On the regularity of the density of electronic wavefunctions

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Abstract. We prove that the electronic density of atomic and molecular eigenfunctions is smooth away from the nuclei. The result is proved without decay assumptions on the eigenfunctions.

1. Introduction and main results

We consider an $N$-electron molecule with $L$ fixed nuclei whose non-relativistic Hamiltonian is given by

$$H = H_{N,L}(\mathbf{R}, \mathbf{Z}) = \sum_{j=1}^{N} \left( -\Delta_j - \sum_{l=1}^{L} \frac{Z_l}{|x_j - R_l|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} + \sum_{1 \leq l < k \leq L} \frac{Z_l Z_k}{|R_l - R_k|},$$

where $\mathbf{R} = (R_1, R_2, \ldots, R_L) \in \mathbb{R}^{3L}$, $R_l \neq R_k$ for $k \neq l$, denote the positions of the $L$ nuclei whose positive charges are given by $\mathbf{Z} = (Z_1, Z_2, \ldots, Z_L)$. The positions of the $N$ electrons are denoted by $(x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}$, where $x_j$ denotes the position of the $j$-th electron in $\mathbb{R}^3$ and $\Delta = \sum_{j=1}^{N} \Delta_j$ is the $3N$-dimensional Laplacian.

For shortness, we will sometimes write (1.1) as

$$H = -\Delta + V.$$

The operator $H$ is selfadjoint on $L^2(\mathbb{R}^{3N})$ with operator domain $W^{2,2}(\mathbb{R}^{3N})$. We consider the eigenvalue problem

$$H \psi = E \psi,$$

with $\psi \in L^2(\mathbb{R}^{3N})$ and $E$ the real eigenvalue. We will assume, without loss, that the eigenfunction $\psi$ is real valued. For $x \in \mathbb{R}^3$ define

$$\psi_j(x) = \psi(x_1, \ldots, x_{j-1}, x, x_{j+1}, \ldots, x_N),$$

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and 
\[ d\hat{x}_j = dx_1 \cdots dx_{j-1} dx_{j+1} \cdots dx_N. \]
Then the density associated with \( \psi \) is defined as:
\[
(1.3) \quad \rho(x) = \sum_{j=1}^{N} \int \psi_j^2 \, d\hat{x}_j.
\]

**Theorem 1.1.** Let \( \psi \) satisfy (1.2). Then the associated density \( \rho \) satisfies
\[
(1.4) \quad \rho \in C^\infty(\mathbb{R}^3 \setminus \{R_1, \ldots, R_L\}).
\]

**Remark 1.2.** We remark that analogous natural smoothness results hold for the 2-electron density and the 1-electron density matrix, see [1].

**Remark 1.3.** The electron density plays the central role in various approximation schemes for the full 3\( N \)-dimensional Schrödinger equation for \( N \)-electron atoms and molecules (Thomas-Fermi, Hartree-Fock, and Density Functional Theory).

Strangely enough, the density \( \rho \) has only rarely been the subject of mathematical analysis, see [1], [2], and references therein. Our present results are not surprising—surprising is the fact that it has not been shown some decades ago. Since the eigenfunction \( \psi \) is real analytic away from the singularities of the potential one would even expect \( \rho \) also to be real analytic away from the nuclei.

**Remark 1.4.** Theorem 1.1 is an improvement of [1, Theorem 1] since we have no decay assumptions on \( \psi \). This improvement will come about by using Sobolev spaces instead of Hölder spaces.

For simplicity we will here only explicitly consider the case of atoms, i.e. we take \( L = 1 \) and can without loss of generality define \( R_1 = 0 \). To prove Theorem 1.1 it clearly suffices to prove
\[
(1.5) \quad \rho \in C^\infty(\mathbb{R}^3 \setminus \{0\})
\]
with \( \rho \) redefined by \( \rho(x) = \int \psi^2(x, x_2, \ldots, x_N) \, dx_2 \cdots dx_N \), which will be done below.

