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by

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HARTREE-FOCK THEORY FOR PSEUDORELATIVISTIC ATOMS

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Abstract. We study the Hartree-Fock model for pseudorelativistic atoms, that is, atoms where the kinetic energy of the electrons is given by the pseudo-relativistic operator $\sqrt{(|\mathbf{p}|c)^2 + (mc^2)^2} - mc^2$. We prove the existence of a Hartree-Fock minimizer, and prove regularity away from the nucleus and pointwise exponential decay of the corresponding orbitals.

1. Introduction and results

We consider a model for an atom with N electrons and nuclear charge Z, where the kinetic energy of the electrons is described by the expression $\sqrt{(|\mathbf{p}|c)^2 + (mc^2)^2} - mc^2$. This model takes into account some (kinematic) relativistic effects; in units where $\hbar = e = m = 1$, the Hamiltonian becomes

$$H = H_{\mathrm{rel}}(N, Z, \alpha) = \sum_{j=1}^{N} \Big\{ \sqrt{-\alpha^{-2}\Delta_j + \alpha^{-4}} - \alpha^{-2} - \frac{Z}{|\mathbf{x}_j|} \Big\} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}$$
$$= \sum_{j=1}^{N} \alpha^{-1} \Big\{ T(-\mathrm{i}\nabla_j) - V(\mathbf{x}_j) \Big\} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} , \tag{1}$$

with $T(\mathbf{p}) = E(\mathbf{p}) - \alpha^{-1} = \sqrt{|\mathbf{p}|^2 + \alpha^{-2}} - \alpha^{-1}$ and $V(\mathbf{x}) = Z\alpha/|\mathbf{x}|$. Here, α is Sommerfeld's fine structure constant; physically, $\alpha \simeq 1/137.036$.

The operator H acts on a dense subspace of the N-particle Hilbert space $\mathcal{H}_F = \wedge_{i=1}^{N} L^2(\mathbb{R}^3; \mathbb{C}^q)$ of antisymmetric functions, where q is the number of spin states. It is bounded from below on this subspace (more details below).

The *(quantum) ground state energy* is the infimum of the spectrum of H considered as an operator acting on $\mathcal{H}_F$:

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

where $\mathfrak{q}$ is the quadratic form defined by H, and $\mathcal{Q}$ the corresponding form domain (see below); $\langle \ , \ \rangle$ is the scalar product in $\mathcal{H}_F \subset L^2(\mathbb{R}^{3N}; \mathbb{C}^{q^N})$.

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:

$$\Psi(\mathbf{x}_1, \sigma_1; \mathbf{x}_2, \sigma_2; \ldots; \mathbf{x}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \det(u_i(\mathbf{x}_j, \sigma_j))_{i,j=1}^{N} , \tag{2}$$

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 $\|\Psi\|_{L^2(\mathbb{R}^{3N}; \mathbb{C}^{q^N})} = 1$.

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

$$E^{\mathrm{HF}}(N,Z,\alpha) := \inf\{\,\mathfrak{q}(\Psi,\Psi)\,|\,\Psi \text{ Slater determinant}\}\,. \tag{3}$$

For the non-relativistic Hamiltonian,

$$H_{\mathrm{cl}}(N,Z) = \sum_{j=1}^{N}\Big\{-\frac{1}{2}\Delta_j - \frac{Z}{|\mathbf{x}_j|}\Big\} + \sum_{1\le i<j\le N}\frac{1}{|\mathbf{x}_i-\mathbf{x}_j|}\,, \tag{4}$$

the mathematical theory of this approximation has been much studied, the ground-breaking work being that of Lieb and Simon [13]; see also [15] 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 [10].

The aim of the present paper is to study the Hartree-Fock approximation for the pseudorelativistic operator H in (1).

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 [7], [9, 5.33 p. 307], and [25]; 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 [7, Theorem 2.1 c)], $\big\||\mathbf{x}|^{-1}(T(-\mathrm{i}\nabla)+1)^{-1}\big\|_{\mathcal{B}(L^2(\mathbb{R}^3))} = 2$. 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 [9, 5.33 p. 307],

$$\int_{\mathbb{R}^3}\frac{|f(\mathbf{x})|^2}{|\mathbf{x}|}\,d\mathbf{x} \le \frac{\pi}{2}\int_{\mathbb{R}^3}|\mathbf{p}||\hat{f}(\mathbf{p})|^2\,d\mathbf{p}\quad\text{for}\quad f\in H^{1/2}(\mathbb{R}^3)\,, \tag{5}$$

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

$$\mathfrak{v}[u,v] := (V^{1/2}u, V^{1/2}v)\quad\text{for}\quad u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q) \tag{6}$$

(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

$$\mathfrak{e}[u,v] := (E(\mathbf{p})^{1/2}u, E(\mathbf{p})^{1/2}v)\quad\text{for}\quad u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,. \tag{7}$$

By abuse of notation, we write $E(\mathbf{p})$ for the (strictly positive) operator $E(-\mathrm{i}\nabla) = \sqrt{-\Delta+\alpha^{-2}}$. Then, using (5) and that $|\mathbf{p}| \le E(\mathbf{p})$,

$$\mathfrak{v}[u,u] \le Z\alpha\frac{\pi}{2}\,\mathfrak{e}[u,u]\quad\text{for}\quad u\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\setminus\{0\}\,. \tag{8}$$

Hence, by the KLMN theorem [18, Theorem X.17], if $Z\alpha < 2/\pi$ 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 $\mathfrak{t} = \mathfrak{e} - \alpha^{-1}$)

$$(u, h_0 v) = \mathfrak{t}[u,v] - \mathfrak{v}[u,v]\quad\text{for}\quad u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,, \tag{9}$$

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 $[0,\infty)$ [7, Theorems 2.2 and 2.3].

As for the N-particle operator in (1), when $Z\alpha < 2/\pi$, (5) implies that the quadratic form

$$\mathfrak{q}(\Psi,\Phi) = \sum_{j=1}^{N} \Big\{ \langle\, E(\mathbf{p}_j)^{1/2}\Psi, E(\mathbf{p}_j)^{1/2}\Phi \,\rangle - \alpha^{-1}\langle \Psi,\Phi\rangle - \langle\, V(\mathbf{x}_j)^{1/2}\Psi, V(\mathbf{x}_j)^{1/2}\Phi \,\rangle \Big\}$$

$$+ \sum_{1\le i<j\le N} \langle\, |\mathbf{x}_i-\mathbf{x}_j|^{-1/2}\Psi, |\mathbf{x}_i-\mathbf{x}_j|^{-1/2}\Phi\rangle\ , \quad \Psi,\Phi \in \bigwedge_{i=1}^{N} H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,,$$

is well-defined, closed, and bounded from below. The operator H can then be defined as the corresponding (unique) self-adjoint operator. It satisfies

$$\bigwedge_{i=1}^{N} H^{1}(\mathbb{R}^3;\mathbb{C}^q) \subset \mathcal{D}(H) \subset \mathcal{Q}(H) = \bigwedge_{i=1}^{N} H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,,$$
$$\mathfrak{q}(\Psi,\Phi) = \langle \Psi, H\Phi\rangle\,, \quad \Phi\in\mathcal{D}(H)\,, \quad \Psi\in\mathcal{Q}(H)\,.$$

For $Z\alpha < 1/2$, $\mathcal{D}(H) = \wedge_{i=1}^{N} H^1(\mathbb{R}^3;\mathbb{C}^q)$. All this follows from (the statements and proofs of) [18, Theorem X.17] and [17, Theorem VIII.15]. See [14] for further references on H. We shall not have anything further to say on H in this paper, however, but will only study the Hartree-Fock problem mentioned above. We now discuss this in more detail.

