# NON-ISOTROPIC CUSP CONDITIONS AND REGULARITY OF THE ELECTRON DENSITY OF MOLECULES AT THE NUCLEI

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Abstract. We investigate regularity properties of molecular one-electron densities $\rho$ near the nuclei. In particular we derive a representation

$$\rho(x) = e^{\mathcal{F}(x)}\mu(x)$$

with an explicit function $\mathcal{F}$, only depending on the nuclear charges and the positions of the nuclei, such that $\mu \in C^{1,1}(\mathbb{R}^3)$, i.e., $\mu$ has locally essentially bounded second derivatives. An example constructed using Hydrogenic eigenfunctions shows that this regularity result is sharp. For atomic eigenfunctions which are either even or odd with respect to inversion in the origin, we prove that $\mu$ is even $C^{2,\alpha}(\mathbb{R}^3)$ for all $\alpha \in (0,1)$. Placing one nucleus at the origin we study $\rho$ in polar coordinates $x = r\omega$ and investigate $\frac{\partial}{\partial r}\rho(r,\omega)$ and $\frac{\partial^2}{\partial r^2}\rho(r,\omega)$ for fixed $\omega$ as $r$ tends to zero. We prove non-isotropic cusp conditions of first and second order, which generalize Kato's classical result.

## 1. Introduction and statement of the results

We consider a non-relativistic $N$-electron molecule with the nuclei fixed in $\mathbb{R}^3$. The Hamiltonian describing the system is given by

$$H = \sum_{j=1}^{N}\Big(-\Delta_j - \sum_{k=1}^{K}\frac{Z_k}{|x_j - R_k|}\Big) + \sum_{1\le i<j\le N}\frac{1}{|x_i - x_j|}. \tag{1.1}$$

Here the $R_k$, $k = 1,\dots,K$, $R_i \neq R_j$ for $i \neq j$, denote the positions of the (fixed) nuclei in $\mathbb{R}^3$ with charges $Z_1,\dots,Z_K$, and the $x_j = (x_{j,1}, x_{j,2}, x_{j,3}) \in \mathbb{R}^3$, $j = 1,\dots,N$, denote the positions of the electrons. The $\Delta_j$, $j = 1,\dots,N$, are the associated Laplacians so that $\Delta = \sum_{j=1}^{N}\Delta_j$ is the $3N$-dimensional Laplacian. Let $\mathbf{x} = (x_1, x_2, \dots, x_N) \in \mathbb{R}^{3N}$ and $\nabla = (\nabla_1,\dots,\nabla_N)$ denote the points in

*Date*: March 7, 2006.

$\mathbb{R}^{3N}$ and the $3N$-dimensional gradient operator respectively. We write $H = -\Delta + V$ where $V$ is the multiplicative potential

$$V(\mathbf{x}) = -\sum_{j=1}^{N}\sum_{k=1}^{K} \frac{Z_k}{|x_j - R_k|} + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}. \tag{1.2}$$

Here we neglect the internuclear repulsion $W = \sum_{1\le k<\ell\le K}^{K} \frac{Z_k Z_\ell}{|R_k - R_\ell|}$ which is just an additive term in the fixed-nuclei approximation.

The operator $H$ is selfadjoint with operator domain $\mathcal{D}(H) = W^{2,2}(\mathbb{R}^{3N})$ and form domain $\mathcal{Q}(H) = W^{1,2}(\mathbb{R}^{3N})$ [14].

Let $\psi$ be an eigenfunction of $H$ corresponding to an eigenvalue $E \in \mathbb{R}$, that is,

$$H\psi = E\psi. \tag{1.3}$$

We shall here only consider eigenfunctions $\psi \in L^2(\mathbb{R}^{3N})$[1].

Note that physical molecular eigenfunctions have to satisfy the Pauli principle. This is however irrelevant to our results and we impose no such condition.

The operator in (1.1) (possibly with the addition of the internuclear repulsion $W$) can be considered as the standard model for atoms and molecules in quantum mechanics. The analysis of $H$ is fundamental for the understanding of the properties of atoms, molecules or, more generally, of matter[2].

It is well known that every eigenfunction $\psi$ of $H$ is Lipschitz-continuous [13] and real analytic away from the points in configuration space $\mathbb{R}^{3N}$ where the potential $V$ defined in (1.2) is singular (see [12, Section 7.5, pp. 177–180]). In this paper we investigate regularity properties of the electron density $\rho$ associated to an eigenfunction $\psi$. The density $\rho$ is defined by

$$\rho(x) = \sum_{j=1}^{N} \rho_j(x) = \sum_{j=1}^{N} \int_{\mathbb{R}^{3N-3}} |\psi(x, \hat{\mathbf{x}}_j)|^2 \, d\hat{\mathbf{x}}_j \tag{1.4}$$

where we use the notation

$$\hat{\mathbf{x}}_j := (x_1, \dots, x_{j-1}, x_{j+1}, \dots, x_N),$$

and

$$d\hat{\mathbf{x}}_j := dx_1 \dots dx_{j-1} dx_{j+1} \dots dx_N,$$

[1]For scattering problems and for solid state physics, solutions to (1.3) which are not in $L^2$ are also important.

[2]For some problems it is of course necessary to include nuclear motion, and in the presence of heavy nuclei relativistic effects have to be accounted for.

and, by abuse of notation, we identify $(x_1, \dots, x_{j-1}, x, x_{j+1}, \dots, x_N)$ with $(x, \hat{\mathbf{x}}_j)$.

We assume throughout when studying $\rho$ stemming from some eigenfunction $\psi$ that

$$|\psi(\mathbf{x})| \le C_0 e^{-\gamma_0 |\mathbf{x}|} \text{ for all } \mathbf{x} \in \mathbb{R}^{3N} \tag{1.5}$$

for some $C_0, \gamma_0 > 0$. By [10, Theorem 1.2] (see also [10, Remark 1.7]) this implies the existence of constants $C_1, \gamma_1 > 0$ such that

$$\big|\nabla\psi(\mathbf{x})\big| \le C_1\, e^{-\gamma_1|\mathbf{x}|} \quad \text{ for almost all } \mathbf{x} \in \mathbb{R}^{3N}. \tag{1.6}$$

Since $\psi$ is continuous, (1.5) is only an assumption on the behaviour at infinity. For references on the exponential decay of eigenfunctions, see e.g. Agmon [1], Froese and Herbst [8], and Simon [19]. The proofs of our results rely (if not indicated otherwise) on some kind of decay-rate for $\psi$; exponential decay is not essential, but assumed for convenience. Note that (1.5) and (1.6) imply that $\rho$ is Lipschitz continuous in $\mathbb{R}^3$ by Lebesgue's theorem on dominated convergence.