Let us recall the definition of Sobolev spaces (with integer exponent).

**Definition 1.5.** Let \( \Omega \subset \mathbb{R}^n \) be an open set. We define \( B^\infty(\Omega) \) as follows
\[
B^\infty(\Omega) = \{ f \in C^\infty(\mathbb{R}^n) \mid \text{supp} \, f \subset \Omega \text{ and } \partial^\alpha f \in L^2(\Omega) \text{ for all } \alpha \in \mathbb{N}^n, |\alpha| \leq k \}.
\]

**2. Differentiation of \( \psi \) ‘along’ singularities of \( V \)**

The key to the smoothness of the density is the understanding that one is allowed to differentiate ‘along’ singularities of the potential. The precise statement of this is given in Lemma 2.2. The statement and proof of this lemma is analogous to a similar result in [1, Proposition 2], the difference being that we here measure regularity of functions by demanding that they be in \( W^{2,2} \), whereas the analogous space in [1, Proposition 2] was the Lipschitz continuous functions \( C^{0,1} \).

**Definition 2.1.** Let \( \Omega \subset \mathbb{R}^n \) be an open set. We define \( B^\infty(\Omega) \) as follows
\[
B^\infty(\Omega) = \{ f \in C^\infty(\mathbb{R}^n) \mid \text{supp} \, f \subset \Omega \text{ and } \partial^\alpha f \in L^\infty(\mathbb{R}^n) \text{ for all } \alpha \in \mathbb{N}^n \}. \]
Lemma 2.2. Let $P, Q$ be a partition of $\{1, \ldots, N\}$ satisfying

\[ P \neq \emptyset, \quad P \cap Q = \emptyset, \quad P \cup Q = \{1, \ldots, N\} \]

Define, for $P, Q$ as above and $\epsilon > 0$

\[ U_P(\epsilon) = \left\{ (x_1, \ldots, x_N) \in \mathbb{R}^{3N} \mid |x_j| > \epsilon \text{ for } j \in P, \right. \]

\[ |x_j - x_k| > \epsilon \text{ for } j \in P, k \in Q \}. \tag{2.1} \]

Define also

\[ x_P = \frac{1}{\sqrt{|P|}} \sum_{j \in P} x_j, \]

and let $T$ be any orthogonal transformation of $\mathbb{R}^{3N}$ such that $T(x_1, \ldots, x_N) = (x_P, x')$ with $x' \in \mathbb{R}^{3N-3}$. Let $\psi$ satisfy (2.2) and let $\phi \in \mathcal{B}^\infty(U_P(\epsilon))$. Then

\[ \partial_{x_P}^\alpha((\phi\psi) \circ T^*) \in W^{2,2}(\mathbb{R}^{3N}) \text{ for all } \alpha \in \mathbb{N}^3. \]

We may assume without loss of generality that $P = \{1, \ldots, N_1\}$, with $N_1 \leq N$. Then the orthogonal transformation $T$ can be written as:

\[ T = \left( \begin{array}{cccc} \frac{1}{\sqrt{N_1}} & \ldots & 0 & \ldots \vspace{0.2cm} \frac{1}{\sqrt{N_1}} \\ t_1 & \ldots & 0 & \ldots \vspace{0.2cm} t_N \end{array} \right), \tag{2.2} \]

with the first row being understood as $3 \times 3$ matrices—first $N_1$ repetitions of $\frac{1}{\sqrt{N_1}} I_3$ and then $N - N_1$ repetitions of the $3 \times 3$ 0-matrix. The remaining part of the matrix,

\[ \tilde{T} = \left( \begin{array}{cccc} t_1 & \ldots & t_N \end{array} \right) \text{ with } t_j \in M_{3N-3,3}(\mathbb{R}), \tag{2.3} \]

is such that the complete matrix $T$ is orthogonal.

