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Third Derivative of the One-Electron Density at the Nucleus

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Abstract. We study electron densities of eigenfunctions of atomic Schrödinger operators. We prove the existence of $\widetilde{\rho}\,'''(0)$, the third derivative of the spherically averaged atomic density $\widetilde{\rho}$ at the nucleus. For eigenfunctions with corresponding eigenvalue below the essential spectrum in any symmetry subspace we obtain the bound $\widetilde{\rho}\,'''(0) \leq -(7/12)Z^3\widetilde{\rho}(0)$, where Z denotes the nuclear charge. This bound is optimal.

1. Introduction and results

In a recent paper [5] the present authors (together with T. Hoffmann-Ostenhof (THO)) proved that electron densities of atomic and molecular eigenfunctions are real analytic away from the positions of the nuclei. Concerning questions of regularity of ρ it therefore remains to study the behaviour of ρ in the vicinity of the nuclei. A general (optimal) structure-result was obtained recently [2]. For more detailed information, two possible approaches are to study limits when approaching a nucleus under a fixed angle $\omega \in \mathbb{S}^2$, as was done in [2], and to study the spherical average of ρ (here denoted $\widetilde{\rho}$), which is mostly interesting for atoms. The existence of $\widetilde{\rho}\,'(0)$, the first derivative of $\widetilde{\rho}$ at the nucleus, and the identity $\widetilde{\rho}\,'(0) = -Z\widetilde{\rho}(0)$ (see (1.12) below) follow immediately from Kato's classical result [12] on the 'Cusp Condition' for the associated eigenfunction (see also [10, 15]). Two of the present authors proved (with THO) the existence of $\widetilde{\rho}\,''(0)$, and, for densities corresponding to eigenvalues below the essential spectrum, a lower positive bound to $\widetilde{\rho}\,''(0)$ in terms of $\widetilde{\rho}(0)$ in [9]. In the present paper we prove the existence of $\widetilde{\rho}\,'''(0)$ and derive a negative upper bound to it (see Theorem 1.2). We prove this bound for eigenvalues below the essential spectrum in any symmetry subspace. In particular, it holds for the physical (fermionic) ground state (see Remark 1.4). A key role in the proof is played by the *a priori* estimate on 2nd order derivatives of eigenfunctions obtained in [6] (see also Remark 1.3 and Appendix B below). Furthermore our investigations lead to an improvement of the lower bound to $\widetilde{\rho}''(0)$ (see Corollary 1.7). The bounds on $\widetilde{\rho}''(0)$ and $\widetilde{\rho}'''(0)$ in terms of $\widetilde{\rho}(0)$ are optimal (see Remarks 1.5 and 1.8).

We turn to the precise description of the problem. We consider a non-relativistic N-electron atom with a nucleus of charge Z fixed at the origin in $\mathbb{R}^3$. The Hamiltonian describing the system is given by

$$H = H_N(Z) = \sum_{j=1}^{N}\left(-\Delta_j - \frac{Z}{|x_j|}\right) + \sum_{1\le i<j\le N}\frac{1}{|x_i - x_j|}\,. \tag{1.1}$$

The positions of the N electrons are denoted by $\mathbf{x} = (x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}$, where $x_j = (x_{j,1}, x_{j,2}, x_{j,3})$ denotes the position of the j'th electron in $\mathbb{R}^3$, and Δ_j denotes the Laplacian with respect to x_j. For shortness, we will sometimes write

$$H = -\Delta + V(\mathbf{x})\,, \tag{1.2}$$

where $\Delta = \sum_{j=1}^{N}\Delta_j$ is the $3N$-dimensional Laplacian, and

$$V(\mathbf{x}) = V_{N,Z}(\mathbf{x}) = \sum_{j=1}^{N} -\frac{Z}{|x_j|} + \sum_{1\le i<j\le N}\frac{1}{|x_i - x_j|} \tag{1.3}$$

is the complete (many-body) potential. With ∇_j the gradient with respect to x_j, $\nabla = (\nabla_1, \ldots, \nabla_N)$ will denote the gradient with respect to $\mathbf{x}$.

It is a standard fact (see e.g. Kato [11]) that H is selfadjoint with operator domain $\mathcal{D}(H) = W^{2,2}(\mathbb{R}^{3N})$ and quadratic form domain $\mathcal{Q}(H) = W^{1,2}(\mathbb{R}^{3N})$.

We consider eigenfunctions ψ of H, i.e., solutions $\psi \in L^2(\mathbb{R}^{3N})$ to the equation

$$H\psi = E\psi\,, \tag{1.4}$$

with $E \in \mathbb{R}$. To simplify notation we assume from now on, without loss, that ψ is real. Apart from the wave function ψ itself, the most important quantity describing the state of the atom is the **one-electron density** ρ. It is defined by

$$\rho(x) = \sum_{j=1}^{N}\rho_j(x) = \sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}}|\psi(x, \hat{\mathbf{x}}_j)|^2 d\hat{\mathbf{x}}_j\,, \tag{1.5}$$

where we use the notation

$$\hat{\mathbf{x}}_j = (x_1, \ldots, x_{j-1}, x_{j+1}, \ldots, x_N) \tag{1.6}$$

and

$$d\hat{\mathbf{x}}_j = dx_1 \ldots dx_{j-1}dx_{j+1} \ldots dx_N \tag{1.7}$$

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

We assume throughout when studying ρ that E and ψ in (1.4) are such that there exist constants $C_0, \gamma > 0$ such that

$$|\psi(\mathbf{x})| \leq C_0 \, e^{-\gamma|\mathbf{x}|} \quad \text{for all} \quad \mathbf{x} \in \mathbb{R}^{3N} \,. \tag{1.8}$$

The *a priori* estimate [9, Theorem 1.2] (see also [9, Remark 1.7]) and (1.8) imply the existence of constants $C_1, \gamma_1 > 0$ such that

$$\big|\nabla\psi(\mathbf{x})\big| \leq C_1 \, e^{-\gamma_1|\mathbf{x}|} \quad \text{for almost all} \quad \mathbf{x} \in \mathbb{R}^{3N} \,. \tag{1.9}$$

Remark 1.1. Since ψ is continuous (see Kato [12]), (1.8) is only an assumption on the behaviour at infinity. The proofs of our results rely on some kind of decay-rate for ψ; exponential decay is not essential, but assumed for convenience. It is known to hold for eigenfunctions associated to non-threshold eigenvalues, in particular, for all eigenvalues below the essential spectrum in any symmetry subspace (see e.g. Froese and Herbst [7] and Simon [14]). Note that (1.8) and (1.9) imply that ρ is Lipschitz continuous in $\mathbb{R}^3$ by Lebesgue's theorem on dominated convergence.

In [5] we proved (with THO) that ρ is real analytic away from the position of the nucleus. More generally, for a molecule with K fixed nuclei at $R_1, \dots, R_K$, $R_j \in \mathbb{R}^3$, it was proved that $\rho \in C^\omega(\mathbb{R}^3 \setminus \{R_1, \dots, R_K\})$; see also [3] and [4]. Note that the proof of analyticity does *not* require any decay of ρ (apart from $\psi \in W^{2,2}(\mathbb{R}^{3N})$). That ρ itself is not analytic at the positions of the nuclei is already clear for the groundstate of 'Hydrogenic atoms' ($N = 1$); in this case, $\nabla\rho$ is not even continuous at $x = 0$. However, as was proved in [2], $e^{Z|x|}\rho \in C^{1,1}(\mathbb{R}^3)$.

To obtain more information about the behaviour of the density at the positions of the nuclei one therefore has to study the regularity of other quantities, derived from ρ.

One possibility is to study the function $r \mapsto \rho(r, \omega) := \rho(r\omega)$ for fixed $\omega = \frac{x}{|x|} \in \mathbb{S}^2$ ($r = |x|$); results in this direction were derived by the authors (with THO) in [2, Theorem 1.5]. In particular, for the case of atoms it was proved that for all $\omega \in \mathbb{S}^2$,

$$\rho(\,\cdot\,, \omega) \in C^{2,\alpha}([0, \infty)) \quad \text{for all} \quad \alpha \in (0, 1) \,, \tag{1.10}$$

and the 1st and 2nd radial derivatives were investigated at $r = 0$.

The main quantity studied in this paper is the spherical average of ρ,

$$\widetilde{\rho}(r) = \int_{\mathbb{S}^2} \rho(r\omega) \, d\omega \,, \quad r \in [0, \infty) \,. \tag{1.11}$$

It follows from the analyticity of ρ mentioned above that also $\widetilde{\rho} \in C^\omega((0, \infty))$, and from the Lipschitz continuity of ρ in $\mathbb{R}^3$ that $\widetilde{\rho}$ is Lipschitz continuous in $[0, \infty)$.

The existence of $\widetilde{\rho}\,'(0)$, the continuity of $\widetilde{\rho}\,'$ at $r = 0$, and the Cusp Condition

$$\widetilde{\rho}\,'(0) = -Z\widetilde{\rho}(0) \,, \tag{1.12}$$

follows from a similar result for ψ itself by Kato [12]; see [10, 15], and [9, Remark 1.13].

To investigate properties of ρ and the derived quantities above it is essential that ρ satisfies a differential equation. Such an equation easily follows via (1.4) from

$$\sum_{j=1}^{N}\int_{\mathbb{R}^{3N-3}}\psi(x,\hat{\mathbf{x}}_j)(H-E)\psi(x,\hat{\mathbf{x}}_j)\,d\hat{\mathbf{x}}_j=0\,. \tag{1.13}$$

This implies that ρ satisfies, in the distributional sense, the (inhomogeneous one-particle Schrödinger) equation

$$-\frac{1}{2}\Delta\rho-\frac{Z}{|x|}\rho+h=0\quad\text{in}\quad\mathbb{R}^3\,. \tag{1.14}$$

The function h in (1.14) is given by

$$h(x)=\sum_{j=1}^{N}h_j(x), \tag{1.15}$$

$$\begin{aligned}h_j(x)=&\int_{\mathbb{R}^{3N-3}}|\nabla\psi(x,\hat{\mathbf{x}}_j)|^2\,d\hat{\mathbf{x}}_j-\sum_{\ell=1,\ell\neq j}^{N}\int_{\mathbb{R}^{3N-3}}\frac{Z}{|x_\ell|}\,|\psi(x,\hat{\mathbf{x}}_j)|^2\,d\hat{\mathbf{x}}_j\\&+\sum_{\ell=1,\ell\neq j}^{N}\int_{\mathbb{R}^{3N-3}}\frac{1}{|x-x_\ell|}\,|\psi(x,\hat{\mathbf{x}}_j)|^2\,d\hat{\mathbf{x}}_j\\&+\sum_{1\le k<\ell\le N,\,k\neq j\neq\ell}\int_{\mathbb{R}^{3N-3}}\frac{1}{|x_k-x_\ell|}\,|\psi(x,\hat{\mathbf{x}}_j)|^2\,d\hat{\mathbf{x}}_j-E\rho_j(x)\,.\end{aligned} \tag{1.16}$$

The equation (1.14) implies that the function $\widetilde{\rho}$ in (1.11) satisfies

$$-\frac{1}{2}\Delta\widetilde{\rho}-\frac{Z}{r}\widetilde{\rho}+\widetilde{h}=0\quad\text{for}\quad r\in(0,\infty)\,, \tag{1.17}$$

where $\Delta=\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}=\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr})$, and

$$\widetilde{h}(r)=\int_{\mathbb{S}^2}h(r\omega)\,d\omega\,. \tag{1.18}$$

In [9, Theorem 1.11] information about the regularity of ψ was used to prove that $\widetilde{h}\in C^0([0,\infty))$, and, using (1.17), that consequently, $\widetilde{\rho}\in C^2([0,\infty))$, and

$$\widetilde{\rho}\,''(0)=\frac{2}{3}\big(\widetilde{h}(0)+Z^2\widetilde{\rho}(0)\big)\,. \tag{1.19}$$

Moreover, denote by $\sigma(H_N(Z))$ the spectrum of $H_N(Z)$, and define

$$\varepsilon:=E_{N-1}^0(Z)-E\,,\quad E_{N-1}^0(Z)=\inf\sigma\big(H_{N-1}(Z)\big)\,. \tag{1.20}$$

Then if $\varepsilon\ge 0$ [9, Theorem 1.11], we have

$$h(x)\ge\varepsilon\rho(x)\quad\text{for all}\quad x\in\mathbb{R}^3\,, \tag{1.21}$$

and so in this case, (1.19) implies that

$$\widetilde{\rho}''(0) \geq \frac{2}{3}\big(Z^2+\varepsilon\big)\widetilde{\rho}(0) \geq \frac{2}{3}\,Z^2\widetilde{\rho}(0)\,. \tag{1.22}$$

Our main result in this paper is the following.

