. Let condition (1.2.21) be fulfilled. In the free nuclei model let \( \bar{l}_N > 0 \). Then

(i) Estimate (6.2.14) holds;

(ii) For \( B \leq Z \) estimate (6.2.16) holds.

6.3 Estimate for ionization energy

Now, let us estimate ionization energy assuming that

(6.3.1) \((Z - N)_+ \) does not exceed the right-hand expression of (6.2.14)\(^{34}\).

Few cases are possible:

(i) \( B \leq Z^{\frac{20}{7}} \) and \((Z - N)_+ \leq C_0 Z^{\frac{1}{3}} \). In this case we act exactly as in Subsection 24.5.2: we pick up \( b = \epsilon Z^{-\frac{x}{7}} \) with a small enough constant \( \epsilon' > 0 \); then

\[
| \int \theta_b(x)(\rho_{\psi} - \rho) \, dx | \leq C b^{\frac{1}{2}} Q^{\frac{3}{2}}
\]

while

\[
\int \theta_b(x) \rho \, dx \asymp b^{-3}
\]

and therefore

\[
\Theta := \int \theta_b(x) \rho_{\psi} \, dx \asymp b^{-3}
\]

and

(6.3.5) \[
| \int \theta(x)(\rho_{\psi} - \rho) \, dx | \leq \epsilon'' \Theta
\]

and (6.2.2), (6.2.6), (6.2.9) yield that \( \bar{l}_N \leq CZ^{\frac{20}{7}} \); so estimate (6.3.15) below in this case is recovered.

In all other cases one needs to replace \( \theta_b \) by function which is not \( b \)-admissible.

(ii) Let \( Z^{\frac{20}{7}} \leq B \leq Z^{3} \) and \( M = 1 \). Let here \( \tilde{r} \) be an exact radius of \( \text{supp} \rho \) which is obtained in Thomas-Fermi theory with \( \nu = 0 \). Recall that

\(^{34}\) Or (6.2.15), or (6.2.16) in the framework of the corresponding theorem.
\( \bar{r} \approx \max(B^{-\frac{1}{2}}; B^{-\frac{3}{2}} Z^{rac{1}{2}}) \) and \( \bar{Q} \approx \max(Z^{\frac{3}{2}}; B^{\frac{3}{2}} Z^{rac{3}{2}}) \) and for \( W \approx G t^4, \rho \approx BG^{\frac{1}{2}} \) for \( r = (1 - t)\bar{r} \) with \( 1 - \epsilon \leq t \leq 1 \) where recall \( G := \min(B; B^{\frac{3}{2}} Z^\frac{3}{2}) \).

We take in this case \( \bar{r}t \)-admissible function \( \theta \), equal 0 as \( |x - y| \leq \bar{r}(1 - t) \) and equal 1 as \( |x - y| \geq \bar{r}(1 - \frac{1}{2}t) \).

(6.3.6) In all the above estimates one needs to replace \( Cb^{-1}\theta_{b(1-\epsilon)} \) by \( C\bar{r}^{-1}t^{-1}\Theta' \) with \( \Theta' \) defined by \( \theta' \) which is also \( \bar{r}t \)-admissible and equal 1 in \( \epsilon \bar{r}t \)-vicinity of \( \text{supp} \theta \).

Then (6.3.2)–(6.3.5) are replaced by

\[
| \int \theta(x)(\rho_y - \rho) \, dx | \leq CQ^\frac{1}{2} \times \| \nabla \theta \| \approx C t^{-\frac{1}{2}} \bar{r}^2 Q^\frac{1}{2}
\]

while

\[
\int \theta(x) \rho \, dx \approx BG^{\frac{1}{2}} \bar{r}^3 t^3
\]

and therefore

\[
\Theta := \int \theta(x) \rho_x \, dx \approx BG^{\frac{1}{2}} \bar{r}^3 t^3
\]

and (6.3.5) holds provided the right-hand expression of (6.3.7) does not exceed the right-hand expression of (6.3.9) multiplied by \( \epsilon \):

\[
t = t_* := C_0 B^{-\frac{3}{2}} G^{-\frac{1}{2}} \bar{r}^{-\frac{5}{2}} Q^\frac{1}{2} = C_1 \max(B^{-\frac{1}{2}} Z^\frac{3}{2}; B^{\frac{3}{2}} Z^{-\frac{5}{2}})
\]

where we picked up the smallest possible value of \( t \). Note that

(6.3.11) \( t \approx 1 \) as either \( B \approx Z^\frac{20}{7} \) or \( B \approx Z^3 \).

Further, let us estimate from above

\[
\mathcal{I}' = -\int (\varphi_x^2(x,y) - \rho \varphi_x(x) \rho(y)) \ell(x) |x - y|^{-1} \theta(x) \, dx \, dy \leq
- \int (\varphi_x^2(x,y) - \rho \varphi_x(x) \rho(y)) (1 - \omega_r(x,y)) \ell(x) |x - y|^{-1} \theta(x) \, dx \, dy +
\int \rho \varphi_x(x) \rho(y) \omega_r(x,y) \ell(x) |x - y|^{-1} \theta(x) \, dx \, dy
\]

with \( \omega = 0 \) as \( |x - y| \geq 2 \tau \bar{r} \) and \( \omega = 1 \) as \( |x - y| \leq \tau \bar{r} \), with \( \tau \in (t, 1) \).
Then due to proposition 6.1.2 with \( \chi(x, y) = (1 - \omega_\tau(x, y))|x - y|^{-1} \) the first term in the right-hand expression does not exceed \( C\tilde{r}^{1\over 2}\tau^{-1\over 2}Q^{1\over 2}\Theta \) as \( \|\nabla_y \chi_x\|_{L^2(\mathbb{R}^2)} \leq (\tilde{r}\tau)^{-1\over 2} \) and also one can prove easily that all other terms in \( (Q + \varepsilon^{-1}N + T)^{1\over 2}\Theta + P^{1\over 2}\Theta^{1\over 2} \) do not exceed \( CQ\Theta \).

Meanwhile the second term in in the right-hand expression of (6.3.12) does not exceed \( CBG^{1\over 2}\tau^{-1\over 2} \times (\tilde{r}\tau)^{1\over 2} \times \) because \( \rho(y) \leq CBG^{1\over 2}\tau^{-1\over 2} \) as \( |x - y| \leq 2\tau\tilde{r}, x \in \text{supp}\, \theta \) and therefore \( \int \rho(y)\omega_\tau(x, y)\, dy \leq CBG^{1\over 2}\tau^{-1\over 2}. \)

Minimizing their sum
\[
C\left(\tilde{r}^{1\over 2}\tau^{-1\over 2}Q^{1\over 2} + BG^{1\over 2}\tau^{3\over 2}\right)\Theta
\]
with respect to \( \tau \geq t^{35} \) we arrive to estimate
\[
I' \leq C\tilde{r}^{1\over 2}Q^{1\over 2}B^{1\over 2}G^{1\over 2}\Theta.
\]

Then as in the proof of Theorem 24.5.3 we have inequality
\[
(6.3.13) \quad \tilde{r}I_N \leq C(Z - N)_+ + C\tilde{r}Q^{1\over 2}B^{1\over 2}G^{1\over 2}
\]
and therefore for \( (Z - N)_+ \leq C\tilde{r}Q^{1\over 2}B^{1\over 2}G^{1\over 2} \) we have \( I_N \leq C\tau^{-1\over 2}Q^{1\over 2}B^{1\over 2}G^{1\over 2}. \)

Thus we have proven estimate (6.3.15) of theorem 6.3.1 below at least as \( N \geq Z \).

**Theorem 6.3.1.** Let \( M = 1. \)

(i) Then as \( B \leq Z^3 \) and
\[
(6.3.14) \quad (Z - N)_+ \leq C_0 \begin{cases} 
Z^{5\over 4} & \text{as } B \leq Z^{20\over 21}, \\
B^{-1\over 2}Z^{5\over 8} & \text{as } Z^{20\over 21} \leq B \leq Z^{4\over 7}, \\
B^{1\over 2}Z^{5\over 8} & \text{as } Z^{4\over 7} \leq B \leq Z^3
\end{cases}
\]
estimate holds
\[
(6.3.15) \quad I_N \leq C \begin{cases} 
Z^{20\over 21} & \text{as } B \leq Z^{20\over 21}, \\
B^{5\over 8}Z^{20\over 27} & \text{as } Z^{20\over 21} \leq B \leq Z^{4\over 7}, \\
B^{26\over 27}Z^{4\over 13} & \text{as } Z^{4\over 7} \leq B \leq Z^3
\end{cases}
\]

\[35)\] One can see easily that minimum is achieved as \( \tau \approx t^{7\over 8}. \)
(ii) Furthermore as \( B \leq Z \) and

\[
(Z - N)_+ \leq C_0 \begin{cases} 
Z^{\frac{5}{2} - \delta} & \text{as } B \leq Z^{\frac{20}{11}}, \\
B^{-\frac{1}{2} + \delta} Z^{\frac{5}{2} - \delta} & \text{as } Z^{\frac{20}{11}} \leq B \leq Z,
\end{cases}
\]

estimate holds

\[
l_N \leq C \begin{cases} 
Z^{\frac{20}{11} - \delta'} & \text{as } B \leq Z^{\frac{20}{11}}, \\
B^{\frac{5}{2} + \delta'} Z^{\frac{20}{11} - \delta'} & \text{as } Z^{\frac{20}{11}} \leq B \leq Z
\end{cases}
\]

Proof in the general settings. To prove estimates (6.3.15) and (6.3.17) in the general settings note that for \( N < Z \)

\[
D(\rho_N^T - \rho_Z^T, \rho_N^T - \rho_Z^T) \leq C(Z - N)^2 \bar{r}^{-1} \times C \max((Z - N)^{\frac{1}{2}}; C(Z - N)^2 B^{\frac{1}{2}}; C(Z - N)^2 B^\frac{3}{2} Z^{-\frac{1}{2}})
\]

because the same estimate holds for \( \mathcal{E}_N^T - \mathcal{E}_Z^T \):

\[
0 \leq \mathcal{E}_N^T - \mathcal{E}_Z^T \leq C(Z - N)^2 \bar{r}^{-1}
\]

which itself follows from

\[
\frac{\partial \mathcal{E}_N^T}{\partial N} = \nu \propto (Z - N) \bar{r}^{-1}.
\]

Therefore to preserve our estimates we need to assume that the right-hand expression of (6.3.18) does not exceed \( Q \) i.e. \((Z - N)_+ \leq \min(Z^{\frac{5}{2}}; Z^{\frac{5}{2}} B^{-\frac{1}{2}})\) as \( B \leq Z^{\frac{5}{2}} \) which is exactly the first and the second cases in (6.3.14) (and these cases in (6.3.16) appear in the same way), and \((Z - N)_+ \leq CB^{\frac{3}{2}} Z^{\frac{5}{2}}\) which is exactly the third case in (6.3.18).

Also there is a term \( C(Z - N)_+ \bar{r}^{-1} \) in the estimate of \( l_N \) but under assumption (6.3.18) it does not exceed the right hand expression of (6.3.18) (or (6.3.20), in fact coincides with it only in the first case.

(iii) Consider now \( M \geq 2 \). Assume that \( B \geq Z^{\frac{20}{11}} \) as an opposite case has been analyzed already.
Let us pick up \( \bar{t} \)-admissible function \( \theta \) such that \( \theta = 1 \) as \( W \leq C_0 G t^4 \) and \( \theta = 0 \) as \( W \geq 2 C_0 G t^4 \). In this case we can claim only that \( \| \nabla \theta \| \leq C t^{-\frac{1}{2}} \bar{r}^\frac{1}{2} | \log t |^\frac{1}{2} \) and therefore

\[(6.3.7)’ \quad | \int \theta(x)(\rho_{\psi} - \rho) \, dx | \leq C t^{-\frac{1}{2}} | \log t |^\frac{1}{2} \bar{r}^\frac{1}{2} Q^\frac{1}{2} \]

while

\[(6.3.8)’ \quad B G^\frac{1}{2} \bar{r}^3 t^3 \leq \int \theta(x)\rho \, dx \leq B G^\frac{1}{2} | \log t | \bar{r}^3 t^3 \]

and therefore

\[(6.3.9)’ \quad \Theta := \int \theta(x)\rho_{\psi} \, dx \geq B G^\frac{1}{2} \bar{r}^3 t^3 \]

as

\[(6.3.10)’ \quad t \geq t_* := C_0 B^{-\frac{1}{2}} G^{-\frac{1}{2}} \bar{r}^{-\frac{1}{2}} Q^\frac{1}{2} | \log t |^\frac{1}{2}. \]

Now we need to look more carefully at \( \bar{Q} \) especially because while it may contain “rogue” factor \( L \) or \( L^2 \), it can also be large as \((Z - N)_+ \) is large. Fortunately, this is not the case in the current framework:

**Proposition 6.3.2.** (i) Under condition (6.3.24) below \( \bar{Q} \) is as in the case \( N = Z \) i.e.

\[(6.3.21) \quad \bar{Q} = \begin{cases} Z^\frac{5}{4} + B^\frac{5}{4} L^2 & \text{as } B \leq Z^\frac{1}{4}, \\ B^\frac{5}{4} Z^\frac{3}{4} L^2 & \text{as } Z^\frac{1}{4} \leq B \leq Z \end{cases} \]

(ii) Furthermore, as \( B \leq Z \) and \( a \geq Z^{-\frac{1}{2}} \) Under condition (6.3.26) below \( \bar{Q} \) is as in the case \( N = Z \), i.e.

\[(6.3.22) \quad \bar{Q} = Z^\frac{5}{2}(Z^{-\delta} + (a Z^\frac{1}{2})^{-\delta} + (B Z^{-1})^\delta). \]

**Proof.** One can either derive it from existing estimates or just repeat estimates with \( \nu = 0 \) adding \((Z - N)^2_+ \bar{r}^{-1} \) to \( \bar{Q} \). \( \square \)