Let us write $\tilde{\psi} = \psi \circ T^*$. Notice that, since $\Delta$ is invariant under orthogonal transformations, $\tilde{\psi}$ satisfies

\[ -\Delta \tilde{\psi} + (V \circ T^*) \tilde{\psi} = E \tilde{\psi}. \tag{2.4} \]

We can now prove Lemma 2.2.

Proof. We will prove that for all $\phi \in \mathcal{B}^\infty(U_P(\epsilon(1-2^{-k})))$ we have $\partial_{x_P}^\alpha(\tilde{\phi}\tilde{\psi}) \in W^{2,2}(\mathbb{R}^{3N})$ for all $\gamma \in \mathbb{N}^3$ with $|\gamma| \leq k$, with $\tilde{\phi} = \phi \circ T^*$. The proof is by induction with respect to $k$. For $k = 0$ there is nothing to prove since $D(H) = W^{2,2}(\mathbb{R}^{3N})$. Let $k \geq 0$ and suppose that $\partial_{x_P}^\alpha(\tilde{\phi}\tilde{\psi}) \in W^{2,2}(\mathbb{R}^{3N})$ for all $\phi \in \mathcal{B}^\infty(U_P(\epsilon(1-2^{-k})))$ and all $\gamma \in \mathbb{N}^3$ with $|\gamma| \leq k$. Take now $\gamma \in \mathbb{N}^3$ with $|\gamma| = k + 1$. Let $\tilde{\phi} \in \mathcal{B}^\infty(U_P(\epsilon(1-2^{-(k+1)})))$. From the eigenfunction equation (2.4) for $\tilde{\psi}$ we get

\[ -\Delta(\tilde{\phi}\tilde{\psi}) = (-2 \nabla \tilde{\phi} \nabla \tilde{\psi} - \tilde{\psi} \Delta \tilde{\phi} + E \tilde{\phi} \tilde{\psi}) \]

\[ - \sum_{j=1}^N \frac{Z}{|x_j| \circ T^*} (\tilde{\phi}\tilde{\psi}) - \sum_{1 \leq j < k \leq N} \left( \frac{1}{|x_j - x_k| \circ T^*} \right) (\tilde{\phi}\tilde{\psi}). \tag{2.5} \]

Now we differentiate equation (2.5) with respect to $x_P$ (in the distributional sense).

By the induction hypothesis it is clear that

\[ \partial_{x_P}^\alpha(-2 \nabla \tilde{\phi} \nabla \tilde{\psi} - \tilde{\psi} \Delta \tilde{\phi} + E \tilde{\phi} \tilde{\psi}) \in L^2(\mathbb{R}^{3N}). \]

Notice that $\partial_{x_P}$ commutes with $|x_j|^{-1} \circ T^*$ for $j \in Q$ and with $|x_j - x_k|^{-1} \circ T^*$ for $j, k \in P$ or $j, k \in Q$. Furthermore, on $\text{supp} \tilde{\phi}$ the remaining parts of the potential, $|x_j|^{-1} \circ T^*$ for $j \in P$ and $|x_j - x_k|^{-1} \circ T^*$ with $j \in P, k \in Q$, are
bounded functions with bounded derivatives of arbitrary order, so we get, using the induction hypothesis that
\[ \partial_{x^p}^\gamma ((V \circ T^*)\tilde{\psi}) = (V \circ T^*)\partial_{x^p}^\gamma (\tilde{\psi}) + g, \]
where \( g \in W^{2,2}(\mathbb{R}^{3N}) \). Furthermore, by assumption we have \( \partial_{x^p}^\gamma (\tilde{\psi}) \in W^{1,2}(\mathbb{R}^{3N}) \). Therefore we obtain \( (V \circ T^*) (\partial_{x^p}^\gamma (\tilde{\psi})) \in L^2(\mathbb{R}^{3N}) \) since the operators \(|x_j|^{-1}\) and \(|x_j - x_k|^{-1}\) are bounded from \( W^{1,2}(\mathbb{R}^{3N}) \) to \( L^2(\mathbb{R}^{3N}) \) (see for instance \cite{3} p. 169).
Thus, in the sense of distributions, (2.5) implies
\[ \Delta \partial_{x^p}^\gamma (\tilde{\psi}) \in L^2(\mathbb{R}^{3N}). \]
Via standard elliptic regularity results, this implies that \( \partial_{x^p}^\gamma (\tilde{\psi}) \in W^{2,2}(\mathbb{R}^{3N}) \) and finishes the proof. \( \square \)