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 (2) 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 $u_1,\dots,u_N$, then the kernel of γ is given by

$$\gamma(\mathbf{x},\sigma;\mathbf{y},\tau) = \sum_{j=1}^{N} u_j(\mathbf{x},\sigma)\overline{u_j(\mathbf{y},\tau)}\,. \tag{10}$$

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

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

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

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

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

$$\mathcal{E}^{\rm HF}(\gamma) = \alpha^{-1}\Big\{ \operatorname{Tr}[E(\mathbf{p})\gamma] - \alpha^{-1}\operatorname{Tr}[\gamma] - \operatorname{Tr}[V\gamma]\Big\} + \mathcal{D}(\gamma) - \mathcal{E}x(\gamma)\,. \tag{11}$$

Here,

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

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

$$\mathcal{D}(\gamma) = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{x})\rho_\gamma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}\,d\mathbf{y}\,, \tag{12}$$

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

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

This way,

$$
\begin{aligned}
E^{\mathrm{HF}}(N,Z,\alpha) &= \inf\{\, \mathcal{E}^{\mathrm{HF}}(\gamma) \,|\, \gamma\in\mathcal{P}\,\}\,, \qquad (13)\\
\mathcal{P} &= \{\gamma : L^2(\mathbb{R}^3;\mathbb{C}^q)\to L^2(\mathbb{R}^3;\mathbb{C}^q) \,|\, \gamma \text{ projection onto } \mathrm{span}\{u_1,\dots,u_N\},\\
&\qquad u_i\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q), (u_i,u_j)=\delta_{i,j}\}\,.
\end{aligned}
$$

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

We now extend the definition of the Hartree-Fock energy functional $\mathcal{E}^{\mathrm{HF}}$, in order to turn the minimization problem (13) (that is, (3)) into a convex problem.

A *density matrix* $\gamma : L^2(\mathbb{R}^3;\mathbb{C}^q)\to L^2(\mathbb{R}^3;\mathbb{C}^q)$ is a self-adjoint trace class operator that satisfies the operator inequality $0\le\gamma\le\mathrm{Id}$. A density matrix γ has the integral kernel

$$\gamma(\mathbf{x},\sigma;\mathbf{y},\tau)=\sum_j \lambda_j u_j(\mathbf{x},\sigma)\overline{u_j(\mathbf{y},\tau)}\,, \qquad (14)$$

where λ_j, u_j are the eigenvalues and corresponding eigenfunctions of γ. We choose the u_j's to be orthonormal in $L^2(\mathbb{R}^3;\mathbb{C}^q)$. As before, let $\rho_\gamma\in L^1(\mathbb{R}^3)$ denote the 1-particle density associated to γ given by

$$\rho_\gamma(\mathbf{x})=\sum_{\sigma=1}^{q}\sum_j \lambda_j\,|u_j(\mathbf{x},\sigma)|^2\ . \qquad (15)$$

Define

$$\mathcal{A}:=\big\{\gamma \text{ density matrix} \;\big|\; \mathrm{Tr}\,\big[E(\mathbf{p})\gamma\big]<+\infty\,\big\}\,, \qquad (16)$$

where, by definition, for γ written as in (14),

$$\mathrm{Tr}[E(\mathbf{p})\gamma]:=\sum_j \lambda_j\,\mathfrak{e}[u_j,u_j]\,. \qquad (17)$$

Notice that if $\gamma\in\mathcal{A}$ then all the terms in $\mathcal{E}^{\mathrm{HF}}(\gamma)$ (see (11)) are finite. Indeed, for $\gamma\in\mathcal{A}$ and written as in (14),

$$\mathrm{Tr}[V\gamma]:=\sum_j\lambda_j\,\mathfrak{v}[u_j,u_j]=Z\alpha\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{x})}{|\mathbf{x}|}\,d\mathbf{x} \qquad (18)$$

is finite, due to (8). In particular,

$$u_j\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\subset L^3(\mathbb{R}^3;\mathbb{C}^q)\,, \qquad (19)$$

the last inclusion by Sobolev's inequality [12, Theorem 8.4].

On the other hand, if $\gamma\in\mathcal{A}$ then

$$\rho_\gamma\in L^1(\mathbb{R}^3)\cap L^{4/3}(\mathbb{R}^3)\,. \qquad (20)$$

This follows from Daubechies' inequality, see [5, pp. 519–520]. By Hölder's inquality, $\rho_\gamma\in L^{6/5}(\mathbb{R}^3)$. The Hardy-Littlewood-Sobolev inequality [12, Theorem 4.3] then implies that $\mathcal{D}(\gamma)$ (see (12)) is finite. Finally, $\mathcal{E}x(\gamma)\le\mathcal{D}(\gamma)$, since

$$
\begin{aligned}
&\mathcal{D}(\gamma)-\mathcal{E}x(\gamma)\\
&\quad=\frac12\sum_{i,j}\lambda_i\lambda_j\sum_{\sigma,\tau=1}^{q}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|u_i(\mathbf{x},\sigma)u_j(\mathbf{y},\tau)-u_j(\mathbf{x},\sigma)u_i(\mathbf{y},\tau)|^2}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y}\ge 0\,.
\end{aligned}
$$

Therefore, $\mathcal{E}^{\mathrm{HF}}$ defined by (11) extends to $\gamma\in\mathcal{A}$. This way, with h_0 defined as in (9),

$$\mathrm{Tr}[h_0\gamma]=\mathrm{Tr}[E(\mathbf{p})\gamma]-\alpha^{-1}\,\mathrm{Tr}[\gamma]-\mathrm{Tr}[V\gamma]\,,$$

and so

$$\mathcal{E}^{\rm HF}(\gamma) = \alpha^{-1}\,{\rm Tr}[h_0\gamma] + \mathcal{D}(\gamma) - \mathcal{E}x(\gamma)\,,\ \gamma\in\mathcal{A}\,. \tag{21}$$

Consider $\gamma\in\mathcal{A}$ and define, with ρ_γ as in (15),

$$R_\gamma(\mathbf{x}) := \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y}\,. \tag{22}$$

We have that

$$R_\gamma \in L^\infty(\mathbb{R}^3)\cap L^3(\mathbb{R}^3)\,. \tag{23}$$

This follows from (8) (for L^∞), and (20) and the weak Young inequality [12, p. 107] (for L^3). Next, define the operator K_γ with integral kernel

$$K_\gamma(\mathbf{x},\sigma;\mathbf{y},\tau) := \frac{\gamma(\mathbf{x},\sigma;\mathbf{y},\tau)}{|\mathbf{x}-\mathbf{y}|}\,. \tag{24}$$

The operator K_γ is Hilbert-Schmidt; we prove this fact in Lemma 2 below.

Note that, using (14) 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

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

Then, using $(u,K_\gamma u)\geq 0$ and (8),

$$0\leq \mathfrak{b}_\gamma[u,u]\leq \alpha(u,R_\gamma u) = \alpha\sum_{\sigma=1}^q\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{y})|u(\mathbf{x},\sigma)|^2}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}\,d\mathbf{y} \leq \alpha\frac{2}{\pi}\,{\rm Tr}[\gamma]\,\mathfrak{e}[u,u]\,.$$

Therefore (by the statements and proofs of [18, Theorem X.17] and [17, 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

$$(u,h_\gamma v) = \mathfrak{t}[u,v] - \mathfrak{v}[u,v] + \mathfrak{b}_\gamma[u,v] \ \text{ for }\ u,v\in H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)\,. \tag{25}$$

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 will be proved in Lemma 2 below.

The main result of this paper is the following theorem.

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 (11)*, that is, $E^{\rm HF}(N,Z,\alpha)$ in* (13) *(and therefore, in* (3)*) is attained. In fact,*

$$\begin{aligned}\mathcal{E}^{\rm HF}(\gamma^{\rm HF}) = E^{\rm HF}(N,Z,\alpha) &= \inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma\in\mathcal{A},\gamma^2=\gamma,{\rm Tr}[\gamma]=N\big\}\\ &= \inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma\in\mathcal{A},\ {\rm Tr}[\gamma]=N\big\}\\ &= \inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma\in\mathcal{A},\ {\rm Tr}[\gamma]\leq N\big\}\,.\end{aligned} \tag{26}$$

Moreover, one can write

$$\gamma^{\rm HF}(\mathbf{x},\sigma;\mathbf{y},\tau) = \sum_{i=1}^N \varphi_i(\mathbf{x},\sigma)\overline{\varphi_i(\mathbf{y},\tau)}\,, \tag{27}$$

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 $h_{\gamma^{\rm HF}}$ as defined in* (25)*,*

$$h_{\gamma^{\rm HF}}\varphi_i = \varepsilon_i\varphi_i\ ,\ i=1,\ldots,N\,, \tag{28}$$

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

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

$$\varphi_i \in C^\infty(\mathbb{R}^3 \setminus \{0\}; \mathbb{C}^q)\,. \tag{29}$$

(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* $i = 1, \ldots, N$,

$$|\varphi_i(\mathbf{x})| \le C\, e^{-\beta|\mathbf{x}|} \quad \textit{for} \quad |\mathbf{x}| \ge R\,. \tag{30}$$

Remark 1.