Therefore all the above arguments could be repeated with this new \( \bar{Q} \) which also acquires factor \( | \log t | \) (due to this factor in the estimate of \( \| \nabla \theta \| \)) and this factor boils to \( L^\frac{1}{2} \) with

\[(6.3.23) \quad L_1 = \begin{cases} | \log B Z^{-\frac{20}{21}} | + 1 & Z^{\frac{20}{21}} \leq B \leq Z^\frac{4}{3}, \\ | \log B Z^{-3} | + 1 & Z^\frac{4}{3} \leq B \leq Z^3 \end{cases} \]

Therefore we arrive to
Theorem 6.3.3. Let \( M \geq 2 \). Then

(i) As

\[
(Z - N)_+ \leq C_0 \begin{cases} 
  Z^\frac{5}{7} & \text{as } B \leq Z^{20}_{21}, \\
  Z^\frac{5}{7} B^{-\frac{3}{7}} + B^\frac{1}{2} L & \text{as } Z^{20}_{21} \leq B \leq Z^4, \\
  B^\frac{1}{2} Z^\frac{2}{7} L & \text{as } Z^4 \leq B \leq Z^3 
\end{cases}
\]

estimate holds

\[
I_N \leq C L^\frac{1}{2} \begin{cases} 
  Z^{20}_{21} & \text{as } B \leq Z^{20}_{21}, \\
  Z^{20}_{21} B^\frac{2}{7} + B^\frac{7}{8} L^\frac{8}{7} & \text{as } Z^{20}_{21} \leq B \leq Z^4, \\
  Z^{4}_{21} B^\frac{26}{45} L^\frac{8}{7} & \text{as } Z^4 \leq B \leq Z^3 
\end{cases}
\]

(ii) Furthermore as \( B \leq Z \), \( a \geq Z^{-\frac{1}{4}} \) and

\[
(Z - N)_+ \leq C_0 \varsigma \begin{cases} 
  Z^\frac{5}{7} & \text{as } B \leq Z^{20}_{21}, \\
  Z^\frac{5}{7} B^{-\frac{3}{7}} & \text{as } Z^{20}_{21} \leq B \leq Z, 
\end{cases}
\]

with

\[
\varsigma = Z^{-1} + BZ^{-1} + a^{-1}Z^{\frac{1}{3}}
\]

estimate holds

\[
I_N \leq C L^\frac{1}{2} \varsigma' \begin{cases} 
  Z^{20}_{21} & \text{as } B \leq Z^{20}_{21}, \\
  Z^{20}_{21} B^\frac{2}{7} & \text{as } Z^{20}_{21} \leq B \leq Z 
\end{cases}
\]

7 Positively charged systems

Now let us estimate from above and below ionization energy in the case when \( N < Z \) and condition (6.3.14) (as \( M = 1 \)) or (6.3.24) (as \( M \geq 2 \)) fails. We also estimate excessive positive charge in the case of \( M \geq 2 \) and free nuclei model. We will follow arguments of and its three subsections of Section 24.6.
7.1 Upper estimate for ionization energy: 

\( M = 1 \)

Consider first the case of \( M = 1 \). Then as \( B = 0 \) arguments are well-known (see Section 24.6) but we repeat them as \( B > 0 \): we pick up \( \beta \)-admissible function \( \theta \) such that \( \theta = 1 \) as \(|x - y_1| \geq \bar{r} - \beta\) and \( \theta = 0 \) as \(|x - y_1| \leq \bar{r} - 2\beta\) where \( \bar{r} \) is an exact radius of support of \( \rho^{\text{TF}} \) (see the very beginning of Subsection 24.6.1) and \( \beta \ll \bar{r} \). Recall that

\[
\bar{r} \approx \begin{cases} 
(Z - N)^{-\frac{1}{3}} & \text{as } B \leq Z^{\frac{2}{3}}, \\
\min((Z - N)^{-\frac{1}{3}}, B^{-\frac{1}{3}}) & \text{as } Z^{\frac{2}{3}} \leq B \leq Z^{\frac{4}{3}}, \\
B^{-\frac{1}{3}} Z^{\frac{4}{3}} & \text{as } Z^{\frac{4}{3}} \leq B \leq Z^{3}
\end{cases}
\]

where in the first case we used that \( Z - N \geq Z^{\frac{5}{2}} \) while in the second case both subcases \((Z - N)^{-\frac{1}{3}} \geq B^{-\frac{1}{3}}\) are possible. We can assume that \( y_1 = 0 \). Now in the spirit of Subsection 24.6.1 we need to select like in Subsection 6.3 the smallest \( \beta \) such that

\[
\Theta^{\text{TF}} := \int \theta(x) \rho^{\text{TF}}(x) \, dx \geq C \beta^{-\frac{1}{3}} \bar{r} \bar{Q}^{\frac{1}{3}}
\]

implying that

\[
\Theta_{\psi} := \int \theta(x) \rho_{\psi}(x) \, dx \approx \Theta^{\text{TF}}
\]

where the right-hand expression of (7.1.2) estimates \( \int \theta(x)(\rho^{\text{TF}} - \rho_{\psi}) \, dx \) (recall that it does not exceed \( \|\nabla \theta\| \cdot D(\rho^{\text{TF}} - \rho_{\psi}, \rho^{\text{TF}} - \rho_{\psi})^{\frac{1}{2}}\)). Again as in Subsection 24.6.1 \( \rho^{\text{TF}} \) is calculated for actual \( N < Z \).

Eventually we arrive to estimate (24.6.8)

\[
(7.1.4) \ 1_N \int \ell(x) \rho_{\psi}(x) \theta(x) \, dx \leq \int \theta(x) V(x) \ell(x) \rho_{\psi}(x) \, dx \\
- \int \left( \rho^{(2)}_{\psi}(x, y) - \rho_{\psi}(x) \rho(y) \right) \ell(x) |x - y|^{-1} \theta(x) \, dxdy \\
- \int \rho_{\psi}(x) \rho(y) \ell(x) |x - y|^{-1} \theta(x) \, dxdy + C \beta^{-2} \bar{r} \Theta.
\]
and then estimate from above the second term in the right-hand expression

\begin{equation}
(7.1.5) \quad - \int \left( \phi^{(2)}_{\psi}(x, y) - \rho_{\psi}(x, y) \right) \ell(x) |x - y|^{-1} \theta(x) \, dx \, dy \leq \\
- \int \left( \phi^{(2)}_{\psi}(x, y) - \rho_{\psi}(x, y) \right) (1 - \omega(x, y)) \ell(x) |x - y|^{-1} \theta(x) \, dx \, dy \\
+ \int \rho_{\psi}(x, y) \omega(x, y) \ell(x) |x - y|^{-1} \theta(x) \, dx \, dy
\end{equation}

with \( \omega = \omega_{\gamma} \): \( \omega = 0 \) as \(|x - y| \geq 2\gamma \) and \( \omega = 1 \) as \(|x - y| \leq \gamma, \gamma \geq \beta \) (see \((24.6.9))

To estimate the first term in the right-hand expression of \((7.1.5)\) one can apply proposition \(24.5.1\). In this case \(\|\nabla_{y} \chi\|_{\mathcal{P}^{2}} \approx C \tilde{r} \gamma^{-\frac{1}{2}}, \|\nabla_{y} \chi\|_{\mathcal{P}^{\infty}} \approx \tilde{r} \gamma^{-2}\) and plugging \(P = \beta^{-2} \Theta\) and \(T = |\nu|, \epsilon = Z^{-\frac{1}{2}}\) we conclude that this term does not exceed \((24.6.10)\)

\begin{equation}
(7.1.6) \quad C \tilde{r} \left( \gamma^{-\frac{1}{2}} Q \frac{1}{3} + Z^{-\frac{1}{2}} \gamma^{-2} \right) \Theta
\end{equation}

(as \(Q \geq Z^{\frac{5}{3}}\); otherwise here we should reset here \(Q := Z^{\frac{5}{3}}\).

Note that as \(0 \leq \tilde{r} - |x| \approx \beta\)

\begin{equation}
(7.1.7) \quad W + \nu \approx \nu := \max \left\{ \left( \frac{|\nu| \beta}{\tilde{r}} \right)^{\frac{1}{2}}, G \left( \frac{\beta}{\tilde{r}} \right)^{4} \right\}
\end{equation}

with \(G\) defined by \((1.3.10)\) and therefore

\begin{equation}
(7.1.8) \quad \rho \approx \max \left\{ \left( \frac{|\nu| \beta}{\tilde{r}} \right)^{\frac{1}{3}}, B \left( \frac{|\nu| \beta}{\tilde{r}} \right)^{\frac{1}{3}}, BG \left( \frac{\beta}{\tilde{r}} \right)^{2} \right\}
\end{equation}

where the first and the second clauses are forks of the first clause in \((7.1.7)\) as in the second clause automatically \(W + \nu \leq B\) as \(0 \leq \tilde{r} - |x| \approx \beta\); therefore

\begin{equation}
(7.1.9) \quad \int \rho(x) \theta(x) \, dx \approx \max \left\{ \left( \frac{|\nu| \beta}{\tilde{r}} \right)^{\frac{1}{2}} \beta^{2}, B \left( \frac{|\nu| \beta}{\tilde{r}} \right)^{\frac{1}{2}}, BG \left( \frac{\beta}{\tilde{r}} \right)^{2} \right\} \beta \tilde{r}^{2}
\end{equation}

and therefore \((7.1.2)\) holds if and only if

\begin{equation}
(7.1.10) \quad \max \left\{ \left( \frac{|\nu|}{\tilde{r}} \right)^{2} \beta^{3}, B \left( \frac{|\nu|}{\tilde{r}} \right)^{3} \beta^{2}, BG \left( \frac{1}{\tilde{r}} \right)^{2} \beta^{2} \right\} \tilde{r} \geq C Q \frac{1}{3};
\end{equation}
then
\[
\beta = \min \left\{ Q^2 |\nu|^{-\frac{1}{2}} \bar{r}^\frac{1}{2}; B^{-\frac{1}{2}} Q^2 |\nu|^{-\frac{1}{2}} \bar{r}^{-\frac{1}{2}}; B^{-\frac{1}{2}} G^{-\frac{1}{2}} Q^2 \bar{r}^{\frac{1}{2}} \right\}
\]

and in the corresponding cases
\[
\nu = \left\{ Q^2 |\nu|^{-\frac{1}{2}} \bar{r}^{-\frac{1}{2}}; B^{-\frac{1}{2}} Q^2 |\nu|^{-\frac{1}{2}} \bar{r}^{-\frac{1}{2}}; B^{-\frac{1}{2}} G^{-\frac{1}{2}} Q^2 \bar{r}^{-\frac{1}{2}} \right\}.
\]

Note however that as \(B \lesssim Q^\frac{2}{3}\) and \(|\nu| \lesssim Q^\frac{2}{3}\) we do not need these arguments; simpler arguments of Subsection 24.5.2 show that in this case \(|N| \leq CQ^\frac{2}{3}\).

On the other hand, as \(B \lesssim Q^\frac{2}{3}\) but \(|\nu| \gtrsim Q^\frac{2}{3}\) we pick like in Subsection 24.6.1 \(\gamma = Q^2 |\nu|^{-\frac{1}{2}}\bar{r}^{-\frac{1}{2}}\) and observe that \(|\nu|\gamma^{-1} \bar{r}^{-1} \gtrsim B\) and therefore \(|N| + \nu \leq CQ^\frac{2}{3}|\nu|\frac{17}{20}\) exactly like in that Subsection. Therefore we arrive to

**Proposition 7.1.1.** Let \(B \leq C_0 Z^\frac{22}{3}\). Then

(i) As \(|\nu| \leq C_0 Z^\frac{22}{3}\) estimate \(|N| \leq CZ^\frac{22}{3}\) holds like in the case \(B = 0\);

(ii) As \(|\nu| \geq C_0 Z^\frac{22}{3}\) estimate \(|N| + \nu \leq CZ^\frac{22}{3}|\nu|\frac{17}{20}\) holds like in the case \(B = 0\).

Therefore in what follows we assume that \(B \gtrsim Q^\frac{2}{3}\). One can see easily that then \(\beta \leq \bar{r}\).

Meanwhile the same arguments imply that the second term in the right-hand expression of (7.1.5) is of magnitude
\[
\max \left\{ \left( \frac{|\nu|}{\bar{r}} \right)^\frac{1}{2}; B \left( \frac{|\nu|}{\bar{r}} \right)^\frac{1}{2}; BG^{\frac{1}{2}} \left( \frac{\gamma}{\bar{r}} \right)^2 \right\} \gamma^2
\]

and we need to minimize
\[
\gamma^{-\frac{1}{2}} Q^\frac{1}{2} + \max \left\{ \left( \frac{|\nu|}{\bar{r}} \right)^\frac{1}{2}, B \left( \frac{|\nu|}{\bar{r}} \right)^\frac{1}{2}; BG^{\frac{1}{2}} \left( \frac{\gamma}{\bar{r}} \right)^2 \right\} \gamma^2
\]

which is achieved when
\[
\gamma^{-\frac{1}{2}} Q^\frac{1}{2} \simeq \max \left\{ \left( \frac{|\nu|}{\bar{r}} \right)^\frac{1}{2}; B \left( \frac{|\nu|}{\bar{r}} \right)^\frac{1}{2}; BG^{\frac{1}{2}} \left( \frac{\gamma}{\bar{r}} \right)^2 \right\} \gamma^2.
\]
Let us compare with equation to $\beta$. It is the same albeit with factor $\bar{r}^2$ rather than $\gamma^2$. Therefore if $\gamma \geq \bar{r}$ then $\gamma \leq \beta \leq \bar{r}$ which is a contradiction. Thus $\gamma \leq \bar{r}$ but then $\gamma \geq \beta$.

Therefore we conclude that this term does not exceed

\[
(7.1.13) \quad \zeta := \max \left\{ Q^{\frac{7}{10}} \left( \frac{|\nu|}{\bar{r}} \right)^{\frac{17}{16}}, \ Q^{\frac{5}{10}} B^{\frac{1}{2}} \left( \frac{|\nu|}{\bar{r}} \right)^{\frac{17}{16}}, \ Q^{\frac{5}{8}} B^{\frac{1}{2}} G^{\frac{2}{5}} \bar{r}^{-\frac{3}{2}} \right\}
\]

and to estimate $I_N + \nu$ we need just to compute its sum with $\nu$ defined by (7.1.12).