3. The differentiation of \( \rho \)

In this section we perform the differentiation of the density, as stated in (1.3). Let \( \phi \in C_0^\infty(\mathbb{R}^3 \setminus \{0\}) \). We will prove that
\[ \partial_{x^p}^\gamma (\phi^2 \rho) \in L^1(\mathbb{R}^3) \] for all \( \gamma \in \mathbb{N}^3 \).

By a Sobolev embedding theorem, we therefore get \( \phi^2 \rho \in C^\infty(\mathbb{R}^3) \), which implies (1.3), since \( \phi \in C_0^\infty(\mathbb{R}^3 \setminus \{0\}) \) was arbitrary.

We use the partition of unity introduced in \cite{1}. Let \( R > 0 \) be such that \( \{x \in \mathbb{R}^3 | |x| \leq R\} \cap \text{supp} \phi = \emptyset \). Let \( \chi_1, \chi_2 \) be a partition of unity in \( \mathbb{R}_+ \): \( \chi_1 + \chi_2 = 1 \), with \( \chi_1(x) = 1 \) on \( [0,R/(4N)] \), \( \text{supp} \chi_1 \subset [0,R/(2N)] \) and \( \chi_j \in C^\infty(\mathbb{R}_+) \) for \( j = 1, 2 \). We combine the \( \chi_j \)'s to make a partition of unity in \( \mathbb{R}^{3N} \). Obviously,
\[ 1 = \prod_{1 \leq j < k \leq N} \left( \chi_1(|x_j - x_k|) + \chi_2(|x_j - x_k|) \right). \]

Multiplying out the above product, we get sums of products of \( \chi_1 \)'s and \( \chi_2 \)'s. We introduce the following index sets to control these sums: Define first
\[ M = \{(j,k) \in \{1, \ldots, N\}^2 | j < k\}, \]
and let
\[ I \subset M, \quad J = M \setminus I. \]

Now define, for each pair \( I, J \) as above,
\[ \phi_I^2(x) = \left( \prod_{(j,k) \in I} \chi_1(|x_j - x_k|) \right) \left( \prod_{(j,k) \in J} \chi_2(|x_j - x_k|) \right). \]

Then we get
\[ 1 = \prod_{1 \leq j < k \leq N} \left( \chi_1 + \chi_2 \right)(|x_j - x_k|) = \sum_{I \subset M} \phi_I^2(x), \]
where the sum is over all subsets \( I \subset M \).

Therefore we have, with \( g_I = \psi^2 \phi_I^2 \),
\[ \rho(x_1) = \sum_{I \subset M} \int g_I(x_1,x_2, \ldots, x_N) \, dx_2 \cdots dx_N \equiv \sum_{I \subset M} \rho_I(x_1). \]

To verify (1.4) we have to prove that for every \( I \subset M \), \( \partial_{x^p}^\gamma (\phi^2 \rho_I) \in L^1(\mathbb{R}^3) \) for all \( \gamma \in \mathbb{N}^3 \). As in \cite{1}, for each \( I \subset M \) we can choose a \( P \) (depending on
This finishes the proof of (1.5) and hence of Theorem 1.1 for the atomic case.

