Habilitationsschrift von

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Non-relativistic and pseudorelativistic quantum mechanics of atoms and molecules

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Ich erkläre hiermit ehrenwörtlich, daß die vorgelegten wissenschaftlichen Arbeiten in dieser Habilitationsschrift von mir ohne andere als die angegebenen Hilfsmittel angefertigt sind (sehe auch die Mitautorerklärungen am Ende der Schrift).

Thomas Østergaard Sørensen

NON-RELATIVISTIC AND PSEUDORELATIVISTIC QUANTUM MECHANICS OF ATOMS AND MOLECULES

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Contents

1. Introduction

This Habilitation-thesis consists of 14 papers ([A]–[N]; see the list on page 3) and this (short) overview of their results and brief ideas of the proofs of these. The overview is, to a large extent, compiled from the introductions to the various papers. For a more thorough discussion of the results in the adjacent papers, we refer to these introductions, and, for the detailed proofs of the results, to the papers themselves. The papers have been grouped under two headlines:

Regularity of atomic and molecular wavefunctions and their associated one-electron densities

and

Pseudorelativistic atoms and molecules

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Three papers which do not really fit under these two headlines are described under

Various themes

All papers deal with certain aspects of Schrödinger operators describing atoms and molecules.

The quantum mechanical Hamiltonian of an N–electron molecule with M fixed nuclei is given by

$$H_{N,M}(\mathbf{X},\mathbf{Z}) = \sum_{j=1}^{N} T(-\mathrm{i}\nabla_j) + V(\mathbf{X},\mathbf{Z}) + U(\mathbf{X},\mathbf{Z})\,,$$

where V, the Coulombic potential, is given by

$$V \equiv V(\mathbf{X},\mathbf{Z}) = -\sum_{j=1}^{N}\sum_{k=1}^{M} \frac{Z_k}{|x_j - X_k|} + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\,, \qquad (1)$$

and the internuclear repulsion U by

$$U(\mathbf{X},\mathbf{Z}) = \sum_{1\le k<\ell\le M} \frac{Z_k Z_\ell}{|X_k - X_\ell|}\,. \qquad (2)$$

The latter is merely an additive term that will be neglected in the sequel and we will henceforth consider

$$H \;\equiv\; H_{N,M}(\mathbf{X},\mathbf{Z}) - U(\mathbf{X},\mathbf{Z})\,. \qquad (3)$$

Above, $\mathbf{x} = (x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}$ denotes the positions of the N electrons, with $x_j = (x_{j,1}, x_{j,2}, x_{j,3}) \in \mathbb{R}^3$ the position of the j^{th} electron. The positions of the M nuclei with the positive charges $\mathbf{Z} = (Z_1, Z_2 \ldots, Z_M) \in \mathbf{R}_+^M$ are denoted by $\mathbf{X} = (X_1, X_2, \ldots, X_M) \in \mathbf{R}^{3M}$ where $X_k = (X_{k,1}, X_{k,2}, X_{k,3}) \in \mathbb{R}^3$ is the (fixed) position of the k^{th} nucleus with charge Z_k, and it is assumed that $X_\ell \neq X_k$ for $\ell \neq k$. The gradient with respect to x_j is denoted ∇_j, and we also introduce the $3N$-dimensional gradient by $\nabla = (\nabla_1, \ldots, \nabla_N)$. The Laplacian corresponding to the j^{th} electron is $\Delta_j = \sum_{i=1}^{3} \frac{\partial^2}{\partial {x_{j,i}}^2}$ and so the Laplacian on $\mathbb{R}^{3N}$ is given by $\Delta = \sum_{j=1}^{N} \Delta_j$.

The operator $T(-\mathrm{i}\nabla_j)$ is the kinetic energy of the j^{th} electron. We will mainly consider two choices for T, namely the non-relativistic kinetic energy given by the Laplacian in $\mathbb{R}^3$,

$$T_{\mathrm{nr}} = \,-\Delta\,, \qquad (4)$$

and the *pseudorelativistic* kinetic energy given by the pseudodifferential operator

$$T_{\psi\mathrm{rel}} = \sqrt{-\hbar^2 \mathrm{c}^2 \Delta + (\mathrm{mc}^2)^2} - \mathrm{mc}^2 \,. \tag{5}$$

Here, m is the mass of the electron, c is the speed of light, and $\hbar$ is Planck's constant. In (4) we have chosen units such that $\mathrm{c} = \hbar = 1$ and $\mathrm{m} = 1/2$. When using the operator in (5), however, we shall retain the units.

Below is the list of papers constituting this Habilitation thesis. They are ordered alphabetically as they (would) appear in MathSciNet. A note on notation. The papers of the thesis will be refered to by *letters*, [A]–[N], whereas references by *numbers*, [1]–[51], are to the list of references at the very end of this overview.

References

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[M] Thomas Østergaard Sørensen, *The large-Z Behavior of pseudorelativistic atoms*, J. Math. Phys. **46** (2005), no. 5, 052307, 24pp.
[N] Thomas Østergaard Sørensen and Edgardo Stockmeyer, *On the convergence of eigenfunctions to threshold energy states*, Proc. Roy. Soc. Edinburgh Sect. A **138** (2008), no. 1, 169–187.

2. Regularity of atomic and molecular wavefunctions and their associated one-electron densities

In quantum chemistry and atomic and molecular physics, the regularity properties of the eigenfunctions ψ of the Hamiltonian in (3), and of their corresponding one-electron densities ρ (defined in (36) below), are of great importance. These regularity properties determine the convergence properties of various (numerical) approximation schemes (see [7, 8, 31, 49, 50, 51] for some recent works). They are also of intrinsic mathematical interest.

The series of papers [B, C, D, E, F, G, J, K] deals with the regularity properties of ψ and ρ in the non-relativistic case when $T(-\mathrm{i}\nabla) = -\Delta$, the Laplacian in $\mathbb{R}^3$. In this case,

$$\sum_{j=1}^{N} T(-\mathrm{i}\nabla_j) = -\sum_{j=1}^{N} \Delta_j = -\Delta\,, \tag{6}$$

the Laplacian in $\mathbb{R}^{3N}$. Therefore, the operator H in (3) can be written as

$$H = -\Delta + V\,, \tag{7}$$

with V as in (1).

2.1. **Regularity of eigenfunctions.** In this section we discuss the results for eigenfunctions ψ—or, more generally, for local solutions to

$$H\psi = (-\Delta + V)\psi = E\psi\,. \tag{8}$$

We first note the following: Let Σ denote the set of points in $\mathbb{R}^{3N}$ where the potential V defined in (1) is singular, the so-called 'coalescence points',

$$\Sigma \equiv \Sigma(\mathbf{X}) := \Big\{ \mathbf{x} \in \mathbb{R}^{3N} \,\Big|\, \prod_{j=1}^{N}\prod_{k=1}^{M} |x_j - X_k| \prod_{1\le i<j\le N} |x_i - x_j| = 0 \Big\}\,. \tag{9}$$

The function V is real analytic in $\mathbb{R}^{3N} \setminus \Sigma$. Therefore, if, for some $\Omega \subset \mathbb{R}^{3N}$, ψ is a distributional solution to (8) in Ω, then [21, Section 7.5, pp. 177–180] ψ is real analytic away from Σ, that is, $\psi \in C^{\omega}(\Omega\setminus\Sigma)$.

It therefore remains to study the regularity properties of ψ in the neighbourhood of points in Σ.

The pioneering work on this is due to Kato [23], who proved that ψ is Lipschitz continuous, i.e., $\psi \in C^{0,1}$, near two-particle coalescence points. Kato's result implies that $\nabla\psi$ is (essentially) bounded, but as the ground state of Hydrogen-like systems ($M = N = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z, E = -Z^2/4$, $\psi(x) = c_0 e^{-Z|x|/2}, x \in \mathbb{R}^3$) shows, it is not in general continuous. Furthermore, Kato proved a cusp condition which plays an important role in the numerical treatment of (8). (Here, and in the sequel, by a 'cusp condition' we understand an equation a solution ψ has to satisfy at a point in the singular set Σ). It says that .....

Something on Kato's Cusp too

Aside from Kato's classical results the local behaviour of electron wavefunctions had been investigated more recently by Hoffmann-Ostenhof et al. [19], [20] before the papers discussed here.

Note that the usual theory of regularity of solutions of elliptic equations, applied to the equation (8), does not yield Kato's result mentioned above. This is due to the many-particle structure of the potential V, which means that V has relatively 'bad' L^p-properties. For instance, with $B_{3N}(\mathbf{y}, r) \subset \mathbb{R}^{3N}$ the ball of (small) radius r and centre $\mathbf{y} = (X_1, 0, \ldots, 0) \in \mathbb{R}^{3N}$,

$$\int_{B_{3N}(\mathbf{y},r)} \Big(\frac{Z_1}{|x_1 - X_1|}\Big)^p \, d\mathbf{x} < \infty \quad \Leftrightarrow \quad p < 3\,, \tag{10}$$

which, for $N = 1$, only implies that solutions to (8) belong to $C^\alpha(B_3(\mathbf{y}, r))$ for $\alpha \in (0, 1)$, and for $N > 1$ does not imply any regularity at all [33, Theorem 11.7 (iv)]. Here, $C^\alpha(B_3(\mathbf{y}, r))$ is the space of Hölder-continuous functions on $B_3(\mathbf{y}, r))$ (see Defintion 2 in the Appendix).

The paper [K] deals with improving Kato's result. It determines explicitely the form of the singularities of $\nabla\psi$ at points in Σ. The main theorem in [K] is the following.

Theorem 1 ([K, Proposition 1.5])**.** *Let V be as in (1). Define $y_{i,k} = x_i - X_k$, $i \in \{1, \ldots, N\}, k \in \{1, \ldots, M\}$, and let*

$$F_2(\mathbf{x}) = -\frac{1}{2} \sum_{i=1}^{N} \sum_{k=1}^{M} Z_k |y_{i,k}| + \frac{1}{4} \sum_{1 \le i < j \le N} |x_i - x_j|\,. \tag{11}$$

Let

$$\mathcal{F} = e^{F_2}\,. \tag{12}$$

Assume $\psi \in W^{1,2}(\Omega)$ is a solution to (8) in $\Omega \subseteq \mathbb{R}^{3N}$. Then

$$\psi = \mathcal{F}\phi_2 \tag{13}$$

with

$$\phi_2 \in C^{1,\alpha}(\Omega) \text{ for all } \alpha \in (0, 1). \tag{14}$$

Note that since $\psi = e^{F_2}\phi_2$ we have $\nabla\psi = \psi\nabla F_2 + e^{F_2}\nabla\phi$, and that both ψ, e^{F_2}, and $\nabla\phi$ are continuous. This result therefore classifies the singularities of $\nabla\psi$ as those coming from ∇F_2. More precisely,

$$\nabla\psi - (\nabla F_2)\psi \in C^\alpha(\Omega) \quad \text{for} \quad \alpha \in (0,1). \tag{15}$$

This is a much more precise result than Kato's cusp condition mentioned above.

The proof of Theorem 1 is surprisingly simple. Make the 'Ansatz' $\psi = e^F\phi$, then (8) implies that ϕ satisfies

$$\Delta\phi + 2\nabla F\cdot\nabla\phi + \big(\Delta F + |\nabla F|^2 + (E-V)\big)\phi = 0. \tag{16}$$

With $F = F_2$ this becomes, since $\Delta F_2 = V$,

$$\Delta\phi_2 + \nabla F_2\cdot\nabla\phi_2 + \big(|\nabla F_2|^2 + E\big)\phi_2 = 0\,, \tag{17}$$

where we have also given ϕ an index 2 to show that it is associated with F_2. This choice of F eliminated the singular term V in (16). The regularity properties of ϕ_2 are now determined by the regularity of ∇F_2, respectively, $|\nabla F_2|^2$. Since ∇F_2 is locally bounded, standard elliptic regularity theory (see Proposition 4 in the Appendix) gives the statement of the theorem. Since ∇F_2 is just bounded and not continuous, one cannot in general expect anything better than (14).

We note here that this 'Ansatz', $\psi = e^{F_2}\phi_2$, was previously used in [19, Lemma 4.1] to prove unique continuation for solutions to the equation (8) in a neighbourhood of points in Σ. It seems to go back to [32]. Attempts to approximate many-particle wave functions by a product as in (12)–(13) are common in computational chemistry and physics. There, such an $\mathcal{F}$ is usually called a 'Jastrow factor'.

As usual for elliptic regularity results, one also has an *a priori* estimate. To prove this, one uses a regularised version of the function F_2 in (11). We refer to [K, Section 2] for the details.

