Upper Estimates for Electronic Density in Heavy Atoms and Molecules*,†

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Abstract

We derive an upper estimate for electronic density $\rho_\Psi(x)$ in heavy atoms and molecules. While not sharp, on the distances $\gtrsim Z^{-1}$ from the nuclei it is still better than the known estimate $CZ^3$ ($Z$ is the total charge of the nuclei, $Z \approx N$ the total number of electrons).

1 Introduction

This paper is a result of my rethinking of three rather old but still remarkable papers [HHT, SI, ILS], which I discovered recently. The first of them derives the estimate electronic density $\rho_\Psi(x)$ from above via some integral also containing $\rho_\Psi$, the second one provides an estimate $\rho_\Psi(x) = O(Z^3)$ where $Z$ is the total charge of nuclei and the third one derives the asymptotic of the averaged electronic density on the distances $O(Z^{-1})$ from the nuclei but its method works also on the larger distances.

The purpose of this paper is to provide a better upper estimate for $\rho_\Psi(x)$ on the distances larger than $Z^{-1}$ from the nuclei.

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Let us consider the following operator (quantum Hamiltonian)

\[(1.1) \quad H = H_N := \sum_{1 \leq j \leq N} H_{V,x_j} + \sum_{1 \leq j < k \leq N} |x_j - x_k|^{-1}\]
on

on

\[(1.2) \quad \mathfrak{H} = \bigwedge_{1 \leq n \leq N} \mathfrak{H}, \quad \mathfrak{H} = L^2(\mathbb{R}^3, \mathbb{C}^q)\]

with

\[(1.3) \quad H_V = -\Delta - V(x)\]

describing \(N\) same type particles in (electrons) the external field with the scalar potential \(-V\) (it is more convenient but contradicts notations of the previous chapters), and repulsing one another according to the Coulomb law.

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

\[(1.4) \quad V(x) = \sum_{1 \leq m \leq M} \frac{Z_m}{|x - y_m|}\]

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

Mass is equal to \(\frac{1}{2}\) and the Plank constant and a charge are equal to 1 here. We assume that \(N \asymp Z = Z_1 + \ldots + Z_M\).

Our purpose is to a pointwise upper estimate for the electronic density

\[(1.5) \quad \rho_\Psi(x) = N \int |\Psi(x, x_2, \ldots, x_N)|^2 \, dx_2 \cdots dx_N.\]

Let

\[(1.6) \quad \ell(x) = \min_{1 \leq m \leq M} |x - y_m|\]

is the distance to the nearest nucleus. Our goal is to prove the following theorem:

**Theorem 1.1.** Let

\[(1.7) \quad \min 1 \leq m < m' \leq M |y_m - y_{m'}| \geq Z^{-1/3+\sigma}\]

with \(\sigma > 0\). Then
(i) For $\ell(x) \leq Z^{-1/3}$ the following estimate holds:

\begin{equation}
\rho_{\Psi}(x) \leq C \left\{ \begin{array}{ll}
Z^3 & \text{for } \ell(x) \leq Z^{-8/9}, \\
Z^{19/9} \ell^{-1} & \text{for } Z^{-8/9} \leq \ell(x) \leq Z^{-7/9}, \\
Z^{197/90} \ell^{-9/10} & \text{for } Z^{-7/9} \leq \ell \leq Z^{-1/3}.
\end{array} \right.
\end{equation}

(ii) For $\ell(x) \geq Z^{-1/3}$ the following estimate holds:

\begin{equation}
\rho_{\Psi}(x) \leq C \left\{ \begin{array}{ll}
Z^{17/9} \ell^{-9/5} & \text{for } Z^{-1/3} \leq \ell \leq Z^{-5/18}, \\
Z^{19/9} \ell^{-1} & \text{for } \ell \geq Z^{-5/18}.
\end{array} \right.
\end{equation}

(iii) Furthermore, if $(Z - N) \geq C_0 Z^{5/6}$ then

\begin{equation}
\rho_{\Psi}(x) \leq Z^{19/9} \ell^{-1} \quad \text{for } \ell(x) \geq C_0 (Z - N)^{-1/3}.
\end{equation}

**Remark 1.2.** (i) We would like to prove an estimate $\rho_{\Psi}(x) \leq C \zeta^3$, or to discover that it does not necessarily hold.

(ii) We marginally improved our estimate (of the previous version) using [Ivr3]. We also added Statement [(iii)].

**Plan of the paper.** In Section 2 we prove a more subtle version of the main estimate of [HHT]. In Section 3 we provide upper estimates and asymptotics of $\rho_{\Psi}$ integrated over small balls. In Section 4 we study energy of electron-to-electron interaction (it involves a two-point correlation function) and in Section 5 we prove upper estimates for $\rho_{\Psi}(x)$.

## 2 Main intermediate inequality

We start from the main intermediate equality.

**Proposition 2.1.** Let $\Psi$ be an eigenfunction of $H_N$ with an eigenvalue $\lambda$. Let $\phi(|x|)$ be a real-valued spherically symmetric function. Then

\begin{equation}
(2\pi)^{-1} N \int (\partial_r K(x)) \Psi(x, x_2, \ldots, x_N) \Psi^*(x, x_2, \ldots, x_N) \phi(|x|) \, dx \, dx_2 \cdots \, dx_N
\end{equation}

\begin{equation}
- (8\pi)^{-1} \int \rho_{\Psi}(x) \phi'''(|x|) \, dx,
\end{equation}

\begin{equation}
= \rho_{\Psi}(0) =
\end{equation}

\begin{equation}
\end{equation}
where

\begin{equation}
(2.2) \quad K(x) := -H_N - (\partial_r^2 + 2r^{-1}\partial_r)
\end{equation}

is an operator in the auxiliary space \( H := \bigotimes_{n=2}^N L^2(\mathbb{R}^3, \mathbb{C}^q) \otimes \mathbb{C}^q \) with an inner product \( \langle ., . \rangle \), \( \phi'''(r) = \partial^3_r \phi(r) \) and \( x = (r, \theta) \in \mathbb{R}^+ \times \mathbb{S}^2 \).

