THE ELECTRON DENSITY IS SMOOTH AWAY FROM THE NUCLEI

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Abstract. We prove that the electron densities of electronic eigenfunctions of atoms and molecules are smooth away from the nuclei.

1. Introduction and Statement of the Results.

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

$$H_{N,L}(\mathbf{R},\mathbf{Z}) = \sum_{j=1}^{N}\Big(-\Delta_j - \sum_{l=1}^{L}\frac{Z_l}{|x_j-R_l|}\Big) + \sum_{1\le i<j\le N}\frac{1}{|x_i-x_j|} + \sum_{1\le l<k\le L}\frac{Z_lZ_k}{|R_l-R_k|}, \tag{1.1}$$

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.

The operator $H_{N,L}(\mathbf{R},\mathbf{Z})$ depends parametrically on $\mathbf{R},\mathbf{Z},L,N$ and the last term in (1.1) corresponds to the internuclear repulsion which is just an additive term. It will play no role in this paper and we will hence neglect it, i.e. from now on we let

$$H = H_{N,L}(\mathbf{R},\mathbf{Z}) - \text{ internuclear repulsion.}$$

The operator H is selfadjoint on $L^2(\mathbb{R}^{3N})$ with operator domain $\mathcal{D}(H)=W^{2,2}(\mathbb{R}^{3N})$ and quadratic form domain $\mathcal{Q}(H)=W^{1,2}(\mathbb{R}^{3N})$, see e.g. Kato [8].

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We consider the eigenvalue problem

$$H\psi = (-\Delta + V)\psi = E\psi, \tag{1.2}$$

where the potential V is given by

$$V = -\sum_{j=1}^{N}\sum_{l=1}^{L} \frac{Z_l}{|x_j - R_l|} + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|}. \tag{1.3}$$

Of course the eigenfunction ψ and the associated eigenvalue E depend parametrically on $\mathbf{R}, \mathbf{Z}, L, N$. Since the potential V has singularities for $x_j = R_l$ and for $x_i = x_j$ one cannot expect classical solutions. In 1957 Kato showed [7] that any local solution ψ to (1.2) is locally Lipschitz, i.e.

$$\psi \in C^0_{\mathrm{loc}}(\mathbb{R}^{3N}) \text{ and } |\nabla\psi| \in L^\infty_{\mathrm{loc}}(\mathbb{R}^{3N}).$$

Kato also characterized the behaviour of such a solution near points where two particles are close to each other (Cusp conditions). (Extensions of these results on the regularity of ψ can be found in M. and T. Hoffmann-Ostenhof and Stremnitzer [6] and M. and T. Hoffmann-Ostenhof and Østergaard Sørensen [5]). Of course, away from the singularities of V, any local solution ψ of (1.2) is smooth by elliptic regularity.

Equation (1.2) is a partial differential equation in $3N$ variables and hence only certain one-electron cases can be solved analytically. (One-electron atoms and diatomic one-electron molecules with equal nuclear charges).

Most of the information about bound states of atoms and molecules that Chemists and Physicists want to know is encoded in equation (1.2). (Of course one can go beyond (1.2), for instance allow for nuclear motion, include relativistic corrections, etc.). Since the electrons are Fermions the physically relevant wavefunctions ψ have to satisfy the Pauli principle. This amounts to requiring that ψ transforms according to some specific irreducible representations of the symmetric group $\mathfrak{S}_N$. Our results will include this.

Already in the early times of quantum mechanics in the 1920's and the 1930's various attempts were made to replace the full $3N$-dimensional equation (1.2) by simpler (usually non-linear) ones in 3 dimensions (Thomas-Fermi theory and Hartree-Fock theory). The relation of these approximations with the N-electron Schrödinger equation has been analysed in detail for big atoms, see e.g. Lieb and Simon [10], Lieb [9], and Lieb and Simon [11].

One important observation and motivation for the development of these and other approximation schemes was the insight that in order to calculate the energy E or one- and two-electron operator expectation values there is no need for the full wave function $\psi(x_1, x_2, \ldots, x_N)$ but only for the **one-electron density** $\rho(x), x \in \mathbb{R}^3$, the **two-electron density** $\rho_2(x, x')$, $(x, x') \in \mathbb{R}^6$ and for the **one-electron density matrix** $\gamma_1(x, x')$, $(x, x') \in \mathbb{R}^6$. These quantities are defined as follows: Defining

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

and

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

and assuming without loss of generality that ψ is real valued (since the coefficients of H are real), the functions ρ, ρ_2, and γ_1 are given by

$$\rho(x) = \sum_{j=1}^{N} \int \psi_j^2 \, d\hat{x}_j, \tag{1.4}$$

$$\rho_2(x, x') = \sum_{1 \le i \ne j \le N} \int \psi_{i,j}^2 \, d\hat{x}_{i,j}, \tag{1.5}$$

and

$$\gamma_1(x, x') = \sum_{j=1}^{N} \int \psi_j(x)\psi_j(x') \, d\hat{x}_j. \tag{1.6}$$

Here $d\hat{x}_j$, respectively $d\hat{x}_{i,j}$, means integration over all variables except x_j, repectively x_i, x_j. Of course $\rho(x) = \gamma_1(x, x)$.

More recently very successful approximation schemes have been developped called Density Functional Theories (DFT). These schemes use some non-linear functionals in which only the one-electron density ρ occurs and lead to surprisingly good approximations to ground state energies and molecular geometries (see e.g. Eschrig [1]). However, their relation to the full Schrödinger equation remains unclear.