Theorem 2 ([K, Theorem 1.2])**.** *Let $\psi \in W^{1,2}(\mathbb{R}^{3N})$ satisfy (8) in $\mathbb{R}^{3N}$, with V as in (1). Then for all $R \in (0,\infty)$, there exists a constant $C = C(R)$ such that*

$$\sup_{\mathbf{y}\in B(\mathbf{x},R)} |\nabla\psi(\mathbf{y})| \leq C \sup_{\mathbf{y}\in B(\mathbf{x},2R)} |\psi(\mathbf{y})| \quad \textit{for all } \mathbf{x}\in\mathbb{R}^{3N}\,.$$

This result complements the result by Simon [42, Thm. C.2.5 (C14)] for the case of operators of the form in (8), but with V in the Kato-class $K^{n,1}(\mathbb{R}^n)$: for $\delta \in [0,2)$ ($\delta = 0 : n \geq 3$),

$$V \in K^{n,\delta}(\mathbb{R}^n) \Leftrightarrow \lim_{\epsilon\to 0}\sup_{x\in\mathbb{R}^n}\int_{|x-y|<\epsilon}\frac{|V(y)|}{|x-y|^{n-2+\delta}}\,dy = 0\,.$$

The Coulomb potential V in (1) is in $K^{3N,\delta}(\mathbb{R}^{3N})$ for all $\delta \in [0,1)$, but is not in $K^{3N,1}(\mathbb{R}^{3N})$. Again, this is an effect of its many-particle structure.

Note that Theorem 2 implies that for those eigenfunctions ψ which decay exponentially, also $\nabla\psi$ decays exponentially. This result is also new.

Corollary 1 ([K, Remark 1.9])**.** *Let ψ satisfy (8) in $\mathbb{R}^{3N}$, with V as in (1). Assume there exist constants $C_0, \gamma_0 > 0$ such that*

$$|\psi(\mathbf{x})| \leq C_0\, e^{-\gamma_0|\mathbf{x}|} \text{ for all } \mathbf{x} \in \mathbb{R}^{3N}\,. \tag{18}$$

Then there exist constants $C_1, \gamma_1 > 0$ such that

$$|\nabla\psi(\mathbf{x})| \leq C_1\, e^{-\gamma_1|\mathbf{x}|} \text{ for all } \mathbf{x} \in \mathbb{R}^{3N}\,. \tag{19}$$

Exponential decay is known to hold for all eigenfunctions except those of so-called 'threshold eigenvalues'. For these nothing is known (see however [18]). For references on the exponential decay of eigenfunctions, see e.g. Agmon [1], Froese and Herbst [9], and Simon [41].

The paper [E] improves the result of Theorem 1. Its main result is the following.

Theorem 3 ([E, Theorem 1.1])**.** *Let V be as in (1), and F_2 as in (11). With $y_{i,k}$ as in Theorem 1, let*

$$F_3(\mathbf{x}) = C_0 \sum_{k=1}^{M} \sum_{1\leq i<j\leq N} Z_k(y_{i,k}\cdot y_{j,k})\, \ln\big(|y_{i,k}|^2 + |y_{j,k}|^2\big)\big), \tag{20}$$

where $C_0 = \frac{2-\pi}{12\pi}$. Let

$$\mathcal{F} = e^{F_2+F_3}\,. \tag{21}$$

Assume ψ is a solution to (8) in $\Omega \subseteq \mathbb{R}^{3N}$. Then

$$\psi = \mathcal{F}\phi_3 \tag{22}$$

with

$$\phi_3 \in C^{1,1}(\Omega)\,. \tag{23}$$

Furthermore this representation is optimal in the following sense: There is no other function $\widetilde{\mathcal{F}}$ depending only on $\mathbf{X}, \mathbf{Z}$ and on N, but not on ψ or E itself, such that $\psi = \widetilde{\mathcal{F}}\phi$ with ϕ having more regularity than $C^{1,1}(\Omega)$.

Note that each term in the sum F_2 (see (11)) is either a term involving the coordinates of one electron and one nucleus, or the coordinates of two electrons, whereas the terms in F_3 involve the coordinates of two electrons and one nucleus. In the representation (20) of F_3 no terms involving the coordinates of three electrons occur (see [E, Section 3]

for details). The fact that no terms involving the coordinates of four and more particles show up in F_3 stems from the fact that in the summands contributing to $|\nabla F_2|^2$ in (17) only terms involving at most three particle coordinates occur (again, see [E, Section 3] for details).

An immediate consequence of Theorem 3 is the following sharpening of (15):

$$\nabla\psi - \psi(\nabla F_2 + \nabla F_3) \in C^{0,1}(\Omega).$$

The proof of Theorem 3 is much more involved than that of Theorem 1. The main idea, however, is the same, namely, choosing the function F_3 as to eliminate the most singular term in the equation (17), and then prove higher regularity of the remaining factor ϕ_3. For the proof of the regularity of ϕ_3 one needs a special regularity result (see Theorem 17 in the Appendix) for solutions of the Poisson equation $\Delta u = g$. Roughly speaking, if $g \in L^\infty$ has a certain multiplicative structure, it was proved in [E, Theorem 2.6] that $u \in C^{1,1}$, and not only $u \in C^{1,\alpha}, \alpha \in (0,1)$ as in general (see Proposition 4 in the Appendix). This result is of independent interest.

The results in Theorem 3 are not well suited for obtaining *a priori* estimates. In particular neither F_2 nor F_3 stay bounded as $|\mathbf{x}|$ tends to infinity so that if, say, $\psi \in L^2(\mathbb{R}^{3N})$ then ϕ_3 is not necessarily in $L^2(\mathbb{R}^{3N})$. These shortcomings are dealt with below in a similar way as in [K].

Definition 1 ([E, Definition 1.3])**.** *Let $\chi \in C_0^\infty(\mathbb{R})$, $0 \leq \chi \leq 1$, with*

$$\chi(x) = \begin{cases} 1 & \text{for } |x| \leq 1 \\ 0 & \text{for } |x| \geq 2. \end{cases} \tag{24}$$

We define

$$F_{\text{cut}} = F_{2,\text{cut}} + F_{3,\text{cut}}, \tag{25}$$

where

$$F_{2,\text{cut}}(\mathbf{x}) = -\frac{1}{2}\sum_{k=1}^{M}\sum_{i=1}^{N} Z_k\, \chi(|y_{i,k}|)\, |y_{i,k}| + \frac{1}{4}\sum_{1\leq i<j\leq N} \chi(|x_i - x_j|)\, |x_i - x_j|, \tag{26}$$

$$F_{3,\text{cut}}(\mathbf{x}) = C_0 \sum_{k=1}^{M} \sum_{1\leq i<j\leq N} Z_k\, \chi(|y_{i,k}|)\chi(|y_{j,k}|)(y_{i,k}\cdot y_{j,k})\, \ln\left(|y_{i,k}|^2 + |y_{j,k}|^2\right), \tag{27}$$

and where C_0 is the constant from (20). *We also introduce $\phi_{3,\mathrm{cut}}$ by*

$$\psi = e^{F_{\mathrm{cut}}}\phi_{3,\mathrm{cut}}. \tag{28}$$

Theorem 4 below strengthens results obtained in [K]. It can be thought of as a *second order cusp condition*.

Theorem 4 ([E, Theorem 1.4])**.** *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,*

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

the following estimate holds:

$$\|\partial^2\psi - \psi\,\partial^2 F_{\mathrm{cut}}\|_{L^\infty(B_{3N}(\mathbf{x}_0,R))} \leq C(R,R')\|\psi\|_{L^\infty(B_{3N}(\mathbf{x}_0,R'))}. \tag{29}$$

To prove Theorem 4 it is shown that

$$\|\phi_{3,\mathrm{cut}}\|_{C^{1,1}(B_{3N}(\mathbf{x}_0,R))} \leq C(R,R')\|\phi_{3,\mathrm{cut}}\|_{L^\infty(B_{3N}(\mathbf{x}_0,R'))}. \tag{30}$$

The estimate (29) is then a trivial consequence of (30).

Theorem 3 is global in nature, inasmuch as it gives a representation of ψ in the vicinity of *all* of Σ, independently of the number of terms which are zero in (9).

The paper [G] on the other hand gives a different representation of ψ in the vicinity of so-called 'two-particle coalescence points'.

More precisely, define, for

$$n, n_1, n_2 \in \{1,\ldots,N\}, n_1 \neq n_2 \ \text{ and } \ m \in \{1,\ldots,M\},$$

the sets

$$\Sigma_n^{m\prime} := \Big\{\mathbf{x}\in\mathbb{R}^{3N}\ \Big|\ \prod_{j=1,j\neq n}^{N}\prod_{k=1,k\neq m}^{M}|x_j - X_k| \prod_{1\leq i<j\leq N}|x_i - x_j| = 0\Big\}, \tag{31}$$

$$\Sigma'_{n_1,n_2} := \Big\{\mathbf{x}\in\mathbb{R}^{3N}\ \Big|\ \prod_{j=1}^{N}\prod_{k=1}^{M}|x_j - X_k| \prod_{1\leq i<j\leq N,\{i,j\}\neq\{n_1,n_2\}}|x_i - x_j| = 0\Big\}. \tag{32}$$

Then we denote

$$\Sigma_n^m := \Sigma \setminus \Sigma_n^{m\prime}\,, \quad \Sigma_{n_1,n_2} := \Sigma \setminus \Sigma'_{n_1,n_2} \tag{33}$$

the two kinds of 'two-particle coalescence points'.

The main result of [G], which completely settles the question of the regularity of ψ in the vicinity of two-particle coalescence points, is the following.

Theorem 5 ([G, Theorem 1.4])**.** *Let V be as in* (1)*, and assume $\psi \in W^{1,2}(\Omega)$ is a solution to* (8) *in $\Omega \subseteq \mathbb{R}^{3N}$. Let the sets Σ_n^m and Σ_{n_1,n_2} be given by* (33)*.*

Then, for all $n \in \{1,\dots,N\}$, $m \in \{1,\dots,M\}$, there exists a neighbourhood $\Omega_n^m \subset \Omega$ of $\Omega \cap \Sigma_n^m$, and real analytic functions $\psi_n^{m,(1)}, \psi_n^{m,(2)} : \Omega_n^m \to \mathbb{C}$ such that

$$\psi(\mathbf{x}) = \psi_n^{m,(1)}(\mathbf{x}) + |x_n - X_m| \psi_n^{m,(2)}(\mathbf{x})\,,\ \mathbf{x} \in \Omega_n^m\,, \tag{34}$$

and for all $n_1, n_2 \in \{1,\dots,N\}$, $n_1 \neq n_2$, there exists a neighbourhood $\Omega_{n_1,n_2} \subset \Omega$ of $\Omega \cap \Sigma_{n_1,n_2}$, and real analytic functions $\psi_{n_1,n_2}^{(1)}, \psi_{n_1,n_2}^{(2)} : \Omega_{n_1,n_2} \to \mathbb{C}$ such that

$$\psi(\mathbf{x}) = \psi_{n_1,n_2}^{(1)}(\mathbf{x}) + |x_{n_1} - x_{n_2}| \psi_{n_1,n_2}^{(2)}(\mathbf{x})\,,\ \mathbf{x} \in \Omega_{n_1,n_2}\,. \tag{35}$$

One should compare the result of the theorem with the ground state of Hydrogen mentioned earlier ($\psi(x) = c_0 e^{-Z|x|/2}, x \in \mathbb{R}^3$).

The proof of Theorem 5 has two ingredients. The first one is the Kustaanheimo-Stiefel (KS) transform $K : \mathbb{R}^4 \to \mathbb{R}^3$ (see [30, Section 2] for the definition). It has the virtue of regularizing the Coulomb-potential. This transform was introduced in the 1960's [30] to regularize the Kepler problem in classical mechanics (see also [29, 46, 28]) and has found applications in problems related to the Coulomb potential in classical mechanics and quantum mechanics, see [4, 11, 14, 15, 16, 22]. For more on the literature on the KS-transform, see [28, 15].

The second ingredient is a result [13] on analytic hypoanalyticity of a certain degenerate elliptic operator, namely the one obtained after applying the KS-transform in the relevant coordinate ($x_n - X_m$ and $x_{n_1} - x_{n_2}$, respectively). Finally, a result on the structure on $\mathbb{R}^3$ of the push-forward via the KS-transform of analytic functions on $\mathbb{R}^4$ is needed; this is proved in [G, Proposition 4.4]. We refer to [G] for further details and discussions.

