POSITIVITY AND LOWER BOUNDS TO THE DECAY OF THE ATOMIC ONE-ELECTRON DENSITY

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Abstract. We investigate properties of the spherically averaged atomic one-electron density $\widetilde{\rho}(r)$. For a $\widetilde{\rho}$ which stems from a physical ground state we prove that $\widetilde{\rho} > 0$. We also give exponentially decreasing lower bounds to $\widetilde{\rho}$ in the case when the eigenvalue is below the corresponding essential spectrum.

1. Introduction and results

Let H be the non-relativistic Schrödinger operator of an N-electron atom with nuclear charge Z in the fixed nucleus approximation,

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

Here 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, and the Δ_j 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 let $\nabla = (\nabla_1, \dots, \nabla_N)$ denote the $3N$-dimensional gradient operator. We write

$$H = -\Delta + V \tag{1.2}$$

where V is the multiplicative potential

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

The operator H is selfadjoint with operator domain $\mathcal{D}(H) = W^{2,2}(\mathbb{R}^{3N})$ and form domain $\mathcal{Q}(H) = W^{1,2}(\mathbb{R}^{3N})$ [9].

For an eigenfunction $\psi \in L^2(\mathbb{R}^{3N})$ of H, with eigenvalue E, i.e.,

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

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we associate the *one-electron density* $\rho \in L^1(\mathbb{R}^3)$. 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

$$\hat{\mathbf{x}}_j := (x_1, \ldots, x_{j-1}, x_{j+1}, \ldots, x_N) \in \mathbb{R}^{3N-3},$$

and

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

and, by abuse of notation, we identify $(x_1, \ldots, x_{j-1}, x, x_{j+1}, \ldots, x_N)$ with $(x, \hat{\mathbf{x}}_j)$. The spherically averaged density $\widetilde{\rho} \in L^1(\mathbb{R}_+; r^2 dr)$ is then defined by

$$\widetilde{\rho}(r) = \sum_{j=1}^{N} \widetilde{\rho}_j(r) = \sum_{j=1}^{N} \int_{\mathbb{S}^2} \rho_j(r\omega) \, d\omega \,, \tag{1.6}$$

where $r = |x|$, $\omega = x/|x| \in \mathbb{S}^2$ for $x = r\omega \in \mathbb{R}^3$.

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

$$|\psi(\mathbf{x})| \leq C_0 \, e^{-\gamma|\mathbf{x}|} \quad \text{for all } \mathbf{x} \in \mathbb{R}^{3N}. \tag{1.7}$$

The *a priori* estimate [7, Theorem 1.2] (see also [7, Remark 1.7]) and (1.7) imply the existence of constants $C_1, \gamma_1 > 0$ such that

$$\big|\nabla\psi(\mathbf{x})\big| \leq C_1 \, e^{-\gamma_1|\mathbf{x}|} \text{ for almost all } \mathbf{x} \in \mathbb{R}^{3N}. \tag{1.8}$$

Remark 1.1. Since ψ is continuous (see [8]), (1.7) is only an assumption on the behaviour at infinity. For references on the exponential decay of eigenfunctions, see e.g. [3] and [12]. The proofs of our results rely (if not indicated otherwise) on some kind of decay-rate for ψ; exponential decay is not essential, but assumed for convenience. Note that (1.7) and (1.8) imply that ρ is Lipschitz continuous in $\mathbb{R}^3$ by Lebesgue's theorem on dominated convergence. This on the other hand implies that $\widetilde{\rho}$ is Lipschitz continuous in $[0, \infty)$.

Since we are interested in atoms (in this non-relativistic description with fixed nucleus) we have to take into account that electrons are fermions. We shall work in the spin-independent description. That is, we split N such that

$$N = N_1 + N_2, \quad N_1, N_2 \geq 0 \,,$$

and proceed as follows: We associate Sobolev-spaces to this splititng. Let $\mathcal{S}(\mathbb{R}^{3N})$ be the space of Schwartz-functions, and define

$$\begin{aligned}\mathcal{S}_{N_1,N_2}(\mathbb{R}^{3N}) = \{\varphi \in \mathcal{S}(\mathbb{R}^{3N}) \mid \varphi(x_1, x_2, x_2, \dots, x_{N_1}, x_{N_1+1}, \dots, x_N)\\ \text{is antisymmetric with respect to the first } N_1 \text{ coordinates}\\ \text{and antisymmetric in the remaining } N_2 \text{ coordinates.}\}\end{aligned}$$

Therefore, for instance,

$$\begin{aligned}&\varphi(x_1, \dots, x_i, \dots, x_j, \dots, x_{N_1}, \dots, x_N)\\ &\qquad = -\varphi(x_1, \dots, x_j, \dots, x_i, \dots, x_{N_1}, \dots, x_N).\end{aligned}$$

Similarily φ changes sign if we interchange the coordinates of two electrons which belong to the other group of N_2 electrons which are labeled with $i = N_1 + 1, \dots, N$. Note that in physical terms this requirement means that the total spin is $\pm|N_2 - N_1|/2$. Define finally the Sobolev-spaces $W^{p,q}_{N_1,N_2}(\mathbb{R}^{3N})$ as the closure in the $W^{p,q}(\mathbb{R}^{3N})$-norm of $\mathcal{S}_{N_1,N_2}(\mathbb{R}^{3N})$.

Let H_{N_1,N_2} be the atomic N-electron Schrödinger operator defined by (1.1), restricted to functions with the above symmetry. Then H_{N_1,N_2} has operator domain $\mathcal{D}(H_{N_1,N_2}) = W^{2,2}_{N_1,N_2}(\mathbb{R}^{3N})$ and form domain $\mathcal{Q}(H_{N_1,N_2}) = W^{1,2}_{N_1,N_2}(\mathbb{R}^{3N})$. We denote E_{N_1,N_2} the infimum of its spectrum (when this is an eigenvalue), and call it *the ground state energy.* A corresponding eigenfunction $\psi = \psi_{N_1,N_2}$ is called a *ground state.* E will henceforth denote any eigenvalue.

Here is the first of our main results.

Theorem 1.2. *Let ψ be a ground state of H_{N_1,N_2}, i.e., $H_{N_1,N_2}\psi = E_{N_1,N_2}\psi$, and let $\widetilde{\rho}$ be the associated spherically averaged density defined by* (1.5)–(1.6).

Then

$$\widetilde{\rho}(r) > 0 \quad \textit{for all } r \in [0, \infty)\,. \tag{1.9}$$

Remark 1.3.

(i) At the origin we derive an explicit, positive lower bound to the density (see (2.13))

$$\rho(0) \geq \frac{2P^4}{3\pi Z N \|\psi\|^2} \quad , \qquad \text{with } P = \Big\| \sum_{j=1}^{N} \nabla_j \psi \Big\|. \tag{1.10}$$

(ii) Note that the choice of *anti-symmetric* in both groups of coordinates in the definition of $\mathcal{S}_{N_1,N_2}(\mathbb{R}^{3N})$ is, in fact, not essential. One could consider functions *symmetric* in each group of coordinates. In fact, the theorem holds for any combination of symmetric/anti-symmetric. This will be clear from the proof. In particular, with $N_1 = N$ and symmetric ($N_2 = 0$), one gets the known result for the absolute (bosonic) ground state.