It is therefore surprising that the eigenfunction ψ and in particular the electron density ρ itself, defined in (1.4), have only rarely been the subject of mathematical analysis (see [5] and references therein).

Here we prove, based on recent work [5], natural smoothness results about the quantities defined in (1.4), (1.5), and (1.6).

We do not assume anything about the eigenvalue E—in particular, it could be an embedded eigenvalue. The only assumption is that ψ satisfies the following decay estimate:

$$|\psi(\mathbf{x})| \le ce^{-\lambda|\mathbf{x}|} \text{ for all } \mathbf{x} \in \mathbb{R}^{3N}, \tag{1.7}$$

for some $c, \lambda > 0$.

Remark 1.1. Since ψ is continuous, (1.7) is only an assumption on the behaviour near infinity. For references on the exponential decay of eigenfunctions, see e.g. Simon [12].

Remark 1.2. We only assume the exponential decay for simplicity. Our proofs extend to the case where the eigenfunction ψ decays faster than polynomially.

The main result of this paper is the following theorem:

Theorem 1.3. *Let ψ be an eigenfunction of H, satisfying (1.7). Let ρ, ρ_2, and γ_1 be as defined in* (1.4), (1.5), *and* (1.6), *and define furthermore $n(x) = \rho_2(x,x)$.*

Let $D = \{(x,x) \in \mathbb{R}^6\} \subset \mathbb{R}^6$, and define

$$\Sigma = \big(\{R_1, \dots, R_L\} \times \mathbb{R}^3\big) \cup \big(\mathbb{R}^3 \times \{R_1, \dots, R_L\}\big) \subset \mathbb{R}^6.$$

Then

$$\rho, n \in C^\infty(\mathbb{R}^3 \setminus \{R_1, \dots, R_L\}) \tag{1.8}$$

and

$$\rho_2 \in C^\infty(\mathbb{R}^6 \setminus (\Sigma \cup D)), \gamma_1 \in C^\infty(\mathbb{R}^6 \setminus \Sigma). \tag{1.9}$$

Furthermore, all the derivatives of ρ satisfy an exponential decay estimate near infinity: Let $\gamma \in \mathbb{N}^3$ be a multi-index. Then for all $\epsilon > 0$ there exists a constant $c = c(\gamma, \epsilon)$ such that

$$|\partial_x^\gamma \rho(x)| \le c e^{-(\lambda-\epsilon)|x|} \quad \textit{for all} \quad |x| > \max\{|R_1|, \dots, |R_L|\} + 1. \tag{1.10}$$

Similar results hold for n-electron densities and for n-electron density matrices.

Remark 1.4. For simplicity we will only prove Theorem 1.3 for atoms (i.e. for $L = 1$, $R_1 = 0$) and only indicate the necessary modifications for the molecular case. Moreover, we only explicitly treat the density ρ, the proofs in the cases of n, ρ_2, and γ_1 being essentially the same. Finally, it is enough to prove smoothness of each term $\int \psi_j^2 \, d\hat{x}_j$ in the sum (1.4), and we therefore restrict ourselves to

$$\int \psi_1^2 \, d\hat{x}_1 = \int \psi^2(x, x_2, \dots, x_N) \, dx_2 \cdots dx_N.$$

2. Additional regularity of eigenfunctions.

We will need to know something about the regularity properties of ψ in order to conclude that ρ is smooth. In order to study the regularity of ψ it is convenient to work in spaces of functions which are Hölder continuous. Let us recall the definition of Hölder continuity:

Definition 2.1. Let Ω be a domain in $\mathbb{R}^n$, $k \in \mathbb{N}$, and $\alpha \in (0,1]$. We say that a function u belongs to $C^{k,\alpha}(\Omega)$ whenever $u \in C^k(\Omega)$, and for all $\beta \in \mathbb{N}^n$ with $|\beta| = k$, and all open balls $B(x_0,r)$ with $\overline{B(x_0,r)} \subset \Omega$, we have

$$\sup_{x,y\in B(x_0,r),\, x\neq y} \frac{|\partial^\beta u(x) - \partial^\beta u(y)|}{|x-y|^\alpha} \leq C(x_0,r).$$

For any domain Ω', with $\overline{\Omega'} \subset \Omega$, we now define the following norms:

$$|u|_{C^{k,\alpha}(\Omega')} = \sum_{|\beta|\leq k} \|\partial^\beta u\|_{L^\infty(\Omega')} + \sum_{|\beta|=k} \sup_{x,y\in\Omega',\, x\neq y} \frac{|\partial^\beta u(x) - \partial^\beta u(y)|}{|x-y|^\alpha}.$$

We will need the following result on elliptic regularity in order to conclude that the solutions of elliptic second order equations with bounded coefficients are $C^{1,\alpha}$. The proposition is a reformulation of Corollary 8.12 in Gilbarg and Trudinger [4], adapted for our purposes:

Proposition 2.2. *Let Ω be a bounded domain in $\mathbb{R}^n$ and suppose $u \in W^{1,2}(\Omega)$ is a weak solution of $\Delta u + \sum_{j=1}^n b_j D_j u + Wu = g$ in Ω, where $b_j, W, g \in L^\infty(\Omega)$. Then $u \in C^{1,\alpha}(\Omega)$ for all $\alpha \in (0,1)$ and for any domain Ω', $\overline{\Omega'} \subset \Omega$ we have*

$$|u|_{C^{1,\alpha}(\Omega')} \leq C\big(\sup_\Omega |u| + \sup_\Omega |g|\big)$$

for $C = C(n, M, \mathrm{dist}(\Omega', \partial\Omega))$, with

$$\max_{j=1,\dots,n} \{1, \|b_j\|_{L^\infty(\Omega)}, \|W\|_{L^\infty(\Omega)}, \|g\|_{L^\infty(\Omega)}\} \leq M.$$

Our regularity result on ψ is the following:

Lemma 2.3. *Let ψ be an N-electron atomic eigenfunction satisfying the decay estimate (1.7). Let P and Q be a partition of $\{1,\dots,N\}$:*

$$\{1,\dots,N\} = P \cup Q, \quad P \cap Q = \emptyset, \quad P \neq \emptyset.$$

Define x_P as

$$x_P = \frac{1}{\sqrt{|P|}} \sum_{j\in P} x_j \in \mathbb{R}^3,$$

and let T be any orthogonal transformation such that $T(x_1,\dots,x_N) = (x_P, x')$ with $x' \in \mathbb{R}^{3N-3}$.

Let $\epsilon > 0$ be given and define $U_P \subset \mathbb{R}^{3N}$ as the open set:

$$
\begin{aligned}
U_P = \Big\{ (x_1, \dots, x_N) \in \mathbb{R}^{3N} \,\Big|\, & |x_j| > \epsilon \text{ for } j \in P, \\
& |x_j - x_k| > \epsilon \text{ for } j \in P, k \in Q \Big\}.
\end{aligned} \tag{2.1}
$$

Then

$$\partial^{\gamma}_{x_P}(\psi \circ T^*) \in C^{0,1}(TU_P) \quad \text{for all } \gamma \in \mathbb{N}^3.$$

Furthermore, the following a priori estimate holds:

$$
\begin{aligned}
\big|\nabla \partial^{\gamma}_{x_P}(\psi \circ T^*)(x_P, x')\big| + \big|\partial^{\gamma}_{x_P}(\psi \circ T^*)(x_P, x')\big| & \\
\le C e^{-\lambda|(x_P, x')|} & \quad \text{for all } (x_P, x') \in TU_P
\end{aligned}
$$

for some $C = C(\gamma) > 0$.

Remark 2.4. One could interpret U_P as a (very large) neighbourhood of a singularity $\mathbf{x}^0$ of V where the electrons with coordinates x_j with $j \in Q$ sit on the nucleus and the electrons with coordinates x_j with $j \in P$ sit on each other away from the nucleus, i.e. $\mathbf{x}^0 = (x_1^0, \cdots, x_N^0)$, with

$$
\begin{aligned}
x_j^0 &= 0 \qquad \text{for all } j \in Q, \\
x_j^0 &= y^0 \neq 0 \qquad \text{for all } j \in P.
\end{aligned}
$$

Notice that x_P is (up to a scalar multiple) the centre of mass of the electrons j with $j \in P$. Loosely speaking Lemma 2.3 then says that in the neighbourhood U_P, ψ is smooth with respect to the centre of mass coordinate x_P.

One can also consider $\mathbf{x}^0$ as a two-cluster singularity—one group of electrons on each other at the nucleus, another group of electrons on top of each other away from the nucleus. It is, of course, possible to have many clusters. Lemma 2.3 is a special case of a more general theorem: If we have any number of clusters which are separated from each other and from the nucleus, then the eigenfunction ψ can be differentiated any number of times with respect to the centre of mass of each cluster.

We only need the two-cluster version (see Lemma 2.3) in the present paper. The more general result will be used in a detailed investigation of the regularity of the wavefunction near all kinds of singularities of the potential (see [3]).

Remark 2.5. In the case of molecules the definition of U_P is slightly different:

$$U_{\mathrm{MOL}} = \Big\{(x_1, \dots, x_N) \in \mathbb{R}^{3N} \;\Big|\; \min_{1\le l\le L} |x_j - R_l| > \epsilon \text{ for } j \in P, \\ |x_j - x_k| > \epsilon \text{ for } j \in P, k \in Q\Big\}.$$

Apart from that, Lemma 2.3 remains unchanged.

Before we prove Lemma 2.3, let us fix some notation. We may assume without loss of generality that $P = \{1, \dots, N_1\}$, with $N_1 \le N$. Then any orthogonal transformation T satisfying the assumptions in the statement of Lemma 2.3 can be written as:

$$T = \begin{pmatrix} \frac{1}{\sqrt{N_1}} & \cdots & \frac{1}{\sqrt{N_1}} & 0 & \cdots & 0 \\ & & & & & \\ & & \tilde{T} & & & \\ & & & & & \end{pmatrix},$$

with the first row being understood as 3×3 matrices—first N_1 repetitions of $\frac{1}{\sqrt{N_1}} I_3$ and then $N - N_1$ repetitions of the 3×3 0-matrix. The remaining part of the matrix, $\tilde{T} \in M_{3N-3,3N}(\mathbb{R})$ is such that the complete matrix T is orthogonal. We will denote the $(3N-3) \times 3$-columns of $\tilde{T}$ by t_j, i.e.