**Proof.** Let us consider \( \Psi \) as a function of \( x \in \mathbb{R}^3 \) with values in the auxiliary space \( H \), and let \( u = r\Psi \) where \( (r, \theta) \) are spherical coordinates in \( \mathbb{R}^3 \). Then similar to (9) of [HHT]

\begin{equation}
(2.3) \quad \langle \Psi(0), \Psi(0) \rangle = -(2\pi)^{-1} \int \langle \partial_r u, \partial_r^2 u \rangle \phi(r) r^{-2} \, dx - (4\pi)^{-1} \int \langle \partial_r u, \partial_r u \rangle \phi'(r) r^{-2} \, dx
\end{equation}

and since \( r^{-1}\partial_r^2 u = r \Delta_r \Psi := r(\partial_r^2 + 2r^{-1}\partial_r)\Psi \), the first term on the right is equal to

\begin{equation}
(2.4) \quad -(2\pi)^{-1} \int \int \langle \partial_r u, r \Delta_r \Psi \rangle \phi(r) \, drd\theta = \pi^{-1} \int \langle \partial_r u, (K + \lambda) u \rangle \phi(r) drd\theta = -(2\pi)^{-1} \int \langle \Psi, (K + \lambda) \Psi \rangle \phi'(r) \, dx
\end{equation}

because \( \Delta_r \Psi = -2(K + \lambda)\Psi \), where \( -K \) is the rest of multiparticle Hamiltonian (including \( -r^{-2}\Delta_\theta \)) and we integrated by parts.

The first term in the latter formula is a corresponding term in [HHT], albeit truncated with \( \phi \), and we have new terms

\[-(4\pi)^{-1} \int \int \langle \partial_r (r\Psi), \partial_r (r\Psi) \rangle \phi'(r) \, drd\theta - (2\pi)^{-1} \int \langle \Psi, (W + \lambda) \Psi \rangle \phi'(r) \, dx \, .\]

Integrating by parts the first term we get

\[ (4\pi)^{-1} \int \int \langle r\Psi, \partial_r^2 (r\Psi) \rangle \phi'(r) \, drd\theta + (4\pi)^{-1} \int \int \langle r\Psi, \partial_r (r\Psi) \rangle \phi''(r) \, drd\theta , \]

where the first term cancels with the second term in (2.4), while the second term integrates by parts one more time resulting in the last term in (2.1). \( \Box \)
Applying (2.1) to our problem, and using skew-symmetry of $\Psi$, we get

\begin{align*}
(2.5) \quad \rho_{\Psi}(0) &= \frac{(2\pi)}{(2\pi)^{-1}} \int \sum_{m} Z_{m} \frac{x \cdot (x - y_{m})}{|x| \cdot |x - y_{m}|^3} \rho_{\Psi}(x) \phi(|x|) \, dx \\
&\quad + (2\pi)^{-1} N(N - 1) \int \frac{x_1 \cdot (x_2 - x_1)}{|x_1| \cdot |x_2 - x_1|^3} \left| \Psi(x_1, x_2, \ldots, x_N)^2 \phi(|x_1|) \right| \, dx_1 \cdots dx_N \\
&\quad - (2\pi)^{-1} N \int |x|^{-3} |\nabla_{\theta} \Psi(x_1, x_2, \ldots, x_N)^2 \phi(|x|) \, dx_1 \cdots dx_N \\
&\quad - (8\pi)^{-1} \int \rho_{\Psi}(x) \phi''(|x|) \, dx.
\end{align*}

Symmetrizing the second term with respect to $x_1$ and $x_2$ we instead of the product of two indicated factors will get

\begin{align*}
&\frac{1}{4} \left( \phi(|x_1|) + \phi(|x_2|) \right) \left( \frac{x_1 \cdot (x_2 - x_1)}{|x_1| \cdot |x_2 - x_1|^3} - \frac{x_2 \cdot (x_2 - x_1)}{|x_2| \cdot |x_2 - x_1|^3} \right) \\
&\quad + \frac{1}{4} \left( \phi(|x_1|) - \phi(|x_2|) \right) \left( \frac{x_1 \cdot (x_2 - x_1)}{|x_1| \cdot |x_2 - x_1|^3} + \frac{x_2 \cdot (x_2 - x_1)}{|x_2| \cdot |x_2 - x_1|^3} \right)
\end{align*}

with the big parenthesis on the first line equal to

\begin{equation}
(2.6) \quad - \frac{|x_1| + |x_2|}{|x_1 - x_2|^3} \left( 1 - \frac{x_1 \cdot x_2}{|x_1| \cdot |x_2|} \right)
\end{equation}

and the big parenthesis on the second line equal to

\begin{equation}
(2.7) \quad - \frac{|x_1| - |x_2|}{|x_1 - x_2|^3} \left( 1 + \frac{x_1 \cdot x_2}{|x_1| \cdot |x_2|} \right).
\end{equation}

One can see that the former is negative, and the latter, multiplied by $\left( \phi(|x_1|) - \phi(|x_2|) \right)$, is non-negative if $\phi$ is non-decreasing function. Let us shift the origin to point $x$ and observe that the first term in (2.5) is equal to

\begin{equation}
(2.8) \quad (2\pi)^{-1} \int \sum_{m} Z_{m} \frac{(x - x) \cdot (x - y_{m})}{|x - x| \cdot |x - y_{m}|^3} \rho_{\Psi}(x) \phi(|x - x|) \, dx.
\end{equation}

Consider first case $\phi = 1$. Then we get

\begin{equation}
(2.9) \quad \rho_{\Psi}(x) \leq (2\pi)^{-1} \int \sum_{m} Z_{m} |x - y_{m}|^{-2} \rho_{\Psi}(x) \, dx.
\end{equation}
Indeed, the second term in the right-hand expression of (2.5) is non-positive due to above analysis, so is the third term, and the fourth term vanishes while the first term does not exceed the right-hand expression.