Theorem 1.2. *Let* $\psi \in L^2(\mathbb{R}^{3N})$ *be an atomic eigenfunction,* $H_N(Z)\psi = E\psi$, *satisfying* (1.8)*, with associated spherically averaged density* $\widetilde{\rho}$ *defined by* (1.5) *and* (1.11)*. Let* $\widetilde{h}$ *be defined by* (1.15)–(1.16)*,* (1.18)*, and let* ε *be given by* (1.20)*. Let finally* $\varphi_j(x,\hat{\mathbf{x}}_j) = e^{\frac{Z}{2}|x|}\psi(x,\hat{\mathbf{x}}_j)$*,* $j=1,\dots,N$*.*

Then $\widetilde{\rho} \in C^3([0,\infty))$*, and*

$$\widetilde{\rho}'''(0) = \widetilde{h}\,'(0) - \frac{Z}{3}\big[\widetilde{h}(0) + Z^2\widetilde{\rho}(0)\big] \tag{1.23}$$

$$= -\frac{7}{12}Z^3\widetilde{\rho}(0) - 4\pi Z\sum_{j=1}^{N}\bigg[\int_{\mathbb{R}^{3N-3}} |\nabla_j\varphi_j(0,\hat{\mathbf{x}}_j)|^2\,d\hat{\mathbf{x}}_j \tag{1.24}$$

$$+\frac{5}{3}\Big\langle \psi(0,\,\cdot\,),\big[H_{N-1}(Z-1)-E\big]\psi(0,\,\cdot\,)\Big\rangle_{L^2(\mathbb{R}^{3N-3}_{\hat{\mathbf{x}}_j})}\bigg]\,.$$

If $\varepsilon \geq 0$*, then*

$$\widetilde{\rho}'''(0) \leq -\frac{Z}{12}\big(7Z^2+20\varepsilon\big)\,\widetilde{\rho}(0) \leq -\frac{7}{12}Z^3\widetilde{\rho}(0)\,. \tag{1.25}$$

Remark 1.3. The existence of $\widetilde{\rho}^{\,(k)}(0)$ for all $k>3$ remains an open problem. The two main steps in the proof of Theorem 1.2 are Propositions 1.6 and 2.1 below. From the latter one sees that the existence of $\widetilde{h}^{\,(k-2)}(0)$ is necessary to prove existence of $\widetilde{\rho}^{\,(k)}(0)$. In Proposition 1.6 the existence of $\widetilde{h}\,'(0)$ is proved and this result already heavily relies on the optimal regularity results for ψ (involving an *a priori* estimate for second order partial derivatives of ψ) obtained in [6] (see also Appendix B below).

Remark 1.4. Note that the inequality

$$\widetilde{\rho}'''(0) \leq -\frac{7}{12}Z^3\widetilde{\rho}(0) \tag{1.26}$$

follows from (1.24) as soon as ψ is such that

$$\sum_{j=1}^{N}\Big\langle \psi(0,\,\cdot\,),\big[H_{N-1}(Z-1)-E\big]\psi(0,\,\cdot\,)\Big\rangle_{L^2(\mathbb{R}^{3N-3}_{\hat{\mathbf{x}}_j})} \geq 0\,. \tag{1.27}$$

There are cases where (1.27) holds even if the assumption $\varepsilon \geq 0$ does not. For instance when E is an embedded eigenvalue for the full operator H ($\varepsilon<0$), but non-embedded for the operator restricted to a symmetry subspace. In particular, (1.26) holds for the fermionic ground state.

Remark 1.5. Compare (1.12), (1.22), and Theorem 1.2 with the fact that for the ground state of 'Hydrogenic atoms' ($N = 1$), the corresponding density $\widetilde{\rho}_1(r) = c\,e^{-Zr}$ satisfies

$$\widetilde{\rho}_1^{\,(k)}(0) = (-Z)^k \widetilde{\rho}_1(0)\,. \tag{1.28}$$

In fact, if $(-\Delta - Z/|x|)\psi_n = E_n\psi_n$, $E_n = -Z^2/4n^2$, $n \in \mathbb{N}$, $\psi_n(x) = e^{-\frac{Z}{2}|x|}\phi_n(x)$, then (1.24) implies that the corresponding density $\widetilde{\rho}_n$ satisfies

$$\begin{aligned}\widetilde{\rho}_n'''(0) &= \Big[-\frac{7}{12}Z^3 + \frac{5}{3}ZE\Big]\,\widetilde{\rho}_n(0) - 4\pi Z|\nabla\phi_n(0)|^2\\ &= -\frac{Z^3}{12}\Big[7 + \frac{5}{n^2}\Big]\,\widetilde{\rho}_n(0) - 4\pi Z|\nabla\phi_n(0)|^2\,.\end{aligned} \tag{1.29}$$

For the ground state, i.e., for $n = 1$, $E_1 = -Z^2/4$, $\phi_1 \equiv 1$, this reduces to (1.28) with $k = 3$.

Furthermore, for s - states (zero angular momentum), we get that $\nabla\phi_n(0) = 0$, since ϕ_n is radial and $C^{1,\alpha}$ (see (3.25) below). Taking n large in (1.29) illustrates the quality of the bound (1.25).

The proof of Theorem 1.2 is based on the following result on h. Its proof is given in Section 3.1.

Proposition 1.6. *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction, $H_N(Z)\psi = E\psi$, satisfying* (1.8)*, and let h be as defined in* (1.15)*–*(1.16)*. Let $\omega \in \mathbb{S}^2$ and $\widetilde{h}(r) = \int_{\mathbb{S}^2} h(r\omega)\,d\omega$.*

Then both $\widetilde{h}$ and the function $r \mapsto h(r,\omega) := h(r\omega)$ belong to $C^1([0,\infty))$.

Furthermore, with $\varphi_j(x,\hat{\mathbf{x}}_j) = e^{\frac{Z}{2}|x|}\psi(x,\hat{\mathbf{x}}_j)$, $j = 1,\dots,N$,

$$\begin{aligned}\widetilde{h}(0) = \frac{Z^2}{4}\widetilde{\rho}(0) + 4\pi\sum_{j=1}^{N}\Big[\int_{\mathbb{R}^{3N-3}} |\nabla_j\varphi_j(0,\hat{\mathbf{x}}_j)|^2\,d\hat{\mathbf{x}}_j\\ + \Big\langle\psi(0,\,\cdot\,),\big[H_{N-1}(Z-1) - E\big]\psi(0,\,\cdot\,)\Big\rangle_{L^2(\mathbb{R}^{3N-3}_{\hat{\mathbf{x}}_j})}\Big],\end{aligned} \tag{1.30}$$

$$\begin{aligned}\widetilde{h}\,'(0) = -Z\widetilde{h}(0) + \frac{Z^3}{12}\widetilde{\rho}(0) + \frac{4\pi}{3}Z\sum_{j=1}^{N}\Big[\int_{\mathbb{R}^{3N-3}} |\nabla_j\varphi_j(0,\hat{\mathbf{x}}_j)|^2\,d\hat{\mathbf{x}}_j\\ - \Big\langle\psi(0,\,\cdot\,),\big[H_{N-1}(Z-1) - E\big]\psi(0,\,\cdot\,)\Big\rangle_{L^2(\mathbb{R}^{3N-3}_{\hat{\mathbf{x}}_j})}\Big].\end{aligned} \tag{1.31}$$

As a byproduct of (1.30) we get the following improvement of (1.22).

Corollary 1.7. *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction, $H_N(Z)\psi = E\psi$, satisfying* (1.8)*, with associated spherically averaged density $\widetilde{\rho}$ defined by* (1.5) *and* (1.11)*. Let ε be given by* (1.20)*, and assume $\varepsilon \geq 0$.*

Then

$$\widetilde{\rho}\,''(0) \geq \frac{2}{3}\left[\frac{5Z^2}{4} + \varepsilon\right]\widetilde{\rho}(0) \geq \frac{5}{6}\,Z^2\widetilde{\rho}(0)\,. \tag{1.32}$$

Proof. Using the HVZ-theorem [13, Theorem XIII.17], (1.30) provides an improvement of the bound (1.21) for $r = 0$ to

$$\widetilde{h}(0) \geq \left[\frac{Z^2}{4} + \varepsilon\right]\widetilde{\rho}(0)\,. \tag{1.33}$$

This, using (1.19), gives (1.32). □

Remark 1.8. For 'Hydrogenic atoms' ($N = 1$) (see Remark 1.5), (1.19) and (1.30) imply

$$\widetilde{\rho}_n''(0) = \frac{Z^2}{6}\left[5 + \frac{1}{n^2}\right]\widetilde{\rho}_n(0) + \frac{8\pi}{3}|\nabla\phi_n(0)|^2\,, \tag{1.34}$$

which illustrates the quality of the bound (1.32) above (see also the discussion in Remark 1.5), and reduces to (1.28) with $k = 2$ for the ground state ($n = 1, \phi_1 \equiv 1$).

We outline the structure of the rest of the paper. In Section 2, we use Proposition 1.6 and the equation for $\widetilde{\rho}$ (see (1.17)) to prove Theorem 1.2. In Section 3 we then prove Proposition 1.6. This is done applying the characterization of the regularity of the eigenfunction ψ up to order $C^{1,1}$ proved in [6] (see also Appendix B and Lemma 3.9) to the different terms in (1.15)–(1.16).

2. Proof of Theorem 1.2

That $\widetilde{\rho} \in C^3([0,\infty))$ and the formula (1.23) follow from Proposition 2.1 below (with $k = 1$), using Proposition 1.6 and (1.19). The formula (1.24) then follows from (1.23) and Proposition 1.6.