$$\tilde{T} = \begin{pmatrix} t_1 & \cdots & t_N \end{pmatrix},$$

with $t_j \in M_{3N-3,3}(\mathbb{R})$. Then we get:

$$T^* = \begin{pmatrix} \frac{1}{\sqrt{N_1}} & t_1^* \\ \vdots & \vdots \\ \frac{1}{\sqrt{N_1}} & t_{N_1}^* \\ 0 & t_{N_1+1}^* \\ \vdots & \vdots \\ 0 & t_N^* \end{pmatrix}. \tag{2.2}$$

Proof. For the proof of Lemma 2.3 we first proceed as in M. and T. Hoffmann-Ostenhof and Østergaard Sørensen [5]: We make the 'Ansatz'

$$\psi = e^{F - F_1} \psi_1, \tag{2.3}$$

with

$$F = \sum_{j=1}^{N} -\frac{Z}{2}|x_j| + \sum_{1\leq j<k\leq N} \frac{1}{4}|x_j - x_k|,$$

and

$$F_1 = \sum_{j=1}^{N} -\frac{Z}{2}\sqrt{|x_j|^2+1} + \sum_{1\leq j<k\leq N} \frac{1}{4}\sqrt{|x_j - x_k|^2+1}.$$

Observing (see (1.3) with $L=1$, $R_1 = 0$),

$$\Delta F = V, \tag{2.4}$$

we get the following equation for ψ_1 using (1.2) and (2.3):

$$\Delta\psi_1 + 2\nabla(F-F_1)\cdot\nabla\psi_1 + \big(|\nabla(F-F_1)|^2 - \Delta F_1 + E\big)\psi_1 = 0. \tag{2.5}$$

Furthermore, F_1 has the same behaviour as F at infinity, so we get the following estimates:

$$\begin{aligned}&\|\partial^\beta F_1\|_{L^\infty(\mathbb{R}^{3N})}, \|F-F_1\|_{L^\infty(\mathbb{R}^{3N})}, \|\nabla(F-F_1)\|_{L^\infty(\mathbb{R}^{3N})}\\ &\qquad\qquad\leq C(N,Z,\beta)\,,\ \beta\in\mathbb{N}^{3N}, |\beta|>0.\end{aligned} \tag{2.6}$$

We will first investigate the necessary regularity properties of the prefactor $e^{F-F_1}\circ T^*$ in TU_P with respect to x_P. Then we will differentiate the equation (2.5) with respect to x_P and analyse the regularity of $\partial_{x_P}^\gamma(\psi_1\circ T^*)$ in TU_P.

In the coordinates defined by T we have

$$x_j = \frac{x_P}{\sqrt{N_1}} + t_j^* x' \qquad \text{for } j\leq N_1, \tag{2.7}$$

$$x_j = t_j^* x' \qquad \text{for } j > N_1. \tag{2.8}$$

So

$$x_j - x_k = (t_j^* - t_k^*)x' \text{ for } j,k\leq N_1 \text{ or } j,k>N_1.$$

In particular these last expressions are independent of x_P. So when we differentiate $F\circ T^*$ with respect to x_P, the only non-vanishing terms come from derivatives of $|x_j|\circ T^*$ with $j\leq N_1$ and $|x_j-x_k|\circ T^*$ with $j\leq N_1$, $k>N_1$. The definition of U_P implies that the function $\mathbf{x}\mapsto |x_j|$ is smooth with bounded derivatives on U_P for $j\leq N_1$, and $\mathbf{x}\mapsto|x_j-x_k|$ is smooth with bounded derivatives on U_P for $j\leq N_1$, $k>N_1$. Thus

$$\begin{aligned}&\|\nabla\partial_{x_P}^\gamma(F-F_1)\circ T^*\|_{L^\infty(TU_P)} + \|\partial_{x_P}^\gamma(F-F_1)\circ T^*\|_{L^\infty(TU_P)}\\ &\qquad\qquad\leq C(\gamma) \text{ for all } \gamma\in\mathbb{N}^3.\end{aligned} \tag{2.9}$$

Furthermore, we get using (2.6) that

$$\partial^{\gamma}_{x_P}\left(e^{F-F_1}\circ T^*\right) \in C^{0,1}(TU_P)\cap L^{\infty}(TU_P) \text{ for all } \gamma\in\mathbb{N}^3. \tag{2.10}$$

Hence, due to (2.3) and (2.9), it remains to study the regularity of $\psi_1 \circ T^*$.

In the rest of the proof we will use the following notation: We will write $\tilde{F}, \tilde{F}_1, \tilde{\psi}_1$ instead of $F\circ T^*, F_1\circ T^*, \psi_1\circ T^*$. In particular we have the following relation

$$\psi\circ T^* = e^{\tilde{F}-\tilde{F}_1}\tilde{\psi}_1.$$

Notice that since the Laplacian is invariant under orthogonal transformations we have the following equation for $\psi\circ T^*$:

$$-\Delta(\psi\circ T^*) + (V\circ T^*)(\psi\circ T^*) = E(\psi\circ T^*).$$

Now, once again using the invariance of the Laplacian and (2.4),

$$\Delta\tilde{F} = V\circ T^*,$$

so we get the following equation for $\tilde{\psi}_1$ (compare with (2.5)):

$$\begin{aligned} &L\tilde{\psi}_1 = 0,\\ &L = \Delta + 2\nabla(\tilde{F}-\tilde{F}_1)\cdot\nabla + \left(|\nabla(\tilde{F}-\tilde{F}_1)|^2 - \Delta\tilde{F}_1 + E\right). \end{aligned} \tag{2.11}$$