Applying Proposition 3.1 below we arrive to the following estimate

\[(2.10)\]
\[\rho \Psi(x) \leq CZ^3.\]

In the general case we arrive to

**Proposition 2.2.** In the framework of Proposition 2.7

\[(2.11)\]
\[\rho \Psi(x) \leq (2\pi)^{-1} \sum_m Z_m \frac{(x - x) \cdot (x - y_m)}{|x - x| \cdot |x - y_m|^2} \rho \Psi(x) \phi(|x - x|) dx + C t^{-1} \int B(x,t) \times B(x,t) \ |x - y|^{-1} \rho^{(2)}(x,y) dxdy + C \int_{B(x,t) \times (\mathbb{R}^3 \backslash B(x,t))} \ |y - x|^{-2} \rho^{(2)}(x,y) dxdy ,\]

where

\[(2.12)\]
\[\rho^{(2)}(x,y) := N(N - 1) \int |\Psi(x, y, x_3, \ldots, x_N)|^2 dx_3 \cdots dx_N\]

is a two-point correlation function.

Recall that

\[(2.13)\]
\[\int \rho^{(2)}(x,y) dy = (N - 1) \rho \Psi(x).\]

**Remark 2.3.** (i) Inequality (2.9) for \(M = 1\) and \(x = y_1\) is the main result of [HHT]. Our main achievement so far is an introduction of the truncation \(\phi\). However it brings three new terms in the right-hand expression of the estimate.

(ii) Estimate (2.10) (with a specified albeit not sharp constant) was proven in [S1] for \(x = y_m\).

(iii) This estimate definitely has a correct magnitude as \(|x - y_m| \lesssim Z^{-1}\) and \(Z_m \asymp Z\).
3 Estimates of the averaged electronic density

We will need the following estimate (3.3) from [Ivr2]:

\begin{equation}
\int U \rho \Psi \, dx \leq \text{Tr}(H_{W+\nu}^\prime) - \text{Tr}(H_{W+U+\nu}^\prime) + CZ^{5/3-\delta}
\end{equation}

with \( \delta = \delta(\sigma) \), \( \delta > 0 \) for \( \sigma > 0 \) and \( \delta = 0 \) for \( \sigma = 0 \).

First, we use this estimate in the very rough form:

**Proposition 3.1.** The following estimate holds:

\begin{equation}
\int |x - y_m|^{-2} \rho \Psi \, dx \leq CZ^2.
\end{equation}

**Proof.** Let \( \psi(x), \psi_0(x) \) be cut-off functions, \( \psi(x) = 0 \) in \( \{x: \ell(x) \leq b\} \), \( \psi_0(x) = 0 \) in \( \{x: \ell(x) \geq 2b\} \), \( \psi + \psi_0 = 1 \), \( b = Z^{-1} \). Then

\begin{equation}
\text{Tr}(H_{W+U+\nu}^\prime) = \text{Tr}(H_{W+U+\nu}^\prime \psi_0) + \text{Tr}(H_{W+U+\nu}^\prime \psi)
\end{equation}

Using the semiclassical methods of [Ivr1], Section 25.4 in the simplest form, we conclude that for \( U = \epsilon |x - y_m|^{-2} \) the second term on the right (with an opposite sign) could be replaced by its Weyl approximation

\begin{equation}
-\frac{2}{5} \kappa \int (W + U + \nu)^{5/2} \psi(x) \, dx
\end{equation}

with an error not exceeding \( CZ^2 \) where here and below \( \kappa = q/(6\pi^2) \). The same is true for \( U = 0 \). One can see easily that the difference between expression (3.4) and the same expression for \( U = 0 \) does not exceed

\begin{equation}
C \int [(W + \nu)^{3/2} U + U^{5/2}] \, dx,
\end{equation}

which does not exceed \( CZ^2 \).