(i) *In fact, we prove that* (29) *holds for* any *eigenfunction* φ *of* $h_{\gamma^{\rm HF}}$, *and* (30) *for those corresponding to negative eigenvalues* ε. *More precisely, if* $h_{\gamma^{\rm HF}}\varphi = \varepsilon\varphi$ *for some* $\varepsilon \in [\varepsilon_N, 0)$, *then* (30) *holds for* φ *for all* $\beta < \nu_\varepsilon := \sqrt{-\varepsilon(2\alpha^{-1} + \varepsilon)}$ *for some* $C = C(R, \beta) > 0$.

(ii) *Note that, in general, eigenfunctions of* $h_{\gamma^{\rm HF}}$ *can be unbounded at* $\mathbf{x} = 0$*; therefore* (29) *and* (30) *can only be expected to hold away from the origin.*

(iii) *Both the regularity and the exponential decay above are similar to the results in the non-relativistic case (i.e., for the operator in* (4)*; see* [13]*). However, the proof of Theorem 1 is considerably more complicated due to, on one hand, the non-locality of the kinetic energy operator* $E(\mathbf{p})$*, and, on the other hand, the fact that the Hartree-Fock operator* $h_{\gamma^{\rm HF}}$ *is only given as a* form *sum for* $Z\alpha \in [1/2, 2/\pi)$.

(iv) *We show the existence of the Hartree-Fock minimizer by solving the minimization problem on the set of density matrices. This method was introduced in* [23]*. The same method was used in* [4] *in the Dirac-Fock case.*

(v) *As mentioned earlier, we have to assume that* $Z\alpha < 2/\pi$*; the reason is that our proof that* $\mathrm{Tr}[E(\mathbf{p})\gamma_n]$ *is uniformly bounded for a minimizing sequence* $\{\gamma_n\}_{n\in\mathbb{N}}$ *does not work in the critical case* $Z\alpha = 2/\pi$.

(vi) *For simplicity of notation, we give the proof of Theorem 1 only in the spinless case. It will be obvious that the proof also works in the general case.*

(vii) *As will be clear from the proofs, the statements of Theorem 1 (appropriately modified) also hold for molecules. More explicitely, for a molecule with* K *nuclei of charges* $Z_1, \ldots, Z_K$*, fixed at* $R_1, \ldots, R_K \in \mathbb{R}^3$*, replace* $\mathfrak{v}$ *in* (6) *by*

$$\mathfrak{v}[u, v] := \sum_{k=1}^{K} (V_k^{1/2} u, V_k^{1/2} v) \quad \textit{for} \quad u, v \in H^{1/2}(\mathbb{R}^3; \mathbb{C}^q)\,, \tag{31}$$

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

2. Proof of Theorem 1

2.1. **Existence of the Hartree-Fock minimizer.** The proof of the existence of an N-dimensional projection $\gamma^{\rm HF}$ minimizing $\mathcal{E}^{\rm HF}$, the equalities in (26), and that the corresponding Hartree-Fock orbitals $\{\varphi_i\}_{i=1}^N$ solve the Hartree-Fock equations (28), will be a consequence of the following two lemmas.

Lemma 1. *Let* $Z\alpha < 2/\pi$ *and* $N \in \mathbb{N}$*. Then*

$$E_{\le}^{\rm HF}(N, Z, \alpha) := \inf\big\{\mathcal{E}^{\rm HF}(\gamma) \,\big|\, \gamma \in \mathcal{A}, \mathrm{Tr}[\gamma] \le N\big\}$$

is attained.

Lemma 2. *Let $\gamma \in \mathcal{A}$. Then the operator K_γ, defined by (24), is Hilbert-Schmidt. If $Z\alpha < 2/\pi$ then the operator h_γ, defined in (25), satisfies $\sigma_{\rm ess}(h_\gamma) = [0,\infty)$. If furthermore $\mathrm{Tr}[\gamma] < Z$, then h_γ has infinitely many eigenvalues in $[-\alpha^{-1}, 0)$.*

Before proving these two lemmas, we use them to prove the parts of Theorem 1 mentioned above.

Proof. For computational reasons we first state and prove a lemma in the spirit of [3, Lemma 1].

Lemma 3. *Let $\gamma \in \mathcal{A}$, $u_1, u_2 \in H^{1/2}(\mathbb{R}^3)$, and let $\epsilon_1, \epsilon_2 \in \mathbb{R}$ be such that $\tilde\gamma$ given by*

$$\tilde\gamma(\mathbf{x},\mathbf{y}) := \gamma(\mathbf{x},\mathbf{y}) + \gamma_u(\mathbf{x},\mathbf{y}) \,, \tag{32}$$

$$\gamma_u(\mathbf{x},\mathbf{y}) := \gamma_{u_1,u_2}(\mathbf{x},\mathbf{y}) = \epsilon_1 u_1(\mathbf{x})\overline{u_1(\mathbf{y})} + \epsilon_2 u_2(\mathbf{x})\overline{u_2(\mathbf{y})} \tag{33}$$

is again an element of $\mathcal{A}$.

Then we have that

$$\mathcal{E}^{\rm HF}(\tilde\gamma) = \mathcal{E}^{\rm HF}(\gamma) + \alpha^{-1}\epsilon_1(u_1, h_\gamma u_1) + \alpha^{-1}\epsilon_2(u_2, h_\gamma u_2) + \epsilon_1\epsilon_2 R_u \,, \tag{34}$$

where h_γ is given in (25), and

$$R_u := R_{u_1,u_2} = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|u_1(\mathbf{x})u_2(\mathbf{y}) - u_2(\mathbf{x})u_1(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \,. \tag{35}$$

Proof of Lemma 3: We have that

$$\begin{aligned}
\mathcal{E}^{\rm HF}(\tilde\gamma) &= \mathcal{E}^{\rm HF}(\gamma) + \alpha^{-1}\mathrm{Tr}[h_0\gamma_u] + \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{x})\rho_{\gamma_u}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\
&\quad - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\gamma(\mathbf{x},\mathbf{y})\overline{\gamma_u(\mathbf{x},\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_{\gamma_u}(\mathbf{x})\rho_{\gamma_u}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\
&\quad - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\gamma_u(\mathbf{x},\mathbf{y})\overline{\gamma_u(\mathbf{x},\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\
&= \mathcal{E}^{\rm HF}(\gamma) + \alpha^{-1}\epsilon_1(u_1, h_\gamma u_1) + \alpha^{-1}\epsilon_2(u_2, h_\gamma u_2) \\
&\quad + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_{\gamma_u}(\mathbf{x})\rho_{\gamma_u}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\gamma_u(\mathbf{x},\mathbf{y})\overline{\gamma_u(\mathbf{x},\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \,.
\end{aligned} \tag{36}$$

Using (33), that $\rho_{\gamma_u}(\mathbf{x}) = \epsilon_1|u_1(\mathbf{x})|^2 + \epsilon_2|u_2(\mathbf{x})|^2$, and (35), we obtain (34). □

By Lemma 1 a minimizer $\gamma^{\rm HF} \in \mathcal{A}$, with $\mathrm{Tr}[\gamma^{\rm HF}] \le N$, exists. We may write

$$\gamma^{\rm HF}(\mathbf{x},\mathbf{y}) = \sum_k \lambda_k \varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})} \,, \tag{37}$$

with $1 \ge \lambda_1 \ge \cdots \ge 0$ and $\{\varphi_k\}_k \subset H^{1/2}(\mathbb{R}^3)$ an orthonormal (in $L^2(\mathbb{R}^3)$) system (it might be finite). Extend $\{\varphi_k\}_k$ to an orthonormal basis $\{\varphi_k\}_k \cup \{u_\ell\}_{\ell\in\mathbb{N}}$ for $L^2(\mathbb{R}^3)$, with $u_\ell \in H^{1/2}(\mathbb{R}^3)$.