(iii) We would expect that the *non-averaged* density ρ of a ground state of H_{N_1,N_2} does not vanish either. Also, the one-electron density ρ associated to fermionic ground states of *molecules* should be strictly positive. However, these are much harder problems and they will not be addressed here.

(iv) It is not clear what to expect for excited states. Consider for instance a two-electron atom with no interelectronic repulsion; that is, $H = -\Delta_1 - \Delta_2 - Z/|x_1| - Z/|x_2|$. Let ϕ_i, $i = 1, 2$, be linearly independent eigenfunctions of the three-dimensional one-electron operator $-\Delta - Z/|x|$ satisfying $\phi_1(0) = \phi_2(0) = 0$. Then $\psi(x_1, x_2) = \phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)$ is an eigenfunction of $H_{2,0}$ such that the associated density satisfies $\rho(0) = 0$. However, it is not clear whether or not ρ still vanishes once the interelectronic repulsion is turned on.

Our next result on the density is in the spirit of [4].

Theorem 1.4. *Let ψ be an eigenfunction of H_{N_1,N_2} with eigenvalue E and let $\widetilde{\rho}$ be the associated spherically averaged density defined by* (1.5)–(1.6). *Define*

$$\alpha_0 = \sup\big\{\alpha \,\big|\, e^{\alpha|\mathbf{x}|}\psi \in L^2(\mathbb{R}^{3N})\big\}. \tag{1.11}$$

Then

$$\limsup_{R\to+\infty}\Big(\frac{\ln\widetilde{\rho}(R)}{R}\Big) \leq -2\alpha_0. \tag{1.12}$$

If furthermore $E < \inf\sigma_{\mathrm{ess}}(H_{N_1,N_2})$, then also

$$\liminf_{R\to+\infty}\Big(\frac{\ln\widetilde{\rho}(R)}{R}\Big) \geq -2\sqrt{N}\alpha_0. \tag{1.13}$$

Remark 1.5. One can make these bounds more explicit using [4]; in fact,

$$\alpha_0^2 \leq |E|\,. \tag{1.14}$$

To see this, we use Theorems 1.1 and 1.2 in [4]. The set of thresholds $\mathcal{T}(H)$ is defined as the closure of the set of eigenvalues of subsystems, i.e., the corresponding ionized systems. We have, according to [4],

$$\alpha_0^2 + E \in \mathcal{T}(H) \quad\text{and}\quad \mathcal{T}(H) \subset (-\infty, 0]\,, \tag{1.15}$$

so that

$$\alpha_0^2 \leq \sup\mathcal{T}(H) - E = |E|. \tag{1.16}$$

We shall discuss in Section 3.1 why the difference beween the upper and lower bounds (1.12), (1.13) is to be expected.

Remark 1.6. It will be clear from the proof of Theorem 1.4 (see Section 3) that the result holds for more general N-body operators. That is, we could replace V in (1.3) by any multiplication operator of the form $\sum_\nu v_\nu(\Pi_\nu \mathbf{x})$, $\mathbf{x} \in \mathbb{R}^{3N}$, where Π_ν is the orthogonal projection of $\mathbb{R}^{3N}$ on a d_ν-dimensional subspace, and the v_ν are real-valued functions on $\mathbb{R}^{d_\nu}$ satisfying that $v_\nu(-\Delta_{d_\nu}+1)^{-1}$ and $(-\Delta_{d_\nu}+1)^{-1}(y \cdot \nabla v_\nu(y))(-\Delta_{d_\nu}+1)^{-1}$ are compact as operators on $L^2(\mathbb{R}^{d_\nu})$. Here $-\Delta_{d_\nu}$ is the usual Laplace operator on $\mathbb{R}^{d_\nu}$, and $y \in \mathbb{R}^{d_\nu}$ (compare with (1.2), (1.3) and (1.4) in [4]).

The above theorem gives upper and lower exponential bounds on $\widetilde{\rho}$ near infinity. Combined with Theorem 1.2 this implies (by continuity of $\widetilde{\rho}$, see Remark 1.1) *global* lower exponential bounds in the case of a ground state. We state this explicitely in the next corollary.

Corollary 1.7. *Let ψ be an eigenfunction of H_{N_1,N_2} with eigenvalue E, let α_0 be as in* (1.11)*, and let $\widetilde{\rho}$ be the associated spherically averaged density defined by* (1.5)–(1.6)*.*

If $E < \inf \sigma_{\mathrm{ess}}(H_{N_1,N_2})$, then for all $\alpha > \alpha_0$ there exists $r_0 \geq 0$ and $c = c(\alpha, r_0) > 0$ such that

$$\widetilde{\rho}(r) \geq c\, e^{-2\sqrt{N}\alpha r} \text{ for all } r \geq r_0 \,. \tag{1.17}$$

If furthermore $E = E_{N_1,N_2}$ (the ground state energy), then (1.17) *holds with $r_0 = 0$.*

More detailed results than (1.12) on upper bounds to $\widetilde{\rho}$ are known. For completeness, we include the following classical result; see [2].

Proposition 1.8. *Let ψ be an eigenfunction of H_{N_1,N_2} with eigenvalue E, satisfying*

$$\epsilon := \inf \sigma_{\mathrm{ess}}(H_{N_1,N_2}) - E > 0 \,, \tag{1.18}$$

and let ρ be the associated density defined by (1.5)*.*

Then for all $r_0 > 0$ there exists a constant $C = C(r_0) > 0$ such that

$$\rho(x) \leq C\, |x|^{\frac{Z-(N-1)}{\sqrt{\epsilon}}} e^{-2\sqrt{\epsilon}|x|} \text{ for all } x \in \mathbb{R}^3 \text{ with } |x| \geq r_0 \,. \tag{1.19}$$

Remark 1.9.

(i) The infimum of the essential spectrum of H_{N_1,N_2} is characterized by the HVZ-theorem [11, Theorem XII.17], which takes symmetry into account, in particular the fact that we consider fermions. Hence,

$$\epsilon \geq \min\left\{E_{N_1-1,N_2}, E_{N_1,N_2-1}\right\} - E.$$

(ii) Note that the bound (1.19) can be asymptotically sharp as has been shown for the ground state density of the Helium-like atom [2], where the physical ground state eigenfunction can be chosen positive.

(iii) If we consider a bosonic ground state, $H\psi = E_0\psi$, for an atomic Hamiltonian which happens to have $E_0 = \inf \sigma_{\rm ess}(H)$ then the associated density can decay like $e^{-\beta\sqrt{r}}$ for some suitable β up to some sub-exponential factors; see [6].