In [6] we showed that $\rho$ is real analytic away from the nuclei ($\rho \in C^\omega(\mathbb{R}^3 \setminus \{R_1, \dots, R_K\})$); for earlier results see also [10], [4] and [5]. Note that the proof of the analyticity does *not* require any decay of $\psi$ (apart from $\psi \in W^{2,2}(\mathbb{R}^{3N})$). That $\rho$ itself is not analytic in all of $\mathbb{R}^3$ is already clear for the ground state of the Hydrogen atom ($N = K = 1; R_1 = 0, Z_1 = 1$): $\psi(x) = e^{-|x|/2}$ so that the associated $\rho$ (up to a normalization constant) equals $e^{-|x|}$; hence $\rho$ is just Lipschitz continuous near the origin.

For the atomic case ($K = 1; R_1 = 0, Z_1 = Z$) a quantity studied earlier is the spherical average of $\rho$ which, in polar coordinates $x = r\omega$ with $r = |x|$ and $\omega = x/|x|$, is defined by

$$\widetilde{\rho}(r) = \int_{\mathbb{S}^2} \rho(r\omega)\, d\omega\ , \quad r \in [0, \infty). \tag{1.7}$$

The above mentioned analyticity result implies that $\widetilde{\rho} \in C^\omega((0,\infty))$. The existence of $\widetilde{\rho}\,'(0)$ and the so-called **cusp condition**

$$\widetilde{\rho}\,'(0) = -Z\widetilde{\rho}(0) \tag{1.8}$$

follow from a similar result of Kato [13] for $\psi$ itself; see also [11] and [10, Remark 1.13]. The existence of $\widetilde{\rho}\,''(0)$ and an implicit formula for it was proved in [10, Theorem 1.11]; see (1.29) below for the exact statement.

In [7] the present authors generalized the results of Kato for $\psi$ considerably for the Hamiltonian in (1.1). In the present paper we obtain results, partly in the spirit of these findings, for the density $\rho$. In particular, we prove results on the regularity of the density $\rho$ at the nuclei and derive identities which the first and second radial derivatives of $\rho$ satisfy. These identities can be interpreted as cusp conditions (analogously to (1.8)). The methods developed in [10] play an essential role in the proofs of these results.

We indicate the importance of the electron density in quantum mechanics. From the eigenfunction $\psi$ it is, in principle, possible to calculate the energy, various expectation values, etc.; but $\psi$ depends on $3N$ variables. Physicists and chemists usually aim at understanding atomic and molecular properties by means of the electron density which is just a function on $\mathbb{R}^3$ and can be visualized. The density also has an immediate probabilistic interpretation.

In computational chemistry density functional methods are of increasing importance for calculations of ground state energies of large molecules. Thereby the energy is approximated by minimizing a 'density functional' which depends nonlinearly and nonlocally upon the density. The minimizing function is believed to be a good approximation to the density itself. The relationship between most of these functionals and the full $N$-electron Schrödinger equation remains unclear though. One exception is of course the archetype density functional theory, the Thomas-Fermi theory, which is mathematically and physically interesting, and very well understood, see [18] and [16]. For an interesting recent review on various mathematical problems related to the many models in computational chemistry, see [15]. For some work on the density $\rho$ from a numerical point of view, related to regularity questions, see [2].

Questions concerning the one-electron density $\rho$, as defined by (1.4), pose some challenging mathematical problems. Results as given in the present paper contribute to a better understanding of the physics of atoms and molecules and in addition should have relevance for computational quantum chemistry.

In the following we use the standard definition and notation for Hölder continuity and Lipschitz continuity, see e.g. [9]. Let $f : \mathbb{R}^n \supset \Omega \to \mathbb{R}$, then $f \in C^{k,\alpha}(\Omega)$ means, for $\alpha = 0$, that $f$ is $k$ times continuously differentiable, for $\alpha \in (0,1]$ that the $k$-th partial derivatives of $f$ are Hölder continuous with exponent $\alpha$. In the case $k = 0$, we often write $C^\alpha(\Omega) := C^{0,\alpha}(\Omega)$ when $\alpha \in (0,1)$.

The main result of the present paper is the following.

**Theorem 1.1.** *Let $\psi \in L^2(\mathbb{R}^{3N})$ be a molecular or atomic $N$-electron eigenfunction, i.e., $\psi$ satisfies* (1.3)*, with associated density $\rho$. Define*

*$\mathcal{F}:\mathbb{R}^3\to\mathbb{R}$ by*

$$\mathcal{F}(x) = -\sum_{k=1}^{K} Z_k|x-R_k|. \tag{1.9}$$

*Then*

$$\rho(x) = e^{\mathcal{F}(x)}\mu(x) \tag{1.10}$$

*with*

$$\mu \in C^{1,1}(\mathbb{R}^3). \tag{1.11}$$

*This representation is optimal in the following sense: There is no function $\widetilde{\mathcal{F}}:\mathbb{R}^3\to\mathbb{R}$ depending only on $Z_1,\dots,Z_K$, $R_1,\dots,R_K$, but neither on $N$, $\rho$, nor $E$, with the property that $e^{-\widetilde{\mathcal{F}}}\rho$ is in $C^2(\mathbb{R}^3)$.*

*Furthermore, $\mu$ admits the following representation:*
*There exist $C_1,\dots,C_K\in\mathbb{R}^3$ and $\nu:\mathbb{R}^3\to\mathbb{R}$ such that*

$$\mu(x) = \nu(x) + \sum_{k=1}^{K}|x-R_k|^2\big(C_k\cdot\frac{x-R_k}{|x-R_k|}\big), \tag{1.12}$$

*with*

$$\nu \in C^{2,\alpha}(\mathbb{R}^3) \text{ for all } \alpha\in(0,1). \tag{1.13}$$

**Remark 1.2.** In the case of atoms ($K=1; R_1=0, Z_1=Z$), the statement of the theorem reads: There exists $C\in\mathbb{R}^3$ such that

$$\rho(x) = e^{-Z|x|}\mu(x), \quad \mu(x) = \nu(x) + |x|^2\big(C\cdot\frac{x}{|x|}\big) \tag{1.14}$$

with

$$\nu \in C^{2,\alpha}(\mathbb{R}^3) \text{ for all } \alpha\in(0,1). \tag{1.15}$$

To simplify the exposition, we shall give the proof of Theorem 1.1 only in the case of atoms. The proof easily generalizes to the case of several nuclei.

**Remark 1.3.** It will be evident from the proof that the result (appropriately reformulated) also holds for each $\rho_j$ seperately (see (1.4)). The same is true for the results below.

*Proof of the optimality*: We study 'Hydrogenic atoms' ($N=K=1; R_1=0, Z_1=Z$) and use the notation (contrary to the rest of the paper) $x=(x_1,x_2,x_3)\in\mathbb{R}^3$, $r=|x|$. In this case, the operator in (1.1) reduces to $H_Z=-\Delta_x - Z/|x|$. We will present an example where, no matter what the choice of $\widetilde{\mathcal{F}}$ (as in the theorem), $\mu=e^{-\widetilde{\mathcal{F}}}\rho$ cannot be $C^2$. The argument resembles the proof of the corresponding result in [7].