Therefore

\[
(7.1.14) \quad I_N + \nu \leq C(\nu + \zeta).
\]

**Remark 7.1.2.** Observe that

\[
(7.1.15) \quad \nu(\bar{Z}, B, |\nu|) = Z^{\frac{20}{11}} \nu(1, Z^{-\frac{20}{11}} B, |\nu|Z^{-\frac{20}{11}}|\nu|) \quad \text{as} \quad Z^{\frac{20}{11}} \leq B \leq Z^{\frac{4}{3}}
\]

and

\[
(7.1.16) \quad \nu(\bar{Z} B^{-3}, |\nu|) = Z^2 \nu(1, Z^{-3} B, |\nu|Z^{-2}|\nu|) \quad \text{as} \quad Z^{\frac{4}{3}} \leq B \leq Z^{3}
\]

and $\zeta$ has the same scaling properties.

Therefore we can make all calculations with $\bar{Z} = 1$ and then scale. Leaving easy calculations to the reader we arrive to

**Proposition 7.1.3.** (i) As $Z^{\frac{20}{11}} \leq B \leq Z^{\frac{4}{3}}$

\[
(7.1.17) \quad I_N + \nu \leq C \begin{cases} 
Z^{\frac{5}{8}} |\nu|^{\frac{17}{16}} & \text{as } |\nu| \geq Z^{-\frac{20}{11}} B^{\frac{24}{11}}, \\
Z^{\frac{5}{11}} B^{-\frac{1}{2}} |\nu|^{\frac{17}{16}} & \text{as } B \leq |\nu| \leq Z^{-\frac{20}{11}} B^{\frac{24}{11}}, \\
Z^\frac{5}{8} B^{\frac{2}{3}} |\nu|^{\frac{17}{16}} & \text{as } Z^{\frac{5}{8}} B^{\frac{2}{3}} \leq |\nu| \leq B, \\
Z^{\frac{20}{11}} B^{\frac{3}{8}} |\nu|^{\frac{1}{16}} & \text{as } Z^{\frac{2}{5}} B^{\frac{3}{8}} \leq |\nu| \leq Z^{\frac{20}{11}} B^{\frac{24}{11}}, \\
Z^{\frac{20}{11}} B^{\frac{2}{5}} |\nu|^{\frac{1}{16}} & \text{as } |\nu| \leq Z^{\frac{20}{11}} B^{\frac{24}{11}};
\end{cases}
\]

(ii) In particular,

\[
(7.1.18) \quad I_N \leq CZ^{\frac{20}{11}} B^{\frac{2}{5}} \quad \text{as } |\nu| \leq Z^{\frac{20}{11}} B^{\frac{24}{11}};
\]

111
(iii) As $Z^\frac{4}{3} \leq B \leq Z^3$

$$I_N + \nu \leq C \left\{ \begin{array}{ll}
Z^\frac{4}{3} B^\frac{8}{9} |\nu|^\frac{1}{3} & \text{as } |\nu| \geq Z^\frac{2}{3} B^\frac{8}{9} \\
Z^\frac{4}{3} B^\frac{26}{45} & \text{as } |\nu| \leq Z^\frac{2}{3} B^\frac{8}{9}.
\end{array} \right. \quad (7.1.19)$$

(iv) In particular,

$$I_N \leq CZ^\frac{4}{3} B^\frac{26}{45} \quad \text{as } |\nu| \leq Z^\frac{2}{3} B^\frac{8}{9}. \quad (7.1.20)$$

Remark 7.1.4. Recall that $Q = Z^\frac{4}{3} (B^{\delta} + 1) Z^{-\delta}$ as $B \leq Z$; therefore we can add factor $(B^{\delta'} + 1) Z^{-\delta'}$ in all estimates of Propositions 7.1.1 and 7.1.3.

## 7.2 Lower estimate for ionization energy: $M = 1$

Now let us prove estimate $I_N + \nu$ from below. Let $\Psi = \Psi_N(x_1, \ldots, x_N)$ be the ground state for $N$ electrons, $||\Psi|| = 1$; consider an antisymmetric test function

$$\tilde{\Psi} = \tilde{\Psi}(x_1, \ldots, x_{N+1}) = \Psi(x_1, \ldots, x_N)u(x_{N+1}) - \sum_{1 \leq j \leq N} \Psi(x_1, \ldots, x_{j-1}, x_{N+1}, x_{j+1}, \ldots, x_N)u(x_j) \quad (7.2.1)$$

Then exactly as in Subsection 24.6.2

$$E_{N+1}||\tilde{\Psi}||^2 \leq \langle H_{N+1} \tilde{\Psi}, \tilde{\Psi} \rangle = N\langle H_{N+1} \Psi u, \tilde{\Psi} \rangle = N\langle H_N \Psi u, \tilde{\Psi} \rangle + N\langle H_{V,x_{N+1}} \Psi u, \tilde{\Psi} \rangle + N\langle \sum_{1 \leq i \leq N} |x_i - x_{N+1}|^{-1} \Psi u, \tilde{\Psi} \rangle = (E_N - \nu')||\tilde{\Psi}||^2 + N\langle H_{W+\nu',x_{N+1}} \Psi u, \tilde{\Psi} \rangle$$

and therefore

$$N^{-1}(I_{N+1} + \nu')||\tilde{\Psi}||^2 \geq -\langle H_{W+\nu',x_{N+1}} \Psi u, \tilde{\Psi} \rangle - \langle \sum_{1 \leq i \leq N} |x_i - x_{N+1}|^{-1} - (V - W)(x_{N+1}) \rangle \Psi u, \tilde{\Psi} \rangle \quad (7.2.2)$$

112
\[
(7.2.3) \quad N^{-1} \| \tilde{\Psi} \|^2 = \| \Psi \|^2 \cdot \| u \|^2 - N \int \Psi(x_1, \ldots, x_{N-1}, x) \Psi^\dagger(x_1, \ldots, x_{N-1}, y) u(y) u^\dagger(x) \, dx_1 \cdots dx_{N-1} \, dx dy
\]

as in (24.6.14) and (24.6.15) respectively where \( ^\dagger \) means a complex or Hermitian conjugation and \( \nu' \geq \nu \) to be chosen later.

Note that every term in the right-hand expression in (7.2.2) is the sum of two terms: one with \( \tilde{\Psi} \) replaced by \( \Psi(x_1, \ldots, x_N) u(x_{N+1}) \) and another with \( \tilde{\Psi} \) replaced by \( -N \Psi(x_1, \ldots, x_{N-1}) u(x_N) \). We call these terms direct and indirect respectively.

Obviously, in the direct and indirect terms \( u \) appears as \( |u(x)|^2 \, dx \) and as \( u(x) u^\dagger(y) \, dx dy \) respectively multiplied by some kernels.

Recall that \( u \) is an arbitrary function. Let us take \( u(x) = \theta_i(x) \phi_j(x) \) where \( \phi_j \) are orthonormal eigenfunctions of \( H_{W+\nu} \) and \( \theta(x) \) is \( \beta \)-admissible function which is supported in \( \{ x : -v \geq W(x) + \nu \geq \frac{3}{2} \nu \} \) and equal 1 in \( \{ x : -2v \geq W(x) + \nu \geq \frac{3}{2} \nu \} \), satisfying (24.5.11), and \( v \) is related to \( \beta \) as in the previous Section 6:

\[
(7.2.4) \quad v = C \max(\nu r^{-1} \beta; G^{-4} \beta^4).
\]

Let us substitute it into (7.2.2), multiply by \( \phi(\lambda_j L^{-1}) \) and take sum with respect to \( j \); then we get the same expressions with \( |u(x)|^2 \, dx \) and \( u(x) u^\dagger(y) \, dx dy \) replaced by \( F(x, x) \, dx \) and \( F(x, y) \, dx dy \) respectively with

\[
(7.2.5) \quad F(x, y) = \int \phi(\lambda L^{-1}) \, d_\lambda e(x, y, \lambda).
\]

Here \( \phi(\tau) \) is a fixed \( \mathcal{C}^\infty_0 \) non-negative function equal to 1 as \( \tau \leq \frac{1}{2} \) and equal to 0 as \( \tau \geq 1 \) and \( L = \nu' - \nu = 6v \).

Under described construction and procedures the direct term generated by \( N^{-1} \| \tilde{\Psi} \|^2 \) is

\[
(7.2.6) \quad \int \theta(x) \phi(\lambda L^{-1}) \, d_\lambda e(x, x, \lambda) \, dx
\]

and applying semiclassical approximation we get

\[
(7.2.7) \quad \Theta_\Psi := \int \phi(\lambda L^{-1}) \, d_\lambda P_\beta'(W + \nu - \lambda) \, dx.
\]
Consider remainder estimate. Assume that $M = 1$ (case $M \geq 2$ will be considered later). Then as $L = C_1v$ the remainder does not exceed

$$Ch^s(\mu h + 1)\beta^{-2}r^2$$

where

$$h = 1/(v^{\frac{1}{2}} \beta)$$

and

$$\mu = B \beta v^{-\frac{1}{2}};$$

one can prove it easily by partition of unity on $\text{supp} \theta$ and applying semiclassical asymptotics with effective semiclassical parameter $h$ and magnetic parameter $\mu$.

On the other hand, an indirect term generated by $N^{-1}\|\tilde{\Psi}\|^2$ is

$$-N \int \theta^{\frac{1}{2}}(x)\theta^{\frac{1}{2}}(y)\Psi(x_1, \ldots, x_{N-1}, x)\Psi^\dagger(x_1, \ldots, x_{N-1}, y) \times F(x, y) \, dx \, dy \, dx_1 \cdots dx_{N-1}$$

and since the operator norm of $F(., ., .)$ is $1$ the absolute value of this term does not exceed

$$N \int \theta(x)\|\Psi(x_1, \ldots, x_{N-1}, x)\|^2 \, dx = \int \theta(x)\rho_{\Psi}(x) \, dx \leq \int \theta(x)\rho_{TF}(x) \, dx + CQ\|\nabla \theta^{\frac{1}{2}}\|$$

where $\rho_{TF} = 0$ on $\text{supp} \theta$ and $\|\nabla \theta^{\frac{1}{2}}\| \asymp \beta^{-\frac{1}{2}}r$.

Recall that $P'(W_{TF} + \nu) = \rho_{TF}$. We will take $\nu' = \nu + L$ to keep $\Theta_{\Psi}$ larger than all the remainders including those due to replacement $W$ by $W_{TF}$ and $\rho$ by $\rho_{TF}$ in the expression above. One can observe easily that then $\beta$ should satisfy (7.1.10); let us define $\beta$ and then $v$ by (7.1.11) and (7.1.12) respectively. Then

$$\Theta_{\Psi} \asymp (v^{\frac{3}{2}} + Bv^{\frac{1}{2}})\beta r^2.$$  

Therefore

$$\Theta_{\Psi} \asymp (v^{\frac{3}{2}} + Bv^{\frac{1}{2}})\beta r^2.$$  

(7.1.11) Let $h \leq \epsilon_0$ (i.e. $v^{\frac{1}{2}} \beta \geq C_0$), and $\beta, v$ be defined by (7.1.11) and (7.1.12) respectively. Then expression (7.2.13) is larger than $C_0 \beta^{-\frac{1}{2}}Q^{\frac{1}{2}}$ and the total expression generated by $N^{-1}\|\tilde{\Psi}\|^2$ is greater than $\epsilon \Theta$ with $\Theta = \Theta_{\Psi}$ defined by (7.2.13).
Now let us consider direct terms in the right-hand expression of (7.2.2). The first of them is like in (24.6.23)

\[(7.2.15) \quad - \int \theta^\frac{1}{2}(x) \varphi(\lambda L^{-1}) d_{\lambda}(H_{W+\nu',x}\theta^\frac{1}{2}(x)e(x,y,\lambda))_{y=x} \, dx =
\]
\[\quad - \int \theta(x) \varphi(\lambda L^{-1}) d_{\lambda}(H_{W+\nu',x}e(x,y,\lambda))_{y=x} \, dx
\]
\[\quad - \frac{1}{2} \int \varphi(\lambda L^{-1})[[H_{W},\theta^\frac{1}{2}],\theta^\frac{1}{2}] d_{\lambda}(x,x,\lambda) \geq
\]
\[\int \theta(x)(\nu' - \nu - \lambda) \varphi(\lambda L^{-1}) d_{\lambda}e(x,x,\lambda) \, dx - C \int |\nabla \theta^\frac{1}{2}|^2 e(x,x,\nu') \, dx.
\]

Note that the absolute value of last term in the right-hand expression of (7.2.15) does not exceed \(C^{\beta^{-1}} \bar{r}^2 (v^\frac{3}{2} + Bv^\frac{1}{2}) \asymp \beta^{-2}\Theta\).

The second direct term in the right-hand expression of (7.2.2) is like in (24.6.24)

\[(7.2.16) \quad - \int \theta(x) \left( \rho_{\Psi} * |x|^{-1} - (V - W)(x) \right) F(x,x) \, dx =
\]
\[\quad - D(\rho_{\Psi} - \bar{\rho}, \theta(x)F(x,x)) \geq
\]
\[\quad - CD(\rho_{\Psi} - \rho, \rho_{\Psi} - \rho)^{\frac{1}{2}} \cdot D(\theta^\frac{1}{2} F(x,x), \theta^\frac{1}{2} F(x,x))^{\frac{1}{2}} \geq - CQ^{\frac{1}{2}} \bar{r}^{-\frac{1}{2}} \Theta
\]

provided \(V - W = |x|^{-1} * \rho\) with \(D(\rho - \rho^{TF}, \rho - \rho^{TF}) \leq CQ\).