2.2. **Regularity of one-electron densities.** Given an eigenfunction $\psi \in L^2(\mathbb{R}^{3N})$ of the operator H in (3) we define the corresponding *one-electron density* $\rho \in L^1(\mathbb{R}^3)$ by

$$\rho(x) = \sum_{j=1}^N \rho_j(x) = \sum_{j=1}^N \int_{\mathbb{R}^{3N}} |\psi(\mathbf{x})|^2\, \delta(x - x_j)\, d\mathbf{x}\,. \tag{36}$$

In this section we describe results on the regularity properties of ρ. Also, in the case of an atom (i.e., one nucleus: $M = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z$), we study its *spherical average* $\widetilde{\rho} \in L^1([0,\infty); r^2\, dr)$ defined by

$$\widetilde{\rho}(r) = \int_{\mathbb{S}^2} \rho(r\omega)\, d\omega \ , \quad r \in [0,\infty)\,. \tag{37}$$

(The results described below for $\widetilde{\rho}$ also hold in the case of more nuclei, when taking the average around some chosen nucleus).

The regularity of ρ away from $\{X_1, \dots, X_M\} \subset \mathbb{R}^3$, the positions of the nuclei, was studied in the papers [B, C, D]. The major idea is the following. As mentioned earlier, ψ is real analytic away from the set Σ, that is, almost everywhere with respect to the integration in (36). To study the regularity of ψ in a neighbourhood of Σ, one uses the equation (16). When studying (16) for some choice of F, one might obtain higher regularity of the ϕ in certain open sets in $\mathbb{R}^{3N}$, at least in certain *directions* in $\mathbb{R}^{3N}$, if one can differentiate the equation (in those directions) without increasing the singularity of the coefficients in the equation. The following result (Proposition 1 below) on *partial analyticity* of the eigenfunction ψ was proved in [D, Lemma 3.1]. The first result in this direction was [B, Lemma 2.3], which, however, provided pointwise estimates, under a decay-assumption on ψ, and not of an analytic type. It did, however, provide the main idea for the subsequent papers [C, D].

In the following we shall work with certain directional derivatives. Let e_s for $s \in \{1,2,3\}$ denote the standard basis for $\mathbb{R}^3$. Let P be a (non-empty) subset of $\{1,\dots,N\}$. We define the coordinate x_P by

$$x_P = \frac{1}{\sqrt{|P|}} \sum_{j \in P} x_j.$$

We will now define $\partial^{e_s}_{x_P} f$ for a function $f \in C^1(\mathbb{R}^{3N})$. For the given P and s let $\mathbf{v} = (v_1, \dots, v_N) \in \mathbb{R}^{3N}$ with $v_j = 0$ for $j \notin P$, and $v_j = e_s/\sqrt{|P|}$ for $j \in P$. Then we define

$$\partial^{e_s}_{x_P} f(x) = \nabla f \cdot \mathbf{v}.$$

The definition of $\partial^{\alpha}_{x_P}$ then follows by iteration for any $\alpha \in \mathbb{N}^3$. This definition of course extends to weak derivatives. (Alternatively, one can use the Fourier transform.)

Proposition 1 ([D, Lemma 3.1])**.** *Let V be as in* (1)*, and assume $\psi \in W^{1,2}(\mathbb{R}^{3N})$ is a solution to* (8) *in $\mathbb{R}^{3N}$ (i.e., ψ is an eigenfunction of H in* (3)*). Let the index sets $P_1, \dots, P_L \subset \{1,\dots,N\}$ satisfy that*

$P_s \neq \emptyset$ for all $s \in \{1, \dots, L\}$. Define for each s, $Q_s = \{1, \dots, N\} \setminus P_s$. Define also, for $\varepsilon > 0$,

$$U_{P_s}(\varepsilon) = \Big\{ \mathbf{x} \in \mathbb{R}^{3N} \,\Big|\, |x_j - X_k| > \varepsilon \text{ for } j \in P_s, k \in \{1, \dots, M\}, \quad |x_j - x_k| > \varepsilon \text{ for } j \in P_s, k \in Q_s \Big\}. \tag{38}$$

Denote

$$U_{P_1,\dots,P_M}(\varepsilon) = \bigcap_{s=1}^{M} U_{P_s}(\varepsilon). \tag{39}$$

Then there exist positive constants C, L (depending on ε) such that for all multiindices, $\alpha = (\alpha_1, \dots, \alpha_L) \in \mathbb{N}^{3L}$, we have

$$\|\partial_{x_{P_1}}^{\alpha_1} \cdots \partial_{x_{P_L}}^{\alpha_L} \psi\|_{L^2(U_{P_1,\dots,P_M}(\varepsilon))} \leq C L^{|\alpha|} (|\alpha| + 1)^{|\alpha|}.$$

This proposition is of independent interest. Its main interest, however, is the fact that, using a somewhat technical localization argument, it allows to prove the following theorem, which completely settles the question of the regularity of ρ away from the positions of the nuclei. For details of the proof we refer to [D].

Theorem 6 ([D, Theorem 1.1])**.** *Let $\psi \in L^2(\mathbb{R}^{3N})$ satisfy* (8) *with V as in* (1)*, and let ρ be the associated one-electron density defined by* (36)*.*

Then ρ is a real analytic function in $\mathbb{R}^3 \setminus \{X_1, \dots, X_M\}$, i.e.,

$$\rho \in C^\omega\big(\mathbb{R}^3 \setminus \{X_1, \dots, X_M\}\big). \tag{40}$$

The theorem also implies that $\widetilde{\rho}$ defined in (37) is real analytic in $(0, \infty)$.

We note that preliminary results on the regularity of ρ and $\widetilde{\rho}$ away from the positions of the nuclei were obtained in [K, B, C]. In [K, Theorem 1.11] it was proved, using Theorem 1 above and assuming that ψ satisfies (18), that

$$\rho \in C^{2,\alpha}\big(\mathbb{R}^3 \setminus \{X_1, \dots, X_M\}\big) \text{ and } \widetilde{\rho} \in C^{2,\alpha}((0,\infty)) \text{ for all } \alpha \in (0,1).$$

Still under the assumption that (18) holds it was then proved in [B, Theorem 1] that ρ is smooth away from the nuclei, that is,

$$\rho \in C^\infty\big(\mathbb{R}^3 \setminus \{X_1, \dots, X_M\}\big),$$

see the discussion of the proof above. This decay assumption was removed in [C, Theorem 1.1] where smoothness was proved to hold for all ρ associated to L^2-eigenfunctions.

We now turn to the regularity question of ρ and $\widetilde{\rho}$ in the vicinity of the nuclei.

We assume from now on, without further mentioning, that ψ satisfies (18), and therefore also (19) holds, by Corollary 1 above. Since ψ is continuous, (18) is only an assumption on the behaviour at infinity. The proofs of the results below rely on some kind of decay-rate for ψ; exponential decay is not essential, but assumed for convenience. Note that (18) and (19) imply that ρ is Lipschitz continuous in $\mathbb{R}^3$ by Lebesgue's theorem on dominated convergence. As can again be seen from the ground state of Hydrogen ($\psi(x) = c_0 e^{-Z|x|/2}, \rho(x) = c_0^2 e^{-Z|x|}, x \in \mathbb{R}^3$), one cannot in general expect higher regularity.

The following result, proved in [F], gives a representation of the leading order singularity of ρ at the positions of the nuclei, similar in spirit to the results for ψ in Theorem 1 and Theorem 3 above.

Theorem 7 ([F, Theorem 1.1])**.** *Let $\psi \in L^2(\mathbb{R}^{3N})$ satisfy (8) with V as in (1), and let ρ be the associated one-electron density defined by (36). Define $\mathcal{F} : \mathbb{R}^3 \to \mathbb{R}$ by*

$$\mathcal{F}(x) = -\sum_{k=1}^{M} Z_k |x - X_k|. \tag{41}$$

Then

$$\rho(x) = e^{\mathcal{F}(x)} \mu(x) \tag{42}$$

with

$$\mu \in C^{1,1}(\mathbb{R}^3). \tag{43}$$

This representation is optimal in the following sense: There is no function $\widetilde{\mathcal{F}} : \mathbb{R}^3 \to \mathbb{R}$ depending only on $Z_1, \ldots, Z_M$, $X_1, \ldots, X_M$, but neither on N, ρ, nor E, with the property that $e^{-\widetilde{\mathcal{F}}}\rho$ is in $C^2(\mathbb{R}^3)$.

Furthermore, μ admits the following representation:
There exist $C_1, \ldots, C_M \in \mathbb{R}^3$ and $\nu : \mathbb{R}^3 \to \mathbb{R}$ such that

$$\mu(x) = \nu(x) + \sum_{k=1}^{M} |x - X_k|^2 \big(C_k \cdot \frac{x - X_k}{|x - X_k|}\big), \tag{44}$$

with

$$\nu \in C^{2,\alpha}(\mathbb{R}^3) \text{ for all } \alpha \in (0, 1). \tag{45}$$

The proof of Theorem 7 uses the fact that ρ satisfies an inhomogeneous Schrödinger equation whose investigation is crucial for regularity results like the above, as well as it was for the results on ρ in [K] mentioned earlier. Let H be given by (3) and consider an eigenfunction ψ satisfying (8). To simplify notation we assume without loss that ψ is real. The equation

$$\int_{\mathbb{R}^{3N}} \psi(\mathbf{x})(H - E)\psi(\mathbf{x})\delta(x - x_j)\, d\mathbf{x} = 0 \tag{46}$$

leads to an equation (in the sense of distributions) for ρ_j, namely,

$$\Big(-\frac{1}{2}\Delta - \sum_{k=1}^{M} \frac{Z_k}{|x-X_k|}\Big)\rho_j + h_j = 0. \tag{47}$$

Summing (47) over j we obtain the equation for ρ,

$$\Big(-\frac{1}{2}\Delta - \sum_{k=1}^{M} \frac{Z_k}{|x-X_k|}\Big)\rho + h = 0, \tag{48}$$

with $h = \sum_{j=1}^{N} h_j$. The function h in (48) is given by

$$h(x) = \sum_{j=1}^{N} h_j(x), \tag{49}$$

$$\begin{aligned} h_j(x) = &\int_{\mathbb{R}^{3N}} |\nabla\psi(\mathbf{x})|^2\, \delta(x-x_j)\, d\mathbf{x} \\ &- \sum_{\ell=1,\ell\neq j}^{N}\sum_{k=1}^{M} \int_{\mathbb{R}^{3N}} \frac{Z_k}{|x_\ell - X_k|}\, |\psi(\mathbf{x})|^2\, \delta(x-x_j)\, d\mathbf{x} \\ &+ \sum_{\ell=1,\ell\neq j}^{N} \int_{\mathbb{R}^{3N}} \frac{1}{|x-x_\ell|}\, |\psi(\mathbf{x})|^2\, \delta(x-x_j)\, d\mathbf{x} \\ &+ \sum_{1\leq k<\ell\leq N,\, k\neq j\neq \ell} \int_{\mathbb{R}^{3N}} \frac{1}{|x_k-x_\ell|}\, |\psi(\mathbf{x})|^2\, \delta(x-x_j)\, d\mathbf{x} - E\rho_j(x)\,. \end{aligned} \tag{50}$$

The proof of Theorem 7 follows from making the 'Ansatz' $\rho = e^{\mathcal{F}}\mu$ (see (42)) and using (48). The resulting equation for μ is

$$\Delta\mu = 2e^{\mathcal{F}}h + 2\Big(\sum_{k=1}^{M} Z_k \frac{x-X_k}{|x-X_k|}\Big)\mu - Z^2\mu\,. \tag{51}$$

One proves the regularity and structure of h needed to conclude from this equation that $\mu \in C^{1,1}(\mathbb{R}^3)$ by carefully using the information on the structure of ψ in Thereom 1 above. Note that this, albeit more explicit, study of h uses ideas similar to the ones in the proof of Theorem 3 above (see also Theorem 17 in the Appendix). The above mentioned initial result [K, Theorem 1.11] that $\rho \in C^{2,\alpha}\big(\mathbb{R}^3 \setminus \{X_1,\ldots,X_M\}\big)$ used the same ideas.

Assume without loss that $X_1 = 0$. The equations (44) and (45) show that it is natural to consider the behaviour of $\rho(r\omega)$ for fixed $\omega \in \mathbb{S}^2$ as r tends to zero. This was also done in [F].

Theorem 8 ([F, Theorem 1.5]). *Let $\psi \in L^2(\mathbb{R}^{3N})$ satisfy (8) with V as in (1), and let ρ be the associated one-electron density defined by (36). Assume without loss that $X_1 = 0$. Let $r_0 = \min_{k>1} |X_k|$ and let $\omega \in \mathbb{S}^2$ be fixed.*

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

$$\rho(\cdot, \omega) \in C^{2,\alpha}([0, r_0)) \text{ for all } \alpha \in (0, 1). \tag{52}$$

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

$$\eta(x) = e^{Z_1|x|}\rho(x) \ , \ \chi = \eta - r^2(C_1 \cdot \omega), \tag{53}$$

where $C_1 \in \mathbb{R}^3$ is the constant in (44).