Consider the first term in the right-hand expression of (3.3). Using variational methods of [Ivr1], Section 9.1 we can reduce it to the analysis of the same operator in \( \lambda^0 := \{x: \ell(x) \leq 4b\} \) with the Dirichlet boundary conditions on \( \partial X \). Observing that eigenvalue counting function for such operator is \( O(1 + \lambda^{3/2} Z^{-3}) \) (for \( \epsilon \) sufficiently small), we conclude that the first term in (3.3) also does not exceed \( CZ^2 \). Estimate (3.2) has been proven. \( \Box \)
Let us return to (3.1) and consider \( U = \zeta^2 \phi_t(x; x) \) where \( x \) is a fixed point with
\[
\ell(x) := \min_{m} |x - y_m| \geq Z^{-1}, \tag{3.6}
\]
\[
\zeta(x) := \max\left(Z^{1/2} \ell(x)^{-1/2}, \ell(x)^{-2}\right) \tag{3.7}
\]
and \( \phi_t(x; x) = \phi_0(t^{-1}|x - x|), \phi \in C_0^\infty([-1, 1]), 0 \leq \phi \leq 1. \) We assume that
\[
\zeta^{-1} \leq t \leq \frac{\ell}{2} \tag{3.8}
\]
with \( \ell = \ell(x), \zeta = \zeta(x), \) where the last inequality allows us to apply semi-classical methods. Consider with \( 0 \leq \varsigma \leq 1 \)
\[
\Tr(H_{W+\nu}) - \Tr(H_{W+\varsigma U+\nu}) = \int_0^\varsigma \Tr\left(U(\theta(-H_{W+\varsigma U+\nu}) - \theta(-H_{W+\nu}))\right) ds \tag{3.9}
\]
and apply semi-classical method to the right-hand expression. Then we get
\[
\Tr(H_{W+\nu}) - \Tr(H_{W+\varsigma U+\nu})
= \kappa \int_0^\varsigma \left(U\left(\left(W + sU + \nu\right)^{3/2} - \left(W + \nu\right)^{3/2}\right)\right) dx ds + O(\zeta^4 t^2)
= \frac{2}{5} \kappa \int \left(\left(W + \varsigma U + \nu\right)^{5/2} - \left(W + \nu\right)^{5/2}\right) dx + O(\zeta^4 t^2). \tag{3.10}
\]
Indeed, factor \( U \) is \( O(\zeta^2) \) and therefore the semiclassical error is \( O(\zeta^4 t^2) \) since the effective semiclassical parameter is \( h = (\zeta t)^{-1}. \) Observe that the principal part in the right-hand expression does is \( O(\zeta^5 t^3). \)

Then after division by \( \varsigma \zeta^2 \) (3.1) becomes
\[
\int \phi_t(x; x) \rho_\Psi(x) \, dx \leq \int \phi_t(x; x) \rho(x) \, dx
+ C\left(\zeta^2 t^2 + \zeta^3 t^3 + \zeta^{-1} Z^{5/3-\delta}\right). \tag{3.11}
\]
Replacing \( \phi_t(x; x) \) by \( -\phi_t(x; x) \) in this inequality and minimizing by \( \varsigma \in (0, 1] \) we arrive to the first statement of the following proposition:
Proposition 3.2. (i) Under assumptions (3.6) – (3.8)

\[ \left| \int (\rho_\Psi(x) - \rho(x))\phi_t(x;x) \, dx \right| \leq C \left( \zeta^2 t^2 + \zeta^{3/2} t^{3/2} Z^{5/6 - \delta/2} + \zeta^{-2} Z^{5/3 - \delta} \right). \]

(ii) Further,

\[ \left| \int \rho_\Psi(x)\phi_t(x;x) \, dx \right| \leq C \left( \zeta^3 t^3 + t^{6/5} Z^{1 - 3\delta/5} \right). \]

(iii) Furthermore, if \( N < Z \) then

\[ \left| \int \rho_\Psi(x)\phi_t(x;x) \, dx \right| \leq C t^{6/5} Z^{1 - 3\delta/5} \quad \text{for} \quad \ell(x) \geq C_0 (Z - N)^{-1/3}. \]

To prove the second statement, we consider \( \varsigma > 0 \) (without restriction \( \varsigma \leq 1 \)); then instead of (3.11) we have

\[ \int \phi_t(x;x)\rho_\Psi(x) \, dx \leq C \left( \varsigma^3 t^3 + \varsigma^{3/2} \varsigma^3 t^3 + \varsigma^{-1} \varsigma^{-2} Z^{5/3 - \delta} \right) \]

and we optimize it by \( \varsigma > 0 \).

The third statement follows from the same arguments and the fact that recall that \( \rho^{TF}(x) = 0 \) for \( \ell(x) \geq C_0 (Z - N)^{-1/3} \) and therefore (3.15) holds without the first term in the right-hand expression.

4 Estimates of the correlation function

We will need the following Proposition 25.5.1 from [Ivr1] (first proven in [RS]):

Proposition 4.1. Let \( \theta \in \mathcal{C}_\infty^\infty(\mathbb{R}^3) \), such that

\[ 0 \leq \theta \leq 1. \]

Let \( \chi \in \mathcal{C}_\infty^\infty(\mathbb{R}^6) \) and

\[ \mathcal{J} = \left| \int \left( \rho_\Psi^{(2)}(x, y) - \rho(y)\rho_\Psi(x) \right)\theta(x)\chi(x,y) \, dxdy \right| \leq \]

\[ C \sup_x \| \nabla_y \chi \|_2(\mathbb{R}^3) \left( (Q + \varepsilon^{-1} N + T)^{1/2} \Theta + P^{1/2} \Theta^{1/2} \right) + C \varepsilon N \| \nabla_y \chi \|_2 \Theta \]
with

\[ Q = D(\rho_\Psi - \rho^{TF}, \rho_\Psi - \rho^{TF}), \]

\[ \Theta = \Theta_\Psi := \int \theta(x) \rho_\Psi(x) \, dx, \]

\[ T = \sup_{\text{supp}(\theta)} W, \]

\[ P = \int |\nabla \theta|^2 \rho_\Psi \, dx. \]

respectively and arbitrary \( \varepsilon \leq Z^{-5/2}. \)

We cannot apply it directly to estimate the second to the last term in (2.11) because of singularities. Let us consider

\[ \int \int_{\mathbb{R}^3 \times \mathbb{R}^3} |x - y|^{-1} \rho_\Psi^{(2)}(x, y) \, dx \, dy. \]

Let us make an \( \ell \)-admissible partition of unity \( \phi_i \) in with \( \ell \)-admissible \( \phi_i^{1/2} \). We set \( \ell(x) = Z^{-1} \) if \( |x - y_m| \leq Z^{-1} \). Let us consider first

\[ \int |x - y|^{-1} \rho_\Psi^{(2)}(x, y) \phi_i(x) \phi_\kappa(y) \, dx \, dy \]

in the case of \( \phi_i \) and \( \phi_\kappa \) having disjoint supports. Without any loss of the generality we can consider \( \ell_x \leq \ell_y \), where subscripts \( x, y \) are referring to supports of \( \phi_i, \phi_\kappa \) respectively.

