Thomas-Fermi approximation to electronic density*, †

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Abstract

In heavy atoms and molecules, on the distances $a \gg Z^{-1}$ from all of the nuclei (with a charge $Z_m$) we prove that $\rho_{\Psi}(x)$ is approximated in $L^1$-norm, by the Thomas-Fermi density.

1 Introduction

This paper is a continuation of [Ivr3]

The purpose of this paper is to provide a more refined asymptotics (with an error estimate in $L^1$-norm) and on the distances $\gg Z^{-1}$ from the nuclei.

Let us consider the following operator (quantum Hamiltonian)

$H = H_N := \sum_{1 \leq j \leq N} H_{V,x^j} + \sum_{1 \leq j < k \leq N} |x_j - x_k|^{-1}$

on

$\mathcal{H} = \bigcap_{1 \leq n \leq N} \mathcal{H}_n$, \hspace{1cm} $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}^q)$

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with
\begin{equation}
H_V = -\Delta - V(x)
\end{equation}
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
\begin{equation}
V(x) = \sum_{1 \leq m \leq M} \frac{Z_m}{|x - y_m|}
\end{equation}
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
\begin{equation}
N \asymp Z = Z_1 + \ldots + Z_M, \quad Z_m \asymp Z \quad \forall m.
\end{equation}

Our purpose is to prove that at the distances \( a \gg Z^{-1} \) from the nuclei the electronic density
\begin{equation}
\rho_\Psi(x) = N \int |\Psi(x, x_2, \ldots, x_N)|^2 dx_2 \cdots dx_N
\end{equation}
is approximated in \( L^1(B(y_m, a)) \)-norm with the relative error by the Thomas-Fermi density.

**Theorem 1.1.** *In the described framework under assumption*
\begin{equation}
\min_{1 \leq m < m' \leq M} |y_m - y_{m'}| \geq Z^{-1/3+\sigma}
\end{equation}
*the following estimate holds:*
\begin{equation}
\|\rho_\Psi(x) - \rho^{\text{TF}}(x)\|_{L^1(Z)} \leq
C \begin{cases} 
Z a & \text{for } Z^{-1} \leq a \leq Z^{-2/3+\delta'}, \\
Z^{11/9-\delta/3} a^{4/3} & \text{for } Z^{-2/3+\delta'} \leq Z^{-1/3}, \\
Z^{5/9-\delta/3} a^{-2/3} & \text{for } Z^{-1/3} \leq a \leq Z^{-5/21+\delta''}.
\end{cases}
\end{equation}
Remark 1.2. (i) In [Ivr3] or $a = |x - y_m| \ll Z^{-1/3}$ we estimated the same norm for $\rho_\Psi - \rho_m$, where $\rho_m$ is the electronic density for a single atom in the model with no interactions between electrons. As $a \geq Z^{-11/21 - \delta}$ (1.8) is better than estimate (1.8) of that paper, which is in this case $Z^{11/6} a^{5/2}$.

(ii) Under assumption (1.7) with $\sigma = 0$ estimate (1.8) holds with $\delta = 0$.

In Section 2 we consider a one-particle Hamiltonian with a potential $V = V^0 + \varsigma U$ where $U$ is supported in $B(0, r)$ and satisfies $|U(x)| \leq 1$, $0 < \varsigma r \ll 1$ and explore its eigenvalues and projectors. In Section 2 we prove Theorem 1.1.

2Proof of Theorem 1.1

Similarly to (2.3) of [Ivr2] under assumption (1.7) we get

$$
\pm \varsigma \int U \rho_\Psi \, dx \leq \text{Tr}[(H_{W+\nu}^-) - \text{Tr}[H_{W+\pm \varsigma U+\nu}^-]] + CZ^{5/3 - \delta}
$$

with $\delta = \delta(\sigma) > 0$ as $\sigma > 0$ and $\delta = 0$ as $\sigma = 0$; now $U$ be supported in $\{x: a \leq \ell(x) \leq 2a\}$ where $Z^{-1} \leq a$ and satisfies $|U(x)| \leq \zeta^2$ and $0 < \varsigma \leq \epsilon$.

We rewrite the right-hand expression as

$$
- \int_0^\infty \text{Tr}(U \Theta(-H_{W\pm \varsigma U+\nu})) \, ds.
$$

After rescaling $x \mapsto xa^{-1}$, $\tau \mapsto \tau \zeta^{-2}$ we are in the semiclassical settings with $\hbar = 1/\alpha \zeta$.

Due to Tauberian method we can rewrite the integrand as

$$
\hbar^{-1} \int_{-\infty}^0 F_{t \to \hbar^{-1}\tau}(\bar{\chi}_T(t) \Gamma(U(x) u_s)) \, d\tau
$$

with an error, essentially not exceeding

$$
C \varsigma \zeta^{-1} \sup_{|\tau| \leq \epsilon_1} |F_{t \to \tau}(\bar{\chi}_T(t) \Gamma(|U(x)| u_s))|
$$

(we will write an exact statement late) where $\bar{\chi}_T(t) = \bar{\chi}(t/T)$, $\bar{\chi} \in \mathcal{C}_0^\infty([-1, 1])$, equal 1 on $[-\frac{1}{2}, \frac{1}{2}]$, $\hbar \leq T \leq \epsilon$ and
(2.5) $u_s(x, y, t)$ is a Schwartz kernel of $\exp(-ih^{-1}tH_{W+sU+\nu})$.