The analysis of $\tilde{\psi}_1$ will be based on the elliptic regularity result from Proposition 2.2. We shall proceed by induction and for this we will need the following open sets indexed by $l\in\mathbb{N}$:

$$U_l = \Big\{(x_1,\dots,x_N)\in\mathbb{R}^{3N}\ \Big|\ |x_j| > \epsilon(1-2^{-(l+1)}) \text{ for } j\in P,\\ |x_j - x_k| > \epsilon(1-2^{-(l+1)}) \text{ for } j\in P, k\in Q\Big\}.$$

It is clear that for $l_1 < l_2$ we have

$$U_P \subset U_{l_2} \subset U_{l_1} \subset U_0.$$

We will prove the following statement:

Statement. For all $\gamma\in\mathbb{N}^3$ we have

(1) $\partial^{\gamma}_{x_P}\tilde{\psi}_1 \in C^{1,\alpha}(TU_{|\gamma|})$ for all $\alpha\in(0,1)$.
(2) $\partial^{\gamma}_{x_P}\tilde{\psi}_1 \in W^{2,2}_{\mathrm{loc}}(TU_{|\gamma|})$.
(3) There exists $c = c(\gamma) > 0$ such that

$$|\nabla\partial^{\gamma}_{x_P}\tilde{\psi}_1(x_P,x')| + |\partial^{\gamma}_{x_P}\tilde{\psi}_1(x_P,x')| \le c e^{-\lambda|(x_P,x')|}$$

for all $(x_P,x')\in TU_{|\gamma|}$.

Let us start by noticing that once this statement is established Lemma 2.3 is proved.

The proof of the statement proceeds by induction with respect to $|\gamma|$.

In order to prove the statement for $|\gamma| = 0$, let us look at the equation (2.11). We get from Proposition 2.2 that

$$\tilde{\psi}_1 \in C^{1,\alpha}(TU_0),$$

since the coefficients of the equation (2.11) are bounded on TU_0, due to (2.6). This proves (1) for $|\gamma| = 0$.

We next prove that $\tilde{\psi}_1 \in W^{2,2}_{\rm loc}(TU_0)$. This is accomplished as follows: If we use that $\tilde{\psi}_1 \in C^{1,\alpha}(TU_0)$ and that the coefficients in the equation (2.11) (derivatives of $\tilde{F} - \tilde{F}_1$) are bounded (again using (2.6)), then it is easily seen from (2.11) that

$$\Delta\tilde{\psi}_1 \in L^2_{\rm loc}(TU_0).$$

Therefrom, we get via standard elliptic regularity results (see for instance Folland [2, Theorem 6.33]) that $\tilde{\psi}_1 \in W^{2,2}_{\rm loc}(TU_0)$.

Next, we verify the exponential decay estimate (3) for $|\gamma| = 0$. We know from the assumption (1.7) that $\tilde{\psi}_1$ decays exponentially, but we also need to prove it for $\nabla\tilde{\psi}_1$. This is done exactly as in the induction step below, using the exponential decay estimate (1.7). In order not to repeat the argument, we refer the reader to the induction step below.

Suppose now that we have proved (1)-(3) for all γ with $|\gamma| \leq k$. Take a γ with length $|\gamma| = k + 1$.

Differentiating the equation (2.11) for $\tilde{\psi}_1$ we get the following equation for $\partial^\gamma_{x_P}\tilde{\psi}_1$ (in the sense of distributions):

$$\begin{aligned}
&L(\partial^\gamma_{x_P}\tilde{\psi}_1) = f_\gamma,\\
&L = \Delta + 2\nabla(\tilde{F} - \tilde{F}_1)\cdot\nabla + \big(|\nabla(\tilde{F} - \tilde{F}_1)|^2 - \Delta\tilde{F}_1 + E\big),\\
&f_\gamma = -\sum_{\sigma+\mu=\gamma, |\mu|<|\gamma|}\Big(2\Big[\partial^\sigma_{x_P}\big(\nabla(\tilde{F} - \tilde{F}_1)\big)\Big]\cdot\nabla\partial^\mu_{x_P}\tilde{\psi}_1\\
&\qquad\qquad + \Big[\partial^\sigma_{x_P}\big(|\nabla(\tilde{F} - \tilde{F}_1)|^2 - \Delta\tilde{F}_1 + E\big)\Big]\,\partial^\mu_{x_P}\tilde{\psi}_1\Big).
\end{aligned} \tag{2.12}$$

In f_γ only partial derivatives of $\tilde{\psi}_1$ of length $\leq k$ occur.