Further, the first indirect term in the right-hand expression of (7.2.2) is like in (24.6.25)

\[(7.2.17) \quad - N \int \theta^\frac{1}{2}(y) \Psi(x_1, ... , x_{N-1}, x) \Psi^\dagger(x_1, ... , x_{N-1}, y) \times
\]
\[\varphi(\lambda L^{-1}) d_{\lambda}(H_{W+\nu',x}\theta^\frac{1}{2}(x)e(x,y,\lambda)) \, dx dy dx_1 \cdots dx_{N-1} =
\]
\[\quad - N \int \theta^\frac{1}{2}(y)^{\frac{1}{2}}(x) \Psi(x_1, ... , x_{N-1}, x) \Psi^\dagger(x_1, ... , x_{N-1}, y) \times
\]
\[\varphi(\lambda L^{-1})(\nu' - \nu - \lambda) d_{\lambda}e(x,y,\lambda) \, dx dy dx_1 \cdots dx_{N-1}
\]
\[\quad - N \int \theta^\frac{1}{2}(y) \Psi(x_1, ... , x_{N-1}, x) \Psi^\dagger(x_1, ... , x_{N-1}, y) \times
\]
\[\varphi(\lambda L^{-1})[H_{W,x}, \theta^\frac{1}{2}(x)] d_{\lambda}e(x,y,\lambda) \, dx dy dx_1 \cdots dx_{N-1}.
\]
Note that one can rewrite the sum of the first terms in the right-hand expressions in (7.2.15) and (7.2.17) as \( \sum_j \varphi(\lambda_j L^{-1})(\nu' - \nu - \lambda_j) \| \Psi_j \|^2 \) with

\[
\hat{\Psi}_j(x_1, \ldots, x_{N-1}) := \int \Psi(x_1, \ldots, x_{N-1}, x) \theta^{\frac{1}{2}}(x) \phi_j(x) \, dx
\]

and therefore this sum is non-negative.

One can see easily that the absolute value of the second term in the right-hand expression of (7.2.17) does not exceed

\[
\int \rho(y) \theta^{\frac{1}{2}}(y) \, dy \times \beta^{-1} \int \theta_1(x) e(x, x, \nu') \, dx \asymp C \Theta \times C (v^{\frac{1}{2}} + B v)^2 \asymp C \beta^{-\frac{1}{2}} r Q^{\frac{1}{2}} \Theta
\]

due the choice of \( \beta \). This is larger than the absolute value of the right-hand expression in (7.2.16). Therefore (cf. 24.6.26)

(7.2.18) The sum of the first direct and indirect terms in the right-hand expression of (7.2.2) is greater than \(- C \beta^{-\frac{1}{2}} r Q^{\frac{1}{2}} \Theta\).

Finally, we need to consider the second indirect term generated by the right-hand expression of (7.2.2):

(7.2.19) \[- \int \left( \sum_{1 \leq i \leq N} |y - x_i|^{-1} - (V - W)(y) \right) \times \]

\[
\Psi(x_1, \ldots, x_N) \Psi^\dagger(x_1, \ldots, x_{N-1}, y) \theta^{\frac{1}{2}}(x_N) \theta^{\frac{1}{2}}(y) F(x_N, y) \, dx_1 \cdots dx_N \, dy = \\
- \int \left( |y|^{-1} * g_x(y) - (V - W)(y) \right) \Psi(x_1, \ldots, x_N) \Psi^\dagger(x_1, \ldots, x_{N-1}, y) \times \\
\theta^{\frac{1}{2}}(x_N) \theta^{\frac{1}{2}}(y) F(x_N, y) \, dx_1 \cdots dx_N \, dy \\
- \int \left( \sum_{1 \leq i \leq N} |y - x_i|^{-1} - |y|^{-1} * g_x(y) \right) \Psi(x_1, \ldots, x_N) \Psi^\dagger(x_1, \ldots, x_{N-1}, y) \times \\
\theta^{\frac{1}{2}}(x_N) \theta^{\frac{1}{2}}(y) F(x_N, y) \, dx_1 \cdots dx_N \, dy;
\]

recall that \( g_x \) is a smeared density, \( x = (x_1, \ldots, x_N) \).
Since $|y|^{-1} * \varphi_\varepsilon(y) - (V - W)(y) = |y|^{-1} * (\varphi_\varepsilon - \rho)$, the first term in the right-hand expression is equal to

\[
(7.2.20) \quad \int \theta^{\frac{1}{2}}(x_N) \Psi(x_1, \ldots, x_N) \times D_y \left( \varphi_\varepsilon(y) - \rho(y), F(x_N, y, \lambda) \theta^{\frac{1}{2}}(y) \Psi(x_1, \ldots, x_{N-1}, y) \right) dx_1 \cdots dx_N;
\]
and its absolute value does not exceed

\[
(7.2.21) \quad \left( N \int D\left( \varphi_\varepsilon(\cdot) - \rho(\cdot), \varphi_\varepsilon(\cdot) - \rho(\cdot) \right) |\Psi(x_1, \ldots, x_N)|^2 \theta(x_N) dx_1 \cdots dx_N \right)^{\frac{1}{2}} \times N^{-\frac{1}{2}} \left( D_y \left( F(x_N, y, \lambda) \theta^{\frac{1}{2}}(y) \Psi(x_1, \ldots, x_{N-1}, y) \right) dx_1 \cdots dx_N \right)^{\frac{1}{2}}.
\]

Recall that the first factor is equivalently defined by (24.5.4) and therefore due to estimate (24.5.24) it does not exceed \(((Q + T + \varepsilon^{-1} N) \Theta + P)\)^{\frac{1}{2}} where we assume that $\varepsilon \leq Z^{-\frac{4}{3}}$ and $\Theta \asymp \beta(v^{\frac{1}{3}} + B v^{\frac{1}{3}}) r^2 \beta \asymp \beta^{-\frac{1}{3}} r Q^{\frac{1}{2}}$ is now an upper estimate for $\int \theta(y) \rho \Psi(y) dy$-like expressions.

Then according to (24.5.25) $P \asymp C \beta^{-2} \Theta \ll Q \Theta$ and according to (24.5.23) $T \ll Q$ and therefore in all such inequalities we may skip $P$ and $T$ terms; so we get $C(Q + \varepsilon^{-1} N)^{\frac{1}{2}} \Theta^{\frac{1}{2}}$.

Meanwhile the second factor in (7.2.21) (without square root) is equal to

\[
N^{-1} \int L^{-2} \varphi'(\lambda L^{-1}) \varphi'(\lambda' L^{-1}) |y - z|^{-1} e(x_N, y, \lambda) \theta^{\frac{1}{2}}(y) \Psi(x_1, \ldots, x_N, \ldots, y) \times e(x_N, z, \lambda') \theta^{\frac{1}{2}}(z) \Psi^i(x_1, \ldots, x_{N-1}, z) dydz \ dx_1 \cdots dx_N \ d\lambda d\lambda';
\]

after integration by $x_N$ we get instead of marked terms $e(y, z, \lambda)$ (recall that $e(\cdot, \cdot, \cdot)$ is the Schwartz kernel of projector and we keep $\lambda < \lambda'$) and then integrating with respect to $\lambda'$ we arrive to

\[
N^{-1} \int |y - z|^{-1} F(y, z) \theta^{\frac{1}{2}}(y) \Psi(x_1, \ldots, x_{N-1}, y) \times \theta^{\frac{1}{2}}(z) \Psi^i(x_1, \ldots, x_{N-1}, z) dydz \ dx_1 \cdots dx_{N-1};
\]

117
where now $F$ is defined by \eqref{eq:7.2.5} albeit with $\varphi^2$ instead of $\varphi$. This latter expression does not exceed
\begin{equation}
N^{-1} \int \left| y - z \right|^{-1} |F(y, z)| \theta^{\frac{1}{2}}(y) |\Psi(x_1, \ldots, x_{N-1}, y)|^2 \times \nonumber \end{equation}
\begin{equation}
dydz \ dx_1 \cdots dx_{N-1}. \nonumber \end{equation}

Then due to proposition 8.D.1 expression $\int \left| y - z \right|^{-1} |F(y, z)| \ dz$ does not exceed $C \beta^{-1}(h^{-1} + \mu) \geq v^\frac{1}{2} + B v^{-\frac{1}{2}}$, and thus expression \eqref{eq:7.2.22} does not exceed $C Z^{-\frac{2}{3}}(v^\frac{1}{2} + B v^{-\frac{1}{2}}) \Theta$ and therefore the second factor in \eqref{eq:7.2.21} does not exceed $CN^{-1}(v^\frac{1}{2} + B^\frac{1}{2} v^{-\frac{1}{2}}) \Theta^{\frac{1}{2}}$ and the whole expression \eqref{eq:7.2.21} does not exceed
\begin{equation}
C(Q + \varepsilon^{-1} N)^\frac{1}{2} \Theta^{\frac{1}{2}} \times N^{-1}(v^\frac{1}{2} + B^\frac{1}{2} v^{-\frac{1}{2}}) \Theta^{\frac{1}{2}} = \nonumber \end{equation}
\begin{equation}
CN^{-1}(Q + \varepsilon^{-1} N)^\frac{1}{2}(v^\frac{1}{2} + B^\frac{1}{2} v^{-\frac{1}{2}}) \Theta \nonumber \end{equation}

and finally we arrive to

**Proposition 7.2.1.** \footnote{Cf. claim \eqref{eq:24.6.31}.} \footnote{C.} Let
\begin{equation}
v \geq \max(Z^{-\frac{4}{3}} Q^\frac{2}{3}; Z^{-\frac{4}{3}} Q^\frac{2}{3} B^\frac{2}{3}) \nonumber \end{equation}
and
\begin{equation}
\varepsilon \geq Z^{-1} \max(v^{-\frac{3}{2}}, B v^{-\frac{5}{2}}). \nonumber \end{equation}
Then the first term in the right-hand expression of \eqref{eq:7.2.19} does not exceed $C v \Theta$.

Further, we need to estimate the second term in the right-hand expression of \eqref{eq:7.2.19}. It can be rewritten in the form
\begin{equation}
\sum_{1 \leq i \leq N^*} \int U(x_i, y) \Psi(x_1, \ldots, x_N) \Psi^\dagger(x_1, \ldots, x_{N-1}, y) \theta^{\frac{1}{2}}(x_N) \theta^{\frac{1}{2}}(y) \times \nonumber \end{equation}
\begin{equation}F(x_N, y) \ dx_1 \cdots dx_N dy \nonumber \end{equation}
where $U(x_i, y)$ is the difference between two potentials, one generated by the charge $\delta(x - x_i)$ and another by the same charge smeared; note that $U(x_i, y)$
is supported in \( \{(x_i, y) : |x_i - y| \leq \varepsilon\} \). Let us estimate the \( i \)-th term in this sum with \( i < N \) first; multiplied by \( N(N - 1) \), it does not exceed

\[
(7.2.26) \quad N \left( \int |U(x_i, y)|^2 |\Psi(x_1, \ldots, x_N)|^2 \theta^\frac{1}{2}(x_N) \theta^\frac{1}{2}(y)|F(x_N, y)| \, dx_1 \cdots dx_N dy \right)^\frac{1}{2} \times
\]

\[
N \left( \int \omega(x_i, y) |\Psi(x_1, \ldots, x_{N-1}, y)|^2 \theta^\frac{1}{2}(x_N) \theta^\frac{1}{2}(y)|F(x_N, y)| \, dx_1 \cdots dx_N dy \right)^\frac{1}{2}
\]

here \( \omega \) is \( \varepsilon \)-admissible and supported in \( \{(x_i, y) : |x_i - y| \leq 2\varepsilon\} \) function. Due to Proposition 8.D.1 in the second factor

\[
\int \theta^\frac{1}{2}(x_N)|F(x_N, y)| \, dx_N \leq C(1 + \mu h) \asymp C(1 + Bu^{-1})
\]

and therefore the whole second factor does not exceed

\[
(7.2.27) \quad C \left( \int \theta^\frac{1}{2}(x) \omega(x, y) \rho^{(2)}(x, y) \, dx dy \right)^\frac{1}{2} (1 + Bu^{-1})^{\frac{1}{2}}
\]

where we replaced \( x_i \) by \( x \). According to Proposition 24.5.1 in the selected expression one can replace \( \rho^{(2)}(x, y) \) by \( \rho(x)\rho(y) \) with an error which does not exceed

\[
C \left( \sup_x \|\nabla_x x\|_{L^2(\mathbb{R}^3)} \left( \mathcal{Q} + \varepsilon^{-1} N \right)^\frac{1}{2} + C\varepsilon N \|\nabla_y x\|_{L^\infty} \right) \Theta
\]

which as we plug \( \sup_x \|\nabla_y x\|_{L^2(\mathbb{R}^3)} \asymp \varepsilon^\frac{1}{2} \), \( \|\nabla_y x\|_{L^\infty} \asymp \varepsilon^{-1} \) becomes \( CN\Theta \). Meanwhile, consider

\[
(7.2.28) \quad \int |U(x_i, y)|^2 \theta^\frac{1}{2}(y)|F(x_N, y)| \, dy.
\]

Again due to Proposition 8.D.1 it does not exceed

\[
C(u^\frac{3}{2} + Bu^\frac{1}{2}) \int |U(x_i, y)|^2 \theta^\frac{1}{2}(y)(|x_N - y|u^\frac{1}{2} + 1)^{-s} \, dy
\]

and this integral should be taken over \( B(x_i, \varepsilon) \), with \( |U(x_i, y)| \leq |x_i - y|^{-1} \), so (7.2.28) does not exceed

\[
C\varepsilon (u^\frac{1}{2} + Bu^\frac{1}{2})\omega'(x_i, x_N)
\]
with \( \omega'(x, y) = (1 + v^{1/2}|x - y|)^{-s} \) (provided \( \varepsilon \leq v^{-1} \frac{1}{2} \) which will be the case). Therefore the first factor in (7.2.26) does not exceed

\[
C \varepsilon^{1/2} \left( v^{1/2} + B^{1/2} v^{1/2} \right) \left( \int \theta^{1/2}(x) \omega'(x, y) \varrho^{(2)}(x, y) \, dx \, dy \right)^{1/2}.
\]

Therefore in the selected expression one can replace \( \varrho^{(2)}(x, y) \) by \( \rho(y) \) with an error which does not exceed what we got before but with \( \varepsilon \) replaced by \( v^{-1} \), i.e. also \( CN\Theta \).

However in both selected expressions (7.2.27) and (7.2.29) replacing \( \varrho^{(2)}(x, y) \) by \( \rho(y) \) we get just 0. Therefore expression (7.2.26) does not exceed \( C \varepsilon^{1/2} (v^{1/2} + B^{1/2} v^{1/2}) Z \Theta \) which, in turn, does not exceed \( C v \Theta \) provided \( \varepsilon \leq C v \left( 1 + B v^{-1} \right)^{-1} Z^{-2} \).