If $\varepsilon \geq 0$, then the HVZ-theorem [13, Theorem XIII.17] implies that

$$\begin{aligned}\sum_{j=1}^{N}\Big\langle \psi(0,\,\cdot\,), \big[H_{N-1}(Z-1) - E\big]\psi(0,\,\cdot\,)\Big\rangle_{L^2(\mathbb{R}^{3N-3}_{\hat{\mathbf{x}}_j})} \\ \geq \varepsilon \sum_{j=1}^{N}\big\langle \psi(0,\,\cdot\,), \psi(0,\,\cdot\,)\big\rangle_{L^2(\mathbb{R}^{3N-3}_{\hat{\mathbf{x}}_j})} = \varepsilon\rho(0)\,,\end{aligned} \tag{2.1}$$

which, together with (1.24), implies (1.25), since $\widetilde{\rho}(0) = 4\pi\rho(0)$.

It therefore remains to prove the following proposition.

Proposition 2.1. *Let* $\psi \in L^2(\mathbb{R}^{3N})$ *be an atomic eigenfunction,* $H_N(Z)\psi = E\psi$, *satisfying* (1.8), *with associated spherically averaged density* $\widetilde{\rho}$ *defined by* (1.5) *and* (1.11), *and let* $\widetilde{h}$ *be as defined in* (1.15)*–*(1.16) *and* (1.18)*. Let* $k \in \mathbb{N} \cup \{0\}$.

If $\widetilde{h} \in C^k([0,\infty))$ *then* $\widetilde{\rho} \in C^{k+2}([0,\infty))$, *and*

$$\widetilde{\rho}^{(k+2)}(0) = \frac{2}{k+3}\big[(k+1)\widetilde{h}^{(k)}(0) - Z\widetilde{\rho}^{(k+1)}(0)\big]\,. \tag{2.2}$$

Proof. Let $r > 0$; multiplying (1.17) with r^2, integrating over $[\delta, r]$ for $0 < \delta < r$, and then taking the limit $\delta \downarrow 0$, using that $\widetilde{h}, \widetilde{\rho}$, and $\widetilde{\rho}\,'$ are all continuous on $[0,\infty)$ (see the introduction), it follows from Lebesgue's theorem on dominated convergence that

$$\begin{aligned}\widetilde{\rho}\,'(r) &= \frac{2}{r^2}\int_0^r \big[-Z\widetilde{\rho}(s)s + \widetilde{h}(s)s^2\big]\,ds\\ &= -2Z\int_0^1 \widetilde{\rho}(r\sigma)\sigma\,d\sigma + \frac{2}{r^2}\int_0^r \widetilde{h}(s)s^2\,ds\,.\end{aligned} \tag{2.3}$$

Using again Lebesgue's theorem on dominated convergence (in the form of Proposition 3.6 below) we get that for $r > 0$,

$$\widetilde{\rho}\,''(r) = 2\left[\widetilde{h}(r) - \int_0^1 \big[Z\widetilde{\rho}\,'(r\sigma) + 2\widetilde{h}(r\sigma)\big]\sigma^2\,d\sigma\right]. \tag{2.4}$$

Since $\widetilde{\rho} \in C^2([0,\infty))$ (see the introduction), (2.4) extends to $r = 0$ by continuity and Lebesgue's theorem. This finishes the proof in the case $k = 0$.

For $k \in \mathbb{N}$, applying Lebegue's theorem to (2.4) it is easy to prove by induction that if $\widetilde{h} \in C^k([0,\infty))$ then $\widetilde{\rho} \in C^{k+2}([0,\infty))$, and that for $r \geq 0$,

$$\widetilde{\rho}^{(k+2)}(r) = 2\left[\widetilde{h}^{(k)}(r) - \int_0^1 \big[Z\widetilde{\rho}^{(k+1)}(r\sigma) + 2\widetilde{h}^{(k)}(r\sigma)\big]\sigma^{k+2}\,d\sigma\right]. \tag{2.5}$$

In particular, (2.2) holds. This finishes the proof of the proposition. □

This finishes the proof of Theorem 1.2. □

It remains to prove Proposition 1.6.

3. Study of the function h

3.1. Proof of Proposition 1.6

It clearly suffices to prove the statements in Proposition 1.6 for each h_j ($j = 1,\ldots,N$) in (1.16). Proposition 1.6 then follows for h by summation. We shall prove the statements in Proposition 1.6 for h_1; the proof for the other h_j is completely analogous.

Recall (see (1.15)–(1.16)) that h_1 is defined by

$$h_1(x) = t_1(x) - v_1(x) + w_1(x) - E\rho_1(x)\,, \tag{3.1}$$

$$t_1(x) = \int_{\mathbb{R}^{3N-3}} |\nabla\psi(x,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\,, \tag{3.2}$$

$$v_1(x) = \sum_{k=2}^{N}\int_{\mathbb{R}^{3N-3}} \frac{Z}{|x_k|}\,|\psi(x,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\,, \tag{3.3}$$

$$\begin{aligned} w_1(x) = &\sum_{k=2}^{N}\int_{\mathbb{R}^{3N-3}} \frac{1}{|x-x_k|}\,|\psi(x,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1 \\ &+ \sum_{2\le k<\ell\le N}\int_{\mathbb{R}^{3N-3}} \frac{1}{|x_k-x_\ell|}\,|\psi(x,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\,, \end{aligned} \tag{3.4}$$

$$\rho_1(x) = \int_{\mathbb{R}^{3N-3}} |\psi(x,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\,. \tag{3.5}$$

Here, $\hat{\mathbf{x}}_1 = (x_2,\dots,x_N) \in \mathbb{R}^{3N-3}$ and $d\hat{\mathbf{x}}_1 = dx_2\dots dx_N$.

We shall look at the different terms in (3.2)–(3.5) separately. The statements on regularity in Proposition 1.6 clearly follow from Proposition 3.1 and Proposition 3.3 below and the regularity properties of ρ, see the discussion in the introduction (in the vicinity of (1.10)–(1.12); see also [2, Theorem 1.5] and [9, Theorem 1.11]). The formulae (1.30)–(1.31) follow from the formulae in Proposition 3.1 and Proposition 3.3, using (3.1)–(3.5), and the fact that

$$\begin{aligned} &\int_{\mathbb{R}^{3N-3}} \Big\{|\nabla_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1)|^2 + \big(V_{N-1,Z-1}(\hat{\mathbf{x}}_1) - E\big)|\psi(0,\hat{\mathbf{x}}_1)|^2\Big\}\, d\hat{\mathbf{x}}_1 \\ &\qquad = \Big\langle \psi(0,\,\cdot\,), \big[H_{N-1}(Z-1) - E\big]\psi(0,\,\cdot\,)\Big\rangle_{L^2(\mathbb{R}^{3N-3}_{\hat{\mathbf{x}}_1})}\,. \end{aligned} \tag{3.6}$$

For the definitions of $V_{N-1,Z-1}$ and $H_{N-1}(Z-1)$, see (1.3) and (1.1), respectively.

Proposition 3.1. *Let v_1 and w_1 be defined as in (3.3)–(3.4) and let $\omega \in \mathbb{S}^2$. Define $\widetilde{v}_1(r) = \int_{\mathbb{S}^2} v_1(r\omega)\,d\omega$, $\widetilde{w}_1(r) = \int_{\mathbb{S}^2} w_1(r\omega)\,d\omega$.*

Then $v_1(\,\cdot\,,\omega), w_1(\,\cdot\,,\omega), \widetilde{v}_1$, and $\widetilde{w}_1$ all belong to $C^1\big([0,\infty)\big)$, and

$$\widetilde{v}_1{}'(0) = -Z\widetilde{v}_1(0)\,, \tag{3.7}$$

$$\widetilde{w}_1{}'(0) = -Z\widetilde{w}_1(0)\,. \tag{3.8}$$

Remark 3.2. Similar statements hold for v_j and w_j ($j = 2,\dots,N$), and therefore, by summation, for $v = \sum_{j=1}^N v_j$, $w = \sum_{j=1}^N w_j$. Compare this with (1.12): $\widetilde{\rho}\,'(0) = -Z\widetilde{\rho}(0)$; that is, three of the four terms in $\widetilde{h}$ (see (1.15)) satisfy the 'Cusp Condition' $\widetilde{f}\,'(0) = -Z\widetilde{f}(0)$.

For the remaining term in (3.1), we have the following.

Proposition 3.3. *Let t_1 be defined as in* (3.2) *and let $\omega \in \mathbb{S}^2$. Define $\widetilde{t_1}(r) = \int_{\mathbb{S}^2} t_1(r\omega)\, d\omega$.*

Then both $\widetilde{t_1}$ and the function $r \mapsto t_1(r,\omega) := t_1(r\omega)$ belong to $C^1\big([0,\infty)\big)$. Furthermore, with $\varphi_1(x,\hat{\mathbf{x}}_1) = e^{\frac{Z}{2}|x|}\psi(x,\hat{\mathbf{x}}_1)$,

$$\widetilde{t_1}(0) = \frac{Z^2}{4}\widetilde{\rho}_1(0) + 4\pi\bigg[\int_{\mathbb{R}^{3N-3}} |\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1 + \int_{\mathbb{R}^{3N-3}} |\nabla_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\bigg], \tag{3.9}$$

$$\widetilde{t_1}'(0) = -Z\widetilde{t_1}(0) + \frac{Z^3}{12}\widetilde{\rho}_1(0) + \frac{4\pi}{3}Z\bigg[\int_{\mathbb{R}^{3N-3}} |\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1 - \int_{\mathbb{R}^{3N-3}} \Big\{ |\nabla_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1)|^2 + \big(V_{N-1,Z-1}(\hat{\mathbf{x}}_1) - E\big)|\psi(0,\hat{\mathbf{x}}_1)|^2\Big\}\, d\hat{\mathbf{x}}_1\bigg], \tag{3.10}$$

with $V_{N-1,Z-1}$ given by (1.3).

Remark 3.4. Note that in the case of Hydrogen ($N = 1$), with $\phi(x) = e^{\frac{Z}{2}|x|}\psi$,

$$\widetilde{t}\,'(0) + Z\widetilde{t}(0) = \frac{Z}{3}\left(\left[\frac{Z^2}{4} + E\right]\widetilde{\rho}_H(0) + 4\pi|\nabla\phi(0)|^2\right), \tag{3.11}$$

with $\nabla\phi \equiv 0$ for the ground state.

3.2. Integrals and limits

In the proofs of Proposition 3.1 and Proposition 3.3 we shall restrict ourselves to proving the existence of the limits of the mentioned derivatives as $r \downarrow 0$ (e.g., $\lim_{r\downarrow 0} v_1'(r,\omega)$). The existence of the limits of the difference quotients (here, $v_1'(0,\omega) := \lim_{r\downarrow 0}\frac{v_1(r,\omega)-v_1(0)}{r}$), and their equality with the limits of the derivatives (i.e., $\lim_{r\downarrow 0} v_1'(r,\omega)$), is a consequence of the following lemma, which is an easy consequence of the mean value theorem.

Lemma 3.5. *Let $f : [a,b] \to \mathbb{R}$ satisfy $f \in C^0\big([a,b]\big)$, $f' \in C^0\big((a,b)\big)$, and that $\lim_{\epsilon\downarrow 0} f'(a+\epsilon)$ exists.*

Then $\lim_{\epsilon\downarrow 0}\frac{f(a+\epsilon)-f(a)}{\epsilon}$ exists and equals $\lim_{\epsilon\downarrow 0} f'(a+\epsilon)$.