The $1s$ eigenfunction is $\psi_{1s}(x) = e^{-Zr/2}$ with $H_Z\psi_{1s} = -(Z^2/4)\psi_{1s}$ and the associated density is $\rho_{1s}(x) = e^{-Zr}$. The $2s$ and $2p$ eigenfunctions are

$$\psi_{2s}(x) = (1 - \tfrac{Z}{4}r)e^{-Zr/4}, \qquad \psi_{2p}(x) = x_1 e^{-Zr/4}.$$

Both satisfy $H_Z\psi = E\psi$ with $E = -Z^2/16$. The associated densities are

$$\rho_{2s}(x) = \psi_{2s}^2(x) = (1 - \tfrac{Z}{4}r)^2 e^{-Zr/2}, \quad \rho_{2p}(x) = \psi_{2p}^2(x) = x_1^2 e^{-Zr/2}.$$

Consider now $\psi_{\mathrm{mixed}} = \psi_{2s} + \psi_{2p}$ and

$$\rho_{\mathrm{mixed}} = \psi_{\mathrm{mixed}}^2 = \rho_{2s} + \rho_{2p} + 2\psi_{2s}\psi_{2p}.$$

A simple calculation shows that

$$e^{Zr}\rho_{2s}, e^{Zr}\rho_{2p} \in C^{2,1}(\mathbb{R}^3),$$

but $e^{Zr}\rho_{\mathrm{mixed}}$ is just $C^{1,1}$, since the mixed derivative $\partial_{x_2}\partial_{x_1}$ of

$$e^{Zr}\psi_{2s}\psi_{2p} = x_1 e^{Zr/2}(1 - \tfrac{Z}{4})$$

does not exist at $x = 0$.

But if $\rho = e^{\widetilde{\mathcal{F}}}\mu$ with $\mu \in C^2$, then

$$\frac{\mu_{\mathrm{mixed}}}{\mu_{1s}} = \frac{e^{-\widetilde{\mathcal{F}}}\rho_{\mathrm{mixed}}}{e^{-\widetilde{\mathcal{F}}}e^{-Zr}} = e^{Zr}\rho_{\mathrm{mixed}}$$

should also be $C^2$, a contradiction. □

Note that $\psi_{2s}(x) = \psi_{2s}(-x)$ and $\psi_{2p}(x) = -\psi_{2p}(-x)$, but their linear combination $\psi$ is neither even nor odd.

**Remark 1.4.** The representation of $\rho$ as a product $\rho = e^{\mathcal{F}}\mu$ with a fixed 'universal' $\mathcal{F}$ such that $\mu$ is by one degree smoother than $\rho$ corresponds to Theorem 1.1 in [7] where a similar result was obtained for the eigenfunction $\psi$ itself. In that case though, the correponding $\mathcal{F}$ is more complicated since many-particle interactions have to be taken into account. For some interesting recent investigation in connection with Jastrow factors from a numerical point of view, see [3].

The proof of Theorem 1.1 will be given in the next section. Here we just mention that $\rho$ satisfies an inhomogeneous Schrödinger equation whose investigation is crucial for regularity results like the above, as well as it was for the results in [10]. Let $H$ be given by (1.1) and consider an eigenfunction $\psi$ satisfying (1.3). To simplify notation we assume without loss that $\psi$ is real. The equation

$$\int_{\mathbb{R}^{3N-3}} \psi(x, \hat{\mathbf{x}}_j)(H - E)\psi(x, \hat{\mathbf{x}}_j)\, d\hat{\mathbf{x}}_j = 0 \tag{1.16}$$

leads to an equation (in the sense of distributions) for $\rho_j$, namely,

$$\Big(-\frac{1}{2}\Delta-\sum_{k=1}^{K}\frac{Z_k}{|x-R_k|}\Big)\rho_j+h_j=0. \tag{1.17}$$

Summing (1.17) over $j$ we obtain the equation for $\rho$,

$$\Big(-\frac{1}{2}\Delta-\sum_{k=1}^{K}\frac{Z_k}{|x-R_k|}\Big)\rho+h=0, \tag{1.18}$$

with $h=\sum_{j=1}^{N}h_j$. The functions $h_j$ will be given explicitely in Section 2; see (2.3).

In [10] we considered the spherically averaged density $\widetilde{\rho}$ (as defined by (1.7)) for the atomic case. The regularity of $\widetilde{h}$ (the spherical average of $h$ above) was crucial for the results obtained there. Here we study the *non-averaged* density $\rho$ for the general case of molecules. Again, the regularity of $h$ is essential for our results.

We continue to consider $\rho$ in the neighbourhood of one nucleus with charge $Z$. Without loss we can place this nucleus at the origin.

The equations (1.12) and (1.13) show that it is natural to consider the behaviour of $\rho(r\omega)$ for fixed $\omega$ as $r$ tends to zero.

**Theorem 1.5.** *Let $\psi\in L^2(\mathbb{R}^{3N})$ be a molecular or atomic eigenfunction, i.e., $\psi$ satisfies* (1.3)*, with associated density $\rho$. Assume without loss that $R_1=0$ and write $Z$ instead of $Z_1$. Let $r_0=\min_{k>1}|R_k|$ ($r_0=\infty$ for atoms) and let $\omega\in\mathbb{S}^2$ be fixed.*

(i) *The function $r\mapsto\rho(r,\omega):=\rho(r\omega)$, $r\in[0,r_0)$, satisfies*

$$\rho(\cdot,\omega)\in C^{2,\alpha}([0,r_0)) \text{ for all } \alpha\in(0,1). \tag{1.19}$$

(ii) *Denote by $'$ the derivative $\frac{d}{dr}$, and define*

$$\eta(x)=e^{Z|x|}\rho(x)\ ,\ \chi=\eta-r^2(C\cdot\omega), \tag{1.20}$$

*where $C\in\mathbb{R}^3$ is the constant $C_1$ in* (1.12) *(resp. $C$ in* (1.14)*). Then*

$$\eta\in C^{1,1}(B(0,r_0))\ ,\ \chi\in C^{2,\alpha}(B(0,r_0)) \text{ for all } \alpha\in(0,1), \tag{1.21}$$

*and*

$$\rho'(0,\omega)=-Z\rho(0)+\omega\cdot(\nabla\eta)(0), \tag{1.22}$$

$$\rho''(0,\omega)=Z^2\rho(0)+2\omega\cdot[C-Z(\nabla\eta)(0)]+\omega\cdot\big((D^2\chi)(0)\omega\big). \tag{1.23}$$