So, we have two restrictions to \( \varepsilon \) from above: the last one and \( \varepsilon \leq Z^{-2} \frac{1}{4} \) and one can see easily that both of them are compatible with restriction to \( \varepsilon \) in (7.2.23); also we can see easily that condition (7.2.23) is weaker than \( v \geq \{ Z^{\frac{20}{51}} : Z^{\frac{20}{51}} B^{\frac{1}{2}} : Z^{\frac{4}{5}} B^{\frac{20}{51}} \} \) as \( \{ B \leq Z^{20}; Z^{\frac{20}{51}} \leq B \leq Z^{\frac{4}{5}}; Z^{\frac{4}{5}} \leq B \leq Z^{3} \} \) respectively.

Finally, consider term in (7.2.25) with \( i = N \) (multiplied by \( N \));

\[
N \int U(x_N, y) |\Psi(x_1, \ldots, x_N)|^2 \theta^{1/2}(x_N) \theta^{1/2}(y) F(x_N, y) \, dx_1 \cdots dx_N \, dy
\]
due to Cauchy inequality it does not exceed

\[
N \left( \int |x_N - y|^{-2} |\Psi(x_1, \ldots, x_N)|^2 \theta^{1/2}(x_N) \theta^{1/2}(y) \, dx_1 \cdots dx_N \, dy \right)^{1/2} \times
\]

\[
N \left( \int |F(x_N, y)|^2 |\Psi(x_1, \ldots, x_N)|^2 \theta^{1/2}(x_N) \theta^{1/2}(y) \, dx_1 \cdots dx_N \, dy \right)^{1/2}
\]

where both integrals are taken over \( \{ |x_N - y| \leq \varepsilon \} \). Integrating with respect to \( y \) there we get that it does not exceed

\[
C \varepsilon^{1/2} \Theta^{1/2} \times (v^{1/2} + B v^{1/2}) \varepsilon^{1/2} \Theta^{1/2} = C (v^{1/2} + B v^{1/2}) \varepsilon \Theta \ll v \Theta.
\]

Therefore the right-hand expression in (7.2.2) is \( \geq -C v \Theta \) and recalling that \( \nu' - \nu = O(\nu) \) we recover a lower estimate \( l_N + \nu \geq -C v \) in Theorem 7.2.2 below. Here \( \nu \) must be found from (7.1.11)–(7.1.12) and must satisfy \( \nu \leq |\nu| \).

Combining this estimate with Proposition 7.1.3 we arrive to

120
**Theorem 7.2.2.** Let $M = 1$. Let condition (1.2.21) be fulfilled. Then

(i) As $B \leq Z \frac{20}{\pi}$ and $|\nu| \geq Z \frac{20}{\pi}$

(7.2.32)  
\[ |l_N + \nu| \leq CZ \frac{\pi}{\nu} |\nu| \frac{17}{34} \]

(ii) As $Z \frac{20}{\pi} \leq B \leq Z^3$ and $|\nu| \geq Z \frac{20}{\pi} B \frac{2}{3}$ estimate (7.1.17) from above and estimate

(7.2.33) \[ l_N + \nu \geq -C \begin{cases} 
Z \frac{\pi}{\nu} |\nu| \frac{17}{34} & \text{as } B \leq Z \frac{\pi}{\nu} |\nu| \frac{17}{34}, \\
Z \frac{\pi}{\nu} B^{-\frac{1}{3}} |\nu| \frac{17}{34} & \text{as } Z \frac{\pi}{\nu} |\nu| \frac{17}{34} \leq B \leq |\nu|, \\
Z \frac{\pi}{\nu} B^{-\frac{3}{5}} |\nu| \frac{2}{3} & \text{as } |\nu| \leq B \leq Z^{-\frac{20}{\pi}} |\nu|^4, \\
Z \frac{\pi}{\nu} & \text{as } Z^{-\frac{20}{\pi}} |\nu|^4 \leq B 
\end{cases} \]

from below hold;

(iii) As $Z \frac{20}{\pi} \leq B \leq Z^3$ and $|\nu| \geq Z \frac{4}{\pi} B \frac{20}{3}$ estimate (7.1.19) from above and estimate

(7.2.34) \[ v = \begin{cases} 
Z^{-\frac{1}{3}} B^\frac{1}{3} |\nu| \frac{2}{3} & \text{as } B \leq Z^{-\frac{1}{3}} |\nu| \frac{2}{3}, \\
Z \frac{4}{\pi} B^{-\frac{20}{3}} & \text{as } Z^{-\frac{1}{3}} |\nu| \frac{2}{3} \leq B 
\end{cases} \]

from below hold.

**Remark 7.2.3.** Recall that $Q = Z^\frac{5}{3} (B^\delta + 1) Z^{-\delta}$ as $B \leq Z$; therefore we can add factor $(B^\delta + 1) Z^{-\delta}$ in all estimates of Theorem 7.2.2.

### 7.3 Estimates for ionization energy: $M \geq 2$

Recall that as $M \geq 2$ we have only estimate (5.4.45):

\[ D(\rho_\psi - \rho, \rho_\psi - \rho \leq \tilde{Q}) := (4.4.2) + (5.4.41). \]

Then exactly the same arguments lead us to

**Theorem 7.3.1.** Let $M \geq 2$. Then

(i) Estimate $l_N + \nu \leq C(\nu + \zeta)$ holds with $\nu$ and $\zeta$ defined by (7.1.11)–(7.1.12) and (7.1.13) albeit with $Q$ replaced by $\tilde{Q}$;
(ii) Estimate $1 + \nu \geq -C \nu$ holds with $\nu$ defined by (7.1.11)-(7.1.12) albeit with $Q$ replaced by $\bar{Q}$.

Therefore case when $\bar{Q} < Q$ is not affected. One can see easily that it happens for sure as $B \leq Z^{mL^{-\kappa}}$ where $\kappa > 0$ is some exponent.

We leave to the reader

**Problem 7.3.2.** (i) Find explicit formula for $\nu + \zeta$ and $\nu$;

(ii) Find $\nu^* = \nu^*(Z, B)$ and $\nu_* = \nu_*(Z, B)$ such that $|\nu| \lesssim \nu + \zeta$ iff and only if $\nu \lesssim \nu^*$ and $|\nu| \lesssim \nu$ iff and only if $\nu \lesssim \nu_*$.

## 7.4 Free nuclei model

In this Subsection we consider two extra problems appearing in the free nuclei model—estimate the minimal distance between nuclei and the maximal excessive positive charge when system does not break apart. We also slightly improve estimates for maximal negative charge and ionization energy.

### 7.4.1 Preliminary arguments

Recall that we assume that

(7.4.1) $Q := \hat{E} - \sum_{1 \leq m \leq M} E_m < 0$

where

(7.4.2) $\hat{E} = E + \sum_{1 \leq m < m' \leq M} \frac{Z_m Z_{m'}}{|y_m - y_{m'}|}$.

We apply estimate from below for $\hat{E}$ delivered by Proposition 5.1.1(ii), and estimates from above for $E_m$, delivered by Theorem 5.3.5(ii); then

$$\hat{E}^{\text{TF}} + \text{Scott} - \sum_{1 \leq m \leq M} \left( E_m^{\text{TF}} - \text{Scott}_m \right) \leq CQ + CB^{\frac{3}{2}}Z^{\frac{3}{2}} + Ca^{-\frac{3}{2}}Z^{\frac{3}{2}}$$

or, equivalently, due to equality $\text{Scott} = \sum_{1 \leq m \leq M} \text{Scott}_m$ and non-binding theorem

(7.4.3) $0 \leq Q := \hat{E}^{\text{TF}} - \sum_{1 \leq m \leq M} E_m^{\text{TF}} \leq CQ + CB^{\frac{1}{2}}Z^{\frac{3}{2}} + Ca^{-\frac{1}{2}}Z^{\frac{3}{2}}$;
Assume that assumption (1.2.21) is fulfilled. Then $Q \approx a \leq \epsilon r^* \leq \epsilon a \leq \epsilon \bar{r}$ with $r^* = \min(Z^{-\frac{1}{3}}; B^{-\frac{2}{3}} Z^\frac{1}{6})$ and therefore in the free nuclei model $a \geq \epsilon r^*$. Then the last term in (7.4.3) is not needed.

Remark 7.4.1. (i) Obviously, the second term $CB^\frac{1}{3} Z^\frac{2}{3}$ in the right-hand expression of (7.4.3) matters only as $Z \leq B \leq Z^{\frac{3}{2}}$; however we will show that it could be skipped even in this case;

(ii) As $B \leq Z$ we can replace the right-hand expression of (7.4.3) by $Z^{\frac{2}{3} - \delta}(1 + B^\delta)$;

(iii) All these estimates hold also for $D(\rho_B - \rho_{TF}, \rho_B - \rho_{TF})$ because this term is present on the estimate from below.

7.4.2 Minimal distance

Consider case $B \leq Z^{\frac{2}{3}}$ first. Then since $Q \geq \epsilon_0 a^{-7}$ for $\epsilon r^* \leq a \leq \epsilon \bar{r}$ (where in this case $r^* = Z^{-\frac{1}{3}} \leq \bar{r} = B^{-\frac{1}{3}}$) we conclude that $a \geq Z^{\frac{5}{6}} \bar{r}$ provided $B \leq Z^{\frac{20}{21}}$.

Furthermore, then we can apply improved remainder estimate $O(Z^{\frac{5}{6} - \delta})$, since the difference between Dirac–Schwinger terms for a molecule and the sum of these terms for atoms as long as $a \geq Z^{\frac{5}{6} + \delta_1}$ which is the case. Then we conclude that $a \geq Z^{\frac{5}{6} - \delta'}$ as long as it is less than $\epsilon \bar{r}$ and we arrive to statement (i) of Proposition 7.4.2:

**Proposition 7.4.2.** Let condition (1.2.21) be fulfilled. Then in the free nuclei model

(i) As $B \leq Z^{\frac{20}{21}}$ the minimal distance satisfies

$$a \geq \min(Z^{-\frac{5}{6} - \delta}, \epsilon B^{-\frac{1}{3}}).$$  

(ii) As $Z^{\frac{20}{21}} \leq B \leq Z^3$ the distances satisfy

$$|y_m - y_{m'}| \geq \bar{r}_m + \bar{r}_{m'} - \epsilon \bar{r} \quad \forall m \neq m'$$

with arbitrarily small constant $\epsilon > 0$ where $\bar{r}_m$ denote the exact radii of $\rho_{TF}$. 

123
Proof. We need to prove Statement (ii). Observe that case $Z^{\frac{50}{11}} \leq B \leq Z$ also follows from the arguments above.

As $Z \leq B \leq CZ^{\frac{4}{3}}$ the remainder estimate is $O(Z^{\frac{4}{3}}B^{\frac{1}{3}})$ and the same arguments imply that $|y_m - y_m'| \geq \varepsilon Z^{-\frac{4}{3}}B^{-\frac{1}{3}}$ unless $a \geq \varepsilon r$ and since the latter is weaker, it must be satisfied. Therefore if (7.4.5) fails then in virtue of Theorem 1.3.3 $Q \geq \varepsilon_1 B^{\frac{4}{3}}$ which is larger than the remainder estimate $CZ^{\frac{4}{3}}B^{\frac{1}{3}}$.

Finally, case $CZ^{\frac{4}{3}} \leq B \leq Z^3$ follows from the fact that if (7.4.5) fails then in virtue of Theorem 1.3.3 $Q \geq \varepsilon_1 Z^{\frac{4}{3}}B^{\frac{1}{3}}$.

Proposition 7.4.3. Let condition (1.2.21) be fulfilled. Then in the free nuclei model

(7.4.6) $Q + D(\rho_\psi - \rho_{\mathrm{TF}}, \rho_\psi - \rho_{\mathrm{TF}}) \leq CQ$.

Proof. We need to cover only case $Z \leq B \leq Z^{\frac{11}{7}}$.

We apply now estimate from below for $E$ delivered by Proposition 5.1.1(i), and estimates from above for $E_m$, delivered by Theorem 5.3.5(i); then we do not have term $CB^{\frac{4}{3}}Z^{\frac{2}{3}}$ but instead of equal to 0 difference of Scott correction terms we get

(7.4.7) $\left( \text{Tr}(H_{A,W} - \nu)^- + \int P_B(W_{\mathrm{TF}} + \nu) dx \right) - \sum_{1 \leq m \leq M} \left( \text{Tr}(H_{A,W_m} - \nu')^- + \int P_B(W_{\mathrm{TF}} + \nu') dx \right)$

where we know that $\nu' = \nu_1 = \ldots = \nu_M$.