$\Gamma v = \int(\Gamma_x v) \, dx$ and $\Gamma_x v = v(x, x.\cdot)$.

Using two-terms successive approximation method with unperturbed operator $H_{W+\nu}$ and perturbation $sU$, we can evaluate

(2.6) $F_{t\to h^{-1}\tau}(\bar{\chi}_T(t)\Gamma(U(x)u_s))$

as

(2.7) $F_{t\to h^{-1}\tau}(\bar{\chi}_T(t)\Gamma(U(x)u_0))$

with an error, not exceeding $Ch^{-1}T^2\varsigma \times h^{-3}$. Indeed, the absolute value of $n$-th term is estimated by $Ch^{-1-n}T^n\varsigma^{n-1} \times h^{-3}$ for $n \geq 1$.

However, (2.7) is estimated by a better expression $Ch^{-2}$. It is due to semiclassical microlocal arguments applied to $\Gamma_x u$, in which case non-smoothness of $U$ plays no role. Indeed, $W \asymp Z\ell^{-1}$, and $0 \leq -\nu \leq CZ^{4/3}$, so for $\ell(x) \leq \epsilon Z^{-1}$ it $H_{W+\nu}$ is $x$-microhyperbolic on energy level 0. It is also $x$-microhyperbolic for $\ell(x) \leq \epsilon|\nu|^{1/4} \asymp \epsilon(Z - N)^{-1/3}$ and elliptic for $\ell(x) \geq \epsilon|\nu|^{1/4}$. Finally, as $(Z - N)_+ \gtrsim Z^{5/7}$ (and $|\nu| \gtrsim Z^{20/21}$) it follows from the partition-rescaling technique of Subsection 5.1.1 of [Ivr1].

Thus

(2.8) The absolute value of expression (2.4) does not exceed $C(T^{-1}h^{-2} + \varsigma Th^{-4})$.

On the other hand, without these microlocal arguments for $\varphi \in C_0^{\infty}([-1, -\frac{1}{2}], LT \geq h$

(2.9) $|\int_{-\infty}^{0} F_{t\to h^{-1}\tau}\varphi_L(\tau)(\bar{\chi}_T(t)\Gamma(U(x)(u_0 - u_s))) \, d\tau| \leq C_{k}\varsigma Ch^{-1}T^2\varsigma h^{-3} \times (h/TL)^kL$

and therefore if we replace here $\varphi_L(\tau)$ by 1 this would not exceed the same expression with $L = h/T$, i.e. $C_{k}\varsigma CT\varsigma h^{-3}$ and therefore

(2.10) $h^{-1}|\int_{-\infty}^{0} F_{t\to h^{-1}\tau}(\bar{\chi}_T(t)\Gamma(U(x)(u_s - u_0))) \, d\tau| \leq C(T^{-1}h^{-2} + \varsigma Th^{-4})$.

Minimizing by $T \in [h, 1]$ we get $C(\varsigma^{1/2}h^{-3} + h^{-2})$ for $T \asymp \min(h\varsigma^{-1/2}, 1)$. 4
Then

\[(2.11) \quad |\int U(x)(\rho(x) - \rho_{\text{TF}}(x))\, dx| \leq C(\zeta^{1/2}\zeta^3a^3 + \zeta^2a^2)\zeta^2 + C\zeta^{-1}Z^{5/3-\delta}\]

where we rescaled back and plugged \( h = 1/\zeta a \). Taking

\[U(x) = \text{sign}(\rho(x) - \rho_{\text{TF}}(x))\phi(x)\zeta^2\]

with \( \phi \geq 0 \) supported in \( \{x: a/3 \leq \ell(x) \leq 3a\} \) and equal 1 in \( Z = \{x: a \leq \ell(x) \leq 2a\} \) we get

\[\|\rho - \rho_{\text{TF}}\|_{L^1(Z)} \leq C(\zeta^{1/2}\zeta^3a^3 + \zeta^2a^2) + C\zeta^{-1}Z^{5/3-\delta}\zeta^{-2}.
\]

Next, optimizing by \( \zeta \propto (Z^{5/3-\delta}\zeta^{-5}a^{-3})^{2/3} \) as

\[(2.12) \quad Z^{5/3-\delta} \leq \zeta^5a^3\]

we get finally

\[(2.13) \quad CZ^{5/9-\delta/3}\zeta^{4/3}a^2 + C\zeta^2a^2\]

under assumptions \( \zeta a \geq 1 \) and \( (2.12) \).

If \( a \leq Z^{-1/3} \) we have \( \zeta = Z^{1/2}a^{-1/2} \) and the first assumption means that \( a \geq Z^{-1} \) and the second is fulfilled automatically so we arrive to the first case in

\[(2.14) \quad \|\rho(x) - \rho_{\text{TF}}(x)\|_{L^1(Z)} \leq \]

\[C \begin{cases}
Z^{11/9-\delta/3}a^{4/3} + Za & \text{for } Z^{-1} \leq a \leq Z^{-1/3}, \\
Z^{5/9-\delta/3}a^{-2/3} + a^{-2} & \text{for } Z^{-1/3} \leq a \leq Z^{-5/21+\delta''},
\end{cases}\]

If \( a \geq Z^{-1/3} \) we have \( \zeta = a^{-2} \) and \( (2.12) \) means that \( a \leq Z^{-5/21+\delta'} \) and we arrive to the second line in \( (2.14) \), and there the first term dominates.

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