*Here $(D^2\chi)(0)$ is the Hessian matrix of $\chi$ evaluated at the origin.*

**Remark 1.6.**

(i) For atoms, $\eta$ equals $\mu$ from Theorem 1.1 and $\chi$ equals $\nu$ from Remark 1.2.
(ii) Note that (1.19) trivially implies that $\rho(r,\omega) = e^{-Zr}\eta(r,\omega)$ with $\eta(\cdot,\omega) \in C^{2,\alpha}([0,r_0))$ for all $\alpha \in (0,1)$. Compare with (1.10), (1.11).
(iii) In [10, Theorem 1.11] it was proved that $\widetilde{\rho}$ defined by (1.7) belongs to $C^2([0,r_0)) \cap C^{2,\alpha}((0,r_0))$ for all $\alpha \in (0,1)$. (The proof in [10] for the atomic case easily generalizes to the molecular case.) Reading the proof of [10, Theorem 1.11] carefully, one sees that it in fact yields $\widetilde{\rho} \in C^{2,\alpha}([0,r_0))$. The statement in (1.19) shows that for fixed $\omega \in \mathbb{S}^2$ this holds already for $\rho(\cdot,\omega)$, i.e., without averaging.
(iv) The identities (1.22) and (1.23) can be considered as **non-isotropic cusp conditions of first and second order**. They generalize the cusp condition (1.8), as well as the previously mentioned result in [10] for $\widetilde{\rho}''(0)$; more on this in Remark 1.8 (ii) below. See also the second order cusp conditions obtained in [7] for the eigenfunction $\psi$ itself.
(v) It is worth noting that (1.22) and (1.23) can be interpreted as a structural result for the density $\rho$: From Theorem 1.5 it follows that in a neighbourhood of a nucleus (which is at the origin), $\rho$ satisfies (for all $\alpha \in (0,1)$)

$$\rho(r,\omega) = \rho(0) + r\phi_1(\omega) + r^2\phi_2(\omega) + O(r^{2+\alpha})\ ,\ r \downarrow 0, \tag{1.24}$$

and (1.22), (1.23) show that $\phi_1$ is a linear and $\phi_2$ a quadratic polynomial restricted to $\mathbb{S}^2$.
It is a natural question whether (1.24) extends to higher orders.

We continue with the atomic case. In view of Remark 1.2, (1.14) and the considerations after the proof of the optimal regularity of $\mu$ in Theorem 1.1, the following theorem is natural.

**Theorem 1.7.** *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction with associated density $\rho$. Suppose that*

$$|\psi(\mathbf{x})| = |\psi(-\mathbf{x})| \text{ for all } \mathbf{x} \in \mathbb{R}^{3N}. \tag{1.25}$$

*Then $\rho$ satisfies*

$$\rho(x) = e^{-Z|x|}\mu(x),\ \ \mu \in C^{2,\alpha}(\mathbb{R}^3) \text{ for all } \alpha \in (0,1). \tag{1.26}$$

*Furthermore,*

$$\rho'(0,\omega) = -Z\rho(0)\ ,\quad \rho''(0,\omega) = Z^2\rho(0) + \omega \cdot \big((D^2\mu)(0)\omega\big). \tag{1.27}$$

*We also have*

$$\rho''(0,\omega) = \frac{2}{3}\big(Z^2\rho(0) + h(0,\omega)\big) + \frac{1}{3}\lim_{r\downarrow 0}\frac{(\mathcal{L}^2\rho)(r,\omega)}{r^2}, \tag{1.28}$$

*with* $h$ *from* (1.18), *and* $\mathcal{L}^2/r^2$ *the angular part of* $-\Delta$, *i.e.,* $\Delta = \partial^2/\partial r^2 + (2/r)\partial/\partial r - \mathcal{L}^2/r^2$.

**Remark 1.8.**

(i) In this case $\mu = \nu = \chi = \eta$ , as can be seen from Remark 1.6 (i) and the proof of the theorem.

(ii) Note that (1.27) shows that the cusp condition (1.8) in this case holds for fixed angle $\omega \in \mathbb{S}^2$ without averaging. Further, taking the spherical average of (1.28), we get the formula for $\widetilde{\rho}''(0)$ obtained in [10, Theorem 1.11 (iv)]:

$$\widetilde{\rho}''(0) = \frac{2}{3}\big(Z^2\widetilde{\rho}(0) + \widetilde{h}(0)\big). \tag{1.29}$$

To see this note that for all $r > 0$

$$\int_{\mathbb{S}^2} 1\cdot(\mathcal{L}^2\rho)(r,\omega)\,d\omega = \int_{\mathbb{S}^2}(\mathcal{L}^2 1)\cdot\rho(r,\omega)\,d\omega = 0.$$

Note that $\widetilde{\rho}''(0) \geq 0$, since

$$\widetilde{h}(r) \geq \epsilon\widetilde{\rho}(r)$$

for some $\epsilon \geq 0$ [10, Theorem 1.11]. This positivity is not an obvious consequence of the formula in (1.27).

(iii) As can be seen from the proof of Theorem 1.7, $h \in C^{\alpha}(\mathbb{R}^3)$ for all $\alpha \in (0,1)$ in this case.

## 2. Proofs

*Proof of Theorem 1.1*: As noted in Remark 1.2, we shall give the proof only in the case of atoms ($K = 1; R_1 = 0, Z_1 = Z$).

For the regularity questions concerning $\rho$ defined in (1.4) it suffices to consider the (non-symmetrized) density $\rho_1$ defined by

$$\begin{aligned}\rho_1(x) &= \int_{\mathbb{R}^{3N-3}} |\psi(x,x_2,\dots,x_N)|^2\,dx_2\cdots dx_N \\ &= \int_{\mathbb{R}^{3N-3}} |\psi(x,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1 \end{aligned} \tag{2.1}$$

with $x \in \mathbb{R}^3, \hat{\mathbf{x}}_1 = (x_2,\dots,x_N) \in \mathbb{R}^{3N-3}$.

As explained in (1.16)–(1.18) $\rho_1$ satisfies the Schrödinger-type equation

$$-\Delta\rho_1 - \frac{2Z}{|x|}\rho_1 + 2h_1 = 0, \tag{2.2}$$

where the function $h_1$ is given by

$$h_1(x) = J_1 - J_2 + J_3 - E\rho_1(x), \tag{2.3}$$

$$J_1(x) = \sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}} |\nabla_j\psi|^2\, d\hat{\mathbf{x}}_1\ , \quad J_2(x) = \sum_{j=2}^{N}\int_{\mathbb{R}^{3N-3}} \frac{Z}{|x_j|}\psi^2\, d\hat{\mathbf{x}}_1,$$

$$J_3(x) = \sum_{k=2}^{N}\int_{\mathbb{R}^{3N-3}} \frac{1}{|x-x_k|}\psi^2\, d\hat{\mathbf{x}}_1 + \sum_{2\le j<k\le N}\int_{\mathbb{R}^{3N-3}} \frac{1}{|x_j-x_k|}\psi^2\, d\hat{\mathbf{x}}_1.$$

(We will henceforth partly omit the variables in the integrands). Using the exponential decay of $\psi$ (1.5) and of $\nabla\psi$ (1.6) one can prove that $h_1 \in L^\infty(\mathbb{R}^3)$ (for details, see [10, Theorem 1.11]).