Let us use partition of unity $\phi_0 + \phi_1 + \ldots + \phi_M = 1$ where $\phi_m = 1$ in $B(y_m, \varepsilon r_m)$ and is supported in $B(y_m, 2\varepsilon r_m)$. Then our standard methods imply that the absolute values of

(7.4.8) $| \text{Tr}((H_{A,W} - \nu)^- \phi_0) + \int P_B(W_{\mathrm{TF}} + \nu) \phi_0(x) dx |$

and

(7.4.9) $\text{Tr}((H_{A,W_m} - \nu')^- \phi_m') + \int P_B(W_{\mathrm{TF}} + \nu') \phi_m' dx$
with \( m = 1, \ldots, M, m' = 0, 1, \ldots, M, m' \neq m \) do not exceed \( CQ^{37} \). Therefore we need to estimate an absolute value of \( (7.4.10) \)

\[
\text{Tr} \left( \left[ (H_{A,W} - \nu)^- - (H_{A,W_m} - \nu')^- \right] \phi_m \right) + \int (P_B(W_{TF} + \nu) - P_B(W_{TF_m} + \nu')) \phi_m \, dx.
\]

Due to Proposition 7.4.2 \( B(y_m, 3\epsilon \tilde{r}) \) does not intersect \( B(y_{m'}, \tilde{r}_{m'}) \) and then in \( B(y_m, 3\epsilon \tilde{r}) \) \( W_{m'} \leq C(Z - N)\tilde{r}^{-1} \). Using this inequality and

\[
(7.4.11)
\]

one can prove easily that there also

\[
|W - W_m| \leq CT := CQ^{\frac{1}{2}}\tilde{r}^{-\frac{1}{2}} + C(Z - N)\tilde{r}^{-1}
\]

and, moreover

\[
(7.4.12)
\]

\[
|\nabla(W - W_m)| \leq CT\tilde{r}^{-1} = CQ^{\frac{1}{2}}\tilde{r}^{-\frac{3}{2}} + C(Z - N)\tilde{r}^{-2},
\]

\[
(7.4.13)
\]

\[
|\nabla^2(W - W_m)| \leq CT\tilde{r}^{-2} = CQ^{\frac{1}{2}}\tilde{r}^{-\frac{5}{2}} + C(Z - N)\tilde{r}^{-3}.
\]

Then using our standard methods one can prove easily that an absolute value of expression \( (7.4.10) \) with \( \phi_m \) replaced by \( \ell \)-admissible function \( \psi_m \) does not exceed

\[
(7.4.15)
\]

\[
CT\tilde{h}^{-2}(1 + \mu h)
\]

with our standard

\[
(7.4.16)
\]

\[
h = Z^{-\frac{1}{2}}r^{-\frac{1}{2}}, \quad \mu = BZ^{\frac{1}{2}}r^{\frac{3}{2}}
\]

as either \( B \leq Z^{\frac{3}{4}}, r \leq r^*Z^{-\frac{1}{4}} \) or \( Z^{\frac{1}{4}} \leq B \leq Z^{3}, r \leq \tilde{r} \) and

\[
(7.4.17)
\]

\[
h = r, \quad \mu = Br^{3}
\]

as \( B \leq Z^{\frac{3}{4}} \). Plugging \( (7.4.16) \) and \( (7.4.17) \) and summing over partition we arrive to \( CTZ^{\frac{1}{2}} \) as \( Z^{\frac{3}{2}} \leq B \leq Z^{\frac{3}{4}} \) and \( CTZ^{\frac{1}{2}}B^{\frac{1}{2}} \) as \( Z^{\frac{1}{4}} \leq B \leq Z^{3} \).

\[37\) Recall that \( W \) and \( W_m \) are approximations to \( W_{TF} \) and \( W_{TF_m} \).
Plugging $T = (Z - N)\bar{r}^{-1}$ we get expressions which are much smaller than $\epsilon(Z - N)^2\bar{r}^{-1}$ due to (7.4.6); plugging $T = Q\frac{1}{2}\bar{r}^{-\frac{3}{2}}$ we get terms smaller than $\epsilon'Q + C(\epsilon')B^\frac{1}{2}Z^\frac{3}{2}$ as $B \leq Z^\frac{3}{2}$ and $\epsilon'Q + C(\epsilon')Z^\frac{3}{2}B^\frac{1}{2}$ as $Z^\frac{3}{2} \leq B \leq Z^3$; here $\epsilon' > 0$ is arbitrarily small and thus term (7.4.10) does not make any difference.

Since $Q \geq \epsilon a^{-1}(Z - N)^2$ we arrive to

**Corollary 7.4.4.** Let condition (1.2.21) be fulfilled. Then

(i) If $(Z - N) \geq C(Qa)^\frac{1}{3}$ where $Q$ is our remainder estimate in the ground state energy, then in free nuclei model minimal distance between nuclei must be at least $a$.

(ii) In particular, if $(Z - N) \geq C(\bar{Q}\bar{r})^\frac{1}{3}$ then in free nuclei model minimal distance between nuclei must be at least $C_0\bar{r}$ and molecule consists of separate atoms.

We leave to the reader

**Problem 7.4.5.** Using Theorem 1.3.3 and arguments used in the proof of Proposition 7.4.2 estimate overlapping of balls $B(y_m, \bar{r}_m)$ as $Z^{-\frac{3}{2}} \geq B^{-\frac{1}{2}}$ in the free nuclei model as $N = Z$ and prove that

(7.4.18) \[(\bar{r}_m + \bar{r}_m' - |y_m - y_m'|) \leq C\bar{r}(K^{-2}\bar{r}^{-1}Q)^\frac{1}{2} = \begin{cases} B^{-\frac{1}{2}}(B^{-\frac{1}{2}}Z^\frac{3}{2} + B^{-\frac{1}{2}}L)\frac{1}{2} & \text{as } Z^{\frac{10}{7}} \leq B \leq Z^\frac{3}{2}, \\ B^{-\frac{7}{10}}Z^\frac{13}{10}L^\frac{1}{10} & \text{as } Z^\frac{3}{2} \leq B \leq Z^3. \end{cases}\]

### 7.4.3 Estimate of excessive positive charge

To estimate excessive positive charge when molecules can still exist in free nuclei model we apply arguments of section 5 of B. Ruskai and J. P. Solovej [RS]. In view of Corollary 7.4.4 for $(Z - N)$ violating (7.4.21) below it is sufficient to assume that (24.6.41) is satisfied:

(7.4.19) \[a = \min_{j<k} |y_j - y_k| \geq C_0\bar{r}\]

i.e. in Thomas-Fermi theory $\rho^{TF}$ is supported in separate “atoms”. Really, it is the case as $C_0Z^{\frac{10}{7}} \leq B \leq Z^3$, but also it is so as $B \leq C_0Z^{\frac{10}{7}}$ and $(Z - N)_+ \geq C_1Z^\frac{5}{2}$ as then $\bar{r} \approx (Z - N)_+^{-\frac{1}{3}}$. 126
Like in Subsection 24.6.3 consider \(a\)-admissible functions \(\theta_m(x)\), supported in \(B(y_m, \frac{1}{3}a)\) as \(m = 1, \ldots, M\) and in \(|x - y_m| \geq \frac{1}{4}a\) \(\forall m' = 1, \ldots, M\) as \(m = 0\), such that

\[
(7.4.20) \quad \theta_0^2 + \ldots + \theta_M^2 = 1.
\]

Then for the ground state \(\Psi\) equality (24.6.43) holds with cluster Hamiltonians \(H_{\alpha_m}\) defined by (24.6.44) and satisfying (24.6.45) and with the intercluster Hamiltonian \(J_{\alpha}\) defined by (24.6.46) and satisfying (24.6.47) with \(J_{ml}\) defined by (24.6.48)–(24.6.49). Furthermore, equality (24.6.50) holds.

Applying proposition 24.5.1 and estimate (24.4.55) (replacing first \(\theta_k\) with \(k = 1, \ldots, M\) by \(\tilde{\theta}_k\) supported in \(B(y_k, \overline{c}r)\) and estimating an error), we conclude that (24.6.51)–(24.6.54) hold with \(Y = Q\overline{a}^2\overline{c}r\) since \(D(\rho_\Psi - \rho_{TF}, \rho_\Psi - \rho_{TF}) \leq CQ\).

The last term in (24.6.51) is estimated by proposition 24.5.1 and estimate (7.4.6) instead of (24.4.55) and the same replacement trick; so we arrive to (24.6.55) and repeating the same trick we get that it is larger than (24.6.56).

Again let us note that the absolute value of the last term in the right-hand expression of (24.6.43) does not exceed \(Ca^{-2}Y\) due to (24.6.52). Now stability condition yields that (5.4.33) must be fulfilled.

Then we conclude that (24.6.57) and (24.6.59) hold with \(J_{ml}\) defined by (24.6.58) provided (24.6.60) is fulfilled as \(|x - y_k| \geq \overline{c}r\).

This inequality, (7.4.19) and proposition 24.6.6 (which is the special case of Theorem 1.2.6) yield that \(Z - N \leq CY = C\overline{r}Q\frac{1}{2}\). Now we need to consider two cases:

(a) \(B \leq (Z - N)^{\frac{1}{4}}\); then \(\overline{r} \sim (Z - N)^{-\frac{1}{4}}\) and we conclude that \((Z - N) \leq CQ^{\frac{3}{2}}\) exactly like in Subsubsection 24.6.3.

(b) \((Z - N)^{\frac{1}{4}} \leq B \leq Z^3\); then plugging \(\overline{r}\) and \(Q\) we arrive to two other cases of (7.4.21).

So we arrive to Statement (i) below; Statement (ii) follows from Remark 7.4.1(ii).

**Theorem 7.4.6.** \(^{38}\) Let condition (1.2.21) be fulfilled.

\(^{38}\) Cf. Theorem 24.6.4.
(i) Then in the framework of free nuclei model with $M \geq 2$ the stable molecule does not exist unless

\begin{equation}
(Z - N)_+ \leq C_1 \begin{cases}
Z^{\frac{20}{21}} & \text{as } B \leq Z^{\frac{20}{21}}, \\
Z^{\frac{5}{8}}B^{-\frac{1}{8}} & \text{as } Z^{\frac{20}{21}} \leq B \leq \frac{7}{4}, \\
Z^{\frac{5}{8}}B^{\frac{1}{8}} & \text{as } \frac{7}{4} \leq B \leq Z^3;
\end{cases}
\end{equation}

(ii) Furthermore for $B \leq Z$ in the framework of free nuclei model with $M \geq 2$ the stable molecule does not exist unless

\begin{equation}
(Z - N)_+ \leq C_1 \begin{cases}
Z^{\frac{20}{21}} - \delta & \text{as } B \leq Z^{\frac{20}{21}}, \\
Z^{\frac{5}{8}} - \delta B^{-\frac{1}{8} + \delta} & \text{as } Z^{\frac{20}{21}} \leq B \leq Z^3.
\end{cases}
\end{equation}

7.4.4 Estimate of excessive negative charge and ionization energy

Estimate (7.4.6) and Remark 7.4.1 imply

Theorem 7.4.7. Let condition (1.2.21) be fulfilled.

(i) Then in the framework of free nuclei model with $M \geq 2$ estimates (6.2.15) for excessive negative charge and (6.3.15) for ionization energy $\hat{\mathcal{N}} = -\hat{\mathcal{E}}_N + \hat{\mathcal{E}}_{N-1}$ hold;

(ii) Furthermore as $B \leq Z$ estimates (6.2.16) for excessive negative charge and (6.3.17) for ionization energy $\hat{\mathcal{N}}$ hold.

8 Appendices

8.A Electrostatic inequalities

There are two kinds of electrostatic inequalities: those which hold for any fermionic state $\Psi$ and those which hold only for the ground-state (or near ground state) $\Psi$. Inequalities of the first kind do not depend on the quantum
Hamiltonian and they are (24.2.1) repeated here:

\[
\sum_{1 \leq j < k \leq N} \int |x_j - x_k|^{-1} |\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots dx_N \geq \frac{1}{2} D(\rho_\Psi, \rho_\Psi) - C \int \rho_\Psi^\frac{3}{2}(x) \, dx
\]

and (8.A.5) below.

Inequalities of the second kind are as \( B = 0 \):

\[
\sum_{1 \leq j < k \leq N} \int |x_j - x_k|^{-1} |\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots dx_N \geq \frac{1}{2} D(\rho_\Psi, \rho_\Psi) - CZ^\frac{3}{2},
\]

and more precise one (8.A.26) below.

As \( \vec{B} = \text{const} \) there is an inequality established in E. Lieb, J. P. Solovej and J. Yngvarsson [LSY2] (p. 122):

**Theorem 8.A.1.** Let \( \vec{B} = \text{const} \). Then for the ground state \( \Psi \)

\[
\int \rho_\Psi^\frac{3}{2} \, dx \leq CZ^{\frac{3}{2}} N^{\frac{3}{2}} (Z + N)^{\frac{3}{2}} (1 + BZ^{-\frac{3}{2}})^{\frac{3}{2}};
\]

In particular for \( c^{-1}N \leq Z \leq cN \) the right-hand expression does not exceed

\[
CZ^{\frac{3}{2}} (1 + BZ^{-\frac{3}{2}})^{\frac{3}{2}} \asymp C \left\{ \begin{array}{ll}
Z^{\frac{3}{2}} & \text{as } B \leq Z^{\frac{3}{2}}, \\
Z^{\frac{3}{2}} B^{\frac{3}{2}} & \text{as } B \geq Z^{\frac{3}{2}}.
\end{array} \right.
\]

We want to establish inequality similar to (24.A.2) but in the magnetic case. We will use for this the following
Theorem 8.A.2. \footnote{Lemma 6 of G. Graf and J. P. Solovej [GS].} Fix \(0 < \delta \leq 1/6\). Then for any density matrix \(F\) an any density \(\rho_0(x) \geq 0\) we have

\[
\sum_{1 \leq j < k \leq N^*} \int |x_j - x_k|^{-1}|\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots dx_N \geq \\
D(\rho_0, \rho) - \frac{1}{2}D(\rho_0, \rho_0) - \frac{1}{2} \sum_{\varsigma, \varsigma'} \int \int |F(x, \varsigma; y, \varsigma')|^2 |x - y|^{-1} \, dx \, dy \\
- C\|\rho\|^{5/6} \cdot \|\rho\|^{1/6+\delta} \, v(\gamma, F)^{1/3-\delta}
\]

where \(\rho = \rho_0 + \rho_F + \rho \nu\), \(v(\gamma, F) := \text{Tr}(\gamma(I - F))\),

\[
\gamma = \gamma_F(x, y) = N \int \Psi(x, x_2, \ldots, x_N) \Psi^\dagger(y, x_2, \ldots, x_N) \, dx_2 \cdots dx_N
\]

is two-point one particle density.

Recall that \(\| \cdot \|_p\) denotes \(L^p\)-norm.

Connection between (8.A.1) and (8.A.5): as we set \(F = 0\) we get \(\varsigma = \|\rho\|_1\) and the last term in (8.A.5) becomes \(\|\rho\|^{5/6} \cdot \|\rho\|^{1/2}\); on the other hand, \(\|\rho\|^{4/3} \leq \|\rho\|^{5/6} \cdot \|\rho\|^{1/2}\), so (8.A.5) is slightly deteriorated (8.A.1) with \(F = 0\) but with “free” \(\rho_0\).

Let us follow G. Graf and J. P. Solovej [GS] further albeit in the case of magnetic field. Let us estimate first \(\|\rho\|_{5/3}\).