Verifying the two first assumptions in Lemma 3.5 in the case of the functions in Proposition 3.1 and Proposition 3.3 follow exactly the same ideas as proving the existence of the limits of the mentioned derivatives as $r \downarrow 0$ (which follows below), and so we will omit the details.

When proving below the existence of the limits of the mentioned derivatives as $r \downarrow 0$, we shall need to interchange first the differentiation $\frac{d}{dr}$, then the limit $\lim_{r\downarrow 0}$, with the integration $\int_{\mathbb{R}^{3N-3}} \cdots\, d\hat{\mathbf{x}}_1$ (or, for the spherical averages, with $\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}} \cdots\, d\hat{\mathbf{x}}_1 d\omega$). We shall use Lebesgue's Theorem of Dominated Convergence in both cases; in the case of $\frac{d}{dr}$ in the form of Proposition 3.6 below, which is a standard result in integration theory (see e. g. [1]). The dominant (in Proposition 3.6, the function g) will be the same in both cases.

Proposition 3.6. *Let $I \subset \mathbb{R}$ be an interval, A any subset of $\mathbb{R}^m$, and f a function defined on $A \times I$, satisfying the three following hypothesis:*

i) *For all $\lambda \in I$, the function $x \mapsto f(x,\lambda)$ is integrable on A.*
ii) *The partial derivative $\partial f/\partial\lambda(x,\lambda)$ exists at all points in $A \times I$.*
iii) *There exists a non-negative function g, integrable on A, such that $|\partial f/\partial\lambda(x,\lambda)| \leq g(x)$ for all $(x,\lambda) \in A \times I$.*

Then the function F defined by

$$F(\lambda) = \int_A f(x,\lambda)\,dx$$

is differentiable in I, and

$$F'(\lambda) = \int_A \frac{\partial f}{\partial\lambda}(x,\lambda)\,dx\,.$$

Remark 3.7. Note that one can remove a set B of measure zero from the domain of integration A, without changing the two integrals above; it is therefore enough to check the three hypothesis on this new domain, $A' = A \setminus B$. Note that the set B of measure zero must be independent of λ.

Note that in (3.2)–(3.5) we can, for $x = r\omega \neq 0$, restrict integration to the set

$$\mathcal{S}_1(\omega) = \Big\{ \hat{\mathbf{x}}_1 \in \mathbb{R}^{3N-3} \,\Big|\, x_k \neq 0\,,\ \frac{x_k}{|x_k|} \neq \omega\,,\ x_\ell \neq x_k\,, \text{ for } k,\ell \in \{2,\dots,N\} \text{ with } k \neq \ell \Big\}\,, \tag{3.12}$$

since $\mathbb{R}^{3N-3} \setminus \mathcal{S}_1(\omega)$ has measure zero. The set $\mathcal{S}_1(\omega)$ will be our A'. From the definition of $\mathcal{S}_1(\omega)$ it follows that for any $r > 0$, $\omega \in \mathbb{S}^2$, and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$, there exists an $\epsilon > 0$ and a neighbourhood $U \subset \mathcal{S}_1(\omega) \subset \mathbb{R}^{3N-3}$ of $\hat{\mathbf{x}}_1$ such that V in (1.3) is C^∞ on $B_3(r\omega,\epsilon) \times U \subset \mathbb{R}^{3N}$. It follows from elliptic regularity [8] that $\psi \in C^\infty(B_3(r\omega,\epsilon) \times U)$. In particular, if $G : \mathbb{R}^{3N} \to \mathbb{R}$ is any of the integrands in (3.2)–(3.5), then, for all $\omega \in \mathbb{S}^2$, the partial derivative $\partial G_\omega/\partial r(r,\hat{\mathbf{x}}_1)$ of the function $(r,\hat{\mathbf{x}}_1) \mapsto G(r\omega,\hat{\mathbf{x}}_1) \equiv G_\omega(r,\hat{\mathbf{x}}_1)$ exists, and satisfies

$$\frac{\partial G_\omega}{\partial r}(r,\hat{\mathbf{x}}_1) = \omega \cdot \big[(\nabla_1 G)(r\omega,\hat{\mathbf{x}}_1)\big] \quad \text{for all} \quad r > 0\,, \quad \hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)\,. \tag{3.13}$$

This assures that the hypothesis ii) in Proposition 3.6 will be satisfied in all cases below where we apply the proposition (the hypothesis i) is trivially satisfied).

We illustrate how to apply this. Let

$$g_\omega(r) = g(r,\omega) = \int_{\mathcal{S}_1(\omega)} G(r\omega,\hat{\mathbf{x}}_1)\,d\hat{\mathbf{x}}_1 \qquad \Big(= \int_{\mathbb{R}^{3N-3}} G(r\omega,\hat{\mathbf{x}}_1)\,d\hat{\mathbf{x}}_1 \Big)\,.$$

Interchanging integration and differentiation as discussed above, we have, for $\omega \in \mathbb{S}^2$ fixed and $r > 0$, that

$$g_\omega{}'(r) = \int_{\mathcal{S}_1(\omega)} \omega \cdot \big[(\nabla_1 G)(r\omega,\hat{\mathbf{x}}_1)\big]\,d\hat{\mathbf{x}}_1\,. \tag{3.14}$$

To justify this, and to prove the existence of $\lim_{r\downarrow 0} g_\omega{}'(r)$ we will need to prove two things.

First, we need to find a dominant to the integrand in (3.14), that is, a function $\Phi_\omega \in L^1(\mathbb{R}^{3N-3})$ such that, for some $R_0 > 0$,

$$\big|\omega \cdot \big(\nabla_1 G\big)(r\omega, \hat{\mathbf{x}}_1)\big| \le \Phi_\omega(\hat{\mathbf{x}}_1) \quad \text{for all} \quad r \in (0, R_0)\,, \quad \hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)\,. \tag{3.15}$$

This will, by Proposition 3.6, also justify the above interchanging of $\frac{d}{dr}$ and the integral ((3.15) ensures that the hypothesis iii) is satisfied). We note that, with one exception, whenever we apply this, in fact $\Phi \equiv \Phi_\omega$ will be *independent* of $\omega \in \mathbb{S}^2$, and therefore $\Phi \in L^1(\mathbb{R}^{3N-3} \times \mathbb{S}^2)$.

Secondly, we need to prove, for all $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$ fixed, the existence of

$$\lim_{r\downarrow 0} \big[\omega \cdot (\nabla_1 G)(r\omega, \hat{\mathbf{x}}_1)\big]\,. \tag{3.16}$$

This, by Lebesgue's Theorem of Dominated Convergence, will prove the existence of $\lim_{r\downarrow 0} g_\omega{}'(r)$.

To study

$$\widetilde{g}(r) = \int_{\mathbb{S}^2} g(r,\omega)\, d\omega = \int_{\mathbb{S}^2} \int_{\mathbb{R}^{3N-3}} G(r\omega, \hat{\mathbf{x}}_1)\, d\hat{\mathbf{x}}_1\, d\omega \tag{3.17}$$

note that, by the above, the set

$$\Big(\mathbb{R}^{3N-3} \times \mathbb{S}^2\Big) \setminus \left(\bigcup_{\omega \in \mathbb{S}^2} \big[\mathcal{S}_1(\omega) \times \{\omega\}\big] \right)$$

has measure zero, and that, also by the above, the partial derivative $\partial\widetilde{G}/\partial r(r, (\hat{\mathbf{x_1}}, \omega))$ of the function

$$\big(r, (\hat{\mathbf{x}}_1, \omega)\big) \mapsto \widetilde{G}\big(r, (\hat{\mathbf{x}}_1, \omega)\big) \equiv G(r\omega, \hat{\mathbf{x}}_1)$$

exists for all $r > 0$ and $(\hat{\mathbf{x}}_1, \omega) \in \cup_{\omega\in\mathbb{S}^2}\big[\mathcal{S}_1(\omega) \times \{\omega\}\big]$. As noted above, the dominants Φ we will exhibit below when studying $g(r,\omega)$ will (except in one case) be independent of $\omega \in \mathbb{S}^2$, and so can also be used to apply both Lebegue's Theorem on Dominated Convergence, Proposition 3.6, and Fubini's Theorem on the integral in (3.17). This implies that

$$\lim_{r\downarrow 0} \widetilde{g}\,'(r) = \int_{\mathbb{R}^{3N-3}} \int_{\mathbb{S}^2} \Big\{ \lim_{r\downarrow 0} \omega \cdot \big[(\nabla_1 G)(r\omega, \hat{\mathbf{x}}_1)\big] \Big\}\, d\omega\, d\hat{\mathbf{x}}_1\,, \tag{3.18}$$

as soon as we have proved the pointwise convergence of the integrand for all $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$, and provided the mentioned dominant. (In the last, exceptional case, we will provide a dominant $\Phi \in L^1(\mathbb{R}^{3N-3} \times \mathbb{S}^2)$).

In the sequel, we shall use all of this without further mentioning, apart from proving the existence of a dominant, and the existence of the pointwise limits of the integrands on $\mathcal{S}_1(\omega)$. Also, for notational convenience, we shall allow ourselves to write all integrals over $\mathbb{R}^{3N-3}$ instead of over $\mathcal{S}_1(\omega)$.

3.3. Additional partial regularity

For the existence of pointwise limits the following lemma will be essential; it gives detailed information about the structure of the eigenfunction ψ in the vicinity of the two-particle singularity $x = 0$. The lemma is reminiscent of more detailed results obtained earlier, see [3, Proposition 2], [4, Lemma 2.2], and [5, Lemma 3.1].

We need to recall the definition of Hölder-continuity.

Definition 3.8. 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 $B_n(x_0, r)$ with $\overline{B_n(x_0, r)} \subset \Omega$, we have

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

When $k = 0$ and $\alpha \in (0,1)$ we also write $C^\alpha(\Omega) \equiv C^{0,\alpha}(\Omega)$.