2. Proof of positivity

Proof of Theorem 1.2. Assume first for contradiction that

$$\widetilde{\rho}(r_0) = 0 \text{ for some } r_0 > 0. \tag{2.1}$$

This implies that $\widetilde{\rho}_j(r_0) = 0$ for all $j = 1, \dots, N$, and therefore, still for all $j = 1, \dots, N$, that

$$|\psi(\mathbf{x})|^2 = 0 \;\text{ if }\; \mathbf{x} \in N_j(r_0) = \big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, |x_j| = r_0\big\}.$$

Here we used (1.5), (1.6), and the continuity of ψ. This means that

$$\psi(\mathbf{x}) = 0 \;\text{ for }\; \mathbf{x} \in N(r_0),$$

where

$$N(r_0) = \bigcup_{j=1}^{N} N_j(r_0) = \bigcup_{j=1}^{N} \big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, |x_j| = r_0\big\}.$$

Let

$$\mathbf{\Omega}_0 \equiv \mathbf{\Omega}_0(r_0) = \big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, \max_{j=1,\dots,N} |x_j| < r_0\big\}.$$

Then $\mathbf{\Omega}_0$ is an open bounded subset of $\mathbb{R}^{3N}$ satisfying

$$\mathbf{x} \in \mathbf{\Omega}_0 \;\Rightarrow\; \mathcal{P}\mathbf{x} \in \mathbf{\Omega}_0$$

for every permutation $\mathcal{P} \in \mathfrak{S}^N$ of the electron coordinates (that is, of the N-tuple $(1, \dots, N)$). This means that the following space is non-trivial ($\neq \{0\}$):

$$\mathcal{Q}_{N_1,N_2}(\mathbf{\Omega}_0) = \{f \in W_0^{1,2}(\mathbf{\Omega}_0) \,\big|\, \exists F \in \mathcal{Q}(H_{N_1,N_2}) \text{ such that } F|_{\mathbf{\Omega}_0} = f\}.$$

In fact, by the above, $\psi = 0$ on $\partial\mathbf{\Omega}_0$. Therefore, the restriction $\psi_{\mathbf{\Omega}_0} := \psi|_{\mathbf{\Omega}_0}$ of $\psi \in \mathcal{Q}(H_{N_1,N_2})$ to $\mathbf{\Omega}_0$ belongs to $\mathcal{Q}_{N_1,N_2}(\mathbf{\Omega}_0)$, and clearly

$$\langle \psi_{\mathbf{\Omega}_0}, H\psi_{\mathbf{\Omega}_0}\rangle = E_{N_1,N_2}\|\psi_{\mathbf{\Omega}_0}\|^2 \,. \tag{2.2}$$

We now claim that we have the strict inequality

$$E_{N_1,N_2}(\mathbf{\Omega}_0) = \min_{\varphi \in \mathcal{Q}_{N_1,N_2}(\mathbf{\Omega}_0)} \frac{\langle \varphi, H\varphi\rangle}{\|\varphi\|^2} > E_{N_1,N_2} = \min_{\varphi \in \mathcal{Q}(H_{N_1,N_2})} \frac{\langle \varphi, H\varphi\rangle}{\|\varphi\|^2}. \tag{2.3}$$

Indeed, assume that we have equality in (2.3). Then, by the variational characterization of the ground state (also in a symmetry subspace), the eigenfunction which minimizes the LHS of (2.3), and which we extend to $\mathbb{R}^{3N}$ by setting it identically equal to zero outside $\mathbf{\Omega}_0$, will have to be an eigenfunction in all of $\mathbb{R}^{3N}$ also. This is a contradiction to unique continuation (see [11, Theorem XIII.57]).

Now, (2.2) and (2.3) imply that $\psi|_{\mathbf{\Omega}_0} = 0$. By unique continuation, $\psi = 0$ (since $r_0 > 0$). This is a contradiction, and therefore settles the case when $r_0 > 0$ (see (2.1)).

We still have to show that

$$\widetilde{\rho}(0) = 4\pi\rho(0) > 0. \tag{2.4}$$

Here we explicitely use the Coulombic nature of the potential V (see (1.3)). Recall that $\mathbf{x} = (x_1, \dots, x_N) \in \mathbb{R}^{3N}$, with $x_j = (x_{j,1}, x_{j,2}, x_{j,3}) \in \mathbb{R}^3$. The gradient with respect to x_j is denoted ∇_j.

Let, for $\alpha \in \mathbb{R}$,

$$F^{(\alpha)} = \sum_{j=1}^{N} (\nabla_j + \alpha x_j)\psi = \big(F_1^{(\alpha)}, F_2^{(\alpha)}, F_3^{(\alpha)}\big) \tag{2.5}$$

with $F_k^{(\alpha)} = \sum_{j=1}^N \big(\frac{\partial \psi}{\partial x_{j,k}} + \alpha x_{j,k}\psi\big), k = 1,2,3$. Using that $\psi \in \mathcal{D}(H) = W^{2,2}(\mathbb{R}^{3N})$, and the exponential decay (1.7) and (1.8), we get that $F_k^{(\alpha)} \in W^{1,2}(\mathbb{R}^{3N})$. Then the following variational expression is well-defined:

$$\mathbf{R}(\alpha) = \sum_{k=1}^{3} \big\langle F_k^{(\alpha)}, (H - E_{N_1,N_2})F_k^{(\alpha)} \big\rangle. \tag{2.6}$$

Note that the $F_k^{(\alpha)}$ are obtained by applying the operator

$$\sum_{j=1}^{N} (\frac{\partial}{\partial x_{j,k}} + \alpha x_{j,k})$$

to ψ, which does not change symmetry properties with respect to permutations of the electron coordinates. Hence $F_k^{(\alpha)}$ has the same permutational properties as ψ itself, and so $F_k^{(\alpha)} \in \mathcal{Q}(H_{N_1,N_2}), k = 1,2,3$. Therefore, by the variational characterization of the ground state ψ (also in a symmetry subspace), we have

$$\mathbf{R}(\alpha) \geq 0 \quad \text{for all } \alpha \in \mathbb{R}. \tag{2.7}$$

We have (since H is self-adjoint) that

$$\begin{aligned}\mathbf{R}(\alpha) &= \sum_{k=1}^{3}\sum_{i,j=1}^{N}\big(a_{i,j,k}+2\alpha b_{i,j,k}+\alpha^2 c_{i,j,k}\big),\\ a_{i,j,k} &= \Big\langle\frac{\partial\psi}{\partial x_{j,k}},(H-E_{N_1,N_2})\frac{\partial\psi}{\partial x_{i,k}}\Big\rangle,\\ b_{i,j,k} &= \Big\langle\frac{\partial\psi}{\partial x_{j,k}},(H-E_{N_1,N_2})(x_{i,k}\psi)\Big\rangle,\\ c_{i,j,k} &= \big\langle(x_{j,k}\psi),(H-E_{N_1,N_2})(x_{i,k}\psi)\big\rangle. \end{aligned} \tag{2.8}$$