Let \( \theta(x) = \phi_i(x) \) and

\[ \chi(x, y) = \bar{\chi}(x, y) := |x - y|^{-1} \phi_i(x) \phi_\kappa(y) \]

where \( \phi_i \) which are \( \ell \)-admissible and equal 1 in the \( \ell \)-vicinity of \( \text{supp}(\phi_i) \). Then \( T = \zeta_x \) and for \( \ell_x \leq Z^{-5/21} \) in virtue of Proposition [3,21]

\[ \Theta_\Psi \asymp \zeta_x^3 \ell_x^3, \quad P \asymp \zeta_x^3 \ell_x \]

and

\[ \| \nabla_y \chi \|_{L^2(\mathbb{R}^3_y)} \asymp d_{x, y}^{-1} \ell_y^{1/2}, \quad \| \nabla \chi \|_{L^\infty} \asymp d_{x, y}^{-1} \ell_y^{-1} \]

1) Indeed, \( \zeta_x^3 \ell^3 \geq Z^{5/3 - \delta} \zeta^{-2} \iff \ell \leq Z^{-5/21 + \delta/7}. \)
where $d_{x,y} \geq \ell_y$ is the distance between supports of $\phi_\iota$ and $\phi_\kappa$. Then the right-hand expression of (4.2) is

$$C\zeta^3 \xi_x \ell_x \left( \ell_y^{-1/2}(Z^{5/6} + \zeta_x) + \varepsilon^{-1/2}\ell_y^{-1/2}\varepsilon^{1/2} + \varepsilon Z\ell_y^{-2} + \ell_y^{-1/2}\ell_x^{-1} \right)$$

and minimizing by $\varepsilon \leq Z^{-2/3}$ we get

$$C\zeta^3 \xi_x \ell_x \left( \ell_y^{-1/2}(Z^{5/6} + \zeta_x) + Z^{2/3}\ell_y^{-1} + \ell_y^{-1/2}Z^{5/6} + \ell_y^{-1/2}\ell_x^{-1} \right).$$

Observe that all powers of $\ell_y$ are negative. Therefore summation over all elements of $y$-partition results in the same expression albeit with $\ell_y$ replaced by $\ell_x = \ell^*$:

$$C\zeta^3 \ell^2 \left( \ell^{1/2}(Z^{5/6} + \zeta) + Z^{2/3} + \ell^{-1/2} + \ell^{1/2}Z^{5/6} \right).$$

For $\ell \leq Z^{-1/3}$ we have $\zeta = Z^{1/2}\ell^{-1/2}$ and all powers are positive with the exception of one term, where the power is 0, and for $\ell \geq Z^{-1/3}$ we have $\zeta = \ell^{-2}$ and all powers are negative. Therefore summation over all elements of $x$-partition results in the same expression albeit with $\ell = Z^{-1/3}$, $\zeta = Z^{2/3}$, with the exception of one term which gains a logarithmic factor. We get $CZ^2$. Then

$$\left| \sum_{\iota,\kappa} \int \int \left( \rho^{(2)}_\Psi(x, y) - \rho(y)\rho_\Psi(x) \right) \phi_\iota(x)\phi_\kappa(y), dxdy \right| \leq CZ^2$$

with summation over indicated pairs of elements of the partition (disjoint, with $\ell_x \leq \min(Z^{-5/21+8/7}, \ell_y)$).

Let us prove that

$$\text{(4.13) Estimate } (4.12) \text{ also holds with } \rho_\Psi(x) \text{ replaced by } \rho(x) \text{ and therefore it holds for a sum over pairs of elements with } \min(\ell_x, \ell_y) \leq \ell^* = Z^{-5/21+5/7}. $$

Indeed, in virtue of the proof of Proposition 3.2 (before minimizing by $\zeta$) the error

$$\left| \int \int (\rho_\Psi(x) - \rho(x))\rho_\Phi(x)\phi_\kappa(y), dxdy \right|$$

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on each pair of elements does not exceed $C\zeta_y^{3/2}$ with all powers of $\ell_y$ positive for $\ell_y \leq Z^{-1/3}$ and negative for $\ell_y \geq Z^{-1/3}$. Then summation with respect to $y$-partition (recall, that $\ell_y \geq \ell_x$) results in

$$C\left(\zeta_x^2 \ell_x^2 + \zeta_y^2 \ell_y^2 + \zeta^{-1} \zeta_x^{-2} Z^{5/3-\delta}\right) \times \begin{cases} Z^{4/3} & \text{for } \ell_x \leq Z^{-1/3}, \\ \zeta_x^3 \ell_x^2 & \text{for } \ell_x \geq Z^{-1/3}, \end{cases}$$

with the first line corresponding to $\ell_y = Z^{-1/3}$, $\zeta_y = Z^{2/3}$ and the second line corresponding to $\ell_y = \ell_x$, $\zeta_y = \zeta_x$.

Powers of $\ell_x$ are positive for $\ell_x \leq Z^{-1/3}$ and negative for $\ell_x \geq Z^{-1/3}$, and summation with respect to $x$-partition results in the value as $\ell_x = Z^{-1/3}$, $\zeta_x = Z^{2/3}$, which is

$$CZ^2 + C\zeta Z^{7/3} + C\zeta^{-1} Z^{5/3-\delta}.$$

Minimizing by $\zeta = Z^{-1/3}$ we conclude that the sum of expressions (4.13) over required pairs does not exceed $CZ^2$, which in turn implies (4.12).