Lemma 3.9. *Let $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1^0 \in \mathcal{S}_1(\omega)$. Then there exists an open neighbourhood $U \subset \mathcal{S}_1(\omega) \subset \mathbb{R}^{3N-3}$ of $\hat{\mathbf{x}}_1^0$ and $\epsilon > 0$ such that*

$$\psi(x, \hat{\mathbf{x}}_1) = e^{-\frac{Z}{2}|x|}\varphi_1(x, \hat{\mathbf{x}}_1) \quad \text{with} \tag{3.19}$$

$$\partial^\beta_{\hat{\mathbf{x}}_1}\varphi_1 \in C^{1,\alpha}\big(B_3(0,\epsilon)\times U\big) \quad \text{for all} \quad \alpha \in (0,1)\,, \quad \beta \in \mathbb{N}^{3N-3}\,. \tag{3.20}$$

Proof. By the definition (3.12) of $\mathcal{S}_1(\omega)$ there exists a neighbourhood $U \subset \mathcal{S}_1(\omega) \subset \mathbb{R}^{3N-3}$ of $\hat{\mathbf{x}}_1^0 \in \mathcal{S}_1(\omega)$, and $\epsilon > 0$ such that

$$\begin{aligned} &x_j \neq x_k \quad \text{for} \quad j,k \in \{2,\dots,N\} \quad \text{with} \quad j \neq k\,, \\ &x_j \neq 0\,, \quad x_j \neq x \quad \text{for} \quad j \in \{2,\dots,N\} \\ &\text{for all} \quad (x, x_2, \dots, x_N) \in B_3(0,\epsilon)\times U \subset \mathbb{R}^{3N}\,. \end{aligned} \tag{3.21}$$

Make the *Ansatz* $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$. Using (1.4), (1.1), and that $\Delta_x(|x|) = 2|x|^{-1}$, we get that φ_1 satisfies the equation

$$\Delta\varphi_1 - Z\frac{x}{|x|}\cdot\nabla_1\varphi_1 + \left(\frac{Z^2}{4} + E - V_1\right)\varphi_1 = 0 \tag{3.22}$$

with

$$V_1(x, \hat{\mathbf{x}}_1) = \sum_{j=2}^N -\frac{Z}{|x_j|} + \sum_{k=2}^N \frac{1}{|x - x_k|} + \sum_{2\leq j<k\leq N}\frac{1}{|x_j - x_k|}\,, \tag{3.23}$$

where, due to (3.21),

$$V_1 \in C^\infty\big(B_3(0,\epsilon)\times U\big)\,. \tag{3.24}$$

Since the coefficients in (3.22) are in $L^\infty(B_3(0,\epsilon)\times U))$, this implies, by standard elliptic regularity [8, Theorem 8.36], that

$$\varphi_1 \in C^{1,\alpha}\big(B_3(0,\epsilon)\times U\big) \quad \text{for all} \quad \alpha \in (0,1)\,. \tag{3.25}$$

Let $\eta \in \mathbb{N}^{3N-3}$, $|\eta| = 1$; differentiating (3.22) we get

$$\Delta(\partial^\eta_{\hat{\mathbf{x}}_1}\varphi_1) - Z\frac{x}{|x|}\cdot\nabla_1(\partial^\eta_{\hat{\mathbf{x}}_1}\varphi_1) = -\left[\left(\frac{Z^2}{4} + E - V_1\right)(\partial^\eta_{\hat{\mathbf{x}}_1}\varphi_1) - (\partial^\eta_{\hat{\mathbf{x}}_1}V_1)\varphi_1\right]. \quad (3.26)$$

By (3.23) and (3.25), the right side in (3.26) belongs to $C^\alpha(B_3(0,\epsilon)\times U)$ for all $\alpha \in (0,1)$ and so, by elliptic regularity, $\partial^\eta_{\hat{\mathbf{x}}_1}\varphi_1 \in C^{1,\alpha}(B_3(0,\epsilon)\times U)$ for all $\alpha \in (0,1)$. An easy induction argument finally gives that

$$\partial^\beta_{\hat{\mathbf{x}}_1}\varphi_1 \in C^{1,\alpha}\big(B_3(0,\epsilon)\times U\big) \quad \text{for all} \quad \alpha\in(0,1)\,, \quad \beta \in \mathbb{N}^{3N-3}\,. \qquad \square$$

3.4. Proof of Proposition 3.1

We will treat the two kinds of terms in (3.4) separately.

For the first one, we make a change of variables. Assume without loss of generality that $k = 2$, and let $y = x_2 - r\omega$, then

$$\int_{\mathbb{R}^{3N-3}} \frac{1}{|r\omega - x_2|}\,|\psi(r\omega,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1 = \int_{\mathbb{R}^{3N-3}} \frac{1}{|y|}\,|\psi(r\omega, y + r\omega, x_3,\dots,x_N)|^2\,dy\,dx_3\dots dx_N\,. \quad (3.27)$$

For $\omega \in \mathbb{S}^2$ fixed, and $r > 0$, interchanging integration and differentiation as discussed above, we get, using (3.27), that

$$\frac{d}{dr}\left[\int_{\mathbb{R}^{3N-3}} \frac{1}{|r\omega - x_2|}\,|\psi(r\omega,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\right] = \int_{\mathbb{R}^{3N-3}}\left[\frac{2}{|y|}\,\psi\big\{\omega\cdot(\nabla_1\psi + \nabla_2\psi)\big\}\right](r\omega, y + r\omega, x_3,\dots,x_N)\,dy\,dx_3\dots dx_N\,. \quad (3.28)$$

Note that, using (1.8), (1.9), and equivalence of norms in $\mathbb{R}^{3N}$, there exists positive constants C, c_1, c_2 such that

$$\left|\frac{2}{|y|}\,\psi\big\{\omega\cdot(\nabla_1\psi + \nabla_2\psi)\big\}(r\omega, y + r\omega, x_3,\dots,x_N)\right| \le C\,e^{c_1 r}\,\frac{1}{|y|}\,e^{-c_2|(y,x_3,\dots,x_N)|}\,, \quad (3.29)$$

which provides a dominant, independent of $\omega \in \mathbb{S}^2$, in the sense of (3.15), uniformly for $r \in (0, R_0)$ for any $R_0 > 0$.

Writing $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$, the integrand in (3.28) equals

$$\frac{1}{|y|}\Big[-Z|\psi|^2 + 2\varphi_1\,e^{-Zr}\big(\omega\cdot\{\nabla_1\varphi_1 + \nabla_2\varphi_1\}\big)\Big](r\omega, y + r\omega, x_3,\dots,x_N)\,,$$

which has a limit as $r \downarrow 0$ (for $\omega \in \mathbb{S}^2$ and $(y, x_3,\dots,x_N)$ fixed) since $\varphi_1 \in C^{1,\alpha}$ by Lemma 3.9. This proves the existence of the limit of the integrand in (3.28), and therefore of the limit as $r \downarrow 0$ of the derivative with respect to r of the first term in (3.4). Note that since $\int_{\mathbb{S}^2} \omega\, d\omega = 0$, the terms proportional to ω vanish by integration over $(y, x_3, \ldots, x_N, \omega)$. The limit of the derivative of the spherical average of this term is therefore (after setting $x_2 = y$)

$$-Z \int_{\mathbb{S}^2} \int_{\mathbb{R}^{3N-3}} \frac{1}{|x_2|} \, |\psi(0, \hat{\mathbf{x}}_1)|^2 \, d\hat{\mathbf{x}}_1 \, d\omega \,. \tag{3.30}$$

For the second term in (3.4), assume without loss that $k = 2$, $\ell = 3$, and write $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$ as before. Then, for $\omega \in \mathbb{S}^2$ fixed, and $r > 0$, interchanging integration and differentiation we get

$$\begin{aligned} &\frac{d}{dr} \left[\int_{\mathbb{R}^{3N-3}} \frac{1}{|x_2 - x_3|} \, |\psi(x, \hat{\mathbf{x}}_1)|^2 \, d\hat{\mathbf{x}}_1 \right] \\ &\quad = \int_{\mathbb{R}^{3N-3}} \frac{2}{|x_2 - x_3|} \, \psi(r\omega, \hat{\mathbf{x}}_1) \big[\omega \cdot \nabla_1 \psi(r\omega, \hat{\mathbf{x}}_1) \big] \, d\hat{\mathbf{x}}_1 \,. &(3.31) \\ &\quad = \int_{\mathbb{R}^{3N-3}} \frac{1}{|x_2 - x_3|} \big[- Z|\psi|^2 + 2\varphi_1 \, e^{-Zr} (\omega \cdot \nabla_1 \varphi_1) \big] (r\omega, \hat{\mathbf{x}}_1) \, d\hat{\mathbf{x}}_1 \,. &(3.32) \end{aligned}$$

As above, (1.8) and (1.9) provides us with a dominant to the integrand in (3.31) in the sense of (3.15).

Also as before, the integrand in (3.32) has a limit as $r \downarrow 0$, since $\varphi_1 \in C^{1,\alpha}$ by Lemma 3.9. This proves the existence of the limit as $r \downarrow 0$ of the derivative of the second term in (3.4). Again, the term in (3.32) proportional to ω vanish when integrating over $(\hat{\mathbf{x}}_1, \omega)$, since $\int_{\mathbb{S}^2} \omega\, d\omega = 0$. The limit of the derivative of the spherical average of this term is therefore

$$-Z \int_{\mathbb{S}^2} \int_{\mathbb{R}^{3N-3}} \frac{1}{|x_2 - x_3|} \, |\psi(0, \hat{\mathbf{x}}_1)|^2 \, d\hat{\mathbf{x}}_1 \, d\omega \,. \tag{3.33}$$

This proves the existence of $\lim_{r\downarrow 0} w_1{}'(r, \omega)$ (for any $\omega \in \mathbb{S}^2$ fixed), and of $\lim_{r\downarrow 0} \widetilde{w}_1{}'(r)$. Furthermore, from (3.30) and (3.33),

$$\begin{aligned} \lim_{r\downarrow 0} \widetilde{w}_1{}'(r) &= -Z \int_{\mathbb{S}^2} \int_{\mathbb{R}^{3N-3}} \left[\sum_{k=2}^{N} \frac{1}{|x_k|} \right] |\psi(0, \hat{\mathbf{x}}_1)|^2 \, d\hat{\mathbf{x}}_1 d\omega \\ &\quad - Z \int_{\mathbb{S}^2} \int_{\mathbb{R}^{3N-3}} \left[\sum_{2 \le k < \ell \le N} \frac{1}{|x_k - x_\ell|} \right] |\psi(0, \hat{\mathbf{x}}_1)|^2 \, d\hat{\mathbf{x}}_1 d\omega \\ &= -Z \widetilde{w}_1(0) \,. \end{aligned}$$

The proof for v_1 is similar, but simpler; we give it for completeness. For $r > 0$ we get, by arguments as for $w_1{}'$, that

$$\begin{aligned} v_1{}'(r, \omega) &= \sum_{k=2}^{N} \int_{\mathbb{R}^{3N-3}} \frac{2Z}{|x_k|} \, \psi(r\omega, \hat{\mathbf{x}}_1) \big[\omega \cdot \nabla_1 \psi(r\omega, \hat{\mathbf{x}}_1) \big] \, d\hat{\mathbf{x}}_1 &(3.34) \\ &= \sum_{k=2}^{N} \int_{\mathbb{R}^{3N-3}} \frac{Z}{|x_k|} \big[- Z|\psi|^2 + 2\varphi_1 \, e^{-Zr} (\omega \cdot \nabla_1 \varphi_1) \big] (r\omega, \hat{\mathbf{x}}_1) \, d\hat{\mathbf{x}}_1 \,. &(3.35) \end{aligned}$$

One provides a dominant to the integrand in (3.34) in a similar way as for w_1. We omit the details. Again, existence of the limit as $r \downarrow 0$ of the integrand in (3.35) is ensured by Lemma 3.9.