Then

$$\eta \in C^{1,1}(B(0, r_0)) \ , \ \chi \in C^{2,\alpha}(B(0, r_0)) \text{ for all } \alpha \in (0, 1), \tag{54}$$

and

$$\rho'(0, \omega) = -Z_1\rho(0) + \omega \cdot (\nabla\eta)(0), \tag{55}$$

$$\rho''(0, \omega) = Z_1^2\rho(0) + 2\omega \cdot [C_1 - Z_1(\nabla\eta)(0)] + \omega \cdot \big((D^2\chi)(0)\omega\big). \tag{56}$$

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

In [K, Theorem 1.11] it was proved that $\widetilde{\rho}$ defined by (37) belongs to $C^2([0, r_0)) \cap C^{2,\alpha}((0, r_0))$ for all $\alpha \in (0, 1)$. (The proof in [K] for the atomic case easily generalizes to the molecular case.) Reading the proof of [K, Theorem 1.11] carefully, one sees that it in fact yields $\widetilde{\rho} \in C^{2,\alpha}([0, r_0))$. The statement in (52) shows that for fixed $\omega \in \mathbb{S}^2$ this holds already for $\rho(\cdot, \omega)$, i.e., without averaging.

The identities (55) and (56) can be considered as *non-isotropic cusp conditions of first and second order*; see also the discussion after Theorem 9 below, as well as (60), (63), and (68) below.

It is worth noting that (55) and (56) can be interpreted as a structural result for the density ρ: From Theorem 8 it follows that in a neighbourhood of a nucleus (which is at the origin), ρ satisfies (for all $\alpha \in (0, 1)$)

$$\rho(r, \omega) = \rho(0) + r\phi_1(\omega) + r^2\phi_2(\omega) + O(r^{2+\alpha}) \ , \ r \downarrow 0, \tag{57}$$

and (55), (56) show that ϕ_1 is a linear and ϕ_2 a quadratic polynomial restricted to $\mathbb{S}^2$. It is a natural question whether (57) extends to higher orders.

In the atomic case ($M = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z$), one gets the following more detailed result in the case of a certain symmetry. The proof uses the same ideas as that of Theorem 8, and additionally uses

the fact that certain singular terms in h vanish due to the assumed symmetry.

Theorem 9 ([F, Theorem 1.7])**.** *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction with associated density ρ. Suppose that*

$$|\psi(\mathbf{x})| = |\psi(-\mathbf{x})| \text{ for all } \mathbf{x} \in \mathbb{R}^{3N}. \tag{58}$$

Then ρ satisfies

$$\rho(x) = e^{-Z|x|}\mu(x), \;\; \mu \in C^{2,\alpha}(\mathbb{R}^3) \text{ for all } \alpha \in (0,1). \tag{59}$$

Furthermore,

$$\rho'(0,\omega) = -Z\rho(0)\;, \quad \rho''(0,\omega) = Z^2\rho(0) + \omega \cdot \big((D^2\mu)(0)\omega\big). \tag{60}$$

We also have

$$\rho''(0,\omega) = \frac{2}{3}\big(Z^2\rho(0) + h(0,\omega)\big) + \frac{1}{3}\lim_{r\downarrow 0}\frac{(\mathcal{L}^2\rho)(r,\omega)}{r^2}, \tag{61}$$

with h from (48)*, and $\mathcal{L}^2/r^2$ the angular part of $-\Delta$, i.e., $\Delta = \partial^2/\partial r^2 + (2/r)\partial/\partial r - \mathcal{L}^2/r^2$.*

We turn to the study of $\widetilde{\rho}$, the spherical average of ρ (see (37)), in the vicinity of the origin in $\mathbb{R}^3$. As mentioned earlier, we restrict the discussion to the atomic case ($M = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z$) for convenience only. We also recall that we assume throughout that (18) holds.

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

$$\widetilde{\rho}\,'(0) = -Z\widetilde{\rho}(0), \tag{62}$$

follows from the earlier mentioned cusp condition for ψ itself proved by Kato [23]; see [45], [20], and [K, Remark 1.13]. As mentioned above it was proved in [K, Theorem 1.11] that $\widetilde{\rho} \in C^2([0,\infty))$ (and, as also mentioned, the proof actually yields $\widetilde{\rho} \in C^{2,\alpha}([0,\infty))$ for all $\alpha \in (0,1)$). Furthermore, the implicit formula,

$$\widetilde{\rho}\,''(0) = \frac{2}{3}\big(Z^2\widetilde{\rho}(0) + \widetilde{h}(0)\big)\,, \tag{63}$$

with $\widetilde{h}$ the spherical average of h in (49),

$$\widetilde{h}(r) = \int_{\mathbb{S}^2} h(r\omega)\, d\omega\,, \tag{64}$$

was proved. Note that in the case of the symmetry in (58), (60) shows that (62) holds even without averaging. Also, in this case, (63) actually follows from (61) by averaging (see [F, Remark 1.8] for details).

Again, the proof of (63) relied on the information on the structure of ψ obtained in Theorem 1 above.

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

$$\varepsilon := E^0_{N-1}(Z) - E \ , \quad E^0_{N-1}(Z) = \inf \sigma(H_{N-1}(Z)) \, . \tag{65}$$

Then if $\varepsilon \geq 0$, we have (see [K, Theorem 1.11])

$$h(x) \geq \varepsilon \rho(x) \ \text{ for all } x \in \mathbb{R}^3 \, , \tag{66}$$

and so in this case, (63) implies that

$$\widetilde{\rho}\,''(0) \geq \frac{2}{3}\big(Z^2 + \varepsilon\big)\widetilde{\rho}(0) \geq \frac{2}{3}\, Z^2 \widetilde{\rho}(0) \, . \tag{67}$$

However, all of this was improved in [J] where the following was proved.

Theorem 10 ([J, Theorem 1.2])**.** *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction, $H_N(Z)\psi = E\psi$, satisfying* (18)*, with associated spherically averaged density $\widetilde{\rho}$ defined by* (36) *and* (37)*. Let $\widetilde{h}$ be defined by* (49)–(50)*,* (64)*, and let ε be given by* (65)*. Let finally $\varphi_j(\mathbf{x}) = e^{\frac{Z}{2}|x_j|}\psi(\mathbf{x})$, $j = 1, \dots, N$.*

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

$$\widetilde{\rho}\,'''(0) = \widetilde{h}\,'(0) - \frac{Z}{3}\big[\widetilde{h}(0) + Z^2\widetilde{\rho}(0)\big] \tag{68}$$

$$= -\frac{7}{12}Z^3\widetilde{\rho}(0) - 4\pi Z \sum_{j=1}^{N} \Big[\int_{\mathbb{R}^{3N}} |\nabla_j \varphi_j(\mathbf{x})|^2 \, \delta(x_j)\, d\mathbf{x} \tag{69}$$

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

If $\varepsilon \geq 0$, then

$$\widetilde{\rho}\,'''(0) \leq -\frac{Z}{12}\big(7Z^2 + 20\varepsilon\big)\,\widetilde{\rho}(0) \leq -\frac{7}{12}Z^3\widetilde{\rho}(0) \, . \tag{70}$$

Here we use the notation

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

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

The existence of $\widetilde{\rho}^{\,(k)}(0)$ for all $k > 3$ remains an open problem. The two main steps in the proof of Theorem 10 are Propositions 2 and 3 below (also proved in [J]). 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 2 the existence of $\widetilde{h}\,'(0)$ is proved and this result already heavily relies on

the optimal regularity results for ψ (involving the *a priori* estimate for second order partial derivatives of ψ in Theorem 4 above) obtained in [E].

Connect to the a priori estimate and Cusp Condition for *psi* in The Monster

Proposition 2 ([J, Proposition 1.6]). *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction, $H_N(Z)\psi = E\psi$, satisfying* (18)*, and let h be as defined in* (49)–(50)*. 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 $\varphi_j(\mathbf{x}) = e^{\frac{Z}{2}|x_j|}\psi(\mathbf{x})$, $j = 1,\dots,N$,

$$\widetilde{h}(0) = \frac{Z^2}{4}\widetilde{\rho}(0) + 4\pi \sum_{j=1}^{N} \Big[\int_{\mathbb{R}^{3N}} |\nabla_j \varphi_j(\mathbf{x})|^2\, \delta(x_j)\, d\mathbf{x} + \langle \psi(0,\cdot), [H_{N-1}(Z-1) - E]\psi(0,\cdot)\rangle_{L^2(\mathbb{R}^{3N-3}_{\mathbf{x}_j})} \Big], \tag{71}$$

$$\widetilde{h}\,'(0) = -Z\widetilde{h}(0) + \frac{Z^3}{12}\widetilde{\rho}(0) + \frac{4\pi}{3} Z \sum_{j=1}^{N} \Big[\int_{\mathbb{R}^{3N}} |\nabla_j \varphi_j(\mathbf{x})|^2\, \delta(x_j)\, d\mathbf{x} - \langle \psi(0,\cdot), [H_{N-1}(Z-1) - E]\psi(0,\cdot)\rangle_{L^2(\mathbb{R}^{3N-3}_{\mathbf{x}_j})} \Big]. \tag{72}$$

Proposition 3 ([J, Proposition 2.1]). *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction, $H_N(Z)\psi = E\psi$, satisfying* (18)*, with associated spherically averaged density $\widetilde{\rho}$ defined by* (36) *and* (37)*, and let $\widetilde{h}$ be as defined in* (49)–(50) *and* (64)*. 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

$$\widetilde{\rho}^{(k+2)}(0) = \frac{2}{k+3}\big[(k+1)\widetilde{h}^{(k)}(0) - Z\widetilde{\rho}^{(k+1)}(0)\big]. \tag{73}$$

As a byproduct of (71) the following improvement of (67) was proved in [F].

Corollary 2 ([J, Corollary 1.7]). *Let $\psi \in L^2(\mathbb{R}^{3N})$ be an atomic eigenfunction, $H_N(Z)\psi = E\psi$, satisfying* (18)*, with associated spherically averaged density $\widetilde{\rho}$ defined by* (36) *and* (37)*. Let ε be given by* (65)*, and assume $\varepsilon \geq 0$.*

Then

$$\widetilde{\rho}\,''(0) \geq \frac{2}{3}\big[\frac{5Z^2}{4} + \varepsilon\big]\widetilde{\rho}(0) \geq \frac{5}{6}\, Z^2\widetilde{\rho}(0). \tag{74}$$

The proof follows using the HVZ-theorem [39, Theorem XIII.17]. Then (71) provides an improvement of the bound (66) for $r = 0$ to

$$\widetilde{h}(0) \geq \big[\frac{Z^2}{4} + \varepsilon\big]\widetilde{\rho}(0)\,. \tag{75}$$

This, using (63), gives (74).

One should compare (62), (67), and (70) with the fact that for the ground state of 'Hydrogenic atoms' ($N = 1$), the corresponding density $\widetilde{\rho}_1(r) = c\,e^{-Zr}$ satisfies

$$\widetilde{\rho}_1^{(k)}(0) = (-Z)^k \widetilde{\rho}_1(0)\,. \tag{76}$$

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 (63) and (71), and (69) and (72), imply that the corresponding density $\widetilde{\rho}_n$ satisfies

$$\widetilde{\rho}_n''(0) = \frac{Z^2}{6}\big[5 + \frac{1}{n^2}\big]\widetilde{\rho}_n(0) + \frac{8\pi}{3}|\nabla\phi_n(0)|^2\,, \tag{77}$$

$$\begin{aligned}\widetilde{\rho}_n'''(0) &= \big[-\frac{7}{12}Z^3 + \frac{5}{3}ZE\big]\widetilde{\rho}_n(0) - 4\pi Z|\nabla\phi_n(0)|^2 \\ &= -\frac{Z^3}{12}\big[7 + \frac{5}{n^2}\big]\widetilde{\rho}_n(0) - 4\pi Z|\nabla\phi_n(0)|^2\,.\end{aligned} \tag{78}$$

For the ground state, i.e., for $n = 1$, $E_1 = -Z^2/4$, $\phi_1 \equiv 1$, (77) reduces to (76) with $k = 2$, and (78) reduces to (76) with $k = 3$.

Furthermore, for s - states (zero angular momentum), we get that $\nabla\phi_n(0) = 0$, since ϕ_n is radial and $C^{1,\alpha}$. Taking n large in (77) and (78) illustrates the optimality of the bounds (74) and (70).

As mentioned above, the existence of $\widetilde{\rho}^{(k)}(0)$ for all $k > 3$, that is, whether $\widetilde{\rho}$ is smooth in $[0, \infty)$, remains an open problem. Proving this, and inequalities related to (76) for these (similar to (62), (74), and (70) for $\widetilde{\rho}'(0)$, $\widetilde{\rho}''(0)$, and $\widetilde{\rho}'''(0)$) is of great interest. Such inequalities could possible even lead to a proof that $\widetilde{\rho}$ is analytic in $[0, \infty)$.