Let $K+1$ be the first index such that $\lambda_{K+1} < 1$. Fix $j \in \{1,\ldots,K\}$, choose $u \in \{\varphi_k\}_{k\ge K+1} \cup \{u_\ell\}_{\ell\in\mathbb{N}}$, and consider, for ϵ to be chosen,

$$\gamma_\epsilon^{(j)}(\mathbf{x},\mathbf{y}) := \sum_{k\ne j} \lambda_k\varphi_k(\mathbf{x})\varphi_k^*(\mathbf{y}) + \frac{1}{1+m\epsilon^2}\big(\varphi_j(\mathbf{x}) + \epsilon u(\mathbf{x})\big)\big(\overline{\varphi_j(\mathbf{y})} + \epsilon\overline{u(\mathbf{y})}\,\big) \,.$$

Choosing $m \ge 1$ assures that $\mathrm{Tr}[\gamma_\epsilon^{(j)}] \le N$. Then $0 \le \gamma_\epsilon^{(j)} \le \mathrm{Id}$ for $|\epsilon|$ small enough (depending on u). Since $\gamma^{\rm HF}$ minimizes $\mathcal{E}^{\rm HF}$, and $\gamma_0^{(j)} = \gamma^{\rm HF}$,

$$0 = \frac{d}{d\epsilon}(\mathcal{E}^{\rm HF})\big(\gamma_\epsilon^{(j)}\big)\Big|_{\epsilon=0} = \alpha^{-1}(\varphi_j, h_{\gamma^{\rm HF}}u) + \alpha^{-1}(u, h_{\gamma^{\rm HF}}\varphi_j) \,.$$

Repeating the computation for iu we get that $(u, h_{\gamma^{\rm HF}}\varphi_j) = 0$, from which it follows that $h_{\gamma^{\rm HF}}$ maps $\mathrm{span}\{\varphi_1, \dots, \varphi_K\}$ into itself. Diagonalising the restriction of $h_{\gamma^{\rm HF}}$ to $\mathrm{span}\{\varphi_1, \dots, \varphi_K\}$, we can choose $\varphi_1, \dots, \varphi_K$ to be eigenfunctions of $h_{\gamma^{\rm HF}}$ with eigenvalues $\varepsilon_{n_1}, \dots, \varepsilon_{n_K}$, $n_j \in \mathbb{N}$ (numbering the eigenvalues of $h_{\gamma^{\rm HF}}$ in increasing order, $-\alpha^{-1} < \varepsilon_1 \le \varepsilon_2 \le \cdots$). Since $\lambda_1 = \cdots = \lambda_K = 1$, this does not change (37).

To show that, for $j > K$, φ_j is also an eigenfunction of $h_{\gamma^{\rm HF}}$ (corresponding to an eigenvalue ε_{n_j}) one repeats the argument above, with $u \in \{\varphi_k\}_{k\neq 1,\dots,K,j} \cup \{u_\ell\}_{\ell\in\mathbb{N}}$, and

$$\gamma_\epsilon^{(j)}(\mathbf{x},\mathbf{y}) = \sum_{k\neq j} \lambda_k \varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})} + \frac{\lambda_j}{1+m\epsilon^2}\big(\varphi_j(\mathbf{x}) + \epsilon u(\mathbf{x})\big)\big(\overline{\varphi_j(\mathbf{y})} + \epsilon\overline{u(\mathbf{y})}\big)\,.$$

Moreover, the eigenvalues ε_{n_k} (of $h_{\gamma^{\rm HF}}$) corresponding to the eigenfunctions φ_k are non-positive. In fact, if $\varepsilon_{n_k} > 0$, then we could lower the energy: Define $\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) - \lambda_k\varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})}$, then, using Lemma 3, we get that $\mathcal{E}^{\rm HF}(\tilde\gamma) = \mathcal{E}^{\rm HF}(\gamma^{\rm HF}) - \alpha^{-1}\lambda_k\varepsilon_{n_k} < \mathcal{E}^{\rm HF}(\gamma^{\rm HF})$.

It remains to show that $\mathrm{Tr}[\gamma^{\rm HF}] = N$, that $\gamma^{\rm HF}$ is a projection, and that the $\{\varphi_j\}_{j=1}^N$ are eigenfunctions corresponding to the *lowest* (negative) eigenvalues of $h_{\gamma^{\rm HF}}$ (that is, to $\varepsilon_1 \le \varepsilon_2 \le \cdots \le \varepsilon_N < 0$).

Consider first the case $N < Z$. Assume, for contradiction, that $\mathrm{Tr}[\gamma^{\rm HF}] < N$. Let $K \in \mathbb{N}$ be the multiplicity of the eigenvalue 1 in (37). Since (by Lemma 2), for $N < Z$, $h_{\gamma^{\rm HF}}$ has infinitely many eigenvalues in $[-\alpha^{-1}, 0)$ we can find a (normalized) eigenfunction u, corresponding to a negative eigenvalue of $h_{\gamma^{\rm HF}}$, and orthogonal to $\varphi_1, \dots, \varphi_K$. Let $\epsilon > 0$ be sufficiently small that $\gamma(\mathbf{x},\mathbf{y}) := \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) + \epsilon u(\mathbf{x})\overline{u(\mathbf{y})}$ defines a density matrix satisfying $\mathrm{Tr}[\gamma] \le N$. By Lemma 3 (with $u_1 = u, \epsilon_1 = \epsilon$ and $\epsilon_2 = 0$) we get that

$$\mathcal{E}^{\rm HF}(\gamma) = \mathcal{E}^{\rm HF}(\gamma^{\rm HF}) + \epsilon\alpha^{-1}(u, h_{\gamma^{\rm HF}}u) < \mathcal{E}^{\rm HF}(\gamma^{\rm HF})\,, \tag{38}$$

leading to a contradiction. Hence, $\mathrm{Tr}[\gamma^{\rm HF}] = N$. That $\gamma^{\rm HF}$ is a projection follows from Lieb's Variational Principle (see [11]) which we prove for completeness. If this is not the case, there exist indices p, q such that $0 < \lambda_p, \lambda_q < 1$. Consider $\tilde\gamma(\mathbf{x},\mathbf{y}) := \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) + \epsilon\varphi_q(\mathbf{x})\overline{\varphi_q(\mathbf{y})} - \epsilon\varphi_p(\mathbf{x})\overline{\varphi_p(\mathbf{y})}$ with ϵ such that $0 \le \tilde\gamma \le \mathrm{Id}$. Choose $\epsilon > 0$ if $\varepsilon_{n_q} \le \varepsilon_{n_p}$ and $\epsilon < 0$ otherwise. By Lemma 3, we get that $\mathcal{E}^{\rm HF}(\tilde\gamma) < \mathcal{E}^{\rm HF}(\gamma^{\rm HF})$.

Consider now the case $Z \le N < Z+1$ (and $N \ge 2$), so that $N - 1 < Z$. Let $\gamma_{N-1}^{\rm HF}$ denote the density matrix where

$$\inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma \in \mathcal{A},\ \mathrm{Tr}[\gamma] \le N-1\big\}$$

is attained. By the above, $\mathrm{Tr}[\gamma_{N-1}^{\rm HF}] = N-1$ and $\gamma_{N-1}^{\rm HF}$ is a projection, so its integral kernel is given by

$$\gamma_{N-1}^{\rm HF}(\mathbf{x},\mathbf{y}) = \sum_{i=1}^{N-1} \phi_i(\mathbf{x})\overline{\phi_i(\mathbf{y})}\,,$$

where the ϕ_i's are eigenfunctions of $h_{\gamma_{N-1}^{\rm HF}}$.