First note that, since $H\psi = E_{N_1,N_2}\psi$, ([;] denoting the commutator)

$$\big(H-E_{N_1,N_2}\big)\frac{\partial\psi}{\partial x_{i,k}} = \Big[(H-E_{N_1,N_2});\frac{\partial}{\partial x_{i,k}}\Big]\psi = \big(-\frac{\partial V}{\partial x_{i,k}}\big)\psi,$$

and so, by partial integration,

$$\begin{aligned}\sum_{k=1}^{3}\sum_{i,j=1}^{N}a_{i,j,k} &= \sum_{k=1}^{3}\sum_{i,j=1}^{N}\Big\langle\frac{\partial\psi}{\partial x_{j,k}},\big(-\frac{\partial V}{\partial x_{i,k}}\big)\psi\Big\rangle\\ &= \frac{1}{2}\sum_{k=1}^{3}\sum_{i,j=1}^{N}\Big\langle\psi,\frac{\partial^2 V}{\partial x_{j,k}\partial x_{i,k}}\psi\Big\rangle.\end{aligned}$$

Strictly speaking, V and ψ are not smooth enough for this and the following computation to be but formal. However, regularizing V and using the exponential decay (1.7)–(1.8), and the continuity of ρ (see Remark 1.1), one easily justifies this.

Note that (for V, see (1.3))

$$\begin{aligned}&\big(\frac{\partial}{\partial x_{i,k}}+\frac{\partial}{\partial x_{j,k}}\big)\big(|x_i-x_j|^{-1}\big)=0,\\ &\sum_{k=1}^{3}\frac{\partial^2(|x_j|^{-1})}{\partial x_{j,k}\partial x_{i,k}} = \delta_{i,j}\Delta_j(|x_j|^{-1}) = -4\pi\delta_{i,j}\delta(|x_j|),\end{aligned}$$

where $\delta_{i,j}$ is Kronecker's delta, and δ is the delta - function. This way,

$$\begin{aligned}\sum_{k=1}^{3}\sum_{i,j=1}^{N}a_{i,j,k} &= \sum_{j=1}^{N}\big\langle\psi,2\pi Z\,\delta(|x_j|)\psi\big\rangle = 2\pi Z\int_{\mathbb{R}^{3N}}|\psi(\mathbf{x})|^2\delta(|x_j|)\,d\mathbf{x}\\ &= 2\pi Z\sum_{j=1}^{N}\rho_j(0) = 2\pi Z\rho(0).\end{aligned} \tag{2.9}$$

Secondly, again since $H\psi = E_{N_1,N_2}\psi$,

$$\big(H - E_{N_1,N_2}\big)(x_{i,k}\psi) = \big[(H - E_{N_1,N_2}); x_{i,k}\big]\psi = -2\frac{\partial\psi}{\partial x_{i,k}}. \tag{2.10}$$

Therefore,

$$\begin{aligned}\sum_{k=1}^{3}\sum_{i,j=1}^{N} b_{i,j,k} &= -2\sum_{k=1}^{3}\Big\langle \sum_{j=1}^{N}\frac{\partial\psi}{\partial x_{j,k}}, \sum_{i=1}^{N}\frac{\partial\psi}{\partial x_{i,k}}\Big\rangle \\ &= -2\Big\|\sum_{j=1}^{N}\nabla_j\psi\Big\|^2 =: -2P^2. \end{aligned}\tag{2.11}$$

Finally, using (2.10) and partial integration,

$$\begin{aligned}\sum_{k=1}^{3}\sum_{i,j=1}^{N} c_{i,j,k} &= -2\sum_{k=1}^{3}\sum_{i,j=1}^{N}\Big\langle x_{j,k}\psi, \frac{\partial\psi}{\partial x_{i,k}}\Big\rangle \\ &= -\sum_{k=1}^{3}\sum_{i,j=1}^{N}\int_{\mathbb{R}^{3N}} x_{j,k}\frac{\partial}{\partial x_{i,k}}\big(\psi^2\big)\,d\mathbf{x} \\ &= \sum_{k=1}^{3}\sum_{i,j=1}^{N}\delta_{i,j}\cdot\|\psi\|^2 = 3N\|\psi\|^2. \end{aligned}\tag{2.12}$$

Combining (2.9), (2.11), and (2.12) with (2.8), we find that

$$\mathbf{R}(\alpha) = 2\pi Z\rho(0) - 4\alpha P^2 + 3\alpha^2 N\|\psi\|^2 \geq 0 \quad \text{for all} \quad \alpha\in\mathbb{R}.$$

Optimizing this expression in α we obtain

$$\rho(0) \geq \frac{2P^4}{3\pi Z N\|\psi\|^2} \quad , \quad P = \Big\|\sum_{j=1}^{N}\nabla_j\psi\Big\|. \tag{2.13}$$

Suppose that $P = 0$. After Fourier transformation, this implies that

$$\sum_{j=1}^{N} p_j\,\hat{\psi}(\mathbf{p}) = 0, \tag{2.14}$$

in $L^2(\mathbb{R}^{3N})$. The equation (2.14) clearly implies that $\hat{\psi} = 0$ (since it has support on the set $\{\,\mathbf{p}\in\mathbb{R}^{3N} \mid \sum_{j=1}^{N} p_j = 0\,\}$ which has zero measure). Since ψ is an eigenfunction, $\psi \neq 0$, so this is a contradiction. We conclude that $P \neq 0$ and (2.13) thus implies (2.4).

This settles the case $r_0 = 0$, and therefore finishes the proof of Theorem 1.2. $\square$

3. Discussion and proof of decay

3.1. **Discussion and examples.**

Before proving Theorem 1.4, we show with some examples why the difference on the right hand sides of (1.12) and (1.13) is natural. Define $\widetilde{\alpha}_0$ as

$$\widetilde{\alpha}_0 = \sup\big\{\alpha \,\big|\, e^{2\alpha r}\widetilde{\rho}(r) \in L^1(\mathbb{R}_+, r^2dr)\big\}. \tag{3.1}$$

For the definition of α_0, see (1.11).

Example 3.1 ($\widetilde{\alpha}_0 = \alpha_0$)**.** Consider first the function,

$$\psi_1(x_1, x_2) = e^{-\alpha_1|x_1|}e^{-\alpha_2|x_2|} \quad , \quad x_1, x_2 \in \mathbb{R}^3.$$

Clearly, the associated density satisfies,

$$\widetilde{\rho}(r) = c_1 e^{-2\alpha_1 r} + c_2 e^{-2\alpha_2 r} \quad , \quad c_1 = \pi/\alpha_2^3\ ,\ c_2 = \pi/\alpha_1^3.$$