If \(\rho = \rho_{\text{TF}}\) direct calculations show that as \(N \asymp Z\)

\[
\int \rho_{\text{TF}} \, dx = \min(Z, N),
\]

\[
\int (\rho_{\text{TF}})^4 \, dx \asymp C \rho^*_{*} \rho^*_{*} = CZ^5 (1 + BZ^{-1})^{1/5},
\]

\[
\int (\rho_{\text{TF}})^5 \, dx \asymp C \rho^*_{*} \rho^*_{*} = CZ^2 (1 + BZ^{-1})^{1/5}
\]

with

\[
\rho^* = \min(Z^{-1}, B^{-1/2}Z^{1/2}) \asymp Z^{-1/2} (1 + BZ^{-1})^{-1/2},
\]

\[
\rho^* = \min(N, Z) r^* - 3
\]
and we have \( \|\rho\|_5/3 \cdot \|\rho\|_1^{1/2} \approx \|\rho\|_4^{4/3} \) for \( \rho = \rho^{TF} \).

If \( \rho = \rho_\psi \) we use magnetic Lieb-Thirring inequality (see f. e. L. Erd\"os [E])

\[
(8.\text{A}.12) \quad \text{Tr}(H_{A,W})^- \geq -C \int P_B(W) \, dx
\]

and therefore

\[
(8.\text{A}.13) \quad \langle H\Psi, \Psi \rangle \geq \text{Tr}^{-1}(H_{A,W}) + \int W \rho_\psi \, dx
\]

\[
- \int V \rho_\psi \, dx + \frac{1}{2} D(\rho_\psi, \rho_\psi) - C\|\rho_\psi\|_4^{4/3}
\]

which due to \( (8.\text{A}.12) \) is greater than

\[
(8.\text{A}.14) \quad \int (-CP_B(W) + W \rho_\psi) \, dx - \int V \rho_\psi \, dx + \frac{1}{2} D(\rho_\psi, \rho_\psi) - C\|\rho_\psi\|_4^{4/3} \geq
\]

\[
3\varepsilon_0 \int \tau_B(\rho_\psi) \, dx - \int V \rho_\psi \, dx + \frac{1}{2} D(\rho_\psi, \rho_\psi) - C\|\rho_\psi\|_4^{4/3}
\]

as we picked up \( W : CP_B(W) = \rho_\psi \).

The first two terms in the right-hand expression are estimated from below by

\[
2\varepsilon_0 \int \tau_B(\rho_\psi) \, dx - C \int P_B(V) \phi \, dx - C \int V \rho_\psi (1 - \phi) \, dx
\]

where \( \text{supp}(\phi) \subset \{x, \ell(x) \leq 2r^* \} \) and \( \text{supp}(1 - \phi) \subset \{x, \ell(x) \geq r^* \} \).

One can see easily that the absolute value of the second term is \( \approx Z^{\frac{5}{2}} (1 + BZ^{-\frac{4}{5}})^{\frac{5}{2}} \) while the absolute value of the third term does not exceed \( CZ \int V(1 - \phi) \, dx \approx C Z^2 r^{*-1} \) which does not exceed the same expression \( Z^{\frac{7}{2}} (1 + BZ^{-\frac{4}{5}})^{\frac{5}{2}} \). Therefore

\[
(8.\text{A}.15) \quad \langle H\Psi, \Psi \rangle + C_1 Z^{\frac{7}{2}} (1 + BZ^{-\frac{4}{5}})^{\frac{5}{2}} \geq
\]

\[
2\varepsilon_0 \int \tau_B(\rho_\psi) \, dx + \frac{1}{2} D(\rho_\psi, \rho_\psi) - C\|\rho_\psi\|_4^{4/3}
\]
Note that \( \| \rho_\psi \|_{4/3}^{4/3} \) calculated over domain \( \{ x : \rho_\psi(x) \geq B^{\frac{4}{3}} \} \) does not exceed \( C \| \rho_\psi \|_{5/3}^{5/6} \cdot \| \rho \|_{1/1}^{1/1} \) with norms calculated over the same domain which does not exceed \( CT^{\frac{1}{3}}Z^{\frac{1}{3}} \) with \( T = \int \tau_B(\rho_\psi) \, dx \).

Meanwhile \( \| \rho_\psi \|_{4/3}^{4/3} \) calculated over domain \( \{ x : \rho_\psi(x) \geq B^{\frac{4}{3}} \} \) does not exceed \( C \| \rho \|_{3}^{1} \cdot \| \rho \|_{3}^{1} \) with norms calculated over the same domain which does not exceed \( CZ^3B^3T^\frac{1}{3} \).

Therefore

\[
(8.A.16) \quad \| \rho_\psi \|_{4/3}^{4/3} \leq C T^{\frac{1}{3}}Z^{\frac{1}{3}} + CZ^3B^3T^\frac{1}{3}.
\]

and therefore (8.A.15) implies that if

\[
(8.A.17) \quad \langle H \Psi, \Psi \rangle \leq C_1Z^{\frac{7}{3}}(1 + BZ^{-\frac{3}{2}})^{\frac{2}{3}}
\]

then

\[
(8.A.18) \quad T = \int \tau_B(\rho_\psi) \, dx \leq C_2Z^{\frac{7}{3}}(1 + BZ^{-\frac{3}{2}})^{\frac{2}{3}}
\]

and

\[
(8.A.19) \quad \| \rho_\psi \|_{4/3}^{4/3} \leq CZ^5(1 + BZ^{-\frac{3}{2}})^{\frac{2}{3}};
\]

taking \( F = 0 \) we arrive to (8.A.3) as \( N \approx Z \).

However on our preparatory step we need to estimate also \( \| \rho_\psi \|_{5/3}^{5/3} \) and due to (8.A.18) we need to consider only norms over \( \{ x : \rho_\psi(x) \geq B^{\frac{4}{3}} \} \). Then

\[
\| \rho_\psi \|_{5/3}^{5/3} \leq C \| \rho_\psi \|_{4/3}^{16/15} \cdot \| \rho_\psi \|_{3}^{3/5}
\]

and plugging the same estimates (8.A.19), (8.A.19) we conclude that

\[
(8.A.20) \quad \| \rho_\psi \|_{5/3}^{5/3} \leq CZ^{7/3}(1 + BZ^{-\frac{3}{2}})^{\frac{2}{3}}.
\]

Now we assume that \( B \leq Z^3 \), take \( F = e(x, y, \nu) \) where \( e(x, y, \nu) \) is the Schwartz kernel of spectral projector for potential \( W \) approximating \( W^{\text{TF}} \) and \( \nu \leq 0 \) is a chemical potential. One can prove easily that \( \| \rho_F \|_{5/3}^{5/3} \) satisfies the same estimate and we need to estimate \( \text{Tr}(\gamma_\psi(l - E(\mu))) \).
Consider

\[ N(H_{A,W(\alpha)}\psi, \psi) - \text{Tr}(HE(\nu)) - \alpha \text{ Tr}(\gamma_{\psi}(I - E(\nu))) \]
\[ \geq \int_{\beta < 0} \beta d_\beta \text{Tr} E(\beta) - \int_{\beta \leq \nu} (\beta - \nu + \alpha) d_\beta \text{Tr} E(\beta) \]
\[ = -\int_{\nu-\alpha < \beta < \nu} (\beta - \nu + \alpha)d_\beta E(\beta) \]
\[ = -\alpha E(\nu) + \int_{\nu-\alpha < \beta < \nu} E(\beta) d\beta. \]

We can replace \( E(\beta) \) by \( \int P'(W + \beta) \, dx \) with a resulting error \( O(Z\alpha h^\delta) \), \( \hbar := BZ^{-3} \). Then the right-hand expression becomes

\[ L(\alpha) := \int \left( -\alpha P'_\beta(W + \nu) + \int_0^\alpha P'_\beta(W + \nu - \beta) \, d\beta \right) \, dx = -\int_0^\alpha (\alpha - \beta) \left( \int P''_\beta(W + \nu - \beta) \, dx \right) \, d\beta. \]

Therefore

\[ \alpha \left( \text{Tr}(\gamma_{\psi}(I - E(\mu))) - C\hbar^\delta \right) \leq N(H_{A,W(\alpha)}\psi, \psi) - \text{Tr}(HE(\nu)) + L(\alpha). \]

Note that adding to the selected terms \( -\frac{1}{2}D(\rho^{TF}, \rho^{T\bar{F}}) \) we obtain exactly the snippet occurring in the lower estimate of \( E_N \) but in virtue of the upper estimate it should not exceed \( Q = CZ^{\frac{5}{2}}(1 + BZ^{-\frac{3}{2}})^{\frac{5}{2}} \leq CZ^{\frac{5}{2}} + Ch^2Z^{\frac{5}{2}} \). and therefore plugging \( \alpha = Z^{\frac{5}{4}}h^\delta \) we conclude that

\[ \text{Tr}(\gamma_{\psi}(I - E(\mu))) \leq Zh^\delta \]

provided we prove that

\[ L(\alpha) \leq Q \quad \text{as} \quad \alpha = Z^{\frac{5}{4}}h^\delta. \]

Therefore modulo proof of (8.A.25) we arrive to the estimate (8.A.26) below:
Theorem 8.A.3. Let $N \approx Z$ and $B \leq Z$. Then for the ground state energy

$$\sum_{1 \leq j < k \leq N} |x_j - x_k|^{-1}|\Psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots dx_N \geq$$

$$\frac{1}{2} D(\rho^{\text{TF}}, \rho^{\text{TF}}) + \text{Dirac} - CZ^{3/4}\delta(1 + B^{3/4}).$$

To prove (8.A.25) we note that $\frac{1}{w} P''(w) \approx w + Bw - \frac{1}{w}$. One can prove easily then that $L(\alpha) \leq C\alpha^{3/2} + C\alpha^{1/2}$ which obviously implies (8.A.25).

8.B Very strong magnetic field case

Let us consider now case $Z^2 \leq B \leq Z^3$.

Proposition 8.B.1. Consider Schrödinger operator $H_{A,W}$ with a constant magnetic field of intensity $B$ and potential $W$: $W \leq Z|x|^{-1}$. Let $\phi(x) := \phi_r(x)$ be $r$-admissible function. Then as $Z^2 \lesssim B \lesssim Z^3$ and $r \approx Z^{-1}$

$$(8.B.1) \quad |e(x, y, 0)| \leq CZB \quad \text{in } B(0, r)$$

and

$$(8.B.2) \quad \text{All eigenvalues are } \geq -CZ^2.$$ 

Proof. Without any loss of the generality one can assume that

$$(8.B.3) \quad H_{A,W} = D_3^2 + D_2^2 + (D_1 - Bx_2)^2 - W.$$ 

Consider $f \in L^2$; then $\|E(\lambda)f\| \leq \|f\|$ and then one can prove easily (8.B.2) and that

$$(8.B.4) \quad \|H_{A,0}E(\lambda)f\| \leq (CZ^2 + \lambda_+)\|f\|.$$ 

Really, $\frac{1}{2} D_2^2 + CZ^2 \geq W$ in the operator sense.

Then (8.B.4) implies that in $B(0, r) \times B(y', r')$ with $r' = B^{-1/2}$

$$|P^\alpha E(\lambda)f| \leq CZ^{\alpha_3}B^{3/2}|\alpha'| \quad \forall \alpha : |\alpha| \leq 2 \forall \lambda \leq Z^2$$ 

with $P = (D_1 - Bx_2, D_2, D_3)$ and therefore $\|E(\lambda)f\|_{\mathcal{C}} \leq CZ^{3/4}B^{3/2}\|f\|$. Then $\|E(x, \ldots, \lambda)\|_{\mathcal{C}} \leq CZ^{3/4}B^{3/2}$.

Repeating the same arguments with respect to $y$ we arrive to estimate (8.B.1). \qed
Corollary 8.B.2. In the framework of Proposition 8.B.1 with \( \phi \in L^\infty(B(0, r)) \), \( \| \phi \|_{L^\infty} \leq 1 \)

\[
| \int \phi(x)e(x, x, 0) \, dx | \leq CZ^{-2}B,
\]

and

\[
D(\phi(x)e(x, x, 0), \phi(x)e(x, x, 0)) \leq CZ^{-3}B^2
\]

8.C Riemann sums and integrals

If \( f \in C^\infty(\mathbb{R}^+) \) and fast decays at \(+\infty\) then

\[
f(0)h + \sum_{n \geq 1} 2f(2nh)h \sim \int_0^\infty f(t) \, dt + \sum_{m \geq 1} \kappa_m f(2^{m-1})(0)h^{2m},
\]

\[
\sum_{n \geq 0} 2f((2n+1)h)h \sim \int_0^\infty f(t) \, dt + \sum_{m \geq 1} \kappa'_m f(2^{m-1})(0)h^{2m}
\]

as \( h \to +0 \). The proofs of both formulae follow from the Taylor’s decompo-
sition and observation that the odd powers of \( h \) should disappear. Taking \( f(t) = e^{-tz/h} \) with \( \Re z > 0 \) we arrive to

\[
1 - \frac{\cosh(z)}{\sinh(z)}z \sim \sum_{m \geq 1} \kappa_m z^{2m},
\]

\[
1 - \frac{1}{\sinh(z)}z \sim \sum_{m \geq 1} \kappa'_m z^{2m}.
\]

as \( |z| \ll 1 \). In particular, \( \kappa_1 = \frac{1}{3} \) and \( \kappa'_1 = -\frac{1}{6} \).

8.D Some spectral function estimates

Proposition 8.D.1. For Schrödinger operator with \( A, W \in C^\infty \) and for \( \phi \in \mathcal{C}_0^\infty([-1, 1]) \) the following estimate holds for any \( s \):

\[
|F(x, y)| \leq C(h + 1)h^{-3}(1 + h^{-1}|x - y|)^{-s},
\]

\[
F(x, y) := \int \phi(\lambda) \, d\lambda e(x, y, \lambda).
\]
Proof. Let \( u(x, y, t) = \int e^{-iHt} d\lambda e(x, y, \lambda) \) be the Schwartz’s kernel of \( e^{-iHt} \).