Also the question whether $\widetilde{\rho}'(r) \leq 0$ for $r \geq 0$ remains open. This is expected to be true for ground state densities, but not known even for the bosonic case, even for the case of Helium ($N = 2$). The inequality in (74), together with (62), imply that $\widetilde{\rho}'(r) \leq 0$ for $r \leq R_0$ for the bosonic case, where R_0 depends on the constant C in Theorem 2 above. Note that because of (48) (with $M = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z$) and (66) we have $\Delta\rho \geq 0$ for $|x| \geq Z/\varepsilon$, and so the Maximum Principle gives that $\widetilde{\rho}'(r) < 0$ for $r > Z/\varepsilon$.

3. Pseudorelativistic atoms and molecules

In this section we discuss three papers in which the kinetic energy $T(-\mathrm{i}\nabla)$ of the electrons in (3) is chosen to be the *pseudorelativistic* operator (see (5))

$$T_{\psi\mathrm{rel}} = \sqrt{-\hbar^2\mathrm{c}^2\Delta + (\mathrm{mc}^2)^2} - \mathrm{mc}^2\,. \tag{79}$$

Here, m is the mass of the electron, c is the speed of light, and $\hbar$ is Planck's constant. Let $a = \hbar^2/\mathrm{me}^2$ be the Bohr radius, $\alpha = \mathrm{e}^2/\hbar\mathrm{c}$ Sommerfeld's fine-structure constant, and $R_\infty = \frac{1}{2}\mathrm{me}^4/\hbar^2$ Rydberg's constant. (Here, e is the fundamental charge, which was set to 1 in (1) and (2).) Then by a change of coordinates $x_j \to x_j/a$, we see that the operator H in (3) can be written as

$$\begin{aligned}(2R_\infty)^{-1}H =:{}& H_{N,M}(\mathbf{X},\mathbf{Z};\alpha) \\ ={}& \sum_{j=1}^{N}\Big\{\big[\sqrt{-\alpha^{-2}\Delta_j + \alpha^{-4}} - \alpha^{-2}\big] - \sum_{k=1}^{M}\frac{Z_k}{|x_j - X_k|}\Big\} \\ &+ \sum_{1\le i<j\le N}\frac{1}{|x_i - x_j|}\,,\end{aligned} \tag{80}$$

where again α is the fine-structure constant. For $\alpha = 0$ the kinetic energy of the j^{th} electron is $-\frac{1}{2}\Delta$, the non-relativistic kinetic energy treated in Section 2 (but with $\mathrm{m} = 1$ here).

The paper [L] deals with the large-Z asymptotics of the ground state energy of the operator $H_{N,M}(\mathbf{X},\mathbf{Z};\alpha)$ in (80). The paper [A] deals with Hartree-Fock theory for this operator. We first discuss the former.

We set $N = Z = \sum_{k=1}^{M} Z_k$ so that the molecule is neutral. In particular, this means that Z must be an integer. From now on we study the operator $H_{Z,M}(\mathbf{X},\mathbf{Z};\alpha)$. This operator acts as an unbounded operator on the anti-symmetric tensor product,

$$\mathcal{H}_F = \bigwedge^{Z} L^2(\mathbb{R}^3 \times \{-1,1\})\,,$$

where ± 1 refers to the spin variables. We are interested in the *quantum ground state energy*

$$E^{\mathrm{QM}}_{Z,M}(\mathbf{X},\mathbf{Z};\alpha) = \inf\sigma_{\mathcal{H}_F}\big(H_{Z,M}(\mathbf{X},\mathbf{Z};\alpha)\big)\,, \tag{81}$$

and, in particular, in an asymptotic expansion of this when $Z \to \infty$.

The ground state energy $E^{\mathrm{QM}}_{Z,M}(\mathbf{X},\mathbf{Z};\alpha)$ is finite if $\max_k\{Z_k\alpha\} \leq 2/\pi$, but $E^{\mathrm{QM}}_{Z,M}(\mathbf{X},\mathbf{Z};\alpha) = -\infty$ if $\max_k\{Z_k\alpha\} > 2/\pi$ (see [17, 35])[1]. Therefore we must require the atomic numbers to be smaller than or equal to $2/(\pi\alpha)$ which is approximately 87. This is of course in contradiction with the experimental fact that larger stable atoms exist and is one reason why this model can only be qualitatively correct.

The main interest here is the behaviour of the total ground state energy of large atoms and molecules. Because of the relativistic instability problem mentioned above one cannot simply consider the limit of large atomic number Z. One is forced to look at the simultaneous limit of small fine-structure constant α in such a way that the product $Z\alpha$ remains bounded. Of course, α has a fixed value which experimentally is approximately $1/137$. Thus considering the limit α tending to zero is strictly speaking not physically correct. Likewise, considering the limit of Z tending to infinity is in contradiction with the fact that the experimentally observed values of Z are bounded (by 92 for the stable atoms). Studying the limit $Z \to \infty$ and $\alpha \to 0$ with $Z\alpha$ bounded allows us to make a precise mathematical statement about the asymptotics. There is numerical evidence that the asymptotics is indeed a good approximation to the total ground state energy for the physical values of Z and α.

The first rigorous treatment of the limit $Z \to \infty$ with $Z\alpha$ bounded was given in the paper [M][2], where the leading asymptotics of the ground state energy was found. It turns out it does not depend on $Z\alpha$. The goal of the paper [L] is the first correction to the leading asymptotics, called the *Scott correction* and, in particular, to show that it depends on $Z\alpha$. The work in [M] was generalized to another relativistic model in [3].

The main result in [L] is the following.

Theorem 11 ([L, Theorem 1])**.** *Let* $\mathbf{z} = (z_1,\ldots,z_M)$ *with* $z_1,\ldots,z_M > 0$, $\sum_{k=1}^M z_k = 1$, *and* $\mathbf{r} = (r_1,\ldots,r_M) \in \mathbb{R}^{3M}$ *with* $\min_{k\neq\ell}|r_k - r_\ell| > r_0$ *for some* $r_0 > 0$ *be given. Define* $\mathbf{Z} = (Z_1,\ldots,Z_M) = Z\mathbf{z}$ *and* $\mathbf{X} = Z^{-1/3}\mathbf{r}$. *Then there exist a constant* $E^{\mathrm{TF}}(\mathbf{z},\mathbf{r})$ *and a universal (independent of* $\mathbf{z}$, $\mathbf{r}$ *and* M*) continuous, non-increasing function* $\mathcal{S} : [0,2/\pi] \to \mathbb{R}$ *with* $\mathcal{S}(0) = 1/4$ *such that as* $Z = \sum_{k=1}^M Z_k \to \infty$ *and*

[1]Here, and in the whole discussion of [L], operators are defined as the Friedrichs extension for the corresponding form sum, originally defined on C_0^∞-functions (here, for instance, $\bigwedge^Z C_0^\infty(\mathbb{R}^3\times\{-1,1\})$).

[2]This paper is included in this thesis for completeness, but has already been assesed for the Master's Degree ('Cand. Scient.') at the Department of Mathematics, University of Aarhus, Denmark.

$\alpha \to 0$ with $\max_k\{Z_k\alpha\} \leq 2/\pi$ we have

$$E^{\mathrm{QM}}_{Z,M}(\mathbf{X},\mathbf{Z};\alpha) = Z^{7/3}E^{\mathrm{TF}}(\mathbf{z},\mathbf{r}) + 2\sum_{k=1}^{M} Z_k^2\mathcal{S}(Z_k\alpha) + \mathcal{O}(Z^{2-1/30})\,. \quad (82)$$

Here the error term means that $|\mathcal{O}(Z^{2-1/30})| \leq CZ^{2-1/30}$, where the constant C only depends on r_0 and M. As before, $\sqrt{-\alpha^{-2}\Delta + \alpha^{-4}} - \alpha^{-2} = -\frac{1}{2}\Delta$ when $\alpha = 0$.

A less detailed version of the result above was announced in [43]. For several important remarks on the theorem we refer to [L, Remark 3]. For a throurough discussion of the history of this problem, in the non-relativistic set-up, as well as for related work on relativistic models, we refer to the introduction in [L].

The proof of Theorem 11 relies on a more general (pseudorelativistic) semi-classical estimate and the use of a correlation estimate (see [L, Theorem 17]) to reduce to the one-body problem.

We consider the semi-classical approximation for the pseudorelativistic operator

$$T_\beta(-\mathrm{i}h\nabla) - V(x)\,,$$

where

$$T_\beta(p) = \begin{cases} \sqrt{\beta^{-1}p^2 + \beta^{-2}} - \beta^{-1}\,, & \beta \in (0,\infty) \\ \frac{1}{2}p^2\,, & \beta = 0 \end{cases}\,. \quad (83)$$

We will consider potentials $V : \mathbb{R}^3 \to \mathbb{R}$ with Coulomb singularities of the form $z_k|x-r_k|^{-1}$, $k = 1,\dots,M$, at points $r_1,\dots,r_M \in \mathbb{R}^3$ and with charges $0 < z_1,\dots,z_M \leq 2/\pi$. Define

$$d_{\mathbf{r}}(x) = \min\left\{|x-r_k| \;\middle|\; k = 1,\dots,M\right\}\,, \quad \mathbf{r} = (r_1,\dots,r_M) \in \mathbb{R}^{3M}\,. \quad (84)$$

We assume that for some $\mu \geq 0$ the potential V satisfies

$$\left|\partial^\eta\big(V(x)+\mu\big)\right| \leq \begin{cases} C_{\eta,\mu}d_{\mathbf{r}}(x)^{-1-|\eta|} & \text{if } \mu \neq 0 \\ C_\eta \min\{d_{\mathbf{r}}(x)^{-1}, d_{\mathbf{r}}(x)^{-3}\}\, d_{\mathbf{r}}(x)^{-|\eta|} & \text{if } \mu = 0 \end{cases} \quad (85)$$

for all $x \in \mathbb{R}^3$ with $d_{\mathbf{r}}(x) \neq 0$ and all multi-indices η with $|\eta| \leq 3$, and

$$\left|V(x) - z_k|x-r_k|^{-1}\right| \leq Cr_{\min}^{-1} + C \quad (86)$$

for $|x-r_k| < r_{\min}/2$ where $r_{\min} = \min_{k\neq\ell}|r_k - r_\ell|$. Note, in particular, that the Thomas-Fermi potential $V^{\mathrm{TF}}(\mathbf{z},\mathbf{r},\cdot)$ discussed in [L, Section 2.2] satisfies these requirements, by [L, Theorem 20]. So does the potential $V(x) = \frac{2}{\pi|x|} - 1$ (with $M = 1$, $r_0 = 0$, and $d_{\mathbf{r}}(x) = |x|$).

The main semi-classical result in [L] is the relativistic Scott correction to the semi-classical expansion for potentials of this form, stated

below. It is proved in [L, Section 4] using the coherent state calculus introduced in [44]. The power -3 in (85) is not optimal.

Theorem 12 ([L, Theorem 4])**.** *There exists a continuous, non-increasing function $\mathcal{S} : [0, 2/\pi] \to \mathbb{R}$ with $\mathcal{S}(0) = 1/4$, such that for all $h > 0$, $0 \leq \beta \leq h^2$, T_β as in* (83)*, and all potentials $V : \mathbb{R}^3 \to \mathbb{R}$ satisfying* (85) *and* (86) *with $r_{\min} > r_0 > 0$ and $\max\{z_1, \ldots, z_M\} \leq 2/\pi$, we have*

$$\Big| \operatorname{Tr}\left[T_\beta(-\mathrm{i}h\nabla) - V(x)\right]_- - (2\pi h)^{-3} \int \left[\tfrac{1}{2}p^2 - V(v)\right]_- dvdp - h^{-2} \sum_{k=1}^{M} z_k^2 \mathcal{S}(\beta^{1/2} h^{-1} z_k) \Big| \leq C h^{-2+1/10} \,. \quad (87)$$

Here, $[x]_- = \min\{x, 0\}$. The constant $C > 0$ depends only on M, r_0, μ and the other constants in (85) *and* (86)*.*

Moreover, we can find a density matrix γ, whose density ρ_γ satisfies (with $\|\cdot\|_{6/5}$ the $L^{6/5}$-norm)

$$\left| \int \rho_\gamma(x)\, dx - 2^{1/2}(3\pi^2)^{-1} h^{-3} \int |V(x)_-|^{3/2}\, dx \right| \leq C h^{-2+1/5} \quad (88)$$

and

$$\left\| \rho_\gamma - 2^{1/2}(3\pi^2)^{-1} h^{-3} |V_-|^{3/2} \right\|_{6/5} \leq C h^{-2-1/10} \,, \quad (89)$$

such that

$$\operatorname{Tr}\left[(T_\beta(-\mathrm{i}h\nabla) - V(x))\gamma\right] \leq (2\pi h)^{-3} \int \left[\tfrac{1}{2}p^2 - V(v)\right]_- dvdp + h^{-2} \sum_{k=1}^{M} z_k^2 \mathcal{S}(\beta^{1/2} h^{-1} z_k) + C h^{-2+1/10} \,. \quad (90)$$

The term proportional to h^{-2} is called the *Scott correction*. If $\beta = h^2$ then it only depends on the charges $z_k, k = 1, \ldots, M$, of the Coulomb-singularities. Notice that the function in the semi-classical integral is the *non-relativistic* energy. This is also the reason why the leading Thomas-Fermi energy is independent of β.