Thus, $\widetilde{\alpha}_0 = \min(\alpha_1, \alpha_2)$. It is not hard to see that in this example also $\alpha_0 = \min(\alpha_1, \alpha_2)$: Clearly, $\alpha_0 \geq \min(\alpha_1, \alpha_2)$. Suppose, without loss of generality, that $\alpha_1 \leq \alpha_2$. If $\alpha > \alpha_1$, then (by continuity) there exists a neighbourhood Γ (in $\mathbb{S}^5$) of $(1, 0, 0, 0, 0, 0)$, and $\epsilon > 0$, such that, for all $(\omega_1, \omega_2) \in \Gamma$,

$$\alpha - \alpha_1|\omega_1| - \alpha_2|\omega_2| > \epsilon.$$

The integral of $|e^{\alpha|\mathbf{x}|}\psi|^2$ over the cone $\mathbb{R}_+\Gamma \subset \mathbb{R}^6$ therefore clearly diverges. Thus,

$$\alpha_0 = \min(\alpha_1, \alpha_2).$$

Example 3.2 ($\widetilde{\alpha}_0 \neq \alpha_0$)**.** Consider now the function

$$\psi_2(x_1, x_2) = e^{-\alpha_1|\frac{x_1+x_2}{\sqrt{2}}|}e^{-\alpha_2|\frac{x_1-x_2}{\sqrt{2}}|} \quad , \quad x_1, x_2 \in \mathbb{R}^3.$$

It is easy to see that $\alpha_0 = \min(\alpha_1, \alpha_2)$ also in this case (the definition of α_0 is invariant under an orthogonal change of coordinates). However, we will see that $\widetilde{\alpha}_0 = \sqrt{2}\min(\alpha_1, \alpha_2)$. We write out

$$\begin{aligned}\int_{\mathbb{R}^3} e^{2\alpha|x_1|}\rho_1(x_1)\,dx_1 &= \int_{\mathbb{R}^6} e^{2\alpha|x_1|}e^{-2\alpha_1|\frac{x_1+x_2}{\sqrt{2}}|}e^{-2\alpha_2|\frac{x_1-x_2}{\sqrt{2}}|}\,dx_1dx_2 \\ &= \int_{\mathbb{R}^6} e^{2\alpha|\frac{y_1+y_2}{\sqrt{2}}|}e^{-2\alpha_1|y_1|}e^{-2\alpha_2|y_2|}\,dy_1dy_2.\end{aligned}$$

Since $|y_1 + y_2| \leq |y_1| + |y_2|$, the above integral is clearly convergent for all α satisfying $\frac{\alpha}{\sqrt{2}} < \min(\alpha_1, \alpha_2)$. It is also easy to see (as in the previous example) that the integral is not convergent (on a suitable cone) if $\frac{\alpha}{\sqrt{2}} > \min(\alpha_1, \alpha_2)$.

Remark 3.3. Example 3.1 would be the correct behaviour (modulo polynomial forefactors) of eigenfunctions of H, if we omitted the terms $|x_j - x_k|^{-1}$ in V. Since our proof works for general N-body operators (see Remark 1.6), it is therefore clear that Example 3.2 is equally relevant, since Example 3.2 is obtained by using a rotation of the coordinates in Example 3.1.

The proof of Theorem 1.4 will rely on the result [4, Theorem 2.1] adapted for our purpose. For $R_1 < R_2$, denote by $\Omega(R_1, R_2)$ the spherical shell (in $\mathbb{R}^{3N}$)

$$\Omega(R_1, R_2) = \big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, R_1 \le |\mathbf{x}| \le R_2\big\}. \tag{3.2}$$

Theorem 3.4. *Suppose ψ is an eigenfunction of H with eigenvalue E and let α_0 be defined by* (1.11)*. Suppose $\delta(R)$ is a positive function satisfying*

$$\liminf_{R\to+\infty} \Big(\frac{\ln \delta(R)}{R}\Big) \ge 0. \tag{3.3}$$

Then

$$\lim_{R\to+\infty} \frac{1}{R} \ln\Big(\int_{\Omega(R,R+\delta(R))} |\psi(\mathbf{x})|^2 \, d\mathbf{x}\Big) = -2\alpha_0. \tag{3.4}$$

The next result, which is a special case of [4, Theorem 2.2], will not be used in the sequel. It is given only in order for the reader to be able to compare the result for the density, Theorem 1.4, with the corresponding result for the spherically averaged eigenfunction.

Theorem 3.5. *Suppose in addition to the hypotheses of Theorem 3.4 that $E < \inf \sigma_{\mathrm{ess}}(H)$.*
Then

$$\lim_{R\to+\infty} \frac{1}{R} \ln\Big(\int_{\mathbb{S}^{3N-1}} |\psi(R\Omega)|^2 \, d\Omega\Big) = -2\alpha_0.$$

Before starting the proof of Theorem 1.4, we state and prove a result similar to Theorem 3.4 for the density $\widetilde{\rho}$.

Theorem 3.6. *Suppose ψ is an eigenfunction of H with associated electron density $\widetilde{\rho}$ and let α_0 be defined by* (1.11)*.*
Then

$$\limsup_{R\to+\infty} \frac{1}{R} \ln\Big(\int_R^\infty \widetilde{\rho}(r) r^2 \, dr\Big) \le -2\alpha_0, \tag{3.5}$$

$$\liminf_{R\to+\infty} \frac{1}{R} \ln\Big(\int_R^\infty \widetilde{\rho}(r) r^2 \, dr\Big) \ge -2\sqrt{N}\alpha_0\,. \tag{3.6}$$

Proof. The proof of (3.5) is a simple calculation:

$$\begin{aligned}\int_R^\infty \widetilde{\rho}(r) r^2\, dr &\leq N \int_{\{\mathbf{x}\,:\,\max_j |x_j| \geq R\}} |\psi(\mathbf{x})|^2\, d\mathbf{x} \\ &\leq N \int_{\{\mathbf{x}\,:\,|\mathbf{x}| \geq R\}} |\psi(\mathbf{x})|^2\, d\mathbf{x}\,.\end{aligned}$$

Therefore, for all $\alpha < \alpha_0$,

$$\int_R^\infty \widetilde{\rho}(r) r^2\, dr \leq N e^{-2\alpha R} \| e^{\alpha |\mathbf{x}|} \psi \|^2_{L^2(\mathbb{R}^{3N})}\,.$$

This clearly implies (3.5).

In order to prove (3.6), we calculate

$$\begin{aligned}&\int_R^\infty \widetilde{\rho}(r) r^2\, dr \\ &\quad = \sum_{j=1}^N \int_R^\infty r^2\, dr \int_{\mathbb{S}^2} d\omega \int_{\mathbb{R}^{3N}} |\psi(x_1, \dots, x_N)|^2 \delta(r\omega - x_j)\, d\mathbf{x} \\ &\quad = \sum_{j=1}^N \int_{\{|x_j| \in [R,\infty),\, \hat{\mathbf{x}}_j \in \mathbb{R}^{3N-3}\}} |\psi(x_1, \dots, x_N)|^2\, d\mathbf{x} \\ &\quad \geq \int_{\{\mathbf{x}\,:\,\max_j |x_j| \geq R\}} |\psi(x_1, \dots, x_N)|^2\, d\mathbf{x}\,.\end{aligned}$$

Using

$$\min_j |x_j| \leq \frac{|\mathbf{x}|}{\sqrt{N}} \leq \max_j |x_j|,$$

we get

$$\big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, \sqrt{N} R \leq |\mathbf{x}|\big\} \subset \big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, \max_j |x_j| \geq R\big\},$$

and so, from the above,

$$\int_R^\infty \widetilde{\rho}(r) r^2\, dr \geq \int_{\{\mathbf{x}\,:\,\sqrt{N} R \leq |\mathbf{x}|\}} |\psi(x_1, \dots, x_N)|^2\, d\mathbf{x}\,.$$

The lower bound (3.6), now follows from Theorem 3.4 by taking $\delta(R) = +\infty$. □

3.2. **Proof of Theorem 1.4.** We now start the proof of Theorem 1.4. It will be based on a number of lemmas.