The last term in (3.35) again vanishes when taking the limit $r \downarrow 0$ and then integrating over $(\hat{\mathbf{x}}_1, \omega)$, since $\int_{\mathbb{S}^2} \omega \, d\omega = 0$, and so

$$\begin{aligned}\lim_{r\downarrow 0} \widetilde{v}_1{}'(r,\omega) &= -Z \sum_{k=2}^{N} \int_{\mathbb{S}^2} \int_{\mathbb{R}^{3N-3}} \frac{Z}{|x_k|} \, |\psi(0,\hat{\mathbf{x}}_1)|^2 \, d\hat{\mathbf{x}}_1 d\omega \\ &= -Z \widetilde{v}_1(0) \, .\end{aligned}$$

This finishes the proof of Proposition 3.1. □

3.5. Proof of Proposition 3.3

We proceed as in the proof of Proposition 3.1. Interchanging integration and differentiation as discussed in Section 3.2 we have, for $\omega \in \mathbb{S}^2$ fixed and $r > 0$, that

$$t_1{}'(r,\omega) = \int_{\mathbb{R}^{3N-3}} \omega \cdot \big[\nabla_1(|\nabla\psi|^2)(r\omega,\hat{\mathbf{x}}_1)\big] \, d\hat{\mathbf{x}}_1 \, . \tag{3.36}$$

Again, to justify this and to prove the existence of $\lim_{r\downarrow 0} t_1{}'(r,\omega)$ we need to prove two things: The existence of the pointwise limit as $r \downarrow 0$ of the integrand above, for $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$ fixed, and the existence of a dominant in the sense of (3.15).

Pointwise limits

We start with the pointwise limit. We allow ourselves to compute the integrals of the found limits, presuming the dominant found. We shall provide the necessary dominants afterwards.

Recall from (the proof of) Lemma 3.9 that $\varphi_1 = e^{\frac{Z}{2}|x|}\psi$ satisfies the equation

$$\Delta\varphi_1 - Z\frac{x}{|x|} \cdot \nabla_1\varphi_1 + \left(\frac{Z^2}{4} + E - V_1\right)\varphi_1 = 0 \tag{3.37}$$

where

$$V_1 \in C^\infty\big(B_3(0,\epsilon) \times U\big)$$

for some $\epsilon > 0$ and $U \subset \mathcal{S}_1(\omega) \subset \mathbb{R}^{3N-3}$ some neighbourhood of $\hat{\mathbf{x}}_1$.

Using Lemma 3.9, we get that $\Delta_{\hat{\mathbf{x}}_1}\varphi_1 \in C^{1,\alpha}(B_3(0,\epsilon) \times U)$ for all $\alpha \in (0,1)$. From this and (3.37) follows that for any $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$ fixed, and some $\epsilon > 0$, the function $x \mapsto \varphi_1(x,\hat{\mathbf{x}}_1)$ satisfies the equation

$$\Delta_x\varphi_1 - Z\frac{x}{|x|} \cdot \nabla_x\varphi_1 = -\Delta_{\hat{\mathbf{x}}_1}\varphi_1 - \left(\frac{Z^2}{4} + E - V_1\right)\varphi_1 \tag{3.38}$$

$$\equiv G_{\hat{\mathbf{x}}_1} \, , \; G_{\hat{\mathbf{x}}_1} \in C^{1,\alpha}\big(B_3(0,\epsilon)\big) \, , \quad \alpha \in (0,1) \, . \tag{3.39}$$

Furthermore, from Lemma 3.9 (with $\beta = 0$) it follows that $\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)$ is well-defined. Note that for $c \in \mathbb{R}^3$ the function

$$v(x) = \frac{1}{4}|x|^2(c\cdot\omega) = \frac{1}{4}|x|(x\cdot c) \tag{3.40}$$

solves $\Delta_x v = c\cdot\omega$. Therefore, with $c = Z\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)$, the function $u = u_{\hat{\mathbf{x}}_1} = \varphi_1(\,\cdot\,,\hat{\mathbf{x}}_1) - v$ satisfies the equation (in x, with $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$ fixed)

$$\begin{aligned}\Delta_x u(x) &= Z\frac{x}{|x|}\cdot\big(\nabla_1\varphi_1(x,\hat{\mathbf{x}}_1) - \nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)\big)\\ &\quad - \Delta_{\hat{\mathbf{x}}_1}\varphi_1(x,\hat{\mathbf{x}}_1) - \left(\frac{Z^2}{4} + E - V_1\right)\varphi_1(x,\hat{\mathbf{x}}_1) \equiv g_{\hat{\mathbf{x}}_1}(x)\,.\end{aligned} \tag{3.41}$$

By the above, and Lemma A.1 in Appendix A (using that $\nabla_1\varphi_1$ is C^α), $g_{\hat{\mathbf{x}}_1} \in C^\alpha(\mathbb{R}^3)$ for all $\alpha \in (0,1)$, and so, by standard elliptic regularity, $u \in C^{2,\alpha}(\mathbb{R}^3)$ for all $\alpha \in (0,1)$. To recapitulate, for any $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$, the function $x \mapsto \varphi_1(x,\hat{\mathbf{x}}_1)$ satisfies

$$\varphi_1(x,\hat{\mathbf{x}}_1) = u_{\hat{\mathbf{x}}_1}(x) + \frac{1}{4}|x|^2\left(c\cdot\frac{x}{|x|}\right)\,,\quad u_{\hat{\mathbf{x}}_1} \in C^{2,\alpha}(\mathbb{R}^3)\,,\quad \alpha \in (0,1)\,. \tag{3.42}$$

Note that

$$c = Z\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1) = Z\nabla_x u_{\hat{\mathbf{x}}_1}(0)\,. \tag{3.43}$$

We now apply the above to prove the existence of the pointwise limit of the integrand in (3.36) for fixed $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$.

First, since $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$, we have, for $j = 2,\dots,N$,

$$\begin{aligned}\omega\cdot\big[\nabla_1(|\nabla_j\psi|^2)(r\omega,\hat{\mathbf{x}}_1)\big] &= \omega\cdot\big[\nabla_1(e^{-Z|x|}|\nabla_j\varphi_1|^2)(r\omega,\hat{\mathbf{x}}_1)\big]\\ &= -Ze^{-Zr}|\nabla_j\varphi_1|^2(r\omega,\hat{\mathbf{x}}_1)\\ &\quad + e^{-Zr}\Big\{\omega\cdot\big[\nabla_1(|\nabla_j\varphi_1|^2)(r\omega,\hat{\mathbf{x}}_1)\big]\Big\}\,.\end{aligned}$$

Because of (3.20) in Lemma 3.9, this has a limit as $r \downarrow 0$ for fixed $\omega \in \mathbb{S}^2$ (recall that $j = 2,\dots,N$). The contribution to $\lim_{r\downarrow 0}\widetilde{t}_1'(r)$ from this is

$$-Z\sum_{j=2}^{N}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla_j\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega\,, \tag{3.44}$$

since terms proportional with ω vanish upon integration.

So we are left with considering $\omega\cdot\nabla_1\big(|\nabla_1\psi|^2\big)$ (see (3.36)). To this end, use again $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$ to get

$$\begin{aligned}\omega\cdot\nabla_x\big(|\nabla_1\psi|^2\big) &= \omega\cdot\nabla_x\left(\left|-\frac{Z}{2}\omega\psi + e^{-\frac{Z}{2}|x|}\nabla_1\varphi_1\right|^2\right)\\ &= \omega\cdot\nabla_x\left(\frac{Z^2}{4}\psi^2 + e^{-Z|x|}|\nabla_1\varphi_1|^2 - Z(\omega\cdot\nabla_1\varphi_1)e^{-Z|x|}\varphi_1\right).\end{aligned} \tag{3.45}$$

(We leave out the variables, $(r\omega, \hat{\mathbf{x}}_1)$). We will study each of the three terms in (3.45) separately.

For the first term in (3.45), again using $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$, we have

$$\omega \cdot \nabla_x \left(\frac{Z^2}{4}\psi^2\right) = -\frac{Z^3}{4}\psi^2 + \frac{Z^2}{2}\psi e^{-\frac{Z}{2}|x|}(\omega \cdot \nabla_1 \varphi_1)\,, \tag{3.46}$$

which has a limit as $r \downarrow 0$ for fixed $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$, since φ_1 is $C^{1,\alpha}$ (see (3.25)). The contribution to $\lim_{r\downarrow 0} \widetilde{t}_1'(r)$ from this is

$$-\frac{Z^3}{4}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}} |\psi(0, \hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\, d\omega = -\frac{Z^3}{4}\widetilde{\rho}_1(0)\,. \tag{3.47}$$

As for the second term in (3.45) we have

$$\omega \cdot \nabla_x\big(e^{-Z|x|}|\nabla_1\varphi_1|^2\big) = -Ze^{-Z|x|}|\nabla_1\varphi_1|^2 + e^{-Z|x|}(\omega \cdot \nabla_1|\nabla_1\varphi_1|^2)\,, \tag{3.48}$$

where the first term has a limit as $r \downarrow 0$ for fixed $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$, since φ_1 is $C^{1,\alpha}$ (see (3.25)). This contributes

$$-Z\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}} |\nabla_1\varphi_1(0, \hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\, d\omega \tag{3.49}$$

to $\lim_{r\downarrow 0} \widetilde{t}_1'(r)$. For the second term (in (3.48)), using that $\varphi_1 = u + \frac{1}{4}r^2(c\cdot\omega)$ (see (3.42)), we get that

$$\begin{aligned} |\nabla_1\varphi_1|^2 = |\nabla_1 u|^2 &+ \frac{1}{2}\big[(\omega \cdot \nabla_1 u)(c\cdot x) + r(c \cdot \nabla_1 u)\big] \\ &+ \frac{3}{16}(c\cdot x)^2 + \frac{1}{16}r^2(c\cdot c)\,, \end{aligned}$$

and so

$$\begin{aligned} \omega \cdot \nabla_1|\nabla_1\varphi_1|^2 = 2\big\langle \omega, (D^2u)\nabla_1 u\big\rangle &+ \frac{3}{8}r(c\cdot\omega)^2 + \frac{1}{8}r(c\cdot c) \\ &+ \frac{1}{2}\Big[\big\langle \omega, (D^2u)\omega\big\rangle(c\cdot x) + (\omega\cdot\nabla_1 u)(c\cdot\omega) \\ &+ (c\cdot\nabla_1 u) + r\big\langle \omega, (D^2u)c\big\rangle\Big]\,. \end{aligned}$$

Here, D^2u is the Hessian matrix of $u = u_{\hat{\mathbf{x}}_1}$ with respect to x, and $\langle\,\cdot\,,\cdot\,\rangle$ is the scalar product in $\mathbb{R}^3$. Since $\varphi_1 \in C^{1,\alpha}$, and $u \in C^{2,\alpha}$, all terms have a limit as $r \downarrow 0$ for fixed $\omega \in \mathbb{S}^2$ and $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$. We get

$$\begin{aligned} \lim_{r\downarrow 0}\big[(e^{-Z|x|}\omega\cdot\nabla_1|\nabla_1\varphi_1|^2)(r\omega, \hat{\mathbf{x}}_1)\big] &= 2\omega\cdot\big[(D^2u_{\hat{\mathbf{x}}_1})(0)\nabla_x u_{\hat{\mathbf{x}}_1}(0)\big] \\ &+ \frac{1}{2}\Big[\big(c\cdot\nabla_x u_{\hat{\mathbf{x}}_1}(0)\big) + \big(\omega\cdot\nabla_x u_{\hat{\mathbf{x}}_1}(0)\big)(c\cdot\omega)\Big]\,. \end{aligned} \tag{3.50}$$

When integrating, this contributes

$$\frac{2Z}{3}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}} |\nabla_1\varphi_1(0, \hat{\mathbf{x}}_1)|^2\, d\hat{\mathbf{x}}_1\, d\omega \tag{3.51}$$

to $\lim_{r\downarrow 0}\widetilde{t}_1{}'(r)$; to see this, use (3.43) and Lemma A.2 in Appendix A, and that $\int_{\mathbb{S}^2}\omega\, d\omega = 0$.