Making the *Ansatz*

$$\rho_1(x) = e^{-Z|x|}\mu_1(x) \tag{2.4}$$

and using (2.2), we get that $\mu_1$ satisfies the equation

$$\Delta\mu_1 = 2e^{Z|x|}h_1 + 2Z\omega\cdot\nabla\mu_1 - Z^2\mu_1. \tag{2.5}$$

Here $\omega = \frac{x}{|x|}$. Since $\rho_1 \in C^{0,1}(\mathbb{R}^3)$ (as mentioned in the introduction), also $\mu_1 \in C^{0,1}(\mathbb{R}^3)$. Clearly, the function $x \mapsto \omega$ belongs to $L^\infty(\mathbb{R}^3)$. The fact that also $x \mapsto h_1(x)$ is in $L^\infty(\mathbb{R}^3)$ gives, by standard elliptic regularity [17, Theorem 10.2], that

$$\mu_1 \in C^{1,\alpha}(\mathbb{R}^3) \text{ for all } \alpha\in(0,1). \tag{2.6}$$

Our aim is to prove more, namely that

$$\Delta\mu_1 = c_1\cdot\omega + g\ ,\ c_1\in\mathbb{R}^3\ ,\ g\in C^\alpha(\mathbb{R}^3) \text{ for all } \alpha\in(0,1). \tag{2.7}$$

Since, by (2.6), $\nabla\mu_1$ is continuous at the origin, the term $2Z\omega\cdot\nabla\mu_1$ behaves like $c_1^{(1)}\cdot\omega$ ($c_1^{(1)} = 2Z\nabla\mu_1(0)\in\mathbb{R}^3$) at the origin. It turns out that generally $h_1$ is discontinuous at the origin, also behaving like $c_1^{(2)}\cdot\omega$ ($c_1^{(2)}\in\mathbb{R}^3$). However, one can solve the equation $\Delta u_1 = c_1\cdot\omega$ ($c_1\in\mathbb{R}^3$) explicitely, and one gets that the solution $u_1$ is $C^{1,1}$. From standard elliptic regularity, the other terms give contributions which belong to $C^{2,\alpha}(\mathbb{R}^3)$. Below we give the details.

First, we write

$$2Z\omega\cdot\nabla\mu_1(x) = c_1^{(1)}\cdot\omega + g_1(x)\ ,\ g_1\in C^\alpha(\mathbb{R}^3)\,,\ \alpha\in(0,1), \tag{2.8}$$
$$c_1^{(1)} = 2Z\nabla\mu_1(0)\ ,\ g_1(x) = 2Z\omega\cdot\big(\nabla\mu_1(x)-\nabla\mu_1(0)\big).$$

That $g_1\in C^\alpha(\mathbb{R}^3)$, $\alpha\in(0,1)$, follows from Lemma A.1 in Appendix A.

We next consider $h_1$ as defined in (2.3). We will show the following:

**Lemma 2.1.** *Let $h_1$ be as in* (2.3)*. Then there exist $c_1^{(2)}\in\mathbb{R}^3$, $G:\mathbb{R}^3\to\mathbb{R}$, such that*

$$h_1 = c_1^{(2)}\cdot\omega + G\,,\ G\in C^\alpha(\mathbb{R}^3)\,,\ \alpha\in(0,1). \tag{2.9}$$

Before proving Lemma 2.1, we finish the proof of Theorem 1.1.

Lemma 2.1 and Lemma A.1 in Appendix A imply that

$$(e^{Z|x|}-1)h_1\in C^\alpha(\mathbb{R}^3)\quad\text{ for all }\alpha\in(0,1),$$

and it therefore follows from (2.5), (2.6), (2.8), and (2.9) that

$$\Delta\mu_1 = c_1\cdot\omega + g\ ,\qquad c_1 = c_1^{(1)} + 2c_1^{(2)}\in\mathbb{R}^3\ , \tag{2.10}$$
$$g\in C^\alpha(\mathbb{R}^3)\,,\ \alpha\in(0,1).$$

This is (2.7), which we aimed to prove.

A simple computation shows that the function $u_1(x) = \frac{1}{6}|x|^2c_1\cdot\omega = \frac{|x|}{6}c_1\cdot x$ satisfies $\Delta u_1 = c_1\cdot\omega$, and so $\nu_1 = \mu_1 - u_1$ solves $\Delta\nu_1 = g$, $g\in C^\alpha(\mathbb{R}^3)$, $\alpha\in(0,1)$. From standard elliptic regularity theory [17, Theorem 10.3] follows that $\nu_1\in C^{2,\alpha}(\mathbb{R}^3)$, $\alpha\in(0,1)$. Note that due to Lemma A.1, $u_1\in C^{1,1}(\mathbb{R}^3)$, and so

$$\mu_1 = \nu_1 + u_1 = \nu_1 + \frac{1}{6}|x|^2(c_1\cdot\omega)\in C^{1,1}(\mathbb{R}^3). \tag{2.11}$$

This finishes the proof of Theorem 1.1 for atoms, with

$$C = \frac{1}{6}\sum_{j=1}^{N}c_j, \tag{2.12}$$

where $c_j$ is the contribution from $\rho_j$. □

It remains to prove Lemma 2.1.

*Proof of Lemma 2.1*: The proof is essentially a tedious but elementary verification, the idea being to isolate and extract the most singular term of $h_1$. Part of this has been carried out in [10], and, in order not to repeat the details, we refer to that paper whenever possible. We also use the same notation.

Define

$$\psi_1 = e^{-(F-F_1)}\psi, \tag{2.13}$$

with

$$F(\mathbf{x}) = -\frac{Z}{2}\sum_{j=1}^{N}|x_j| + \frac{1}{4}\sum_{1\le j<k\le N}|x_j - x_k|, \tag{2.14}$$

$$F_1(\mathbf{x}) = -\frac{Z}{2}\sum_{j=1}^{N}\sqrt{|x_j|^2+1} + \frac{1}{4}\sum_{1\le j<k\le N}\sqrt{|x_j - x_k|^2+1}. \tag{2.15}$$

Then it follows from [10, Proposition 1.5] that $\psi_1 \in C^{1,\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$.
In [10, Lemma 3.5 (i)] it is proven that (with the notation from (2.3)) $J_2, J_3 \in C^{\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$. Furthermore, using (2.13), $J_1$ is written as

$$J_1(x) = \int_{\mathbb{R}^{3N-3}} |\nabla\psi|^2\, d\hat{\mathbf{x}}_1 = I_1 + I_2 + I_3 + I_4 + I_5 + I_6,$$

where

$$\begin{aligned}
I_1(x) &= \sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}} |\nabla_j F|^2\psi^2\, d\hat{\mathbf{x}}_1,\\
I_2(x) &= \sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}} |\nabla_j F_1|^2\psi^2\, d\hat{\mathbf{x}}_1,\\
I_3(x) &= -2\sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}} (\nabla_j F\cdot\nabla_j F_1)\psi^2\, d\hat{\mathbf{x}}_1,\\
I_4(x) &= \sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}} e^{2(F-F_1)}|\nabla_j\psi_1|^2\, d\hat{\mathbf{x}}_1,\\
I_5(x) &= 2\sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}} (\nabla_j F\cdot\nabla_j\psi_1)e^{2(F-F_1)}\psi_1\, d\hat{\mathbf{x}}_1,\\
I_6(x) &= -2\sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}} (\nabla_j F_1\cdot\nabla_j\psi_1)e^{2(F-F_1)}\psi_1\, d\hat{\mathbf{x}}_1.
\end{aligned}$$