Fix \( y \). Note first that \( \mathcal{L}^2 \)-norm\(^{40}\) of \( \phi(hD_t)\chi(t)\omega(x)u(x, y, t) \) is less than \( Ch^s \) as \( \chi \in C_0^\infty([-\epsilon, \epsilon]) \) and \( \omega \in C^\infty \) supported in \( \{|x-y| \geq \epsilon_1\} \) (with \( \epsilon_1 = C\epsilon \)) due to the finite speed of propagation of singularities.

We conclude then that \( \mathcal{L}^2 \)-norm of \( \phi(hD_t)\chi(t)\omega(x)u(x, y, t) \) does not exceed \( C(\mu h+1)h^s \) for \( \omega \in C^\infty \) supported in \( \{|x-y| \geq \epsilon_0\} \).

Then \( \mathcal{L}^2 \)-norm of \( \partial_t^s \nabla^a \phi(hD_t)\chi(t)\omega(x)u \) does not exceed \( C(\mu h+1)h^s \). Therefore due to imbedding inequality \( \mathcal{L}^{\infty} \)-norm of \( \phi(hD_t)\chi(t)\omega(x)u \) also does not exceed \( C(\mu h+1)h^s \). Setting \( t = 0 \) and using this inequality and \( |F(x, y)| \leq C(\mu h+1)h^{-3} \) (due to Chapter \ref{chap5}) we conclude that \( |F(x, y)| \leq C(\mu h+1)h^s \) for \( |x-y| \geq \epsilon_0 \).

Now let us consider general \( |x-y| = r \geq Ch \). Rescaling \((x-y) \mapsto (x-y)r^{-1}\) we need to rescale \( h \mapsto hr^{-1} \), \( \mu \mapsto \mu r \) and rescaling above inequality and keeping in mind that \( F(x, y) \) is a density with respect to \( x \) we conclude that \( |F(x, y)| \leq Ch^s r^{3-s} \) which is equivalent to \((8.D.1)-(8.D.2)\).\(\square\)

8.E Zhislin’s theorem with constant magnetic field

We provide just a scheme to prove Zhislin’s theorem in the case of the constant magnetic field. In this analysis \( Z, y, N \) and \( B \) are constant.

Proposition 8.E.1. Let \( \Psi \) be a ground state with energy \( E_N < E_{N-1} \). Then

(i) \( \Psi \in \mathcal{C} \) and \( \Psi = O(e^{-\varepsilon|x|}) \) as \( |x| \to \infty \);

(ii) Let \( N < Z \). Then \( V_\Psi \in \mathcal{C}^2 \) and \( V_\Psi = (Z-N)|x|^{-1} + O(|x|^{-2}) \),\( \nabla V_\Psi = (Z-N)|x|^{-2} + O(|x|^{-3}) \) as \( |x| \to \infty \).

Proof. Obvious proof is left to the reader. \(\square\)

Theorem 8.E.2 (Zhislin’s theorem). \( E_{N+1} < E_N \) as \( N < Z \).

Proof. We can assume that \( E_N < 0 \) and ground state energy exists. Really, it is true for some \( N < Z \) and if we prove that \( E_{N+1} < E_N \) then it would be true for \((N+1)\) as well, so we may go by induction.

\(^{40}\) With respect to \( x, t \) here and below.
Consider \( \Psi = \Psi_N(x_1, \ldots, x_N) \) and \( \tilde{\Psi}_{N+1} \) which is an antisymmetrized \( \Psi_N(x_1, \ldots, x_N)u(x_{N+1}) \) (cf. (7.2.1)):

(8.E.1) \[
\tilde{\Psi} = \tilde{\Psi}(x_1, \ldots, x_{N+1}) = \Psi(x_1, \ldots, x_N)u(x_{N+1}) - \sum_{1 \leq i \leq N} \Psi(x_1, \ldots, x_{j-1}, x_{N+1}, x_{j+1}, \ldots, x_N)u(x_j).
\]

Then like in the estimate of the ionization energy (cf. (7.2.2)–(7.2.3)):

(8.E.2) \[
N^{-1} \| \tilde{\Psi} \|^2 \geq -\langle H_{W_N} \Psi u, \tilde{\Psi} \rangle - \langle \sum_{1 \leq i \leq N} |x_i - x_{N+1}|^{-1} \Psi u, \tilde{\Psi} \rangle
\]
and

(8.E.3) \[
N^{-1} \| \tilde{\Psi} \|^2 = \| \Psi \|^2 \| u \|^2 - N \int \Psi(x_1, \ldots, x_{N-1}, x)\Psi^\dagger(x_1, \ldots, x_{N-1}, y)u(y)u^\dagger(x) \, dx_1 \cdots dx_{N-1} \, dx dy
\]

Now we consider \( u \) supported in \( \{ \frac{1}{2} a \leq |x| \leq 3a \} \) with \( a \) to be chosen later. Then in virtue of Proposition 8.E.1(i) modulo \( O(e^{-\epsilon a}) \) we can replace in the right-hand expressions \( \tilde{\Psi} \) by \( \Psi_N(x_1, \ldots, x_N)u(x_{N+1}) \) resulting in \( -\langle H_{W} u, u \rangle \) and \( \| u \|^2 \) respectively with \( W = V_{\Psi} \) defined in Proposition 8.E.1(ii).

Therefore all we need to prove Theorem is to be able to select \( u \) with \( \| u \| \asymp 1 \), supported \( \{ a \leq |x| \leq 3a \} \) in and with \( \langle H_{W} u, u \rangle \leq -\epsilon_0 a^{-1} \).

In virtue of Proposition 8.E.1(ii) \( V_{\Psi} \geq \epsilon_0 a^{-1} \) in \( \{ a \leq |x| \leq 3a \} \); so we can replace \( W \) by \( \epsilon_0 a^{-1} \). Without any loss of the generality one can assume that \( A = (Bx_2, 0, 0) \). Recall that for linear \( A \) operator \( H_0 = ((i\nabla - A) \cdot \sigma)^2 \) is a direct sum of \( H_0^- = (i\nabla - A)^2 + B \) and \( H_0^+ = (i\nabla - A)^2 - B \); so we can consider only the latter. Note that \( H_0^- = (i\partial_1 - Bx_2)^2 - \partial_2^2 - \partial_3^2 \) and \( H_0^- v = 0 \) with \( v = \exp(-\frac{1}{2} B(x_2 - a)^2 + iBx_1) \).

Then \( u = v(x) \chi(r^{-1}(\bar{x} - \bar{x})) \) with \( \chi \in \mathcal{C}^\infty(B(0, 1)), \chi = 1 \) in \( B(0, \frac{1}{2}), \bar{x} = (0, 2a, 0), r = \frac{1}{3}a \) is a required function.

\[ \square \]

**Bibliography**

[A] V. I. Arnold: *Mathematical Methods of Classical Mechanics*. Springer-Verlag (1990).
[Ba] V. Bach: Error bound for the Hartree-Fock energy of atoms and molecules, Commun. Math. Phys. 147:527–548 (1992).

[Be] R. Benguria: Dependence of the Thomas-Fermi energy on the nuclear coordinates, Commun. Math. Phys., 81:419–428 (1981).

[BeL] R. Benguria and E. H. Lieb: The positivity of the pressure in Thomas-Fermi theory, Commun. Math. Phys., 63:193–218 (1978).

[BrL] H. Brezis and E. H. Lieb: Long range potentials in Thomas-Fermi theory, Commun. Math. Phys. 65, 231-246 (1979).

[E] L. Erdős, Magnetic Lieb-Thirring inequalities. Commun. Math. Phys., 170:629–668 (1995).

[ES3] L. Erdős, J.P. Solovej, Ground state energy of large atoms in a self-generated magnetic field. Commun. Math. Phys. 294, No. 1, 229-249 (2009) arXiv:0903.1816

[EFS1] L. Erdös, S. Fournais, J.P. Solovej: Stability and semiclassics in self-generated fields. arXiv:1105.0506

[EFS2] L. Erdös, S. Fournais, J.P. Solovej: Second order semiclassics with self-generated magnetic fields. arXiv:http://arxiv.org/abs/1105.0512

[EFS3] L. Erdös, S. Fournais, J.P. Solovej: Scott correction for large atoms and molecules in a self-generated magnetic field arXiv:1105.0521

[FS] C. Fefferman and L.A. Seco: On the energy of a large atom, Bull. AMS 23, 2, 525–530 (1990).

[FSW1] R. L. Frank, H. Siedentop, S. Warzel: The ground state energy of heavy atoms: relativistic lowering of the leading energy correction. Commun. Math. Phys. 278 no. 2, 549–566 (2008)

[FSW2] R. L. Frank, H. Siedentop, S. Warzel: The energy of heavy atoms according to Brown and Ravenhall: the Scott correction. Doc. Math. 14, 463–516 (2009).

[FLL] J. Fröhlich, E. H. Lieb, and M. Loss: Stability of Coulomb systems with magnetic fields. I. The one-electron atom. Commun. Math. Phys. 104 251–270 (1986)
[GS] G. M. Graf and 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.

[H] W. Hughes: *An atomic energy bound that gives Scott’s correction*, Adv. Math. 79, 213–270 (1990).

[Ivr1] V. Ivrii, Asymptotics of the ground state energy of heavy molecules in the strong magnetic field. I. Russian Journal of Mathematical Physics, 4(1):29–74 (1996).

[Ivr2] Asymptotics of the ground state energy of heavy molecules in the strong magnetic field. II. Russian Journal of Mathematical Physics, 5(3):321–354 (1997).

[Ivr3] V. Ivrii, Heavy molecules in the strong magnetic field. Russian Journal of Math. Phys., 4(1):29–74 (1996).

[Ivr4] V. Ivrii, Heavy molecules in the strong magnetic field. Estimates for ionization energy and excessive charge 6(1):56–85 (1999).

[Ivr5] Sharp spectral asymptotics for operators with irregular coefficients. Pushing the limits. II. Comm. Part. Diff. Equats., 28 (1&2):125–156, (2003).

[Ivr6] V. Ivrii Sharp spectral asymptotics for operators with irregular coefficients. III. Schrödinger operator with a strong magnetic field, arXiv:math/0510326 (Apr. 11, 2011), 101pp.

[Ivr7] V. Ivrii Local trace asymptotics in the self-generated magnetic field, arXiv:math/1108.4188 (December 23, 2011), 24pp.

[Ivr8] V. Ivrii Global trace asymptotics in the self-generated magnetic field in the case of Coulomb-like singularities, arXiv:math/1112.2487 (December 23, 2011), 19pp.

[Ivr9] V. Ivrii Asymptotics of the ground state energy for atoms and molecules in the self-generated magnetic field, arXiv:math/1112.5538 (December 23, 2011), 11pp.
[Ivr10] V. Ivrii Asymptotics of the ground state energy of heavy molecules and related topics, arXiv:math/0510326 (October 03, 2012), 70pp.

[Ivr11] V. Ivrii Microlocal Analysis and Sharp Spectral Asymptotics, in progress: available online at http://www.math.toronto.edu/ivrii/futurebook.pdf

[IS] Ivrii, V. and Sigal, I. M Asymptotics of the ground state energies of large Coulomb systems. Ann. of Math., 138:243–335 (1993).

[L] E. H. Lieb: Thomas-Fermi and related theories of atoms and molecules, Rev. Mod. Phys. 65. No. 4, 603-641 (1981)

[L2] E. H. Lieb: Variational principle for many-fermion systems, Phys. Rev. Lett. 46, 457–459 (1981) and 47 69(E) (1981)

[L2] The stability of matter: from atoms to stars (Selecta). Springer-Verlag (1991).

[LLS] E. H. Lieb, M. Loss and J. P. Solovej: Stability of Matter in Magnetic Fields, Phys. Rev. Lett. 75, 985–989 (1995)

[LO] E. H. Lieb and S. Oxford: Improved Lower Bound on the Indirect Coulomb Energy, Int. J. Quant. Chem. 19, 427–439, (1981)

[LS] E. H. Lieb and B. Simon: The Thomas-Fermi theory of atoms, molecules and solids, Adv. Math. 23, 22-116 (1977)

[LSY1] E. H. Lieb, J. P. Solovej and J. Yngvarsson: Asymptotics of heavy atoms in high magnetic fields: I. Lowest Landau band regions, Comm. Pure Appl. Math. 47:513–591 (1994).

[LSY2] E. H. Lieb, J. P. Solovej and J. Yngvarsson:. Asymptotics of heavy atoms in high magnetic fields: II. Semiclassical regions, Comm. Math. Phys., 161: 77–124 (1994).

[RS] M. B. Ruskai, M. B. and J. P. Solovej: Asymptotic neutrality of polyatomic molecules. In Schrödinger Operators, Springer Lecture Notes in Physics 403, E. Balslev (Ed.), 153–174, Springer Verlag (1992).

[SW1] H. Siedentop and R. Weikard: On the leading energy correction for the statistical model of an atom: interacting case, Commun. Math. Phys. 112, 471–490 (1987)
[SW2] H. Siedentop and R. Weikard: *On the leading correction of the Thomas-Fermi model: lower bound*, Invent. Math. 97, 159–193 (1990).

[SW3] H. Siedentop and R. Weikard: *A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators*, Ann. Sci. École Norm. Sup. (4), 24, no. 2, 215–225 (1991).

[Sob1] A. V. Sobolev: *Quasi-classical asymptotics of local Riesz means for the Schrödinger operator in a moderate magnetic field*. Ann. Inst. H. Poincaré, 62 no. 4, 325-360, (1995).

[Sob] A. V. Sobolev: *Discrete spectrum asymptotics for the Schrödinger operator with a singular potential and a magnetic field*, Rev. Math. Phys 8 (1996) no. 6, 861–903.

[SS] J. P. Solovej, W. Spitzer: *A new coherent states approach to semiclassics which gives Scott’s correction*. Comm. Math. Phys. 241 (2003), no. 2-3, 383–420.

[SSS] J. P. Solovej, T.Ø. Sørensen, W. Spitzer: *Relativistic Scott correction for atoms and molecules*. Comm. Pure Appl. Math. Vol. LXIII. 39-118 (2010).

[Zh] G. Zhislin, *Discussion of the spectrum of Schrodinger operator for systems of many particles*. Tr. Mosk. Mat. Obs., 9, 81–128 (1960).