Applying this theorem to the potential $V(x) = \frac{2}{\pi|x|} - 1$ (which satisfies (85) and (86) with $M = 1$, $r_0 = 0$, and $d_{\mathbf{r}}(x) = |x|$), and using a simple scaling argument, gives the following explicit characterization of the function $\mathcal{S}$ in Theorem 12 (see details in [L, Lemma 27, Section 4]).

Corollary 3 ([L, Corollary 6]). *The function $\mathcal{S}$ satisfies, uniformly for $\alpha \in [0, 2/\pi]$,*

$$\mathcal{S}(\alpha) = \lim_{\kappa\to 0}\Big(\operatorname{Tr}\big[H_{\mathrm{C}} + \kappa\big]_- - (2\pi)^{-3}\int \big[\tfrac{1}{2}p^2 - |v|^{-1} + \kappa\big]_- \, dpdv \Big)\,, \tag{91}$$

where

$$H_{\mathrm{C}}(\alpha) = \begin{cases} \sqrt{-\alpha^{-2}\Delta + \alpha^{-4}} - \alpha^{-2} - |x|^{-1}\,, & \alpha \in (0, 2/\pi] \\ -\tfrac{1}{2}\Delta - |x|^{-1}\,, & \alpha = 0 \end{cases}\,. \tag{92}$$

We turn to the paper [A]. For simplicity of notation, we restrict to the case of atoms ($M = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z$); on the other hand, we allow for q spin states, so that $\mathcal{H}_F = \wedge_{i=1}^N L^2(\mathbb{R}^3; \mathbb{C}^q)$.

The quantum ground state energy defined in (81) is the infimum of the quadratic form defined by the many-body operator,

$$E^{\mathrm{QM}}(N, Z, \alpha) = \inf\{\, \mathfrak{q}(\Psi, \Psi) \,|\, \Psi \in \mathcal{Q}(H), \langle \Psi, \Psi\rangle = 1\}\,,$$

where $\mathfrak{q}$ is the quadratic form defined by $H \equiv H_{\mathrm{rel}}(N, Z, \alpha)$, and $\mathcal{Q}$ the corresponding form domain (see below); $\langle\ ,\ \rangle$ is the scalar product in $\mathcal{H}_F \subset L^2(\mathbb{R}^{3N}; \mathbb{C}^{q^N})$. The many-body operator is now

$$\begin{aligned} H &= H_{\mathrm{rel}}(N, Z, \alpha) \qquad (93)\\ &= \sum_{j=1}^N \Big\{ \sqrt{-\alpha^{-2}\Delta_j + \alpha^{-4}} - \alpha^{-2} - \frac{Z}{|x_j|} \Big\} + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|} \\ &= \sum_{j=1}^N \alpha^{-1}\Big\{ T(-\mathrm{i}\nabla_j) - V(x_j) \Big\} + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\,, \end{aligned}$$

with $T(-\mathrm{i}\nabla) = E(-\mathrm{i}\nabla) - \alpha^{-1} = \sqrt{-\Delta + \alpha^{-2}} - \alpha^{-1}$ and $V(x) = Z\alpha/|x|$ (we changed the notation for T and V). Here, α is again Sommerfeld's fine-structure constant.

In the Hartree-Fock approximation, instead of minimizing the functional $\mathfrak{q}$ in the entire N-particle space $\mathcal{H}_F$, one restricts to wavefunctions Ψ which are pure wedge products, also called Slater determinants:

$$\Psi(x_1, \sigma_1; x_2, \sigma_2; \ldots; x_N, \sigma_N) = \frac{1}{\sqrt{N!}} \det(u_i(x_j, \sigma_j))_{i,j=1}^N\,, \tag{94}$$

with $\{u_i\}_{i=1}^N$ orthonormal in $L^2(\mathbb{R}^3; \mathbb{C}^q)$ (called *orbitals*). Notice that this way, $\Psi \in \mathcal{H}_F$ and $\|\Psi\|_{L^2(\mathbb{R}^{3N}; \mathbb{C}^{q^N})} = 1$.

The *Hartree-Fock ground state energy* is the infimum of the quadratic form $\mathfrak{q}$ defined by H over such Slater determinants:

$$E^{\mathrm{HF}}(N, Z, \alpha) := \inf\{\, \mathfrak{q}(\Psi, \Psi) \,|\, \Psi \text{ Slater determinant}\}\,. \tag{95}$$

For the non-relativistic Hamiltonian,

$$H_{\rm cl}(N,Z) = \sum_{j=1}^{N} \Big\{ -\frac{1}{2}\Delta_j - \frac{Z}{|x_j|} \Big\} + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}\,, \qquad (96)$$

the mathematical theory of this approximation has been much studied, the groundbreaking work being that of Lieb and Simon [34]; see also [36] for work on excited states. For a comprehensive discussion of Hartree-Fock (and other) approximations in quantum chemistry, and an extensive literature list, we refer to [31].

The aim of the paper [A] is to study the Hartree-Fock approximation for the pseudorelativistic operator H in (93).

We turn to the precise description of the problem. The one-particle operator $h_0 = T(-\mathrm{i}\nabla) - V(\mathbf{x})$ is bounded from below (by $\alpha^{-1}[(1 - (\pi Z\alpha/2)^2)^{1/2} - 1]$) if and only if $Z\alpha \le 2/\pi$ (see [17], [24, 5.33 p. 307], and [48]; we shall have nothing further to say on the critical case $Z\alpha = 2/\pi$). More precisely, if $Z\alpha < 1/2$, then V is a small *operator* pertubation of T. In fact [17, Theorem 2.1 c)], $\big\||x|^{-1}(T(-\mathrm{i}\nabla)+1)^{-1}\big\|_{\mathcal{B}(L^2(\mathbb{R}^3))} = 2$. As a consequence, h_0 is selfadjoint with $\mathcal{D}(h_0) = H^1(\mathbb{R}^3;\mathbb{C}^q)$ when $Z\alpha < 1/2$. It is essentially selfadjoint on $C_0^\infty(\mathbb{R}^3;\mathbb{C}^q)$ when $Z\alpha \le 1/2$.

If, on the other hand, $1/2 \le Z\alpha < 2/\pi$, then V is only a small *form* pertubation of T: Indeed [24, 5.33 p. 307],

$$\int_{\mathbb{R}^3} \frac{|f(x)|^2}{|x|}\,dx \le \frac{\pi}{2}\int_{\mathbb{R}^3} |p||\hat f(p)|^2\,dp \quad \text{for} \quad f \in H^{1/2}(\mathbb{R}^3)\,, \qquad (97)$$

where $\hat f$ denotes the Fourier transform of f. Hence, the quadratic form $\mathfrak{v}$ given by

$$\mathfrak{v}[u,v] := (V^{1/2}u, V^{1/2}v) \quad \text{for} \quad u,v \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q) \qquad (98)$$

(multiplication by $V^{1/2}$ in each component) is well defined (for all values of $Z\alpha$). Here, $(\ ,\ )$ denotes the scalar product in $L^2(\mathbb{R}^3;\mathbb{C}^q)$. Let $\mathfrak{e}$ be the quadratic form with domain $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$ given by

$$\mathfrak{e}[u,v] := (E(p)^{1/2}u, E(p)^{1/2}v) \quad \text{for} \quad u,v \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,. \qquad (99)$$

By abuse of notation, we write $E(p)$ for the (strictly positive) operator $E(-\mathrm{i}\nabla) = \sqrt{-\Delta + \alpha^{-2}}$. Then, using (97) and that $|p| \le E(p)$,

$$\mathfrak{v}[u,u] < \mathfrak{e}[u,u] \quad \text{for} \quad u \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q) \setminus \{0\} \quad \text{if} \quad Z\alpha < 2/\pi\,. \qquad (100)$$

Hence, by the KLMN theorem [38, Theorem X.17], there exists a unique self-adjoint operator h_0 whose quadratic form domain is $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$ such that (with $\mathfrak{t} = \mathfrak{e} - \alpha^{-1}$)

$$(u, h_0 v) = \mathfrak{t}[u,v] - \mathfrak{v}[u,v] \quad \text{for} \quad u,v \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,, \qquad (101)$$

and h_0 is bounded below by $-\alpha^{-1}$. Moreover, if $Z\alpha < 2/\pi$ then the spectrum of h_0 is discrete in $[-\alpha^{-1}, 0)$ and absolutely continuous in $[0, \infty)$ [17, Theorems 2.2 and 2.3].

It is convenient to use the one-to-one correspondence between Slater determinants and projections onto finite dimensional subspaces of $L^2(\mathbb{R}^3; \mathbb{C}^q)$. Indeed, if Ψ is given by (94) with $\{u_i\}_{i=1}^N \subset H^{1/2}(\mathbb{R}^3; \mathbb{C}^q)$, orthonormal in $L^2(\mathbb{R}^3; \mathbb{C}^q)$, and γ is the projection onto the subspace spanned by $u_1, \ldots, u_N$, then the kernel of γ is given by

$$\gamma(x, \sigma; y, \tau) = \sum_{j=1}^{N} u_j(x, \sigma)\overline{u_j(y, \tau)}\,. \tag{102}$$

Let $\rho_\gamma \in L^1(\mathbb{R}^3)$ denote the 1-particle density associated to γ given by

$$\rho_\gamma(x) = \sum_{\sigma=1}^{q} \gamma(x, \sigma; x, \sigma) = \sum_{\sigma=1}^{q}\sum_{j=1}^{N} |u_j(x, \sigma)|^2\,. \tag{103}$$

Then the energy expectation of Ψ depends only on γ, more precisely,

$$\mathfrak{q}(\Psi, \Psi) = \langle \Psi, H\Psi \rangle = \mathcal{E}^{\mathrm{HF}}(\gamma)\,,$$

where $\mathcal{E}^{\mathrm{HF}}$ is the Hartree-Fock energy functional defined by

$$\mathcal{E}^{\mathrm{HF}}(\gamma) = \alpha^{-1}\big\{\,\mathrm{Tr}[E(p)\gamma] - \alpha^{-1}\,\mathrm{Tr}[\gamma] - \mathrm{Tr}[V\gamma]\big\} + \mathcal{D}(\gamma) - \mathcal{E}x(\gamma)\,. \tag{104}$$

Here,

$$\mathrm{Tr}[E(p)\gamma] := \sum_{j=1}^{N} \mathfrak{e}[u_j, u_j]\ ,\ \mathrm{Tr}[V\gamma] := \sum_{j=1}^{N} \mathfrak{v}[u_j, u_j] = Z\alpha \int_{\mathbb{R}^3} \frac{\rho_\gamma(x)}{|x|}\,dx\,,$$

$\mathcal{D}(\gamma)$ is the *direct* Coulomb energy,

$$\mathcal{D}(\gamma) = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy\,, \tag{105}$$

and $\mathcal{E}x(\gamma)$ is the *exchange* Coulomb energy,

$$\mathcal{E}x(\gamma) = \frac{1}{2}\sum_{\sigma,\tau=1}^{q}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\gamma(x, \sigma; y, \tau)|^2}{|x-y|}\,dx\,dy\,.$$

This way,

$$E^{\mathrm{HF}}(N, Z, \alpha) = \inf\{\,\mathcal{E}^{\mathrm{HF}}(\gamma)\,|\,\gamma \in \mathcal{P}\,\}\,, \tag{106}$$

$$\mathcal{P} = \{\gamma : L^2(\mathbb{R}^3; \mathbb{C}^q) \to L^2(\mathbb{R}^3; \mathbb{C}^q)\,|\,\gamma \text{ projection onto } \mathrm{span}\{u_1, \ldots, u_N\}, u_i \in H^{1/2}(\mathbb{R}^3; \mathbb{C}^q), (u_i, u_j) = \delta_{i,j}\}\,. \tag{107}$$

(Notice that if one of the orbitals u_i of γ is not in $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$, then $\mathcal{E}^{\rm HF}(\gamma)=+\infty$ (since $Z\alpha<2/\pi$).)