It is proven in [10, p. 93, bottom] that

$$I_2, I_4, I_6 \in C^{\alpha}(\mathbb{R}^3)\ ,\ \alpha \in (0,1).$$

It is also proven in [10] that

$$
\begin{aligned}
I_1(x) &= \int_{\mathbb{R}^{3N-3}} |\nabla_1 F|^2 \psi^2 \, d\hat{\mathbf{x}}_1 + \tilde{I}_1(x), \\
I_3(x) &= -2\int_{\mathbb{R}^{3N-3}} (\nabla_1 F \cdot \nabla_1 F_1)\psi^2 \, d\hat{\mathbf{x}}_1 + \tilde{I}_3(x), \\
I_5(x) &= 2\int_{\mathbb{R}^{3N-3}} (\nabla_1 F \cdot \nabla_1 \psi_1) e^{2(F-F_1)}\psi_1 \, d\hat{\mathbf{x}}_1 + \tilde{I}_5(x),
\end{aligned}
\tag{2.16}
$$

with $\tilde{I}_j \in C^\alpha(\mathbb{R}^3), \alpha \in (0,1)$. (For $\tilde{I}_1$, this is [10, (3.52) and until (3.53)]; for $\tilde{I}_3$ and $\tilde{I}_5$, this is [10, (3.55) and (3.56), and between]).

Now, (see (2.14))

$$
|\nabla_1 F|^2(x, \hat{\mathbf{x}}_1) = \frac{Z^2}{4} - \frac{Z}{4}\frac{x}{|x|} \cdot \sum_{j=2}^{N} \frac{x - x_j}{|x - x_j|} + \frac{1}{16}\Big(\sum_{j=2}^{N} \frac{x - x_j}{|x - x_j|}\Big)^2.
$$

Therefore, we write

$$
\begin{aligned}
\int_{\mathbb{R}^{3N-3}} |\nabla_1 F|^2 \psi^2 \, d\hat{\mathbf{x}}_1 &= I_{1,1}(x) + I_{1,2}(x), \\
I_{1,1}(x) &= -\frac{Z}{4}\frac{x}{|x|} \cdot \int_{\mathbb{R}^{3N-3}} \sum_{j=2}^{N} \frac{x - x_j}{|x - x_j|}\psi^2 \, d\hat{\mathbf{x}}_1, \\
I_{1,2}(x) &= \int_{\mathbb{R}^{3N-3}} \Big\{\frac{Z^2}{4} + \frac{1}{16}\Big(\sum_{j=2}^{N} \frac{x - x_j}{|x - x_j|}\Big)^2\Big\}\psi^2 \, d\hat{\mathbf{x}}_1.
\end{aligned}
$$

The proof that $I_{1,2}$ belongs to $C^\alpha(\mathbb{R}^3)$, $\alpha \in (0,1)$, is also in [10] (between (3.52) and (3.55)).

For $I_{1,1}$, we write $I_{1,1}(x) = \frac{Z}{4}\frac{x}{|x|} \cdot \mathrm{Int}_1(x)$, with

$$
\mathrm{Int}_1(x) = -\int_{\mathbb{R}^{3N-3}} \sum_{j=2}^{N} \frac{x - x_j}{|x - x_j|}\psi^2 \, d\hat{\mathbf{x}}_1. \tag{2.17}
$$

The function $\mathrm{Int}_1$ belongs to $C^\alpha(\mathbb{R}^3)$, $\alpha \in (0,1)$. This follows by arguments as for the integral

$$
\int \frac{1}{|x - x_k|}\big(x \cdot (x - x_k)\psi^2\big) \, dx_2 \cdots dx_N
$$

in [10] (see between (3.54) and (3.55)).

Therefore (with $\omega = \frac{x}{|x|}$),

$$
I_{1,1}(x) = c_{1,1} \cdot \omega + g_{1,1}(x) \ , \ g_{1,1} \in C^\alpha(\mathbb{R}^3) \ , \ \alpha \in (0,1), \tag{2.18}
$$

$$
c_{1,1} = \frac{Z}{4}\mathrm{Int}_1(0) \ , \ g_{1,1}(x) = \frac{Z}{4}\omega \cdot \big(\mathrm{Int}_1(x) - \mathrm{Int}_1(0)\big). \tag{2.19}
$$

That $g_{1,1} \in C^{\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$, follows from Lemma A.1 in Appendix A.

Next we consider $I_3$ (see (2.16)). Since

$$\nabla_1 F(x, \hat{\mathbf{x}}_1) = -\frac{Z}{2}\frac{x}{|x|} + \frac{1}{4}\sum_{j=2}^{N} \frac{x - x_j}{|x - x_j|}, \tag{2.20}$$
$$\nabla_1 F_1(x, \hat{\mathbf{x}}_1) = -\frac{Z}{2}\frac{x}{\sqrt{|x|^2+1}} + \frac{1}{4}\sum_{j=2}^{N} \frac{x - x_j}{\sqrt{|x - x_j|^2+1}},$$

we have

$$\int_{\mathbb{R}^{3N-3}} (\nabla_1 F \cdot \nabla_1 F_1)\psi^2 \, d\hat{\mathbf{x}}_1 = I_{3,1}(x) + I_{3,2}(x),$$
$$I_{3,1}(x) = -\frac{Z}{8}\sum_{j=2}^{N} \frac{x}{|x|} \cdot \int_{\mathbb{R}^{3N-3}} \frac{x - x_j}{\sqrt{|x - x_j|^2+1}} \psi^2 d\hat{\mathbf{x}}_1,$$
$$I_{3,2}(x) = \int_{\mathbb{R}^{3N-3}} \Big\{ \frac{Z^2|x|}{4\sqrt{|x|^2+1}} + \big(\frac{1}{4}\sum_{j=2}^{N} \frac{x - x_j}{|x - x_j|}\big) \cdot \nabla_1 F_1 \Big\} \psi^2 \, d\hat{\mathbf{x}}_1.$$

That the first term in $I_{3,2}$ belongs to $C^{\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$ follows by arguments as in [10] (by applying Lemma 3.4 as done after (3.50); note that the function $x \mapsto |x|/\sqrt{|x|^2+1}$ belongs to $C^{0,1}(\mathbb{R}^3)$).