It is clear that in (2.9) we may replace TU_P by TU_0. Therefore we get, using the induction hypothesis for (1), that $f_\gamma \in L^\infty(TU_{|\gamma|-1})$. A priori $\partial^\gamma_{x_P}\tilde{\psi}_1$ only satisfies the equation (2.12) in the distributional sense. In order to apply Proposition 2.2 we need that $\partial^\gamma_{x_P}\tilde{\psi}_1 \in W^{1,2}_{\rm loc}(U_{|\gamma|-1})$. However, this follows from the induction hypotheses for (2), and the definition of Sobolev spaces. Now, due to (2.9), the coefficients of L are bounded, and therefore we get from Proposition 2.2 that $\partial_{x_P}^{\gamma}\tilde{\psi}_1 \in C^{1,\alpha}(TU_{|\gamma|-1})$ for all $\alpha \in (0,1)$, proving (1). This together with (2.9) implies that $f_\gamma \in L^2_{\mathrm{loc}}(TU_{|\gamma|-1})$. Therefore, we get (invoking once again that $\partial_{x_P}^{\gamma}\tilde{\psi}_1 \in C^{1,\alpha}(TU_{|\gamma|-1})$ for all $\alpha \in (0,1)$ and (2.9)),

$$\Delta(\partial_{x_P}^{\gamma}\tilde{\psi}_1) \in L^2_{\mathrm{loc}}(TU_{|\gamma|-1}).$$

As before, via a standard elliptic regularity theorem (e.g. Folland [2, Lemma 6.32]), we see that $\partial_{x_P}^{\gamma}\tilde{\psi}_1 \in W^{2,2}_{\mathrm{loc}}(TU_{|\gamma|-1})$, and therefore (2) is proved.

Finally, we prove the exponential decay of $\partial_{x_P}^{\gamma}\tilde{\psi}_1$. Let us write $\epsilon_l = \epsilon/2^{l+3}$. Then we have for all $\mathbf{x} \in U_l$ that $\overline{B(\mathbf{x}, 2\epsilon_l)} \subset U_{l-1}$.

Since the equation (2.12) is satisfied on $TU_{|\gamma|-1}$ it is in particular satisfied on $TB(\mathbf{x}, 2\epsilon_{|\gamma|})$ for any $\mathbf{x} \in U_{|\gamma|}$. Applying Proposition 2.2 with $\Omega' = TB(\mathbf{x}, \epsilon_{|\gamma|})$, $\Omega = TB(\mathbf{x}, 2\epsilon_{|\gamma|})$, we get that

$$|\partial_{x_P}^{\sigma}\tilde{\psi}_1|_{C^{1,\alpha}(\Omega')} \leq C\left(\sup_{\Omega}|\partial_{x_P}^{\sigma}\tilde{\psi}_1| + \sup_{\Omega}|f_\sigma|\right).$$

Notice, using (2.9), that the coefficients in the differential operator L are uniformly bounded on all of TU_0. Furthermore, the derivatives of $\tilde{F}$ and $\tilde{F}_1$ in the expression for f_γ are also uniformly bounded on U_0—once again using (2.9). Therefore, using the induction hypothesis (3), we get for all $(x_P, x') \in TU_{|\gamma|}$:

$$\begin{aligned}
|\nabla\partial_{x_P}^{\sigma}\tilde{\psi}_1(x_P, x')| &\leq |\partial_{x_P}^{\sigma}\tilde{\psi}_1|_{C^{1,\alpha}(\Omega')} \\
&\leq C\left(\sup_{\Omega}|\partial_{x_P}^{\sigma}\tilde{\psi}_1| + \sup_{\Omega}|f_\sigma|\right) \\
&\leq C \sup_{(y_P,y')\in TB((x_P,x'),2\epsilon_{|\gamma|})} e^{-\lambda|(y_P,y')|} \\
&= Ce^{-\lambda|(x_P,x')|}.
\end{aligned}$$

In this last line the constant C does not depend on the position (x_P, x') of the ball, since the coefficients of the equation (2.12) are uniformly bounded on all TU_0. This proves (3) and thus finishes the induction. □

Remark 2.6. In the case of molecules we modify F and F_1 as follows:

$$F = \sum_{l=1}^{L}\sum_{j=1}^{N} -\frac{Z_l}{2}|x_j - R_l| + \sum_{1\leq j<k\leq N}\frac{1}{4}|x_j - x_k|,$$

and

$$F_1 = \sum_{l=1}^{L}\sum_{j=1}^{N} -\frac{Z_l}{2}\sqrt{|x_j - R_l|^2+1} + \sum_{1\leq j<k\leq N}\frac{1}{4}\sqrt{|x_j-x_k|^2+1}.$$

The rest of the proof is analogous.

3. The proof of Theorem 1.3

As noted in Remark 1.4 it is enough to prove smoothness of each individual term in (1.4). We therefore redefine ρ by

$$\rho(x) = \int \psi^2(x, x_2, \ldots, x_N)\, dx_2 \cdots dx_N.$$

Lemma 2.3 will be essential in order to prove the smoothness of ρ. It suffices to prove that $\rho \in C^\infty(\mathbb{R}^3 \setminus \overline{B(0,R)})$ for all $R > 0$. Therefore, let us assume that $|x| > R > 0$.

Remark 3.1. In the case of molecules we assume

$$\min_{1\leq l\leq L} |x - R_l| > R > 0,$$

and prove that $\rho \in C^\infty(\mathbb{R}^3 \setminus \left(\cup_{l=1}^{L}\overline{B(R_l,R)}\right))$.

Let χ_1, χ_2 be a partition of unity in $\mathbb{R}_+$: $\chi_1 + \chi_2 = 1$, $\chi_1(x) = 1$ on $[0, R/(4N)]$, $\operatorname{supp}\chi_1 \subset [0, R/(2N)]$ and $\chi_j \in C^\infty(\mathbb{R}_+)$ for $j = 1, 2$.