We first prove that

$$\inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma \in \mathcal{A},\ \mathrm{Tr}[\gamma] \le N\big\} \tag{39}$$

is not attained at the density matrix $\gamma_{N-1}^{\rm HF}$ by constructing a density matrix $\tilde\gamma$ with $\mathrm{Tr}[\tilde\gamma] \le N$ such that $\mathcal{E}^{\rm HF}(\tilde\gamma) < \mathcal{E}^{\rm HF}(\gamma_{N-1}^{\rm HF})$. Indeed, since $h_{\gamma_{N-1}^{\rm HF}}$ has infinitely many strictly negative eigenvalues (by Lemma 2; $N-1 < Z$) there exists a (normalized) eigenfunction u of $h_{\gamma_{N-1}^{\rm HF}}$ corresponding to a negative eigenvalue, and orthogonal to span$\{\phi_1,\ldots,\phi_{N-1}\}$. Let $\tilde\gamma$ be defined by

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma^{\rm HF}_{N-1}(\mathbf{x},\mathbf{y}) + u(\mathbf{x})\overline{u(\mathbf{y})}\,.$$

Then $\mathrm{Tr}[\tilde\gamma]=N$ and, by a computation like in (38),

$$\mathcal{E}^{\rm HF}(\tilde\gamma) = \mathcal{E}^{\rm HF}(\gamma^{\rm HF}_{N-1}) + \alpha^{-1}(u, h_{\gamma^{\rm HF}_{N-1}}u) < \mathcal{E}^{\rm HF}(\gamma^{\rm HF}_{N-1})\,.$$

Hence,

$$\inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma\in\mathcal{A}, \mathrm{Tr}[\gamma]\le N\big\} < \inf\big\{\mathcal{E}^{\rm HF}(\gamma)\,\big|\,\gamma\in\mathcal{A}, \mathrm{Tr}[\gamma]\le N-1\big\}\,. \tag{40}$$

Let γ_N be a density matrix where (39) is attained (the existence of such a minimizer follows, as before, from Lemma 1). By the above it follows that $N-1 < \mathrm{Tr}[\gamma_N]\le N$. We now show that there exists a minimizer $\gamma^{\rm HF}$ with $\mathrm{Tr}[\gamma^{\rm HF}]=N$.

The integral kernel of γ_N is given by

$$\gamma_N(\mathbf{x},\mathbf{y}) = \sum_j \lambda_j\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})}\,,$$

where $1\ge\lambda_1\ge\cdots\ge 0$ and the φ_j's are (orthonormal) eigenfunctions of h_{γ_N}. If $\mathrm{Tr}[\gamma_N]<N$ we can define a new density matrix $\tilde\gamma$ with $\mathrm{Tr}[\tilde\gamma]\le N$ and $\mathcal{E}^{\rm HF}(\tilde\gamma)\le\mathcal{E}^{\rm HF}(\gamma_N)$. Indeed, if $\mathrm{Tr}[\gamma_N]<N$ (and bigger than $N-1$) then there exists a (first) j_0 such that $0<\lambda_{j_0}<1$. We define $\tilde\gamma$ with integral kernel

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma_N(\mathbf{x},\mathbf{y}) + r\varphi_{j_0}(\mathbf{x})\overline{\varphi_{j_0}(\mathbf{y})}\,, \tag{41}$$

with $r=\min\{1-\lambda_{j_0}, N-\mathrm{Tr}[\gamma_N]\}>0$. Recall that $h_{\gamma_N}\varphi_j=\varepsilon_{n_j}\varphi_j$, $\varepsilon_{n_j}\le 0$, for all j. By Lemma 3 we have that

$$\mathcal{E}^{\rm HF}(\tilde\gamma) = \mathcal{E}^{\rm HF}(\gamma_N) + \alpha^{-1}r\varepsilon_{n_{j_0}}\,.$$

If $\varepsilon_{n_{j_0}}<0$, it follows that $\mathcal{E}^{\rm HF}(\tilde\gamma)<\mathcal{E}^{\rm HF}(\gamma_N)$. On the other hand, if $\varepsilon_{n_{j_0}}=0$, then $\mathcal{E}^{\rm HF}(\tilde\gamma)=\mathcal{E}^{\rm HF}(\gamma_N)$, and $\mathrm{Tr}[\gamma_N]<\mathrm{Tr}[\tilde\gamma]\le N$. Either $\mathrm{Tr}[\tilde\gamma]=N$, in which case we let $\gamma^{\rm HF}:=\tilde\gamma$, and, as above, we are done. Or, we repeat all of the above argument on

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \sum_{j=1}^{j_0}\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})} + \sum_{j>j_0}\lambda_j\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})}\,.$$

Since the trace stays bounded by N, this procedure has to stop eventually. Hence, with $\gamma^{\rm HF}$ the resulting density matrix, $\mathrm{Tr}[\gamma^{\rm HF}]=N$ and by Lieb's Variational Principle it follows (as above) that $\gamma^{\rm HF}$ is a projection.

Finally, let $\{\varphi_j\}$ be the eigenfunctions of $h_{\gamma^{\rm HF}}$, now numbered corresponding to the eigenvalues $\varepsilon_1\le\varepsilon_2\le\cdots$, where ε_1 is the lowest eigenvalue of $h_{\gamma^{\rm HF}}$. We know that, for some $j_1,\ldots,j_N\in\mathbb{N}$,

$$\gamma^{\rm HF}(\mathbf{x},\mathbf{y}) = \sum_{k=1}^N \varphi_{j_k}(\mathbf{x})\overline{\varphi_{j_k}(\mathbf{y})}\,.$$

Suppose for contradiction that $\{\varepsilon_{j_1},\ldots,\varepsilon_{j_N}\}\ne\{\varepsilon_1,\ldots,\varepsilon_N\}$. Then there exists a $k\in\{1,\ldots,N\}$ with $\varepsilon_{j_k}>\varepsilon_k$. For $\delta\in(0,1)$ define

$$\tilde\gamma(\mathbf{x},\mathbf{y}) = \gamma^{\rm HF}(\mathbf{x},\mathbf{y}) + \delta\varphi_k(\mathbf{x})\overline{\varphi_k(\mathbf{y})} - \delta\varphi_{j_k}(\mathbf{x})\overline{\varphi_{j_k}(\mathbf{y})}\,.$$

By Lemma 3,

$$\mathcal{E}^{\rm HF}(\tilde\gamma) = \mathcal{E}^{\rm HF}(\gamma^{\rm HF}) + \delta\alpha^{-1}(\varepsilon_k-\varepsilon_{j_k}) - \delta^2 R_{\varphi_j,\varphi_{j_k}} < \mathcal{E}^{\rm HF}(\gamma^{\rm HF})\,,$$

where the last inequality follows by choosing δ small enough.

It remains to prove that $\varepsilon_1, \ldots, \varepsilon_N$ are strictly negative. For $N < Z$ this follows directly from Lemma 2. In the case $Z \le N < Z+1$, assume, for contradiction, that $\varepsilon_N = 0$; then the density matrix

$$\tilde{\gamma}(\mathbf{x}, \mathbf{y}) := \gamma^{\mathrm{HF}}(\mathbf{x}, \mathbf{y}) - \varphi_N(\mathbf{x})\overline{\varphi_N(\mathbf{y})}$$

satisfies $\mathcal{E}^{\mathrm{HF}}(\tilde{\gamma}) = \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})$ (by Lemma 3) and $\mathrm{Tr}[\tilde{\gamma}] = N - 1$. This is a contradiction to (40).

This finishes the proof of the first part of Theorem 1. □

It remains to prove Lemma 1 and Lemma 2.

Proof of Lemma 1: We minimize on density matrices following the method in [23]. In the pseudorelativistic context one faces the problem that the Coulomb potential is not relatively compact with respect to the kinetic energy. This problem has been adressed in [4] and we follow the idea therein.