That the last term in $I_{3,2}$ belongs to $C^{\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$, is proved in [10, (3.55), and after].

For $I_{3,1}$, we write $I_{3,1}(x) = -\frac{Z}{8}\frac{x}{|x|} \cdot \mathrm{Int}_3(x)$, with

$$\mathrm{Int}_3(x) = \sum_{j=2}^{N} \int_{\mathbb{R}^{3N-3}} \frac{x - x_j}{\sqrt{|x - x_j|^2+1}} \psi^2 d\hat{\mathbf{x}}_1. \tag{2.21}$$

Similar arguments as for the first integral in $I_{3,2}$ above show that $\mathrm{Int}_3$ belongs to $C^{\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$.

This implies, by Lemma A.1, that

$$I_{3,1}(x) = c_{3,1} \cdot \omega + g_{3,1}(x) \ , \ g_{3,1} \in C^{\alpha}(\mathbb{R}^3) \, , \, \alpha \in (0,1), \tag{2.22}$$
$$c_{3,1} = -\frac{Z}{8}\mathrm{Int}_3(0) \ , \ g_{3,1}(x) = -\frac{Z}{8}\omega \cdot \big(\mathrm{Int}_3(x) - \mathrm{Int}_3(0)\big). \tag{2.23}$$

Finally, we consider $I_5$ (see (2.16)). We use the same kind of analysis. Using (2.20), we write

$$\int_{\mathbb{R}^{3N-3}} (\nabla_1 F \cdot \nabla_1 \psi_1) e^{2(F-F_1)} \psi_1 \, d\hat{\mathbf{x}}_1 = I_{5,1}(x) + I_{5,2}(x),$$
$$I_{5,1}(x) = -\frac{Z}{4}\frac{x}{|x|} \cdot \int_{\mathbb{R}^{3N-3}} e^{2(F-F_1)} \nabla_1(\psi_1^2) \, d\hat{\mathbf{x}}_1,$$
$$I_{5,2}(x) = \frac{1}{4}\sum_{j=2}^{N} \int_{\mathbb{R}^{3N-3}} \frac{x-x_j}{|x-x_j|} \cdot (\nabla_1 \psi_1) e^{2(F-F_1)} \psi_1 \, d\hat{\mathbf{x}}_1.$$

Again, the proof that $I_{5,2}$ belongs to $C^{\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$, is in [10, (3.56), and after]. As before, we write $I_{5,1}(x) = -\frac{Z}{4}\frac{x}{|x|} \cdot \mathrm{Int}_5(x)$ with

$$\mathrm{Int}_5(x) = \int_{\mathbb{R}^{3N-3}} e^{2(F-F_1)} \nabla_1(\psi_1^2) \, d\hat{\mathbf{x}}_1. \tag{2.24}$$

The integral $\mathrm{Int}_5$ belongs to $C^{\alpha}(\mathbb{R}^3)$, $\alpha \in (0,1)$. This follows by arguments as in [10] (the term in (3.56) with $j = 1$). Therefore, by Lemma A.1,

$$I_{5,1}(x) = c_{5,1} \cdot \omega + g_{5,1}(x) \ , \ g_{5,1} \in C^{\alpha}(\mathbb{R}^3) \, , \, \alpha \in (0,1), \tag{2.25}$$
$$c_{5,1} = -\frac{Z}{4}\mathrm{Int}_5(0) \ , \ g_{5,1}(x) = -\frac{Z}{4}\omega \cdot \big(\mathrm{Int}_5(x) - \mathrm{Int}_5(0)\big). \tag{2.26}$$

It follows from all of the above that

$$\begin{aligned} h_1 = (c_{1,1} - 2c_{3,1} + 2c_{5,1}) \cdot \omega + \big[&(g_{1,1} - 2g_{3,1} + 2g_{5,1}) \\ &+ (I_{1,2} - 2I_{3,2} + 2I_{5,2}) + (I_2 + I_4 + I_6) \\ &+ (\tilde{I}_1 + \tilde{I}_3 + \tilde{I}_5) - J_2 + J_3\big] - E\rho_1 \\ = (c_{1,1} - 2c_{3,1} + 2c_{5,1}) \cdot \omega + f - E\rho_1,& \text{ with } f \in C^{\alpha}(\mathbb{R}^3) \ , \ \alpha \in (0,1). \end{aligned} \tag{2.27}$$

Since $\rho_1 \in C^{0,1}(\mathbb{R}^3)$, (2.27) shows that $h_1$ indeed can be written as in (2.9); that is, this finishes the proof of Lemma 2.1. $\square$

*Proof of Theorem 1.5*: That $\eta \in C^{1,1}(B(0,r_0))$ follows from (1.9)–(1.11). That $\chi \in C^{2,\alpha}(B(0,r_0)), \alpha \in (0,1)$, is a consequence of (1.12)–(1.13). It remains to prove (1.19), (1.22), (1.23).

As for Theorem 1.1, we shall only give the proof for the case of atoms ($K = 1; R_1 = 0, Z_1 = Z, \eta = \mu$ and $\chi = \nu$).

Let in the sequel $\omega = \frac{x}{|x|} \in \mathbb{S}^2$ be arbitrary, but fixed. Note that (1.14) and (1.15) imply that $\rho(r,\omega) = e^{-Zr}\mu(r,\omega)$ with $\mu(\,\cdot\,,\omega) \in C^{2,\alpha}([0,\infty))$. It follows that $\rho(\,\cdot\,,\omega) \in C^{2,\alpha}([0,\infty))$ since $r \mapsto e^{-Zr}$

belongs to $C^\infty([0,\infty))$. In particular, $\rho'(0,\omega) = \lim_{r\downarrow 0}\rho'(r,\omega)$ and $\rho''(0,\omega) = \lim_{r\downarrow 0}\rho''(r,\omega)$. (All the above for all $\alpha\in(0,1)$).

Next, by the above,

$$\begin{aligned}\lim_{r\downarrow 0}\rho'(r,\omega) &= \lim_{r\downarrow 0}\big[\omega\cdot\nabla\rho(r,\omega)\big]\\ &= \lim_{r\downarrow 0}\big[-Z\rho(r,\omega)+e^{-Zr}\omega\cdot\nabla\mu(x)\big] = -Z\rho(0)+\omega\cdot\nabla\mu(0),\end{aligned}$$

which is (1.22).