We start by defining an operator T_R which maps functions from $H^{1/2+\epsilon}(\mathbb{R}^{3N})$ continuously to $L^2(\mathbb{S}^2 \times \mathbb{R}^{3N-3})$. T_R is the restriction map

$$[T_R f](\omega, \hat{\mathbf{x}}_1) = f(R\omega, \hat{\mathbf{x}}_1)\,, \quad R > 0\,, \omega \in \mathbb{S}^2\,, \hat{\mathbf{x}}_1 \in \mathbb{R}^{3N-3}\,. \tag{3.7}$$

Lemma 3.7 will allow us to get the upper bound (1.12).

Lemma 3.7. *Suppose ψ is an eigenfunction of H with eigenvalue E. Then there exists $c > 0$ such that, for all $R > 1$ and all $j \in \{1, \dots, N\}$,*

$$\widetilde{\rho}_j(R) \leq cR^{-2} \int_{R-1}^{\infty} \widetilde{\rho}_j(r) r^2 \, dr \,. \tag{3.8}$$

In particular,

$$\widetilde{\rho}(R) \leq cR^{-2} \int_{R-1}^{\infty} \widetilde{\rho}(r) r^2 \, dr. \tag{3.9}$$

Proof. Since (3.9) follows from (3.8) by summation over j, it clearly suffices to prove the latter. Without loss of generality, we will restrict attention to the case $j = 1$. It is well-known that the restriction map T_R from (3.7) defines a bounded map between Sobolev spaces with loss of a half ($+\epsilon$) derivative. We need some control of how the constants depend on R, but not the optimal regularity result, so we state and prove the following (elementary, not optimal) lemma.

Lemma 3.8. *The map T_R defines a bounded operator from $H^1(\mathbb{R}^{3N})$ to $L^2(\mathbb{S}^2 \times \mathbb{R}^{3N-3})$, with the estimate*

$$\|T_R f\|_{L^2(\mathbb{S}^2 \times \mathbb{R}^{3N-3})} \leq R^{-1}\big(\|\nabla f\|_{L^2(\mathbb{R}^{3N})} + \|f\|_{L^2(\mathbb{R}^{3N})}\big) \,. \tag{3.10}$$

Proof of Lemma 3.8. (The proof is a repetition of the proof of [4, Lemma 3.1]). For $f \in C_0^\infty(\mathbb{R}^{3N})$, we have

$$\begin{aligned}
&\int_{\mathbb{S}^2 \times \mathbb{R}^{3N-3}} |f(R\omega, \hat{\mathbf{x}}_1)|^2 \, d\omega \, d\hat{\mathbf{x}}_1 \\
&= \int_R^\infty \int_{\mathbb{S}^2 \times \mathbb{R}^{3N-3}} -\frac{d}{dr} |f(r\omega, \hat{\mathbf{x}}_1)|^2 \, d\omega \, d\hat{\mathbf{x}}_1 \, dr \\
&= \int_R^\infty \int_{\mathbb{S}^2 \times \mathbb{R}^{3N-3}} -2\mathrm{Re}\big\{\overline{f(r\omega, \hat{\mathbf{x}}_1)} \frac{d}{dr} f(r\omega, \hat{\mathbf{x}}_1)\big\} \, d\omega \, d\hat{\mathbf{x}}_1 \, dr \\
&\leq R^{-2} \int_R^\infty \int_{\mathbb{S}^2 \times \mathbb{R}^{3N-3}} \big(|f(r\omega, \hat{\mathbf{x}}_1)|^2 + |\nabla f(r\omega, \hat{\mathbf{x}}_1)|^2\big) r^2 \, d\omega \, d\hat{\mathbf{x}}_1 \, dr \,.
\end{aligned}$$

This clearly implies (3.10), from which Lemma 3.8 follows. $\square$

We now finish the proof of Lemma 3.7. Let $\chi \in C^\infty(\mathbb{R})$ be monotone, $0 \leq \chi \leq 1$, such that

$$\chi(t) = 0 \text{ for } t \leq 1/2 \quad , \quad \chi(t) = 1 \text{ for } t \geq 1. \tag{3.11}$$

Define $\chi_R(\mathbf{x}) = \chi(|x_1| - (R-1))$. With ψ being the eigenfunction of H, we have $T_R \psi = T_R(\chi_R \psi)$, and therefore (using the relative form boundedness of V with respect to the Laplacian [10, Theorem X.19]) we get, using Lemma 3.8,

$$\begin{aligned}
\widetilde{\rho}_1(R) &= \|T_R\psi\|^2_{L^2(\mathbb{S}^2\times\mathbb{R}^{3N-3})} \leq R^{-2}\langle \chi_R\psi, (-\Delta+1)\chi_R\psi\rangle \\
&\leq cR^{-2}\langle \chi_R\psi, (H+1)\chi_R\psi\rangle \\
&= cR^{-2}\langle \psi, \big(\tfrac{1}{2}(\chi_R^2 H + H\chi_R^2) + \chi_R^2 + |\nabla\chi_R|^2\big)\psi\rangle \\
&= cR^{-2}\langle \psi, \big((E+1)\chi_R^2 + |\nabla\chi_R|^2\big)\psi\rangle \\
&\leq c' R^{-2}\int_{\{\mathbf{x}\,:\,|x_1|>R-1\}} |\psi(\mathbf{x})|^2\,d\mathbf{x}\,.
\end{aligned}$$

From this (3.8) follows, and therefore Lemma 3.7 is proved. □

Next, we define an operator $\mathcal{E}_R$, which will harmonically extend functions defined on $\mathbb{S}^2\times\mathbb{R}^{3N-3}$ (see (3.15) and (3.16) below).

We define by $Y_{\ell,m}(\omega)$ the normalised (in $L^2(\mathbb{S}^2)$) real valued spherical harmonics of degree ℓ, $\ell\in\mathbb{N}_0$, with $m=0,1,\dots,2\ell{+}1$. Then $\{Y_{\ell,m}\}_{\ell,m}$ constitutes an orthonormal basis in $L^2(\mathbb{S}^2)$; they are the eigenfunctions for $\mathcal{L}^2$, the Laplace-Beltrami operator on $\mathbb{S}^2$ ($\mathcal{L}^2 Y_{\ell,m} = \ell(\ell+1)Y_{\ell,m}$).