Consider now the case when supports of elements are not disjoint. Then we take

$$\chi(x, y) = \bar{\chi}(x, y)\eta(|x - y|/s) = |x - y|^{-1} \bar{\phi}_\epsilon(x) \phi_\kappa(y)\eta(|x - y|/s)$$

with $\eta(t)$ smooth function, equal 0 at $(0, \frac{1}{2})$ and 1 at $(1, \infty)$; $s \leq Z^{-1/3}$ will be selected later\(^2\). Then while (4.10) is preserved, (4.11) should be replaced by

$$\|\nabla_y \chi\|_{L^2(\mathbb{R}^d_x)} \asymp s^{-1/2}, \quad \|\nabla_y \chi\|_{L^\infty} \asymp s^{-2}.$$  

Then the right-hand expression (4.2) is

$$Cs^{-1/2} \zeta^3 \ell^3 \left((Z^{5/6} + \zeta) + \epsilon^{-1/2} Z^{1/2} + \epsilon s^{-3/2} Z + \ell^{-1}\right),$$

and minimizing by $\epsilon \leq Z^{-2/3}$ we get

$$|\int \phi_\epsilon(x) \chi(x, y) \left(\rho^{(2)}_\Phi(x, y) - \rho_\Phi(x) \rho(y)\right) dxdy| \leq Cs^{-1/2} \zeta^3 \ell^3 \left(Z^{5/6} + \zeta + s^{-1/2} Z^{2/3} + \ell^{-1}\right).$$

\(^2\) Since in this case $\ell_x = \ell_y$ and $\zeta_x = \zeta_y$ we skip subscripts.
Note that summation of (4.17) over partition returns its value as \( \ell = Z^{-1/3} \), namely, \( C s^{-1} Z^{5/3} \).

Consider for \( t: s \leq t \leq \ell \) zone \( \{(x, y): |x - y| \asymp y\} \) and make there \( t \)-admissible subpartition with respect to \( x, y \). Then contribution of each pair of subelements to

\[
\left| \int \phi_t(x) \chi(x, y) \left( \rho(x) - \rho(y) \right) \rho(y) \, dx \, dy \right|
\]

does not exceed

\[
C \left( \zeta^2 t^2 + \zeta^3 t^3 + \zeta^{-1} \zeta^{-2} Z^{5/3-\delta} \right) \zeta^3 t^2
\]

and since there are \( \asymp \ell^3 t^{-3} \) of such pairs, we get

\[
C \left( \zeta^2 t^2 + \zeta^3 t^3 + \zeta^{-1} \zeta^{-2} Z^{5/3-\delta} \right) \zeta^3 \ell^3 t^{-1}.
\]

Then summation over \( t: s \leq t \leq \ell \) returns

\[
C \left( \zeta^2 \ell + \zeta^3 \ell^2 + \zeta^{-1} s^{-1} \zeta^{-2} Z^{5/3-\delta} \right) \zeta^3 \ell^3
\]

and summation over over partition returns its value as \( \ell = Z^{-1/3} \), namely

\[
C \left( Z^2 + \zeta Z^{7/3} + \zeta^{-1} s^{-1} Z^{4/3-\delta} \right).
\]

Minimizing by \( \zeta = (s Z)^{-1/2} \) we get \( C \left( Z^2 + s^{-1/2} Z^{11/6-\delta} \right) \).

On the other hand,

\[
\int \int \phi_t(x) \left( \overline{\chi}(x, y) - \chi(x, y) \right) \rho(x) \rho(y) \, dx \, dy \asymp s^2 \zeta^6 \ell^3,
\]

and summation over \( \ell \geq Z^{-1/3} \) returns its value at \( Z^{-1/3} \), which is \( C s Z^3 \), but summation over \( \ell \leq Z^{-1/3} \) returns \( s^2 Z^3 \log Z \). To remedy this we replace for \( \ell \leq Z^{-1/3} \) constant \( s \) by \( s_x = s (\ell_x Z^{1/3})^{\delta'} \) with small \( \delta' > 0 \). It will not affect our previous estimates.

Consider the sum of these three right-hand expressions

\[
C \left( Z^2 + s^{-1} Z^{5/3} + s^{-1/2} Z^{11/6-\delta} + s^2 Z^3 \right)
\]

and minimize it by \( s \); we get \( C Z^{19/9} \) achieved as \( s = Z^{-4/9} \).

Since we want \( s \leq \ell \) we finally set

\[
(4.18) \quad s_x = \begin{cases} 
Z^{-4/9} & \text{for } \ell_x \geq Z^{-1/3}, \\
\min(Z^{-4/9} (\ell_x Z^{1/3})^{\delta'}, \ell_x) & \text{for } \ell_x \leq Z^{-1/3}.
\end{cases}
\]
Observe that
\[ \int \int_{\{x : \ell_x \geq Z^{-5/21}\}} |x - y|^{-1} \rho(x) \rho(y) \sim Z^{11/21} \]

and we arrive to
\[ (4.19) \quad \int \int_{\Omega} |x - y|^{-1} (\rho_\Psi^{(2)}(x, y) - \rho(x) \rho(y)) \, dx \, dy \leq CZ^{19/9} \]
and
\[ (4.20) \quad \int \int_{\mathbb{R}^3 \times \mathbb{R}^3 \setminus \Omega} |x - y|^{-1} \rho(x) \rho(y) \, dx \, dy \leq CZ^{19/9} \]

with
\[ (4.21) \quad \Omega = \{(x, y) : \ell_x \leq Z^{-5/21}, |x - y| \geq s_y\} \]