Finally, the proof of (1.23). Due to $\rho = e^{-Zr}\mu$ and (1.14)–(1.15) we have

$$\begin{aligned}\rho''(r,\omega) &= Z^2\rho(r,\omega) - 2Ze^{-Zr}\omega\cdot\nabla\mu(x)\\ &\quad + e^{-Zr}\big[\omega\cdot\nabla(\omega\cdot\nabla\nu(x)) + 2C\cdot\omega\big].\end{aligned}$$

A simple computation shows that $\omega\cdot\nabla(\omega\cdot\nabla\nu(x)) = \omega\cdot\big((D^2\nu)(x)\omega\big)$, and, since $\mu\in C^{1,1}(\mathbb{R}^3)$ and $\nu\in C^{2,\alpha}(\mathbb{R}^3)$, $\alpha\in(0,1)$, we get (1.23). $\square$

*Proof of Theorem 1.7*: We will show that the symmetry assumption (1.25) for $\psi$ implies that $c_1 = 0\in\mathbb{R}^3$ in (2.7). Then

$$\Delta\mu_1 = g\ ,\ \ g\in C^\alpha(\mathbb{R}^3)\,,\ \alpha\in(0,1), \tag{2.28}$$

and so standard elliptic regularity implies that $\mu_1\in C^{2,\alpha}(\mathbb{R}^3)$ for all $\alpha\in(0,1)$. This will prove (1.26).

Recall that (see (2.8), (2.9), (2.10), (2.27) (2.19), (2.23), and (2.26))

$$c_1 = c_1^{(1)} + 2c_1^{(2)} = c_1^{(1)} + 2c_{1,1} - 4c_{3,1} + 4c_{5,1}, \tag{2.29}$$

$$c_1^{(1)} = 2Z\nabla\mu_1(0)\ ,\ \ c_{1,1} = \frac{Z}{4}\mathrm{Int}_1(0), \tag{2.30}$$

$$c_{3,1} = -\frac{Z}{8}\mathrm{Int}_3(0)\ ,\ \ c_{5,1} = -\frac{Z}{4}\mathrm{Int}_5(0). \tag{2.31}$$

We first consider $c_1^{(1)}$. The assumption (1.25) clearly implies that $\rho_1$ is an even function on $\mathbb{R}^3$. It follows from $\mu_1 = e^{Z|x|}\rho_1$ that $\mu_1\in C^{1,1}(\mathbb{R}^3)$ is even and therefore $\nabla\mu_1\in C^{0,1}(\mathbb{R}^3;\mathbb{R}^3)$ is odd. In particular, $\nabla\mu_1(0)=0$, and so $c_1^{(1)}=0$.

It was shown in the proof of Theorem 1.1 that $\mathrm{Int}_j\in C^\alpha(\mathbb{R}^3;\mathbb{R}^3)$, $j=1,3,5$, $\alpha\in(0,1)$ (see (2.17), (2.21), and (2.24)). Furthermore, the symmetry condition (1.25) clearly implies that all three functions are odd (for $\mathrm{Int}_5$, use (2.13)). It follows that $\mathrm{Int}_j(0)=0$, $j=1,3,5$, and therefore (see (2.30) and (2.31)) $c_{j,1}=0$, $j=1,3,5$. Therefore $c_1^{(2)}=0$

and hence $c_1 = 0$ in (2.29). This, and (2.7), implies (2.28), which, as mentioned above, proves (1.26).

Note that $c_1^{(2)} = 0$ implies that $h \in C^{\alpha}(\mathbb{R}^3)$ for all $\alpha \in (0,1)$ (see Lemma 2.1).

The above clearly implies that $\nabla\mu(0) = 0$ and $C = \sum_{j=1}^{N} c_j = 0$, and so (1.22) and (1.23) imply (1.27).

It remains to prove (1.28). With $\Delta = \partial^2/\partial r^2 + (2/r)\partial/\partial r - \mathcal{L}^2/r^2$, (2.2) becomes (after multiplication by $-r$)

$$r\rho''(r,\omega) + 2\rho'(r,\omega) + 2Z\rho(r,\omega) - 2rh(r,\omega) = \frac{(\mathcal{L}^2\rho)(r,\omega)}{r}.$$

This implies, using the fact that $h \in L^{\infty}(\mathbb{R}^3)$ and (1.27), that

$$\lim_{r\downarrow 0} \frac{(\mathcal{L}^2\rho)(r,\omega)}{r} = 2\big(\rho'(0,\omega) + Z\rho(0,\omega)\big) = 0.$$

Let $\mathcal{R}(r,\omega) := \frac{(\mathcal{L}^2\rho)(r,\omega)}{r^2}$, then (2.2) reads

$$\rho''(r,\omega) + \frac{2}{r}\big(\rho'(r,\omega) + Z\rho(r,\omega)\big) - 2h(r,\omega) = \mathcal{R}(r,\omega)\ ,\ r > 0. \quad (2.32)$$

Note that, by l'Hôpital's rule and (1.27),

$$\lim_{r\downarrow 0} \frac{2}{r}\big(\rho'(r,\omega) + Z\rho(r,\omega)\big) = 2\big(\rho''(0,\omega) + Z\rho'(0,\omega)\big),$$

and so (2.32) implies that $\mathcal{R}(0,\omega) := \lim_{r\downarrow 0}\mathcal{R}(r,\omega)$ exists, and

$$\mathcal{R}(0,\omega) = 3\rho''(0,\omega) + 2Z\rho'(0,\omega) - 2h(0,\omega).$$

The existence of $h(0,\omega) := \lim_{r\downarrow 0} h(r,\omega)$ follows from Lemma 2.1. Therefore, using (1.27), we obtain (1.28). $\square$

## Appendix A. A useful lemma

The following lemma is Lemma 2.9 in [7]; we include it, without proof, for the convenience of the reader. (The proof is simple, and can be found in [7]).

**Lemma A.1.** *Let $G : U \to \mathbb{R}^n$ for $U \subset \mathbb{R}^{n+m}$ a neighbourhood of a point $(0, y_0) \in \mathbb{R}^n \times \mathbb{R}^m$. Assume $G(0, y) = 0$ for all $y$ such that $(0, y) \in U$. Let*

$$f(x,y) = \begin{cases} \frac{x}{|x|}\cdot G(x,y) & x \neq 0, \\ 0 & x = 0. \end{cases}$$

*Then, for* $\alpha \in (0,1]$,

$$G \in C^{0,\alpha}(U;\mathbb{R}^n) \Rightarrow f \in C^{0,\alpha}(U). \tag{A.1}$$

*Furthermore,* $\|f\|_{C^\alpha(U)} \leq 2\|G\|_{C^\alpha(U)}$.

**Acknowledgement.** Parts of this work have been carried out at various institutions, whose hospitality is gratefully acknowledged: Mathematisches Forschungsinstitut Oberwolfach (SF, TØS), The Erwin Schrödinger Institute (SF, TØS), Université Paris-Sud (TØS), and the IHÉS (TØS). Financial support from the European Science Foundation Programme *Spectral Theory and Partial Differential Equations* (SPECT), and EU IHP network *Postdoctoral Training Program in Mathematical Analysis of Large Quantum Systems*, contract no. HPRN-CT-2002-00277, is gratefully acknowledged. TØS was partially supported by the embedding grant from The Danish National Research Foundation: Network in Mathematical Physics and Stochastics, and by the European Commission through its 6th Framework Programme *Structuring the European Research Area* and the contract Nr. RITA-CT-2004-505493 for the provision of Transnational Access implemented as Specific Support Action.

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