We combine the χ_j's to make a partition of unity in $\mathbb{R}^{3N}$. Obviously:

$$1 = \prod_{1\leq j<k\leq N} (\chi_1+\chi_2)(|x_j - x_k|).$$

Multiplying out the above product, we get sums of products of χ_1's and χ_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

$$\begin{aligned} I &\subset M,\\ J &= M \setminus I. \end{aligned}$$

Now define, for each pair I, J as above,

$$\phi_I(\mathbf{x}) = \left(\prod_{(j,k)\in I}\chi_1(|x_j-x_k|)\right)\left(\prod_{(j,k)\in J}\chi_2(|x_j-x_k|)\right).$$

Then we get

$$1 = \prod_{1\leq j<k\leq N} (\chi_1 + \chi_2)(|x_j - x_k|) = \sum_{I\subset M} \phi_I(\mathbf{x}),$$

where the sum is over all subsets $I \subset M$.

Therefore we obtain:

$$\begin{aligned}\rho(x_1) &= \int_{\mathbb{R}^{3(N-1)}} \psi^2(x_1, x_2, \ldots, x_N)\, dx_2 \cdots dx_N \\ &= \sum_{I\subset M} \int \psi^2(x_1, x_2, \ldots, x_N)\phi_I(x_1, x_2, \ldots, x_N)\, dx_2 \cdots dx_N \\ &\equiv \sum_{I\subset M} \rho_I(x_1).\end{aligned}$$

We will prove smoothness of each of the individual ρ_I's, so let us pick and fix an arbitrary $I \subset M$. Our strategy is to associate to I a subset P of $\{1, \ldots, N\}$ such that Lemma 2.3 is applicable, i.e. such that $\operatorname{supp}\phi_I \subset U_P$ with U_P defined in (2.1) with a suitable $\epsilon > 0$.

Remark 3.2. To motivate the determination of P and hence the coordinate x_P with respect to which we are allowed to differentiate, let us consider the following example: Let $N = 3$ and $I = \{(1, 2), (2, 3)\}$ and $J = \{(1, 3)\}$. Then we have on the support of ϕ_I that $|x_1 - x_2| \leq \frac{R}{6}$ (due to the $\operatorname{supp}\chi_1$) and since $|x_1| > R$, $|x_2| \geq \frac{5R}{6}$. Further, due to the $\operatorname{supp}\chi_2$, we have $|x_1 - x_3| \geq \frac{R}{12}$. Suppose now, we would choose $P = \{1, 2\}$ and $Q = \{3\}$, then, according to (2.1),

$$U_P = \{(x_1, x_2, x_3)\big||x_1| > \epsilon, |x_2| > \epsilon, |x_1 - x_3| > \epsilon, |x_2 - x_3| > \epsilon\},$$

for some $\epsilon > 0$. But then $\operatorname{supp}\phi_I \not\subset U_P$, since $\operatorname{supp}\phi_I$ contains points with $x_2 = x_3$. On the other hand one easily checks that the choice $P = \{1, 2, 3\}$ is the right one. This example shows that we cannot just choose P to be $\{1\} \cup \{j \leq N\big|(1, j) \in I\}$. On the other hand P cannot be too big: For $N = 3$, $I = \{(1, 2)\}$, $J = \{(1, 3), (2, 3)\}$ it is easily seen that with $P = \{1, 2, 3\}$, $\operatorname{supp}\phi_I$ contains points with $x_3 = 0$ and therefore $\operatorname{supp}\phi_I \not\subset U_P$.

Physically speaking, we divide the N electrons into 2 clusters. The electrons j with $j \in P$ define the 'maximal cluster' of electrons containing the electron 1. This will be done via an equivalence relation below. Note that the (three-dimensional) variable $x_P = \frac{1}{\sqrt{|P|}} \sum_{j\in P} x_j$ is (up to a scalar multiple) the centre (centre of mass) of the maximal cluster.

Let $\sim$ denote the equivalence relation on $\{1, \ldots, N\}^2$ generated by I and let P denote the equivalence class of 1.

Explicitly this means that $j \sim k$ if either $j = k$ or there exists a sequence $j_1, \dots, j_l$ with $j_s \in \{1, \dots, N\}$ for $1 \le s \le l$ and with $j_s \neq j_t$ for $s \neq t$, such that

(i) $(j, j_1) \in I$ or $(j_1, j) \in I$,
(ii) $(j_s, j_{s+1}) \in I$ or $(j_{s+1}, j_s) \in I$, for $1 \le s \le l-1$,
(iii) $(j_l, k) \in I$ or $(k, j_l) \in I$.

Clearly

$$l \le N - 2. \tag{3.1}$$

Thus $P = \{j \,|\, j \sim 1\}$, $Q = \{1, \dots, N\} \setminus P$. Notice that $P \neq \emptyset$. In order to be able to apply Lemma 2.3, we have to show that $\operatorname{supp} \phi_I \subset U_P$ (with a suitable choice of ϵ in the definition of U_P).