For the third and last term in (3.45), using that $\varphi_1 = u + \frac{1}{4}r^2(c\cdot\omega)$ (see (3.42)) and $\omega\cdot\nabla_x = \partial_r$, we get that

$$\begin{aligned}\omega\cdot\nabla_x\big(-Z(\omega\cdot\nabla_1\varphi_1)e^{-Z|x|}\varphi_1\big) &= Z^2(\omega\cdot\nabla_1\varphi_1)e^{-Z|x|}\varphi_1\\ &\quad - Ze^{-Z|x|}\varphi_1\Big[\big\langle\omega,(D^2u)\omega\big\rangle + \frac{1}{2}(c\cdot\omega)\Big]\\ &\quad - Z(\omega\cdot\nabla_x\varphi_1)^2e^{-Z|x|}\,.\end{aligned}$$

Again, since $\varphi_1 \in C^{1,\alpha}$, and $u \in C^{2,\alpha}$, all terms have a limit as $r\downarrow 0$ for fixed $\omega\in\mathbb{S}^2$ and $\hat{\mathbf{x}}_1\in\mathcal{S}_1(\omega)$.

The contribution from this to $\lim_{r\downarrow 0}\widetilde{t}_1{}'(r)$ is, using Lemma A.2, and $\int_{\mathbb{S}^2}\omega\, d\omega = 0$,

$$\begin{aligned}&-\frac{Z}{3}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega\\ &\qquad\qquad -\frac{Z}{3}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}\Delta_x u_{\hat{\mathbf{x}}_1}(0)\varphi_1(0,\hat{\mathbf{x}}_1)\,d\hat{\mathbf{x}}_1\,d\omega\,. \end{aligned}\tag{3.52}$$

Here we used that $\mathrm{Tr}(D^2f) = \Delta f$.

This proves the existence of the pointwise limit of the integrand in (3.36) for fixed $\omega\in\mathbb{S}^2$ and $\hat{\mathbf{x}}_1\in\mathcal{S}_1(\omega)$. Also, from (3.44), (3.47), (3.49) (3.51), and (3.52),

$$\begin{aligned}\lim_{r\downarrow 0}\widetilde{t}_1{}'(r) = &-\Big[Z\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega + \frac{Z^3}{4}\widetilde{\rho}_1(0)\Big]\\ &+\frac{Z}{3}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega\\ &-\frac{Z}{3}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}\Delta_x u_{\hat{\mathbf{x}}_1}(0)\varphi_1(0,\hat{\mathbf{x}}_1)\,d\hat{\mathbf{x}}_1\,d\omega\,.\end{aligned}\tag{3.53}$$

Note that, due to (3.41) and $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$,

$$\Delta_x u_{\hat{\mathbf{x}}_1}(0) = -\Delta_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1) - \Big(\frac{Z^2}{4} + E - V_{N-1,Z-1}(\hat{\mathbf{x}}_1)\Big)\psi(0,\hat{\mathbf{x}}_1)\,,$$

since $V_1(0,\hat{\mathbf{x}}_1) = V_{N-1,Z-1}(\hat{\mathbf{x}}_1)$ (see (1.3)). This implies that

$$\begin{aligned}\lim_{r\downarrow 0}\widetilde{t}_1{}'(r) = &-\Big[Z\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega + \frac{Z^3}{4}\widetilde{\rho}_1(0)\Big]\\ &+\frac{Z}{3}\Big[\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega + \frac{Z^2}{4}\widetilde{\rho}_1(0)\\ &-\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}\Big[|\nabla_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1)|^2 + \big(V_{N-1,Z-1}(\hat{\mathbf{x}}_1)-E\big)|\psi(0,\hat{\mathbf{x}}_1)|^2\Big]d\hat{\mathbf{x}}_1\,d\omega\Big]\,.\end{aligned}\tag{3.54}$$

Here we used that

$$-\int_{\mathbb{R}^{3N-3}} \psi(0,\hat{\mathbf{x}}_1)\big(\Delta_{\hat{\mathbf{x}}_1}\psi\big)(0,\hat{\mathbf{x}}_1)\,d\hat{\mathbf{x}}_1 = \int_{\mathbb{R}^{3N-3}} |\nabla_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,. \tag{3.55}$$

Before we provide a dominant in the sense of (3.15) to the integrand in (3.36) we now compute $\widetilde{t}_1(0)$. Note that for $r>0$,

$$\begin{aligned}\widetilde{t}_1(r) = &\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}} |\nabla_1\psi(r\omega,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega \\ &+\sum_{j=2}^{N}\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}} |\nabla_j\psi(r\omega,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1\,d\omega\,.\end{aligned} \tag{3.56}$$

Use $\psi = e^{-\frac{Z}{2}|x|}\varphi_1$, then, for all $\omega\in\mathbb{S}^2$ and $\hat{\mathbf{x}}_1\in\mathcal{S}_1(\omega)$ fixed, and $j=2,\dots,N$, Lemma 3.9 gives that

$$|\nabla_j\psi(r\omega,\hat{\mathbf{x}}_1)|^2 = e^{-Zr}|\nabla_j\varphi_1(r\omega,\hat{\mathbf{x}}_1)|^2 \quad\xrightarrow{r\to 0}\quad |\nabla_j\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,. \tag{3.57}$$

In particular, this proves the existence of

$$|\nabla_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1)|^2 = \sum_{j=2}^{N}|\nabla_j\psi(0,\hat{\mathbf{x}}_1)|^2 = \sum_{j=2}^{N}|\nabla_j\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,. \tag{3.58}$$

Similarly,

$$\begin{aligned}|\nabla_1\psi(r\omega,\hat{\mathbf{x}}_1)|^2 \;=\;& \frac{Z^2}{4}|\psi(r\omega,\hat{\mathbf{x}}_1)|^2 + e^{-Zr}|\nabla_1\varphi_1(r\omega,\hat{\mathbf{x}}_1)|^2 \\ &- Ze^{-\frac{Z}{2}r}\psi(r\omega,\hat{\mathbf{x}}_1)\big(\omega\cdot\nabla_1\varphi_1(r\omega,\hat{\mathbf{x}}_1)\big) \\ \xrightarrow{r\to 0}\;& \frac{Z^2}{4}|\psi(0,\hat{\mathbf{x}}_1)|^2 + |\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)|^2 - Z\psi(0,\hat{\mathbf{x}}_1)\big(\omega\cdot\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)\big)\,.\end{aligned} \tag{3.59}$$

Using again $\int_{\mathbb{S}^2}\omega\,d\omega = 0$, it follows from (3.56)–(3.59), and Lebesgue's Theorem of Dominated Convergence that

$$\begin{aligned}\lim_{r\downarrow 0}\widetilde{t}_1(r) = &\frac{Z^2}{4}\widetilde{\rho}_1(0) + \int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla_1\varphi_1(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1 d\omega \\ &+\int_{\mathbb{S}^2}\int_{\mathbb{R}^{3N-3}}|\nabla_{\hat{\mathbf{x}}_1}\psi(0,\hat{\mathbf{x}}_1)|^2\,d\hat{\mathbf{x}}_1 d\omega\,.\end{aligned} \tag{3.60}$$

This proves (3.9). Combining this with (3.54) (using (3.58)) proves (3.10).

Dominant

We turn to finding a dominant to the integrand in (3.36). We shall apply results from [6], recalled in Appendix B.

From the *a priori* estimate (B.8) in Theorem B.3 and (3.36) follows that, for almost all $(x, \hat{\mathbf{x}}_1) = \mathbf{x} \in \mathbb{R}^{3N}$ (choose, e.g., $R = 1, R' = 2$)

$$\begin{aligned}\big|\omega \cdot \nabla_1\big(|\nabla\psi|^2\big)(x, \hat{\mathbf{x}}_1)\big| &\le C\,\big|\nabla\psi(x, \hat{\mathbf{x}}_1)\big|\,\|\psi\|_{L^\infty(B_{3N}((x,\hat{\mathbf{x}}_1),2))} \\ &\quad + \left|\left(\sum_{\ell=1}^{N}\sum_{k=1}^{3}\sum_{m=1}^{3} 2\frac{x_{1,k}}{|x_1|}\left(\frac{\partial\psi}{\partial x_{\ell,m}}\right)\psi\frac{\partial^2 F_{\mathrm{cut}}}{\partial x_{1,k}\partial x_{\ell,m}}\right)(x, \hat{\mathbf{x}}_1)\right|,\end{aligned} \tag{3.61}$$

with $F_{\mathrm{cut}} = F_{2,\mathrm{cut}} + F_{3,\mathrm{cut}}$ as in Definition B.2.

Now, using the exponential decay of ψ (1.8) (assumed), and of $\nabla\psi$ (1.9), we get that there exist constants $C, \gamma > 0$ such that

$$\big|\nabla\psi(x, \hat{\mathbf{x}}_1)\big|\,\|\psi\|_{L^\infty(B_{3N}((x,\hat{\mathbf{x}}_1),2))} \le Ce^{-\gamma|\hat{\mathbf{x}}_1|} \quad \text{for almost all} \quad x \in \mathbb{R}^3\,. \tag{3.62}$$

This provides a dominant (in the sense of (3.15)) for the first term in (3.61).

We need to find a dominant for the second term in (3.61). First recall that $F_{\mathrm{cut}} = F_{2,\mathrm{cut}} + F_{3,\mathrm{cut}}$. With F_2 as in (B.1) we have $F_{2,\mathrm{cut}} = F_2 + (F_{2,\mathrm{cut}} - F_2)$, with

$$\begin{aligned}(F_{2,\mathrm{cut}} - F_2)(\mathbf{x}) &= \sum_{i=1}^{N} -\frac{Z}{2}\big(\chi(|x_i|) - 1\big)\,|x_i| \\ &\quad + \sum_{1\le i<j\le N}\frac{1}{4}\big(\chi(|x_i - x_j|) - 1\big)\,|x_i - x_j|\,.\end{aligned} \tag{3.63}$$

Note that $\partial^2\big[(\chi(|x|) - 1)|x|\big]$ is bounded in $\mathbb{R}^3$ for all second derivatives ∂^2, due to the definition (B.3) of χ. Using the exponential decay of ψ (1.8), and $\nabla\psi$ (1.9), we therefore get a dominant for the term

$$\left(\sum_{\ell=1}^{N}\sum_{k=1}^{3}\sum_{m=1}^{3} 2\frac{x_{1,k}}{|x_1|}\left(\frac{\partial\psi}{\partial x_{\ell,m}}\right)\psi\frac{\partial^2(F_{2,\mathrm{cut}} - F_2)}{\partial x_{1,k}\partial x_{\ell,m}}\right)(x, \hat{\mathbf{x}}_1)\,.$$