The quantity $E^{\mathrm{HF}}_{\le}(N, Z, \alpha)$ is finite since for any density matrix γ, with $\mathrm{Tr}[\gamma] \le N$,

$$\mathcal{E}^{\mathrm{HF}}(\gamma) \ge \alpha^{-1}\big\{\,\mathrm{Tr}[E(\mathbf{p})\gamma] - \alpha^{-1}N - \mathrm{Tr}[V\gamma]\big\} \ge \, -\alpha^{-2}N\,.$$

Here we used that $\mathcal{D}(\gamma) - \mathcal{E}x(\gamma) \ge 0$, and (8) (see also (17) and (18)).

Let $\{\gamma_n\}_{n=1}^{\infty}$ be a minimizing sequence for $E^{\mathrm{HF}}_{\le}(N, Z, \alpha)$, more precisely, $\gamma_n \in \mathcal{A}$ (with $\mathcal{A}$ as defined in (16)), $\mathrm{Tr}[\gamma_n] \le N$, and $\mathcal{E}^{\mathrm{HF}}(\gamma_n) \le E^{\mathrm{HF}}_{\le}(N, Z, \alpha) + 1/n$.

The sequence $\mathrm{Tr}[E(\mathbf{p})\gamma_n]$ is uniformly bounded. Indeed, for every $n \in \mathbb{N}$, using (8),

$$\begin{aligned} E^{\mathrm{HF}}(N, Z, \alpha) + 1 \ge \mathcal{E}^{\mathrm{HF}}(\gamma_n) &\ge \alpha^{-1}\big\{\,\mathrm{Tr}[E(\mathbf{p})\gamma_n] - \alpha^{-1}N - \mathrm{Tr}[V\gamma_n]\big\} \\ &\ge \alpha^{-1}(1 - Z\alpha\frac{\pi}{2})\,\mathrm{Tr}[E(\mathbf{p})\gamma_n] - \alpha^{-2}N\,. \end{aligned}$$

The claim follows since $Z\alpha < 2/\pi$. It is this argument that prevents us from proving Theorem 1 for the critical case $Z\alpha = 2/\pi$.

Define $\tilde{\gamma}_n := E(\mathbf{p})^{1/2}\gamma_n E(\mathbf{p})^{1/2}$. Then, by the above, $\{\tilde{\gamma}_n\}_{n\in\mathbb{N}}$ is a sequence of Hilbert-Schmidt operators with uniformly bounded Hilbert-Schmidt norm. Hence, by Banach-Alaoglu's theorem, there exist a subsequence, which we denote again by $\tilde{\gamma}_n$, and a Hilbert-Schmidt operator $\tilde{\gamma}_{(\infty)}$, such that for every Hilbert-Schmidt operator W,

$$\mathrm{Tr}[W\tilde{\gamma}_n] \to \mathrm{Tr}[W\tilde{\gamma}_{(\infty)}]\ ,\ n \to \infty\,.$$

Let $\gamma_{(\infty)} := E(\mathbf{p})^{-1/2}\tilde{\gamma}_{(\infty)}E(\mathbf{p})^{-1/2}$. We are going to show that $\gamma_{(\infty)}$ is a minimizer of $\mathcal{E}^{\mathrm{HF}}$ (in fact, of $\alpha\mathcal{E}^{\mathrm{HF}}$, which is equivalent). We first prove that $\gamma_{(\infty)} \in \mathcal{A}$, then that $\mathcal{E}^{\mathrm{HF}}$ is weak lower semicontinuous on $\mathcal{A}$.

Let $\{\psi_k\}_{k\in\mathbb{N}}$ be a basis of $L^2(\mathbb{R}^3)$ with $\psi_k \in H^{1/2}(\mathbb{R}^3)$. Then, for all $k \in \mathbb{N}$,

$$\begin{aligned} \lim_{n\to\infty}(\psi_k, \gamma_n\psi_k) &= \lim_{n\to\infty}(\psi_k, E(\mathbf{p})^{-1/2}\tilde{\gamma}_n E(\mathbf{p})^{-1/2}\psi_k) \\ &= (\psi_k, \gamma_{(\infty)}\psi_k)\,. \end{aligned}$$

From this follows, by Fatou's lemma, that

$$\mathrm{Tr}[\gamma_{(\infty)}] = \sum_k(\psi_k, \gamma_{(\infty)}\psi_k) \le \liminf_{n\to\infty}\sum_k(\psi_k, \gamma_n\psi_k) = \liminf_{n\to\infty}\mathrm{Tr}[\gamma_n] \le N\,,$$

and

$$\mathrm{Tr}[E(\mathbf{p})^{1/2}\gamma_{(\infty)}E(\mathbf{p})^{1/2}] \le \liminf_{n\to\infty}\mathrm{Tr}[E(\mathbf{p})^{1/2}\gamma_n E(\mathbf{p})^{1/2}] < \infty\,.$$

Since also $0 \le \gamma_{(\infty)} \le \mathrm{Id}$ we see that $\gamma_{(\infty)} \in \mathcal{A}$.

To reach the claim it remains to show the weak lower semicontinuity of the functional $\mathcal{E}^{\mathrm{HF}}$. As mentioned in the introduction, the spectrum of the one-particle operator h_0, defined in (9), is discrete in $[-\alpha^{-1}, 0)$ and purely absolutely continuous in $[0,\infty)$. Let $\Lambda_-(\alpha)$ denote the projection on the pure point spectrum of h_0 and $\Lambda_+(\alpha) := \mathrm{Id} - \Lambda_-(\alpha)$. We write

$$\alpha\mathcal{E}^{\mathrm{HF}}(\gamma_n) = T_1(\gamma_n) + T_2(\gamma_n) + \alpha T_3(\gamma_n)\,, \tag{42}$$

with

$$T_1(\gamma_n) = \mathrm{Tr}[\Lambda_+(\alpha)h_0\Lambda_+(\alpha)\gamma_n]\,, \quad T_2(\gamma_n) = \mathrm{Tr}[\Lambda_-(\alpha)h_0\Lambda_-(\alpha)\gamma_n]\,,$$
$$T_3(\gamma_n) = \mathcal{D}(\gamma_n) - \mathcal{E}x(\gamma_n)\,.$$

We consider these three terms separately.

For the first term in (42), fix (as above) a basis $\{\psi_k\}_{k\in\mathbb{N}}$ of $L^2(\mathbb{R}^3)$, with $\{\psi_k\}_{k\in\mathbb{N}} \subset H^{1/2}(\mathbb{R}^3)$. Defining

$$f_k := \big(\Lambda_+(\alpha)h_0\Lambda_+(\alpha)\big)^{1/2}\psi_k\,,$$

we have that

$$\begin{aligned}T_1(\gamma_n) &= \mathrm{Tr}\left[\big(\Lambda_+(\alpha)h_0\Lambda_+(\alpha)\big)^{1/2}\gamma_n\big(\Lambda_+(\alpha)h_0\Lambda_+(\alpha)\big)^{1/2}\right]\\ &= \sum_k (f_k, \gamma_n f_k) = \sum_k (E(\mathbf{p})^{-1/2}f_k, \tilde{\gamma}_n E(\mathbf{p})^{-1/2}f_k)\,.\end{aligned}$$

Since the projection

$$H_k := \left|E(\mathbf{p})^{-1/2}f_k\right\rangle\left\langle E(\mathbf{p})^{-1/2}f_k\right|$$

is a non-negative Hilbert-Schmidt operator, we find, by Fatou's lemma, that

$$\liminf_{n\to\infty} T_1(\gamma_n) = \liminf_{n\to\infty}\sum_k \mathrm{Tr}[H_k\tilde{\gamma}_n] \geq \sum_k \mathrm{Tr}[H_k\tilde{\gamma}_{(\infty)}] = T_1(\gamma_{(\infty)})\,.$$

As for the second term in (42), we have $\lim_{n\to\infty} T_2(\gamma_n) = T_2(\gamma_{(\infty)})$ since the operator $\Lambda_-(\alpha)h_0\Lambda_-(\alpha)$ is Hilbert-Schmidt; see Lemma 7 in Appendix A.