Since $L^2(\mathbb{S}^2\times\mathbb{R}^{3N-3}) \cong L^2(\mathbb{S}^2; L^2(\mathbb{R}^{3N-3}))$, we have, for $\phi\in L^2(\mathbb{S}^2\times\mathbb{R}^{3N-3})$,

$$\begin{aligned}
\phi(\omega,\hat{\mathbf{x}}_1) &= \sum_{\ell=0}^{\infty}\sum_{m=0}^{2\ell+1} Y_{\ell,m}(\omega)\phi_{\ell,m}(\hat{\mathbf{x}}_1)\,, \\
\phi_{\ell,m}(\hat{\mathbf{x}}_1) &= \int_{\mathbb{S}^2} Y_{\ell,m}(\omega)\phi(\omega,\hat{\mathbf{x}}_1)\,d\omega\,.
\end{aligned}$$

Note that, with $\mathcal{F}$ the Fourier-transform on $L^2(\mathbb{R}^{3N-3})$,

$$\phi_{\ell,m}(\hat{\mathbf{x}}_1) = \frac{1}{(\sqrt{2\pi})^{3N-3}}\int_{\mathbb{R}^{3N-3}} e^{i\hat{\mathbf{k}}_1\cdot\hat{\mathbf{x}}_1}(\mathcal{F}\phi_{\ell,m})(\hat{\mathbf{k}}_1)\,d\hat{\mathbf{k}}_1\,. \tag{3.12}$$

Define

$$\begin{aligned}
&[\mathcal{E}_R\phi](r,\omega,\hat{\mathbf{x}}_1) \qquad (3.13)\\
&\quad= \frac{1}{(\sqrt{2\pi})^{3N-3}}\sum_{\ell=0}^{\infty}\sum_{m=0}^{2\ell+1}\int_{\mathbb{R}^{3N-3}} Y_{\ell,m}(\omega)e^{i\hat{\mathbf{k}}_1\cdot\hat{\mathbf{x}}_1}(\mathcal{F}\phi_{\ell,m})(\hat{\mathbf{k}}_1)f_{\ell,\hat{\mathbf{k}}_1,R}(r)\,d\hat{\mathbf{k}}_1,
\end{aligned}$$

where $f=f_{\ell,\hat{\mathbf{k}}_1,R}$ is the solution (given by Lemma A.1 in Appendix A) to the equation

$$f'' + \frac{2}{r}f' - \big[\frac{\ell(\ell+1)}{r^2} + \hat{\mathbf{k}}_1^2\big]f = 0\,, \quad r\in(R,+\infty), \tag{3.14}$$

satisfying $f(R)=1$, $|f(r)|\leq 1$ for all $r\geq R$.

Using again Lemma A.1 we find that

$$\mathcal{E}_R\phi \in L^\infty\big([R,\infty); L^2(\mathbb{S}^2 \times \mathbb{R}^{3N-3})\big).$$

Furthermore, by the definition of $f_{\ell,\hat{\mathbf{k}}_1,R}$, $\mathcal{E}_R\phi$ satisfies (in the sense of distributions)

$$\Delta\mathcal{E}_R\phi = 0 \quad \text{in} \quad \big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, |x_1| > R\big\}. \tag{3.15}$$

We also have that

$$T_R\mathcal{E}_R\phi = \phi. \tag{3.16}$$

By analogy with $\Omega(R_1, R_2)$ from (3.2), we define

$$\widetilde{\Omega}(R_1, R_2) = \big\{\mathbf{x} \in \mathbb{R}^{3N} \,\big|\, R_1 < |x_1| < R_2\big\}. \tag{3.17}$$

With this notation we have the following L^2 - bound:

Lemma 3.9. *For all $R > 0$ and $\phi \in L^2(\mathbb{S}^2 \times \mathbb{R}^{3N-3})$,*

$$\|\mathcal{E}_R\phi\|_{L^2(\widetilde{\Omega}(R,3R))} \leq 3R^{3/2}\|\phi\|_{L^2(\mathbb{S}^2\times\mathbb{R}^{3N-3})}. \tag{3.18}$$

Proof. Using the definition (see (3.13)) of $\mathcal{E}_R$, the Plancherel theorem, and Lemma A.1, we get

$$\begin{aligned}
&\int_R^{3R} \Big(\int_{\mathbb{R}^{3N-3}} \int_{\mathbb{S}^2} |\mathcal{E}_R\phi(r,\omega,\hat{\mathbf{x}}_1)|^2 \,d\omega\, d\hat{\mathbf{x}}_1\Big) r^2\,dr \\
&= (2\pi)^{3-3N} \int_R^{3R} \Big(\sum_{\ell=0}^{\infty}\sum_{m=0}^{2\ell+2} \int_{\mathbb{R}^{3N-3}} \int_{\mathbb{S}^2} \big|Y_{\ell,m}(\omega)\big|^2 \,\big|(\mathcal{F}\phi_{\ell,m})(\hat{\mathbf{k}}_1)\big|^2 \\
&\qquad\qquad \times |f_{\ell,\hat{\mathbf{k}}_1,R}(r)|^2 \,d\omega\, d\hat{\mathbf{k}}_1\Big) r^2\,dr \\
&\leq \|\phi\|^2_{L^2(\mathbb{S}^2\times\mathbb{R}^{3N-3})} \int_R^{3R} r^2\,dr.
\end{aligned}$$

This implies the conclusion of the lemma. □

Lemma 3.10. *Let ψ be an eigenfunction of H_{N_1,N_2} with eigenvalue E and assume that $E < \inf\sigma_{\mathrm{ess}}(H_{N_1,N_2})$.*

Then there exist constants $R_0, c > 0$ such that for all $R > R_0$ and all $j \in \{1,\dots,N\}$,

$$\int_R^\infty \widetilde{\rho}_j(r) r^2\,dr \leq cR^3\widetilde{\rho}_j(R). \tag{3.19}$$

In particular,

$$\int_R^\infty \widetilde{\rho}(r) r^2\,dr \leq cR^3\widetilde{\rho}(R). \tag{3.20}$$

Proof. Clearly (3.20) follows from (3.19) by summation over j, so we will only prove (3.19). Without loss of generality, we only consider $j = 1$ and therefore aim to prove

$$\int_R^\infty \widetilde{\rho}_1(r) r^2\, dr \leq c R^3 \widetilde{\rho}_1(R). \tag{3.21}$$

We define (with the previously defined operators $\mathcal{E}_R$, T_R, see (3.7) and (3.13))

$$u = \mathcal{E}_R T_R \psi,$$

as a function on $\mathbb{R}^{3N}$. The function u does not necessarily satisfy the antisymmetry properties from $\mathcal{Q}(H_{N_1,N_2})$. Therefore, denote, for $x \in \mathbb{R}^3$, by u_x the function on $\mathbb{R}^{3N-3}$ defined by

$$u_x(x_2, \ldots, x_N) = u(x, x_2, \ldots, x_N).$$

We stress that u_x is *not* a derivative of u. With this definition u_x has the useful symmetry property

$$u_x \in \mathcal{Q}(H_{N_1-1,N_2})\,. \tag{3.22}$$

From Lemma 3.9 we get the inequality

$$\int_{\widetilde{\Omega}(R,3R)} |u(\mathbf{x})|^2\, d\mathbf{x} \leq 9R^3 \|T_R\psi\|^2_{L^2(\mathbb{S}^2\times\mathbb{R}^{3N-3})} = 9R^3\widetilde{\rho}_1(R). \tag{3.23}$$