Let \( u \in C_0^\infty(\mathbb{R}^3) \). Choose \( f \in C_0^\infty(\mathbb{R}^{3N-3}) \), with \( f \equiv 1 \) for \( |x| < 1 \), and let \( f_K(x) = f(x/K) \), \( K > 0 \). We calculate

\[
\int_{\mathbb{R}^3} (\partial_{x_1}^\gamma u)(x_1) (\phi^2 \rho_1)(x_1) \, dx_1 = \int_{\mathbb{R}^{3N}} (\partial_{x_1}^\gamma u)(x_1) (\phi^2 \gamma_1)(x_1, \ldots, x_N) \, dx_1 \cdots dx_N
\]

(3.2)

\[
= N_1^{-|\gamma|/2} \int_{\mathbb{R}^{3N}} (\partial_{x_p}^\gamma \tilde{u})(\phi^2 \gamma_1)(x_p, x') \, dx_p \, dx',
\]

depending on the coordinate transform given in Lemma 2.2 as specified in (2.2) and (2.3). Here \( \tilde{u} = u \circ T^* \) and similarly for the other functions. By Lebesgue integration theory it follows that (3.2) equals

\[
N_1^{-|\gamma|/2} \lim_{K \to \infty} \int_{\mathbb{R}^{3N}} (h_K \phi^2 \gamma_1)(x_p, x') \, dx_p \, dx',
\]

(3.3)

with \( h_K(x_p, x') = (\partial_{x_p}^\gamma \tilde{u})(x_p, x')f_K(x') \).

Noting that \( x_p = \sqrt{N_1} (x_1 - t_1' x') \), \( t_1' \) being the transposed of \( t_1 \), and that \( u \) and \( f_K \) are \( C_0^\infty \) functions, \( h_K \in C_0^\infty(\mathbb{R}^{3N}) \). Hence (3.3) equals

\[
(-1)^{|\gamma|} N_1^{-|\gamma|/2} \lim_{K \to \infty} \int_{\mathbb{R}^{3N}} \tilde{u} f_K v \, dx_p \, dx',
\]

(3.4)

with \( v(x_p, x') = \partial_{x_p}^\gamma (\phi^2 \gamma_1)(x_p, x') \). Here the derivative is taken in the distributional sense.

Suppose we have shown that \( v \in L^1(\mathbb{R}^{3N}) \), then by Lebesgue integration theory (3.4) equals

\[
(-1)^{|\gamma|} N_1^{-|\gamma|/2} \int_{\mathbb{R}^3} \tilde{u} v \, dx_1 \, dx',
\]

(3.5)

and by transforming again and applying Fubini’s theorem (3.3) equals

\[
(-1)^{|\gamma|} N_1^{-|\gamma|/2} \int_{\mathbb{R}^3} \tilde{u} v \, dx_1,
\]

(3.6)

with \( w(x_1) = \int_{\mathbb{R}^{3N-3}} (v \circ T)(x_1, \ldots, x_N) \, dx_2 \cdots dx_N, \, w \in L^1(\mathbb{R}^3) \). Combining (3.2) and (3.6) follows.

So to finish the proof of (1.3) it remains to verify that \( v \in L^1(\mathbb{R}^{3N}) \), which will follow via Lemma 2.2. In order to apply the lemma we need the following.

**Proposition 3.1.** Let \( u, v \in L^2(\mathbb{R}^n) \) and \( \partial_{x_i} u, \partial_{x_i} v \in L^2(\mathbb{R}^n) \) (distributional sense). Then

\[
\partial_{x_i}(uv) = (\partial_{x_i} u)v + u \partial_{x_i} v, \text{ in the distributional sense}.
\]

Proposition 3.1 is easy to prove by standard density arguments.

Remember that \( v = \partial_{x_p}^\gamma (\phi^2 \gamma_1) \), and that \( P \) was chosen such that \( \text{supp } \phi \cap \{ |x| \leq R \} = \emptyset \). This will be essential in the considerations below in order to apply Lemma 2.2.

This finishes the proof of (1.3) and hence of Theorem 1.1 for the atomic case.
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