Finally, for the last term in (42), following the reasoning in [4, pp.142–143] (here we need that $N \in \mathbb{N}$), we get that

$$\liminf_{n\to\infty} T_3(\gamma_n) \geq T_3(\gamma_{(\infty)})\,.$$

This finishes the proof of Lemma 1. □

Proof of Lemma 2: In order to prove that K_γ is Hilbert-Schmidt it is enough to prove that its integral kernel belongs to $L^2(\mathbb{R}^6)$. We have that (see (24) and (14))

$$\begin{aligned}\int_{\mathbb{R}^6} |K_\gamma(\mathbf{x},\mathbf{y})|^2\,d\mathbf{x}d\mathbf{y} &= \int_{\mathbb{R}^6} \frac{|\gamma(\mathbf{x},\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|^2}\,d\mathbf{x}d\mathbf{y} \\ &= \sum_{j,k}\lambda_j\lambda_k\int_{\mathbb{R}^6}\frac{\overline{u_k(\mathbf{x})}u_j(\mathbf{x})u_k(\mathbf{y})\overline{u_j(\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|^2}\,d\mathbf{x}d\mathbf{y} =: \sum_{j,k}\lambda_j\lambda_k I_{j,k}\,.\end{aligned} \tag{43}$$

The last integral can be estimated using the Hardy-Littlewood-Sobolev, Hölder, and Sobolev inequalities (in that order), to get

$$I_{j,k} \leq \|u_k u_j\|_{3/2}^2 \leq \|u_k\|_3^2\|u_j\|_3^2 \leq C\|u_k\|_{H^{1/2}}^2\|u_j\|_{H^{1/2}}^2\,. \tag{44}$$

Inserting (44) in (43) we obtain (since $\gamma \in \mathcal{A}$)

$$\begin{aligned}\int_{\mathbb{R}^6} |K_\gamma(\mathbf{x},\mathbf{y})|^2\,d\mathbf{x}d\mathbf{y} &\leq C\sum_{j,k}\lambda_j\lambda_k\|u_k\|_{H^{1/2}}^2\|u_j\|_{H^{1/2}}^2 = C\Big(\sum_j \lambda_j\|u_j\|_{H^{1/2}}^2\Big)^2\\ &= C\big(\mathrm{Tr}[E(\mathbf{p})\gamma]\big)^2 < \infty\,.\end{aligned}$$

To prove the statement on the essential spectrum, define $\tilde{h}_\gamma := h_\gamma + \alpha K_\gamma$. Since K_γ is Hilbert-Schmidt, and $\sigma_{\mathrm{ess}}(h_0) = [0,\infty)$ (see the introduction), it is enough to prove that $(\tilde{h}_\gamma+\eta)^{-1}-(h_0+\eta)^{-1}$ is compact for some $\eta>0$ large enough [20, Theorem XIII.14]. Since $\mathcal{D}(h_0)=\mathcal{D}(\tilde{h}_\gamma)\subset\mathcal{D}(R_\gamma)$, we have that

$$(\tilde{h}_\gamma+\eta)^{-1}-(h_0+\eta)^{-1} = -(\tilde{h}_\gamma+\eta)^{-1}\alpha R_\gamma(h_0+\eta)^{-1}\,. \tag{45}$$

From Tiktopoulos's formula (see [22, (II.8), Section II.3]), it follows that

$$\begin{aligned}&(h_0+\eta)^{-1}\\ &\quad=(T(\mathbf{p})+\eta)^{-1/2}[1-(T(\mathbf{p})+\eta)^{-1/2}V(T(\mathbf{p})+\eta)^{-1/2}]^{-1}(T(\mathbf{p})+\eta)^{-1/2}\,.\end{aligned} \tag{46}$$

Since, by (5), $\|(T(\mathbf{p})+\eta)^{-1/2}V^{1/2}\|<1$ for $Z\alpha<2/\pi$ and $\eta>\alpha^{-1}$, the right side of (46) is well defined. Inserting (46) in (45) one sees that it suffices to prove that $R_\gamma(T(\mathbf{p})+\eta)^{-1/2}$ is compact. That this is indeed the case follows by using [19, Theorem XI.20] together with the observation that, for $\varepsilon>0$ and $\eta>\alpha^{-1}$, R_γ and $(T(\mathbf{p})+\eta)^{-1/2}$ (as a function of $\mathbf{p}$) belong to the space $L^{6+\varepsilon}(\mathbb{R}^3)$ (for R_γ, see (23)).

Finally, we show that if $\mathrm{Tr}[\gamma]=N<Z$ then h_γ has infinitely many eigenvalues in $[-\alpha^{-1},0)$. By the min-max principle [20, Theorem XIII.1] and since $\sigma_{\mathrm{ess}}(h_\gamma)=[0,\infty)$, it is sufficient to show that for every $n\in\mathbb{N}$ we can find n orthogonal functions $u_1,\dots,u_n$ in $L^2(\mathbb{R}^3)$ such that $(u_i,h_\gamma u_i)<0$ for $i=1,\dots,n$.

Let $n\in\mathbb{N}$. Fix $\delta:=1-N/Z$ and let $h_{0,\delta}$ be the unique self-adjoint operator whose quadratic form domain is $H^{1/2}(\mathbb{R}^3)$ such that

$$(u,h_{0,\delta}v)=\mathfrak{t}[u,v]-\delta\,\mathfrak{v}[u,v] \text{ for } u,v\in H^{1/2}(\mathbb{R}^3)\,.$$

By [7, Theorems 2.2 and 2.3], $\sigma_{\mathrm{ess}}(h_{0,\delta})=[0,\infty)$. Moreover, $h_{0,\delta}$ has infinitely many eigenvalues in $[-\alpha^{-1},0)$. This follows by the min-max principle and the inequality $h_{0,\delta}\le\alpha/2(-\Delta)-\delta Z\alpha/|\mathbf{x}|$. Hence, we can find $u_1,\dots,u_n$ spherically symmetric and orthonormal such that $(u_i,h_{0,\delta}u_i)<0$ for $i=1,\dots,n$. Then, by the positivity of K_γ, by Newton's Theorem [12, p. 249], and since $\mathrm{Tr}[\gamma]=N$ we get, for $i=1,\dots,n$, that

$$\begin{aligned}(u_i,h_\gamma u_i)&\le\mathfrak{t}[u_i,u_i]-\mathfrak{v}[u_i,u_i]+\alpha(u_i,R_\gamma u_i)\\ &\le\mathfrak{t}[u_i,u_i]-\mathfrak{v}[u_i,u_i]+\frac{N}{Z}\,\mathfrak{v}[u_i,u_i]=(u_i,h_{0,\delta}u_i)<0\,.\end{aligned}$$

The claim follows. □

2.2. **Regularity of the Hartree-Fock orbitals.** Here we prove that any eigenfunction of $h_{\gamma^{\mathrm{HF}}}$ is in $C^\infty(\mathbb{R}^3\setminus\{0\})$.

Proof. Let φ be a solution of $h_{\gamma^{\mathrm{HF}}}\varphi=\varepsilon\varphi$ for some $\varepsilon\in\mathbb{R}$. Then φ belongs to the domain of the operator and in particular to $H^{1/2}(\mathbb{R}^3;\mathbb{C}^q)$. We are going to prove that $\varphi\in H^k(\Omega)$ for all bounded smooth $\Omega\subset\mathbb{R}^3\setminus\{0\}$ and all $k\in\mathbb{N}$. The claim will then follow from the Sobolev imbedding theorem [2, Theorem 4.12]. We will use results on pseudodifferential operators; see Appendix B. We briefly summarize these here.