Therefore
\[ (4.22) \quad \int_{\Omega} |x - y|^{-1} \rho_\Psi^{(2)}(x, y) \, dx \, dy \geq \int_{\mathbb{R}^6} |x - y|^{-1} \rho(x) \rho(y) \, dx \, dy - CZ^{19/9}. \]

However we know that (see, e.g. Section 25.2 of [Ivr1])
\[ (4.23) \quad E_N \geq \text{Tr}((H_W - \nu^-) - D(\rho_\Psi, \rho) + \frac{1}{2} \int |x - y|^{-1} \rho_\Psi^{(2)}(x, y) \, dx \, dy \]
and
\[ (4.24) \quad E_N \leq \text{Tr}((H_W - \nu^-) - \frac{1}{2} D(\rho, \rho) + CZ^{5/3} \]

with \( \rho = \rho^{TF}, \ W = W^{TF}, \ D(f, g) : \iint |x - y|^{-1} f(x) g(x) \, dx. \) Then
\[ \int |x - y|^{-1} \rho_\Psi^{(2)}(x, y) \, dx \, dy \leq 2D(\rho_\Psi - \rho, \rho) + D(\rho, \rho) + CZ^{5/3} \]

and from
\[ |D(\rho_\Psi - \rho, \rho)| \leq D(\rho_\Psi - \rho, \rho_\Psi - \rho)^{1/2} D(\rho, \rho)^{1/2} \leq CZ^{5/6} \times Z^{7/6} = CZ^2 \]
we conclude that
\[ (4.25) \quad \int |x - y|^{-1} \rho_\Psi^{(2)}(x, y) \, dx \, dy \leq D(\rho, \rho) + CZ^2. \]

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Combining with (4.22) we conclude that

\[
\int_Z |x - y|^{-1} \rho^{(2)}_\Psi (x, y) \, dx dy \leq CZ^{19/9}
\]

for \( Z = \mathbb{R}^3_x \times \mathbb{R}^3_y \setminus \Omega \).

5 Proof of Theorem 1.1

Now in the last two terms

\[
Ct^{-1} \int \int_{B(x,t) \times B(x,t)} |x - y|^{-1} \rho^{(2)}_\Psi (x, y) \, dx dy
\]

\[
+ C \int \int_{B(x,t) \times (\mathbb{R}^3 \setminus B(x,t))} |y - x|^{-2} \rho^{(2)}_\Psi (x, y) \, dx dy,
\]

in (2.11) we replace \( \rho^{(2)}_\Psi (x, y) \) by \( \rho(x) \rho(y) \) and get

\[
Ct^{-1} \int \int_{B(x,t) \times B(x,t)} |x - y|^{-1} \rho(x) \rho(y) \, dx dy
\]

\[
+ C \int \int_{B(x,t) \times (\mathbb{R}^3 \setminus B(x,t))} |y - x|^{-2} \rho(x) \rho(y) \, dx dy
\]

and the first term does not exceed \( C \zeta^6 t^4 \), while the second term does not exceed

\[
C \zeta^3 t^3 \int_{\mathbb{R}^3 \setminus B(x,t)} |x - y|^{-2} \rho(y) \, dy.
\]

The largest error comes from the first term when integral is taken over \( B(x, t) \times B(x, t) \cap Z \) and in virtue of of (4.26) it does not exceed \( Ct^{-1} Z^{19/9} \), all other errors are lesser (to prove it we need just to repeat arguments of the previous section).

Observe that for \( \ell := \ell_x \leq Z^{-1/3} \) the largest contribution to the integral in (5.2) comes from the layer \( \{ y : \ell_y \approx \ell_x \} \) and it is of magnitude \( \zeta^3 \ell_x \). On the other hand, for \( \ell_x \geq Z^{-1/3} \) the largest contribution to the integral in (5.1) comes from the layer \( \{ y : \ell_y \approx Z^{-1/3} \} \) and it is of magnitude \( Z \ell^{-2} \); the first term in (5.1) is smaller.
Therefore we estimate two last terms in (2.11) by

\[ Ct^{-1}Z^{19/9} + C \left\{ \begin{array}{ll} Z^3 \ell^{-2/3} & \text{for } \ell \leq Z^{-1/3}, \\ Z \ell^{-8} \ell^3 & \text{for } \ell \geq Z^{-1/3}. \end{array} \right. \]

Consider the second term in (2.11):

\[
(2\pi)^{-1} \int \sum_m Z_m \frac{(x - x) \cdot (x - y_m)}{|x - x| \cdot |x - y_m|^3} \rho(x) \phi(|x - x|) \, dx.
\]

We replace in the integral in the right-hand expression \( \rho(x) \) by \( \rho(x) \) and get

\[ (2\pi)^{-1} \sum_m Z_m \int \frac{(x - x) \cdot (x - y_m)}{|x - x| \cdot |x - y_m|^3} \rho(x) \phi(|x - x|) \, dx
\]

with an error

\[ (2\pi)^{-1} \sum_m Z_m \int \frac{(x - x) \cdot (x - y_m)}{|x - x| \cdot |x - y_m|^3} (\rho(x) - \rho(x)) \phi(|x - x|) \, dx
\]

and one can see easily that (5.4) does not exceed \( CZ \zeta^3 \ell^{-3} \ell^4 \).