Define $H_{N_1,N_2}(R)$ as the operator obtained by restricting H to the space

$$\mathcal{H}_{N_1,N_2}(R) := \\ \Big(W^{2,2}\big(\mathbb{R}^3 \setminus \overline{B(0,R)}\big) \cap W_0^{1,2}\big(\mathbb{R}^3 \setminus \overline{B(0,R)}\big)\Big) \otimes W^{2,2}_{N_1-1,N_2}(\mathbb{R}^{3N-3})\,.$$

That is, we impose Dirichlet conditions at radius R on the first electron coordinate, and the symmetry conditions on the last $N-1$ electron coordinates.

Let $\varphi \in \mathcal{H}_{N_1,N_2}(R)$ be normalised (in $L^2(\mathbb{R}^{3N})$). Then, since $|x_1| \geq R$, it follows that

$$\langle \varphi, H_{N_1,N_2}(R)\varphi\rangle \geq \Big\langle \varphi, \Big\{ \sum_{j=2}^N \big(-\Delta_j - \frac{Z}{|x_j|}\big) \\ + \sum_{2\leq j<k\leq N} \frac{1}{|x_j - x_k|}\Big\}\varphi\Big\rangle - \frac{Z}{R}.$$

By the HVZ-theorem (see [11, Theorem XIII.17']) the term in $\langle\,\cdot\,,\,\cdot\,\rangle$ (on the right side) is bounded below by $\inf \sigma_{\mathrm{ess}}(H_{N_1,N_2})$. Thus, for any $\epsilon > 0$ there exists $R' > 0$ such that for all $R > R'$,

$$\inf \sigma(H_{N_1,N_2}(R)) > \inf \sigma_{\mathrm{ess}}(H_{N_1,N_2}) - \epsilon.$$

Since, by assumption, $E < \inf \sigma_{\rm ess}(H_{N_1,N_2})$, the operator $H_{N_1,N_2}(R)-E$ is invertible for R sufficiently large, i.e., for all $R \geq R_0$ for some $R_0 > 0$.

Let $\zeta \in C^\infty(\mathbb{R}), 0 \leq \zeta \leq 1$, be a function such that

$$\zeta(t) = 1 \text{ for } |t| \leq 2, \qquad \zeta(t) = 0 \text{ for } |t| \geq 3. \tag{3.24}$$

With ζ as above and $R > 0$, we define $\zeta_R(x_1, \dots, x_N) := \zeta(|x_1|/R)$. Let $v := \psi - \zeta_R u$. Then $T_R v = 0$, so we see using (3.22) that $v \in \mathcal{H}_{N_1,N_2}(R)$. A calculation gives

$$(-\Delta + V - E)v = -(V-E)\zeta_R u + 2\nabla\zeta_R \nabla u + (\Delta\zeta_R)u. \tag{3.25}$$

Since $H_{N_1,N_2}(R) - E$ is invertible and $v \in \mathcal{H}_{N_1,N_2}(R)$, we find

$$v = (H_{N_1,N_2}(R) - E)^{-1}\big(-(V-E)\zeta_R u + 2\nabla\zeta_R\nabla u + (\Delta\zeta_R)u\big).$$

It is easy to see, using that V is relatively bounded with respect to the Laplacian, (3.23), and the support properties of ζ_R, that there exist c, c' such that

$$\|v\|^2_{L^2(\{\mathbf{x}\,:\,R<|x_1|\})} \leq c\|u\|^2_{L^2(\{\mathbf{x}\,:\,R<|x_1|<3R\})} \leq c' R^3 \widetilde{\rho}_1(R). \tag{3.26}$$

Combining (3.23) and (3.26) we get

$$\begin{aligned}
\|\psi\|^2_{L^2(\{\mathbf{x}\,:\,R<|x_1|\})} &= \|\zeta_R u + v\|^2_{L^2(\{\mathbf{x}\,:\,R<|x_1|\})} \\
&\leq 2\big(\|\zeta_R u\|^2_{L^2(\{\mathbf{x}\,:\,R<|x_1|\})} + \|v\|^2_{L^2(\{\mathbf{x}\,:\,R<|x_1|\})}\big) \\
&\leq cR^3\widetilde{\rho}_1(R).
\end{aligned}$$

This is the inequality (3.21). The proof of Lemma 3.10 is therefore finished. $\square$

The estimate (1.12) follows from (3.9) and (3.5). The lower bound (1.13) clearly follows from Lemma 3.10 upon inserting (3.6). This finishes the proof of Theorem 1.4.

Appendix A

Lemma A.1. *For all $\ell \in \mathbb{N}\cup\{0\}$, all $R > 0$ and all $\kappa \geq 0$, the equation*

$$f'' + \frac{2}{r}f' - \Big[\frac{\ell(\ell+1)}{r^2} + \kappa^2\Big]f = 0, \quad f(R) = 1 \tag{A.1}$$

has a solution f vanishing at infinity and satisfying

$$|f(r)| \leq 1 \quad \textit{for all } r \geq R.$$

Proof. Actually, if f is a solution of (3.14), then rf is a Whittaker function (see [1] for details). This implies that a solution f exists vanishing at infinity.

Define, for $x \in \mathbb{R}^3$, $u(x) := f(|x|)$, then u satisfies

$$-\Delta u + W u = 0, \qquad\qquad u\big|_{|x|=R} = 1$$

with $W(x) = \frac{\ell(\ell+1)}{|x|^2} + \kappa^2 \geq 0$. By Kato's inequality [10, Theorem X.27] we get

$$-\Delta|u| + W|u| \leq 0. \tag{A.2}$$

Let v_κ, $\kappa \geq 0$, be the function on $\mathbb{R}^3 \setminus \{0\}$,

$$v_\kappa(x) = \frac{R}{|x|} e^{-\kappa(|x|-R)}.$$

Then

$$-\Delta v_\kappa + \kappa^2 v_\kappa = 0, \quad v_\kappa\big|_{|x|=R} = 1, \quad \text{and } v_\kappa(x) \leq 1 \text{ for } |x| \geq R.$$

So

$$(-\Delta + W)(v_\kappa - |u|) \geq \frac{\ell(\ell+1)}{|x|^2} v_\kappa \geq 0,$$
$$(v_\kappa - |u|)\big|_{|x|=R} = 0.$$

The maximum principle (see e. g. [5, Theorem 8.1]) implies (since f and v_κ vanish at infinity) that for all $|x| \geq R$,

$$|u(x)| \leq v_\kappa(x). \tag{A.3}$$

This implies the statement of Lemma A.1. □

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