Let $j \in P$, then $j \sim 1$ and we can choose a sequence $j_1, \dots, j_l$ according to the above. Taking into account $|x_1| > R$ we have

$$|x_j| \ge R - |x_1 - x_j|.$$

Further, with

$$|x_1 - x_j| \le |x_1 - x_{j_1}| + \sum_{s=1}^{l-1} |x_{j_s} - x_{j_{s+1}}| + |x_{j_l} - x_j|,$$

the length scale of the cut-off's and (3.1) we obtain that

$$j \in P \Rightarrow \operatorname{supp} \phi_I \subset \{(x_1, \dots, x_N) \in \mathbb{R}^{3N} \,\big|\, |x_j| > R/4\}. \tag{3.2}$$

Remark 3.3. In the case of molecules we get

$$j \in P \Rightarrow \operatorname{supp} \phi_I \subset \{(x_1, \dots, x_N) \in \mathbb{R}^{3N} \,\big|\, \min_{1 \le l \le L} |x_j - R_l| > R/4\}.$$

Furthermore, suppose $j \in P$, $k \in Q$, then it is clear that $(j,k) \in J$ or $(k,j) \in J$ (because if $(j,k) \in I$, then $1 \sim j \sim k$ and therefore $k \in P$), and therefore:

$$j \in P, k \in Q \Rightarrow \operatorname{supp} \phi_I \subset \{(x_1, \dots, x_N) \in \mathbb{R}^{3N} \,\big|\, |x_j - x_k| > R/(4N)\}. \tag{3.3}$$

Using (3.2) and (3.3) we see that $\operatorname{supp} \phi_I \subset U_P$, with $\epsilon = \frac{R}{4N}$ in the definition (2.1) of U_P. Hence we get from Lemma 2.3 that $\psi \circ T^*$ is (infinitely often) differentiable with respect to the coordinate $x_P = \frac{1}{\sqrt{|P|}} \sum_{j \in P} x_j$ on the support of $\phi_I \circ T^*$.

Denote $g_I = \psi^2 \phi_I$, and note that all partial derivatives of ϕ_I are bounded. We get from Lemma 2.3 that

$$\begin{aligned} &\partial_{x_P}^{\gamma}(g_I \circ T^*) \in C^{0,1}(\mathbb{R}^{3N}), \\ &|\partial_{x_P}^{\gamma}(g_I \circ T^*)(x_P, x')| \le c_\gamma e^{-\lambda|(x_P, x')|} \text{ for all } (x_P, x') \in \mathbb{R}^{3N}. \end{aligned} \tag{3.4}$$

Now, we are ready to prove the smoothness of the electron density. We calculate (using the notation from (2.2), and (2.7) and (2.8)):

$$
\begin{aligned}
\rho_I(x) &= \int_{\mathbb{R}^{3N-3}} g_I(x, x_2, \dots, x_N)\, dx_2 \cdots dx_N \\
&= \int_{\mathbb{R}^{3N}} g_I(x_1, \dots, x_N)\delta(x - x_1)\, dx_1 dx_2 \cdots dx_N \\
&= \int_{\mathbb{R}^{3N}} (g_I \circ T^*)(x_P, x')\delta(x - \tfrac{x_P}{\sqrt{N_1}} - t_1^* x')\, dx_P\, dx' \\
&= \int_{\mathbb{R}^{3N-3}} (g_I \circ T^*)(\sqrt{N_1}(x - t_1^* x'), x')\, dx' \qquad (3.5)
\end{aligned}
$$

Using (3.4) and Lebesgue integration theory, we obtain via the chain rule:

$$
\begin{aligned}
\partial_x^\gamma \rho_I(x) =& \partial_x^\gamma \Big(\int \big(g_I \circ T^*\big)\big(\sqrt{N_1}(x - t_1^* x'), x'\big)\, dx' \Big) \\
=& \big(\sqrt{N_1}\big)^{|\gamma|} \int \big(\partial_{x_P}^\gamma (g_I \circ T^*)\big)\big(\sqrt{N_1}(x - t_1^* x'), x'\big)\, dx'.
\end{aligned}
$$

This proves that ρ is smooth away from the nucleus.

The exponential decay of the derivatives of ρ_I is a consequence of (3.4). This can be seen by a similar calculation as in (3.5) but in reversed order:

$$
\begin{aligned}
|\partial_x^\gamma \rho_I(x)| &\le \big(\sqrt{N_1}\big)^{|\gamma|} \int \Big| \big(\partial_{x_P}^\gamma (g_I \circ T^*)\big)\big(\sqrt{N_1}(x - t_1^* x'), x'\big) \Big|\, dx' \\
&\le c \int e^{-\lambda |(\sqrt{N_1}(x - t_1^* x'), x')|}\, dx' \\
&= c \int (e^{-\lambda |\mathbf{x}|} \circ T^*)(x_P, x')\delta\big(x - \tfrac{x_P}{\sqrt{N_1}} - t_1^* x'\big)\, dx_P\, dx' \\
&= c \int e^{-\lambda |\mathbf{x}|}\delta(x - x_1)\, dx_1 \cdots dx_N \\
&= c \int e^{-\lambda |(x, x_2, \dots, x_N)|}\, dx_2 \cdots dx_N.
\end{aligned}
$$

Let us write $(x, x_2, \dots, x_N) = (x, z)$. Then for all $\epsilon \in (0, 1)$:

$$
|(x, z)| = (1 - \epsilon)|(x, z)| + \epsilon|(x, z)| \ge (1 - \epsilon)|x| + \epsilon|z|.
$$

Therefore

$$
\begin{aligned}
\int e^{-\lambda |(x,z)|}\, dz &\le e^{-\lambda(1-\epsilon)|x_1|} \int e^{-\lambda \epsilon |z|}\, dz \\
&= c e^{-\lambda(1-\epsilon)|x_1|}.
\end{aligned}
$$

This verifies inequality (1.10) and finishes the proof of Theorem 1.3. ☐

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