To estimate (5.5) we make a partition in \( B(x, t) \) with subelements supported in the layers \( \{ x : |x - x| \approx t' \} \) with \( p < t' \leq t \) and in \( B(x, p) \) with \( \zeta^{-1} \leq p \leq t \). According to (3.12), the contribution of each layer does not exceed \( CZt^{-2}(\zeta^2 t^2 + \zeta^{-2} Z^{5/3-\delta}) \) and summation over layers returns its value as \( t' = t \), with \( \zeta^{-2} Z^{5/3-\delta} \) acquiring logarithmic factor with we compensate by decreasing \( \delta \):

\[ CZt^{-2}(\zeta^2 t^2 + \zeta^{-2} Z^{5/3-\delta}). \]

Meanwhile, contribution of the ball \( B(x, p) \) into (5.5) does not exceed \( CZt^{-2} \| \rho - \rho \|_{L^1(B(x, p))} \) and to estimate it we use Theorem 1.1 of \[Ivr3\] with \( a = \ell \) and \( \mu = p^3 \ell^{-3} \):

\[ \| \rho - \rho^p \|_{L^1(B(x, s))} \leq C \left\{ \begin{array}{ll} p^2 \ell^{-2/3} Z^{11/9-\delta/3} + p^2 Z \ell^{-2} & \text{as } p \geq Z^{-5/18-\delta} \ell^{5/6}, \ Z^{-1} \leq \ell \leq Z^{-1/3}, \\ p^2 \ell^{-8/3} Z^{5/9-\delta/3} & \text{as } p \geq Z^{5/9-\delta} \ell^{10/3}, \ Z^{-1/3} \leq \ell \leq Z^{-5/21}. \end{array} \right. \]

\[3\) Indeed, it suffices to take a half-sum of the integrand in (5.4) with its value at symmetric about \( x \) point, because both \( |x - y_m| \) and \( \rho(x) \) satisfy \( |\nabla f| \leq C \ell^{-1}. \)
Therefore (2.11) implies

\[
\rho_\Psi(x) \leq C \left( Z \zeta^3 \ell^{-3} t^4 + Z^{19/9} \ell^{-1} + Z \zeta^2 \ell^{-2} t^2 \right)
+ C \left( \zeta^3 + Z^{8/3 - \delta} \ell^{-2} + Z \ell^{-2} \| \rho_\Psi - \rho \|_{L^1(B(x,\ell))} \right),
\]

where only first line depends on \( t \). One can see easily that the third term in the first line does not exceed the sum of two first terms. Further, the second term there is larger than \( Z^{19/9} \ell^{-1} \) which is larger than \( CZ^3 \) as \( \ell \leq Z^{-8/9} \) and since we already have an estimate (2.10), we should consider only \( \ell \geq Z^{-8/9} \). Furthermore, \( Z^{19/9} \ell^{-1} \geq \zeta^3 \).

Finally, optimizing remaining two terms in the first line of (5.8) by \( t: \zeta^{-1} \leq t \leq \ell \), we get

\[
\rho_\Psi(x) \leq C \left( Z^{17/9} \zeta^{3/5} \ell^{-3/5} + Z \zeta^{-1} \ell^{-3} + Z^{19/9} \ell^{-1} \right)
+ C \left( Z^{8/3 - \delta} \ell^{-2} + Z \ell^{-2} \| \rho_\Psi - \rho \|_{L^1(B(x,\ell))} \right).
\]

Let us compare terms there.

(i) Let \( Z^{-8/9} \leq \ell \leq Z^{-1/3} \). Then one can see easily that the first line is defined by the third term \( Z^{19/9} \ell^{-1} \) for \( Z^{-8/9} \leq \ell \leq Z^{-7/9} \) and by the first term, which is \( Z^{197/90} \ell^{-9/10} \), for \( Z^{-7/9} \leq \ell \leq Z^{-1/3} \).

One can see easily that the first term in the second line of (5.9) is smaller than \( Z \ell^{-1} \). Using the first case in (5.7) with \( p = \max(\zeta^{-1}, \ell^{10/3} Z^{-5/18}) \) and \( \delta = 0 \), we see that the second term in the second line is smaller than the first line as well. Thus we arrive to Theorem 1.1, Statement (i).

(ii) Let \( \ell \geq Z^{-1/3} \). Then one can see easily that the first line of (5.9) is defined by the first term, which is \( Z^{17/9} \ell^{-9/5} \) for \( Z^{-1/3} \leq \ell \leq Z^{-5/18} \) and by \( Z \ell^{-1} \) for \( \ell \geq Z^{-5/18} \).

Consider the second line and impose condition \( \ell \leq Z^{-2/9} \). Then the first line dominates the first term here. Using the second case in (5.7) with \( p = \max(\zeta^{-1}, \ell^{10/3} Z^{5/9}) \) and \( \delta = 0 \), we see that the first line dominates the last term in the second line as well.

Further, let \( \ell \geq Z^{-2/9} \). Recall that the second line (except \( C \zeta^3 \)) was a result of the estimate of the second term in (2.11), which, however, could
be estimated by

\begin{equation}
CZ \ell^{-2} \int_{B(x, \ell(x))} \rho_\Psi(x) \, dx.
\end{equation}

It is well known that \( \int \rho_\Psi \leq CZ \) and therefore (5.10) does not exceed \( CZ^2 \ell^{-2} \) which covers \( \ell \geq Z^{-1/9} \).

Furthermore, in the remaining range \( Z^{-2/9} \leq \ell \leq Z^{-1/9} \) we can use Proposition 3.2(ii) to show, that the first term in the second line does not exceed \( Z^{19/9} \ell^{-1} \) while the second term there is estimated again by the second case in (5.7). Thus we arrive to Theorem 1.1 Statement (ii).

(iii) Finally, using Proposition 3.2(iii) we prove Theorem 1.1 Statement (iii).

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