A tedious, but straightforward computation gives that

$$\begin{aligned}&\sum_{\ell=1}^{N}\sum_{k=1}^{3}\sum_{m=1}^{3} 2\frac{x_{1,k}}{|x_1|}\left(\frac{\partial\psi}{\partial x_{\ell,m}}\right)\psi\frac{\partial^2 F_2}{\partial x_{1,k}\partial x_{\ell,m}} \\ &\qquad = \frac{1}{2}\psi\sum_{i=2}^{N}\bigg[\frac{1}{|x_1 - x_i|}\frac{x_1}{|x_1|}\cdot\big(\nabla_1\psi - \nabla_i\psi\big) \\ &\qquad\quad - \left(\frac{x_1}{|x_1|}\cdot\frac{x_1 - x_i}{|x_1 - x_i|^3}\right)\big[(\nabla_1\psi - \nabla_i\psi)\cdot(x_1 - x_i)\big]\bigg]\,.\end{aligned} \tag{3.64}$$

We first remark that, again using exponential decay of ψ and $\nabla\psi$, we get the estimate

$$\left|\left(\frac{1}{2}\psi\sum_{i=2}^{N}\frac{1}{|x_1-x_i|}\frac{x_1}{|x_1|}\cdot\big(\nabla_1\psi-\nabla_i\psi\big)\right)(r\omega,\hat{\mathbf{x}}_1)\right| \leq C\sum_{i=2}^{N}\left[\frac{e^{-c|x_i|}}{\operatorname{dist}(L(\omega),x_i)}\left(\prod_{j=2,j\neq i}^{N}e^{-c|x_j|}\right)\right], \quad (3.65)$$

where $\operatorname{dist}(L(\omega),y)$ is the distance from $y\in\mathbb{R}^3$ to the line $L(\omega)$ spanned by $\omega\in\mathbb{S}^2$. Note that for fixed $\omega\in\mathbb{S}^2$, the function $e^{-c|y|}/\operatorname{dist}(L(\omega),y)$ is integrable in $\mathbb{R}^3$, and its integral is independent of $\omega\in\mathbb{S}^2$. Therefore the right side of (3.65) is integrable in $\mathbb{R}^{3N-3}$ for fixed $\omega\in\mathbb{S}^2$, and is integrable in $\mathbb{R}^{3N-3}\times\mathbb{S}^2$ (all uniformly for $r\in\mathbb{R}$).

The argument is similar for the second term in (3.64).

We are left with considering the terms in (3.61) with $F_{3,\mathrm{cut}}$. Let

$$f_3(x,y)=C_0Z(x\cdot y)\ln\big(|x|^2+|y|^2\big)$$

(so that $F_3(\mathbf{x})=\sum_{i<j}f_3(x_i,x_j)$, see (B.2)). For all second derivatives ∂^2 we easily get, due to the definition (B.3) of χ,

$$\begin{aligned}\partial^2\big[\chi(|x|)\chi(|y|)f_3(x,y)\big] &= \chi(|x|)\chi(|y|)\partial^2 f_3(x,y)+g_3(x,y)\\ &= C_0Z\chi(|x|)\chi(|y|)\ln\big(|x|^2+|y|^2\big)\partial^2(x\cdot y)+\widetilde{g}_3(x,y)\,,\end{aligned}$$

with $g_3,\widetilde{g}_3$ bounded on $\mathbb{R}^6$. Therefore, defining, for all second derivatives ∂^2 and with χ as above,

$$\widetilde{\partial^2 F}_{3,\mathrm{cut}}(\mathbf{x}):=C_0Z\sum_{1\leq i<j\leq N}\chi(|x_i|)\chi(|x_j|)\ln\big(|x|^2+|y|^2\big)\partial^2(x\cdot y)\,, \quad (3.66)$$

we get a dominant for the term

$$\left[\sum_{\ell=1}^{N}\sum_{k=1}^{3}\sum_{m=1}^{3}2\frac{x_{1,k}}{|x_1|}\left(\frac{\partial\psi}{\partial x_{\ell,m}}\right)\psi\left(\frac{\partial^2F_{3,\mathrm{cut}}}{\partial x_{1,k}\partial x_{\ell,m}}-\frac{\widetilde{\partial^2F}_{3,\mathrm{cut}}}{\partial x_{1,k}\partial x_{\ell,m}}\right)\right](x,\hat{\mathbf{x}}_1)\,,$$

using the exponential decay of ψ and $\nabla\psi$. We find that

$$\sum_{\ell=1}^{N}\sum_{k=1}^{3}\sum_{m=1}^{3}2\frac{x_{1,k}}{|x_1|}\left(\frac{\partial\psi}{\partial x_{\ell,m}}\right)\psi\frac{\widetilde{\partial^2F}_{3,\mathrm{cut}}}{\partial x_{1,k}\partial x_{\ell,m}} = 2C_0Z\psi\sum_{i=2}^{N}\chi(|x_1|)\chi(|x_i|)\left[\ln(|x_1|^2+|x_i|^2)\left(\frac{x_1}{|x_1|}\cdot\nabla_i\psi\right)\right]. \quad (3.67)$$

Note that, by the definition of χ,

$$\chi(|x|)\chi(|y|)\,\big|\ln(|x|^2+|y|^2)\big|\leq\chi(|y|)\big[|\ln(|y|^2)|+3\big]\,,$$

and so, again by the exponential decay of ψ and $\nabla\psi$,

$$\left|2C_0 Z\psi \sum_{i=2}^{N}\left[\chi(|x_1|)\chi(|x_i|)\ln(|x_1|^2+|x_i|^2)\left(\frac{x_1}{|x_1|}\cdot\nabla_i\psi\right)\right](r\omega,\hat{\mathbf{x}}_1)\right|$$

$$\leq C\left(\sum_{i=2}^{N}\chi(|x_i|)\big[|\ln(|x_i|^2)|+3\big]\right)\left(\prod_{j=2}^{N}e^{-c|x_j|}\right) \tag{3.68}$$

for all $\omega \in \mathbb{S}, r \in \mathbb{R}$ and (almost) all $\hat{\mathbf{x}}_1 \in \mathcal{S}_1(\omega)$. This provides a dominant for the term

$$\left[\sum_{\ell=1}^{N}\sum_{k=1}^{3}\sum_{m=1}^{3} 2\frac{x_{1,k}}{|x_1|}\left(\frac{\partial\psi}{\partial x_{\ell,m}}\right)\left(\psi\frac{\widetilde{\partial^2 F_{3,\mathrm{cut}}}}{\partial x_{1,k}\partial x_{\ell,m}}\right)\right](x,\hat{\mathbf{x}}_1)\,,$$

and we have therefore provided a dominant, in the sense of of (3.15), for the integrand in (3.36).

This finishes the proof of Proposition 3.3. □

Appendix A. Two useful lemmas

The following lemma is Lemma 2.9 in [6]; we include it, without proof, for the convenience of the reader. (The proof is simple, and can be found in [6]).

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

The following lemma is used to evaluate certain integrals.

Lemma A.2. *Let $a, b \in \mathbb{R}^3$ and let $A \in M_{3\times3}(\mathbb{C})$.*

Then

$$\int_{\mathbb{S}^2}(\omega\cdot a)(\omega\cdot b)\,d\omega=\frac{4\pi}{3}(a\cdot b)=\frac{1}{3}(a\cdot b)\int_{\mathbb{S}^2}d\omega\,, \tag{A.2}$$

$$\int_{\mathbb{S}^2}\omega\cdot(A\omega)\,d\omega=\frac{4\pi}{3}\mathrm{Tr}(A)=\frac{1}{3}\mathrm{Tr}(A)\int_{\mathbb{S}^2}d\omega\,. \tag{A.3}$$

Proof. Both (A.2) and (A.3) follow from the identity

$$\int_{\mathbb{S}^2}\omega_i\omega_j\,d\omega=\frac{4\pi}{3}\,\delta_{i,j}\,, \tag{A.4}$$

which we now prove.

For $i \neq j$, the integrand $\omega_i\omega_j$ is odd as a function of ω_j, which implies (A.4) in that case. For $i = j$ we calculate, using rotational symmetry,

$$\int_{\mathbb{S}^2} \omega_i^2\, d\omega = \frac{1}{3}\int_{\mathbb{S}^2} (\omega_1^2+\omega_2^2+\omega_3^2)\, d\omega = \frac{4\pi}{3}\,.$$

This finishes the proof of (A.4) and by consequence of Lemma A.2. □

Appendix B. Regularity of the eigenfunction ψ

The following two theorems were proved in [6].

Theorem B.1 ([6, Theorem 1.1 for atoms]). *Suppose ψ is a solution to $H\psi = E\psi$ in $\Omega \subseteq \mathbb{R}^{3N}$ where H is given by (1.2). Let $\mathcal{F} = e^{F_2+F_3}$ with*

$$F_2(\mathbf{x}) = \sum_{i=1}^{N} -\frac{Z}{2}|x_i| + \sum_{1\le i<j\le N} \frac{1}{4}\,|x_i - x_j|\,, \tag{B.1}$$

$$F_3(\mathbf{x}) = C_0 \sum_{1\le i<j\le N} Z\,(x_i\cdot x_j)\, \ln(|x_i|^2+|x_j|^2)\,, \tag{B.2}$$

where $C_0 = \frac{2-\pi}{12\pi}$. Then $\psi = \mathcal{F}\phi_3$ with $\phi_3 \in C^{1,1}(\Omega)$.

Definition B.2. Let $\chi \in C_0^\infty(\mathbb{R})$, $0 \le \chi \le 1$, with

$$\chi(x) = \begin{cases} 1 & \text{for} \quad |x| \le 1 \\ 0 & \text{for} \quad |x| \ge 2\,. \end{cases} \tag{B.3}$$

We define

$$F_{\rm cut} = F_{2,\rm cut} + F_{3,\rm cut}\,, \tag{B.4}$$

where

$$F_{2,\rm cut}(\mathbf{x}) = \sum_{i=1}^{N} -\frac{Z}{2}\,\chi(|x_i|)\,|x_i| + \frac{1}{4}\sum_{1\le i<j\le N} \chi(|x_i-x_j|)\,|x_i-x_j|\,, \tag{B.5}$$

$$F_{3,\rm cut}(\mathbf{x}) = C_0 \sum_{1\le i<j\le N} Z\,\chi(|x_i|)\chi(|x_j|)(x_i\cdot x_j)\, \ln(|x_i|^2+|x_j|^2)\,, \tag{B.6}$$

and where C_0 is the constant from (B.2). We also introduce $\phi_{3,\rm cut}$ by

$$\psi = e^{F_{\rm cut}}\phi_{3,\rm cut}\,. \tag{B.7}$$

Theorem B.3 ([6, Theorem 1.5 for atoms]). *Suppose ψ is a solution to $H\psi = E\psi$ in $\mathbb{R}^{3N}$. Then for all $0 < R < R'$ there exists a constant $C(R,R')$, not depending on ψ nor $\mathbf{x}_0 \in \mathbb{R}^{3N}$, such that for any second order derivative,*

$$\partial^2 = \frac{\partial^2}{\partial x_{i,k}\partial x_{j,\ell}}\,, \quad i,j = 1,2,\dots,N\,, \quad k,\ell = 1,2,3\,,$$

the following a priori *estimate holds:*

$$\|\partial^2\psi - \psi\,\partial^2 F_{\rm cut}\|_{L^\infty(B_{3N}(\mathbf{x}_0,R))} \le C(R,R')\|\psi\|_{L^\infty(B_{3N}(\mathbf{x}_0,R'))}\,. \tag{B.8}$$

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