Define, with ρ_γ as in (103),

$$R_\gamma(x):=\int_{\mathbb{R}^3}\frac{\rho_\gamma(y)}{|x-y|}\,dy\,. \tag{108}$$

We have that

$$R_\gamma\in L^\infty(\mathbb{R}^3)\cap L^3(\mathbb{R}^3)\,. \tag{109}$$

Next, define the operator K_γ with integral kernel (recall (102))

$$K_\gamma(x,\sigma;y,\tau):=\frac{\gamma(x,\sigma;y,\tau)}{|x-y|}\,. \tag{110}$$

The operator K_γ is Hilbert-Schmidt [A, Lemma 2].

Note that, using (102) and the Cauchy-Schwarz inequality, $(u,R_\gamma u)\geq (u,K_\gamma u)$ (multiplication by R_γ is in each component). Denote by $\mathfrak{b}_\gamma$ the (non-negative) quadratic form given by

$$\mathfrak{b}_\gamma[u,v]:=\alpha(u,R_\gamma v)-\alpha(u,K_\gamma v)\quad\text{for}\quad u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,.$$

Then, using $(u,K_\gamma u)\geq 0$ and (100),

$$\begin{aligned}0\leq\mathfrak{b}_\gamma[u,u]\leq\alpha(u,R_\gamma u)&=\alpha\sum_{\sigma=1}^q\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\gamma(y)|u(x,\sigma)|^2}{|x-y|}\,dx\,dy\\&\leq\alpha\frac{2}{\pi}\,\mathrm{Tr}[\gamma]\,\mathfrak{e}[u,u]\,.\end{aligned}$$

Therefore (by the statements and proofs of [38, Theorem X.17] and [40, Theorem VIII.15]), there exists a unique self-adjoint operator h_γ (called the *Hartree-Fock operator associated to* γ), which is bounded below (by $-\alpha^{-1}$), with quadratic form domain $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$ and such that

$$(u,h_\gamma v)=\mathfrak{t}[u,v]-\mathfrak{v}[u,v]+\mathfrak{b}_\gamma[u,v]\quad\text{for}\quad u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,. \tag{111}$$

The operator h_γ has infinitely many eigenvalues in $[-\alpha^{-1},0)$ (when $N<Z$), and $\sigma_{\rm ess}(h_\gamma)=[0,\infty)$; both of these facts are proved in [A, Lemma 2].

The main result of the paper [A] is the following theorem.

Theorem 13 ([A, Theorem 1])**.** *Let $Z\alpha<2/\pi$, and let $N\geq 2$ be a positive integer such that $N<Z+1$.*

Then there exists an N-dimensional projection $\gamma^{\rm HF}=\gamma^{\rm HF}(N,Z,\alpha)$ minimizing the Hartree-Fock energy functional $\mathcal{E}^{\rm HF}$ given by (104)*, that*

is, $E^{\mathrm{HF}}(N,Z,\alpha)$ *in* (106) *(and therefore, in* (95)*) is attained, i.e.,*

$$\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) = E^{\mathrm{HF}}(N,Z,\alpha) = \inf\{\, \mathcal{E}^{\mathrm{HF}}(\gamma) \,|\, \gamma \in \mathcal{P} \,\}\,, \tag{112}$$

with $\mathcal{P}$ *as in* (107).

Moreover, one can write

$$\gamma^{\mathrm{HF}}(x,\sigma;y,\tau) = \sum_{i=1}^{N} \varphi_i(x,\sigma)\overline{\varphi_i(y,\tau)}\,, \tag{113}$$

with $\varphi_i \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q), i = 1,\ldots,N$*, orthonormal, such that the* Hartree–Fock orbitals $\{\varphi_i\}_{i=1}^N$ *satisfy:*

(i) *With* $h_{\gamma^{\mathrm{HF}}}$ *as defined in* (111),

$$h_{\gamma^{\mathrm{HF}}}\varphi_i = \varepsilon_i\varphi_i\ ,\ i = 1,\ldots,N\,, \tag{114}$$

with $0 > \varepsilon_N \geq \ldots \geq \varepsilon_1 > -\alpha^{-1}$ *the* N *lowest eigenvalues of* $h_{\gamma^{\mathrm{HF}}}$.

(ii) *For* $i = 1,\ldots,N$,

$$\varphi_i \in C^\infty(\mathbb{R}^3 \setminus \{0\};\mathbb{C}^q)\,. \tag{115}$$

(iii) *For all* $R > 0$ *and* $\beta < \nu_{\varepsilon_N} := \sqrt{-\varepsilon_N(2\alpha^{-1} + \varepsilon_N)}$*, there exists* $C = C(R,\beta) > 0$ *such that for* $i = 1,\ldots,N$,

$$|\varphi_i(x)| \leq C\, e^{-\beta|x|} \quad \textit{for} \quad |x| \geq R\,. \tag{116}$$

Both the regularity and the exponential decay above are similar to the results in the non-relativistic case (i.e., for the operator in (96); see [34]). However, the proof of Theorem 13 is considerably more complicated due to, on one hand, the non-locality of the kinetic energy operator $E(p)$, and, on the other hand, the fact that the Hartree-Fock operator $h_{\gamma^{\mathrm{HF}}}$ is only given as a *form* sum for $Z\alpha \in [1/2, 2/\pi)$. We refer to [A, Section 2] for more details.

As is easily from the proof in [A], the statements of Theorem 13 (appropriately modified) also hold for molecules. More explicitely, for a molecule with M nuclei of charges $Z_1,\ldots,Z_M$, fixed at $X_1,\ldots,X_M \in \mathbb{R}^3$, replace $\mathfrak{v}$ in (98) by

$$\mathfrak{v}[u,v] := \sum_{k=1}^{M} (V_k^{1/2}u, V_k^{1/2}v) \ \text{ for } \ u,v \in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,, \tag{117}$$

with $V_k(x) = Z_k\alpha/|x - X_k|$, $Z_k\alpha < 2/\pi$. Then, for $N < 1 + \sum_{k=1}^M Z_k$, there exists a Hartree-Fock minimizer, and the corresponding Hartree-Fock orbitals have the regularity and decay properties as stated in Theorem 13, away from each nucleus.

We refer to [A, Remark 1] for more remarks. Work is in progress on proving that the Hartree-Fock orbitals in Theorem 13 above are actually real analytic away from the nuclei. An open and interesting question is to prove the existence of minimizers (and study their properties) for the critical case $Z\alpha = 2/\pi$.

4. Various themes

In this section we present the results from the papers [I, H, N].

In [I] it was proved that $\widetilde{\rho} > 0$ for a $\widetilde{\rho}$ which stems from a physical ground state of an atom (that is, $M = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z$). In this paper it is taken into account that electrons are fermions. We work in the spin-independent description. That is, we split N (the number of electrons) such that

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

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

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

Therefore, for instance,

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

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 $i = N_1 + 1, \ldots, N$. 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 (3) (with $M = 1, X_1 = 0 \in \mathbb{R}^3, Z_1 \equiv Z$), 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.

The following theorem is the main results of [I].

Theorem 14 ([I, 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* (36) *and* (37)*.*

Then

$$\widetilde{\rho}(r) > 0 \quad \textit{for all } r \in [0,\infty)\,. \tag{118}$$

At the origin an explicit, positive lower bound to the density was also derived in [I, (1.10)]:

$$\rho(0) \geq \frac{2P^4}{3\pi Z N \|\psi\|^2} \quad , \quad \text{with } P = \Big\| \sum_{j=1}^{N} \nabla_j \psi \Big\|. \tag{119}$$

We 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. In particular, with $N_1 = N$ and symmetric ($N_2 = 0$), one gets the known result for the absolute (bosonic) ground state.

One 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, which remain open.

The proof of Theorem 14 is by contradiction. One assumes that $\widetilde{\rho}$ vanish for some value $r_0 > 0$ of the radial coordinate. This implies that the total wave function ψ satisfies a Dirichlet boundary condition on a suitable hypercube. By the variational principle and the unique continuation theorem one finally arrives at a contradiction. For $r_0 = 0$ positivity of $\widetilde{\rho}$ is proved by exploiting explicit features of the Coulomb potential. For details we refer to [I]. The extension of the proof to the non-averaged one-electron density ρ is out of the scope of this approach, since in the latter case there is no boundary value problem with which to compare: The set in $\mathbb{R}^{3N}$ on which ψ is zero if $\rho(x_0) = 0$ for some $x_0 \in \mathbb{R}^3$ is of co-dimension 3 in $\mathbb{R}^{3N}$, not co-dimension 1 as in the case of $\widetilde{\rho}(r_0) = 0$, and so it does not constitute the boundary of an open set in $\mathbb{R}^{3N}$.

The paper [H] (a refereed conference proceeding) reviews some of the results on the regularity of molecular eigenfunctions ψ, their corresponding one-electron densities ρ, and the spherically average $\widetilde{\rho}$ of these, all discussed in Section 2, as well as the positivity result discussed above.

However, it also contains a proof of an exponentially decreasing lower bound for $\widetilde{\rho}$ in the case when the eigenvalue is below the essential

spectrum. This result also holds when the Hamiltonian is restricted to symmetry subspaces.

Theorem 15 ([H, Theorem 6]). *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* (36) *and* (37)*. Define*

$$\alpha_0 = \sup\left\{\alpha \,\middle|\, e^{\alpha|\mathbf{x}|}\psi \in L^2(\mathbb{R}^{3N})\right\}. \tag{120}$$

Then

$$\limsup_{R\to+\infty}\left(\frac{\ln\widetilde{\rho}(R)}{R}\right) \leq -2\alpha_0. \tag{121}$$

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

$$\liminf_{R\to+\infty}\left(\frac{\ln\widetilde{\rho}(R)}{R}\right) \geq -2\sqrt{N}\alpha_0. \tag{122}$$

One can make these bounds more explicit using [10]; in fact,

$$\alpha_0^2 \leq |E|\,. \tag{123}$$

To see this, we use Theorems 1.1 and 1.2 in [10]. The set of thresholds $\mathcal{T}(H)$ (mentioned in Section 2) is defined as the closure of the set of eigenvalues of subsystems, i.e., the corresponding ionized systems. We have, according to [10],

$$\alpha_0^2 + E \in \mathcal{T}(H) \quad \text{and} \quad \mathcal{T}(H) \subset (-\infty, 0]\,, \tag{124}$$

so that

$$\alpha_0^2 \leq \sup\mathcal{T}(H) - E = |E|. \tag{125}$$

The above theorem gives upper and lower exponential bounds on $\widetilde{\rho}$ near infinity. Combined with Theorem 14 above this implies (by continuity of $\widetilde{\rho}$, see Theorem 10 in Section 2) *global* lower exponential bounds in the case of a ground state. We state this explicitely in the next corollary.

Corollary 4 ([H, Corollary 9]). *Let ψ be an eigenfunction of H^{N_1,N_2} with eigenvalue E, let α_0 be as in* (120)*, and let $\widetilde{\rho}$ be the associated spherically averaged density defined by* (36) *and* (37)*.*

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

$$\widetilde{\rho}(r) \geq c\, e^{-2\sqrt{N}\alpha r} \text{ for all } r \geq r_0\,. \tag{126}$$

If furthermore $E = E_{N_1,N_2}$ (the ground state energy), then (126) *holds with $r_0 = 0$.*

It remains a (probably hard) open and interesting problem to prove lower exponential bounds like (126) for *non*-averaged densities. For more discussions on known *upper* exponential bounds for ρ we refer to [H].

The final paper described in this section, [N], deals with completely different issues. In this paper we consider a family of Hamiltonians

$$H \equiv H(\lambda) = T - \lambda V \tag{127}$$

where $\lambda > 0$ is the coupling constant and $V \geq 0$ is a bounded and integrable potential. Different choices of physical kinetic energies T are considered but for the moment, to fix ideas, we set $T = -\Delta$, the Laplace operator in three dimensions. The essential spectrum of H is equal to the interval $[0, \infty)$ and (for λ sufficiently large) H has negative discrete eigenvalues $E_i < 0$, $i = 1, 2, \ldots$. We shall henceforth fix an $i \in \mathbb{N}$ and consider the λ-dependence of $E(\lambda) := E_i(\lambda)$. Due to monotonicity, there is a $\lambda_c \in \mathbb{R}$ such that, as $\lambda \downarrow \lambda_c$, $E(\lambda) \uparrow 0$. We call λ_c a *coupling constant threshold*.

Let $\varphi_E = \varphi_{E(\lambda)} \in L^2(\mathbb{R}^3)$ be an eigenfunction of $H(\lambda)$ with eigenvalue $E = E(\lambda)$. A detailed study of the behaviour of E as $\lambda \downarrow \lambda_c$ for various choices of T was carried out in [25, 26, 27, 37]. In [N] we studied the behaviour of φ_E as $E \uparrow 0$ (that is, as $\lambda \downarrow \lambda_c$). It is easy to prove (using closedness of the kinetic energy T) that if φ_E converges in $L^2(\mathbb{R}^3)$, then the limit function φ_0 is an eigenfunction of $H(\lambda_c)$, i.e., a boundstate with zero energy. If there is no L^2-convergence, however, one might expect some other kind of convergence of the φ_E's. In particular, we were interested in considering the convergence properties of $w(-\mathrm{i}\nabla)\varphi_E$ where w is a suitable function of the kinetic energy. (For the question of existence of zero energy eigenstates, see e.g. [2], and the above mentioned papers).

Such questions are, apart from being of independent interest, important for problems pertaining to enhanced binding and the Efimov-effect; see e.g. [5, 47]. We shall not comment further on this here. The paper [N] partially use the techniques used in [26, 27], and [25] for the relativistic case (see also [37]). In these papers the authors investigated the relationship between the analytic properties of the eigenvalues near the threshold energy and the existence of eigenvalues at the threshold.

Let us introduce the three different choices of kinetic energy T which we study in [N]. Let $\mathrm{m} > 0$ be the mass of the electron.

Schrödinger case: As earlier mentioned, the free one-particle non-relativistic kinetic energy (in units when $\hbar = 1$) is given by $-\frac{\Delta}{2\mathrm{m}}$.

Choosing units such that $2\mathrm{m} = 1$, the operator is just the Laplace-operator in three dimensions mentioned above,

$$T_{\mathrm{nr}} := -\Delta. \tag{128}$$

Pseudorelativistiv case: A naïve choice of a free one-particle (pseudo)relativistic kinetic energy is (in units when $\hbar = \mathrm{c} = 1$) given by the pseudodifferential operator discussed in Section 3,

$$T_{\psi\mathrm{rel}} := \sqrt{-\Delta + \mathrm{m}^2} - \mathrm{m}. \tag{129}$$

Dirac case: The free one-particle Dirac operator (again, in units when $\hbar = \mathrm{c} = 1$) is given by

$$T_D := \alpha \cdot (-i\nabla) + \mathrm{m}\beta - \mathrm{m}, \tag{130}$$

acting on $L^2(\mathbb{R}^3; \mathbb{C}^4)$. Here α, β are the usual Dirac matrices (note that α is here *not* the fine-structure constant).

Consider, for $E \notin \sigma(T)$ and $\|\varphi_E\|_2 = 1$, the eigenvalue equation

$$(T(-i\nabla) - \lambda V)\varphi_E = E\varphi_E. \tag{131}$$

An elementary manipulation shows that this equation can be rewritten as

$$\varphi_E = \lambda(T(-i\nabla) - E)^{-1} V\varphi_E. \tag{132}$$

The latter equation is known (in the Physics literature) as the Lipmann-Schwinger equation.

We recall the following: For $E \notin \sigma(T)$ there is a solution φ_E of (131) if, and only if, for

$$\mu_E := V^{1/2}\varphi_E, \tag{133}$$

the equation

$$K_E\mu_E = \lambda^{-1}\mu_E \tag{134}$$

holds, where

$$K_E = V^{1/2}(T(-i\nabla) - E)^{-1}V^{1/2} \tag{135}$$

is the *Birman-Schwinger operator*.

Let us now state the condition on the weight functions w. We denote $\chi_< := \chi_{[0,1)}$ and $\chi_> := \chi_{[1,\infty)}$, with χ_A the characteristic function of the set A.

Let $w_S : \mathbb{R}^3 \to \mathbb{C}$ (Schrödinger), $w_{\psi rel} : \mathbb{R}^3 \to \mathbb{C}$ (pseudorelativistic), and $w_D : \mathbb{R}^3 \to M_{4\times 4}(\mathbb{C})$ (4×4 matrices over $\mathbb{C}$) (Dirac) satisfy

$$\frac{w_S(p)\chi_<(|p|)}{p^2} \in L^2(\mathbb{R}^3) \quad \text{and} \quad \frac{w_S(p)\chi_>(|p|)}{p^2} \in L^\infty(\mathbb{R}^3)\,, \tag{136}$$

$$\frac{w_{\psi rel}(p)\chi_<(|p|)}{p^2} \in L^2(\mathbb{R}^3) \quad \text{and} \quad \frac{w_{\psi rel}(p)\chi_>(|p|)}{p} \in L^\infty(\mathbb{R}^3)\,, \tag{137}$$

$$\frac{|w_D(p)|\chi_<(|p|)}{p^2} \in L^2(\mathbb{R}^3;\mathbb{C}^4) \quad \text{and} \quad \frac{|w_D(p)|\chi_>(|p|)}{|p|} \in L^\infty(\mathbb{R}^3;\mathbb{C}^4)\,, \tag{138}$$

where in the last expression $|w_D(p)|$ denotes any norm of the matrix $w_D(p)$. We write in general $w(p)$ for one of the three above defined functions.

The main result of [N] is the following.

Theorem 16 ([N, Theorem 1.2])**.** *Let $H(\lambda) = T - \lambda V$, with T one of the kinetic energy operators mentioned above, and $V \in L^1 \cap L^\infty$. Let λ_c be a coupling constant threshold, let $\lambda_n \downarrow \lambda_c$, and $\{\varphi_n\}_{n\in\mathbb{N}} \subset L^2$ such that $H(\lambda_n)\varphi_n = E(\lambda_n)\varphi_n$. Let $\{\mu_n\}_{n\in\mathbb{N}}$ be the corresponding Birman-Schwinger eigenfunctions defined by* (133) *, and assume that $\mu_n \to \mu_0$ in L^2 as $n \to \infty$. Define*

$$\varphi_0(x) := \lambda_c \int_{\mathbb{R}^3} T^{-1}(x,y)V^{1/2}(y)\mu_0(y)\,dy, \tag{139}$$

where $T^{-1}(x,y) := \lim_{E\to 0}(T-E)^{-1}(x,y)$. Let finally w satisfy the conditions (136)–(138)*.*

Then

$$w\hat{\varphi}_n \to w\hat{\varphi}_0 \quad \text{in } L^2 \quad \text{as } n \to \infty. \tag{140}$$

Furthermore, φ_0 satisfies

$$H\varphi_0 = 0 \quad \text{in} \quad \mathcal{S}'. \tag{141}$$

Note that not all solutions of $H\varphi_0 = 0$ in the distributional sense have the form (139).

In contrast to the Laplacian, the pseudorelativistic kinetic energy behaves as p^2 for small (momenta) p and as p for large momenta. The conditions in (137) are enough to ensure that

$$\|w(\mathbf{p})\chi_<(p)/(\sqrt{p^2+m^2}-m)\|_2$$

and

$$\|w(\mathbf{p})\chi_>(p)/(\sqrt{p^2+m^2}-m)\|_\infty$$

are finite.

Examples of weight functions are

$$w_S(\mathbf{p}) = p^{2s}\ ,\ w_{\psi rel}(\mathbf{p}) = (\sqrt{p^2+m^2}-m)^s\,,$$

and

$$w_D(\mathbf{p}) = |\alpha\cdot\mathbf{p}+m\beta-m|^s\,,$$

all for $s \in (\frac{1}{2}, 2]$. Thus, in general we have that $w(\mathbf{p}) = |T(\mathbf{p})|^s$, $s \in (\frac{1}{2}, 2]$, satisy the conditions (136)–(138).

In the Schrödinger case, convergence of $\nabla\varphi_E$ and $\Delta\varphi_E$ is known; see e. g. [47]. These cases are covered by our results.

It is important to note that our convergence statements are independent of whether there is an eigenvalue at the threshold when $\lambda \to \lambda_c$ or not. Conditions for the limit function φ_0 (or φ_{-2m}) to be in L^2 are well known. In case $\varphi_0 \notin L^2$, φ_0 is called a zero resonance, or a half-bound state.

Appendix A

Here we collect various general facts about elliptic regularity, of which Theorem 17 below is new [E, Theorem 2.6].

Definition 2. *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*

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

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

$$\|u\|_{C^{k,\alpha}(\Omega')} = \sum_{|\beta|\leq k} \|D^\beta u\|_{L^\infty(\Omega')} + [u]_{k,\alpha,\Omega'},$$

$$[u]_{k,\alpha,\Omega'} = \sum_{|\beta|=k} \sup_{x,y\in\Omega',\, x\neq y} \frac{|D^\beta u(x) - D^\beta u(y)|}{|x-y|^\alpha}.$$

For $k = 0$ we use the notation $C^\alpha(\Omega) \equiv C^{0,\alpha}(\Omega)$ and $[u]_{\alpha,\Omega'} \equiv [u]_{0,\alpha,\Omega'}$.

Furthermore, for a function $u \in C^\alpha(\mathbb{R}^n \setminus \{0\})$ we define

$$\|u\|_{C^\alpha(\mathbb{S}^{n-1})} = \sup_{\mathbb{S}^{n-1}} |u| + [u]_{\alpha,\mathbb{S}^{n-1}}, \tag{142}$$

$$[u]_{\alpha,\mathbb{S}^{n-1}} = \sup_{x,y\in\mathbb{S}^{n-1},\, x\neq y} \frac{|u(x)-u(y)|}{|x-y|^\alpha}.$$

The following proposition is a reformulation of Corollary 8.36 in Gilbarg and Trudinger [12], adapted for our purposes:

Proposition 4. *Let Ω_0 be a bounded domain in $\mathbb{R}^n$ and suppose $u \in W^{1,2}(\Omega_0)$ is a weak solution of $\Delta u + \sum_{j=1}^n b_j D_j u + Wu = g$ in Ω_0, where $b_j, W, g \in L^\infty(\Omega_0)$. Then $u \in C^{1,\alpha}(\Omega_0)$ for all $\alpha \in (0,1)$ and for any domains Ω', Ω, $\overline{\Omega'} \subset \Omega$, $\overline{\Omega} \subset \Omega_0$ we have*

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

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

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

The following result proved in [E] shows that one can push the $C^{1,\alpha}, \alpha \in (0,1)$, in Proposition 4 to $C^{1,1}$ in certain cases.

Theorem 17 ([E, Theorem 2.6])**.** *Let $g \in L^\infty(\mathbb{R}^k)$, $k \geq 2$, be a homogeneous function of degree 0 which has the properties $g \in C^\alpha(\mathbb{R}^k \setminus \{0\})$ and $g|_{\mathbb{S}^{k-1}}$ is orthogonal to $\mathfrak{h}_2^{(k)}$ (the subspace of $L^2(\mathbb{S}^{k-1})$ spanned by the spherical harmonics of degree 2). Let $f \in C^\alpha(\mathbb{R}^d)$ for some $d \geq 0$ and let $u \in C^{1,\alpha}(\mathbb{R}^{k+d})$ be a weak solution of the equation*

$$\Delta u(x', x'') = g(x') f(x'') \tag{143}$$

where $x' \in \mathbb{R}^k$, $x'' \in \mathbb{R}^d$, $\Delta = \Delta_{x'} + \Delta_{x''}$.

Then $u \in W^{2,\infty}_{\mathrm{loc}}(\mathbb{R}^n)$, $n = k + d$, and the following a priori estimate holds:
For all balls $B_n(z, R)$ and $B_n(z, R_1)$ in $\mathbb{R}^n$ where $0 < R < R_1$, $z \in \mathbb{R}^n$,

$$\sup_{B_n(z,R)} |D_{ij} u| \leq C \Big(\sup_{B_n(z,R_1)} |u| + \big(\sup_{\mathbb{S}^{k-1}} |g|\big) \, \|f\|_{C^\alpha(\pi_d B_n(z,R_1))} + \big(\sup_{\pi_d B_n(z,R_1)} |f| \big) \, \|g\|_{C^\alpha(\mathbb{S}^{k-1})} \Big) \tag{144}$$

with $C = C(n, \alpha, R, R_1)$. Here $\pi_d(x', x'') = x''$ for $x' \in \mathbb{R}^k$, $x'' \in \mathbb{R}^d$ for $d > 0$; for $d = 0$, $\pi_d(x') = 0$.

The case $d = 0$ means that f is a constant and the terms in (144) with f then equal this constant.

Note that if $k = 0, d \geq 2$, one has stronger conclusions: Equation (143) becomes $\Delta u(y) = f(y)$ with $f \in C^\alpha(\mathbb{R}^d)$, so by Proposition 4, $u \in C^{2,\alpha}(\mathbb{R}^d)$. The *a priori* estimate analogous to (144) is then a consequence of Hölder-estimates for u (see e. g., [12, Corollary 6.3]).

Using the standard fact ([6, Theorem 4 in 5.8]) that $W^{2,\infty}_{\mathrm{loc}}(\mathbb{R}^n) = C^{1,1}_{\mathrm{loc}}(\mathbb{R}^n)$ (with equivalent norms) we may replace the term $\sup_{B_n(z,R)} |D_{ij} u|$ by $[u]_{1,1,B_n(z,R)}$ on the left hand side in (144).

For the special solution to (143) given by the Newton potential of gf, the estimate (144) holds without the term $\sup_{B_n(z,R_1)} |u|$ on the right hand side.

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