1) For all $k,\ell\in\mathbb{R}$, $E(\mathbf{p})^\ell$ maps $H^k(\mathbb{R}^3)$ to $H^{k-\ell}(\mathbb{R}^3)$.
2) For all $k,\ell\in\mathbb{R}$, and any $\chi\in C_0^\infty(\mathbb{R}^3)$, the commutator $[\chi,E(\mathbf{p})^\ell]$ maps $H^k(\mathbb{R}^3)$ to $H^{k-\ell+1}(\mathbb{R}^3)$.
3) For all $k,\ell,m\in\mathbb{R}$ and $\chi_1,\chi_2\in C_0^\infty(\mathbb{R})$ with $\operatorname{supp}\chi_1\cap\operatorname{supp}\chi_2=\emptyset$, $\chi_1E(\mathbf{p})^\ell\chi_2$ maps $H^k(\mathbb{R}^3)$ to $H^m(\mathbb{R}^3)$. Such an operator is called 'smoothing'.

Fix Ω a bounded smooth subset of $\mathbb{R}^3\setminus\{0\}$. We proceed by induction on $k\in\mathbb{N}$. Assume that $\varphi\in H^k(\Omega)$ for some $k\ge0$, i.e., $\chi\varphi\in H^k(\mathbb{R}^3)$ for all $\chi\in C_0^\infty(\Omega)$. Notice that $H^k(\mathbb{R}^3)=D(E(\mathbf{p})^k)$.

Since $\chi\varphi \in H^{k+1}(\mathbb{R}^3)$ is equivalent to $\chi\varphi \in D(E(\mathbf{p})^{k+1})$, and $D(E(\mathbf{p})^{k+1}) = D((E(\mathbf{p})^{k+1})^*)$, it is sufficient to prove that $\chi\varphi \in D((E(\mathbf{p})^{k+1})^*)$, or equivalently, that there exists $v \in L^2(\mathbb{R}^3)$ such that

$$(\chi\varphi, E(\mathbf{p})^{k+1} f) = (v, f) \quad \text{for all } f \in H^{k+1}(\mathbb{R}^3)\,.$$

Let $f \in H^{k+1}(\mathbb{R}^3)$. Then

$$\begin{aligned}(\chi\varphi, E(\mathbf{p})^{k+1} f) &= \mathfrak{e}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\\ &= (\varepsilon + \alpha^{-1})(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) + \mathfrak{v}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\\ &\quad - \mathfrak{b}_{\gamma^{\mathrm{HF}}}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\,,\end{aligned} \tag{47}$$

where we use that $h_{\gamma^{\mathrm{HF}}}\varphi = \varepsilon\varphi$. We study the terms in (47) separately. In the following, $\tilde{\chi}$ denotes a function in $C_0^\infty(\Omega)$ with $\tilde{\chi} \equiv 1$ on $\operatorname{supp}\chi$.

For the first term in (47) we find that

$$\begin{aligned}&(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) = (\chi E(\mathbf{p})^{-1}\varphi, E(\mathbf{p})^{k+1} f)\\ &\quad= ([\chi, E(\mathbf{p})^{-1}]\varphi, E(\mathbf{p})^{k+1} f) + (E(\mathbf{p})^{-1}\chi\varphi, E(\mathbf{p})^{k+1} f)\,.\end{aligned} \tag{48}$$

Since $\chi\varphi \in H^k(\mathbb{R}^3)$ by the induction hypothesis, we have that $E(\mathbf{p})^{-1}\chi\varphi \in H^{k+1}(\mathbb{R}^3)$ and hence there exists $w_1 \in L^2(\mathbb{R}^3)$ such that

$$(E(\mathbf{p})^{-1}\chi\varphi, E(\mathbf{p})^{k+1} f) = (w_1, f)\,.$$

It remains to study the first term in (48). We have that

$$\begin{aligned}&([\chi, E(\mathbf{p})^{-1}]\varphi, E(\mathbf{p})^{k+1} f)\\ &\quad= ([\chi, E(\mathbf{p})^{-1}]\tilde{\chi}\varphi, E(\mathbf{p})^{k+1} f) + ([\chi, E(\mathbf{p})^{-1}](1-\tilde{\chi})\varphi, E(\mathbf{p})^{k+1} f)\,.\end{aligned}$$

Since $\tilde{\chi}\varphi \in H^k(\mathbb{R}^3)$ by the induction hypothesis, it follows from Proposition 2 that $[\chi, E(\mathbf{p})^{-1}]\tilde{\chi}\varphi$ belongs to $H^{k+2}(\mathbb{R}^3)$. On the other hand since the supports of χ and $\tilde{\chi}$ are disjoint the operator $[\chi, E(\mathbf{p})^{-1}](1-\tilde{\chi})$ is a smoothing operator. Hence there exists a $w_2 \in L^2(\mathbb{R}^3)$ such that

$$([\chi, E(\mathbf{p})^{-1}]\varphi, E(\mathbf{p})^{k+1} f) = (w_2, f)\,.$$

As for the second term in (47), we find, with $\tilde{\chi}$ as before,

$$\begin{aligned}\mathfrak{v}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) &= (\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\\ &= (\tilde{\chi}\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\\ &\quad + ((1-\tilde{\chi})\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\,.\end{aligned} \tag{49}$$

Since $\tilde{\chi}$ has support away from zero, $V\tilde{\chi}\varphi \in H^k(\mathbb{R}^3)$ and hence there exists $w_3 \in L^2(\mathbb{R}^3)$ such that

$$(\tilde{\chi}\varphi, VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) = (w_3, f)\,.$$

For the second term in (49) we proceed via an approximation. Let $\{\varphi_n\}_{n=1}^\infty \subset C_0^\infty(\mathbb{R}^3)$ such that $\varphi_n \to \varphi, n \to \infty$, in $L^2(\mathbb{R}^3)$. Since $(1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f$ belongs to $L^2(\mathbb{R}^3)$, we have that

$$(\varphi, (1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f) = \lim_{n\to+\infty}(\varphi_n, (1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\,.$$

For each $n \in \mathbb{N}$, $V(1-\tilde{\chi})\varphi_n \in H^m(\mathbb{R}^3)$ for all m, since $\varphi_n \in C_0^\infty(\mathbb{R}^3)$, and V maps $H^k(\mathbb{R}^3)$ into $H^{k-1}(\mathbb{R}^3)$ for all k. Therefore, $E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}V(1-\tilde{\chi})\varphi_n \in L^2(\mathbb{R}^3)$, and so

$$\begin{aligned}&(\varphi_n, (1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1} f)\\ &\quad= (E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}V(1-\tilde{\chi})\varphi_n, f)\\ &\quad= (E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})E(\mathbf{p})E(\mathbf{p})^{-1}V\varphi_n, f)\,.\end{aligned}$$

Here $E(\mathbf{p})^{-1}V$ is bounded by (8), and $\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})$ is a smoothing operator by the choice of the supports of χ and $\tilde{\chi}$. It then follows that $\{E(\mathbf{p})^{k+1}\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})E(\mathbf{p})E(\mathbf{p})^{-1}V\varphi_n\}_{n\in\mathbb{N}}$ is a uniformly bounded sequence in $L^2(\mathbb{R}^3)$ and hence there exists $w_4 \in L^2(\mathbb{R}^3)$ such that

$$\lim_{n\to+\infty}(\varphi_n, ((1-\tilde{\chi})VE(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) = (w_4, f)\,.$$

For the third term in (47), we have to separate the cases $k=0$ and $k\geq 1$.

Let $k=0$. The terms $R_{\gamma^{\mathrm{HF}}}\varphi$ and $K_{\gamma^{\mathrm{HF}}}\varphi$ belong to $L^2(\mathbb{R}^3)$, since $R_{\gamma^{\mathrm{HF}}}\in L^\infty(\mathbb{R}^3)$ (see (23)) and $K_{\gamma^{\mathrm{HF}}}$ is Hilbert-Schmidt (see Lemma 2), and therefore

$$\mathfrak{b}_{\gamma^{\mathrm{HF}}}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})f) = \alpha\,(E(\mathbf{p})\chi E(\mathbf{p})^{-1}(R_{\gamma^{\mathrm{HF}}}-K_{\gamma^{\mathrm{HF}}})\varphi, f)\,.$$

Assume now $k\geq 1$. With $\tilde{\chi}$ as before,

$$\begin{aligned}\mathfrak{b}_{\gamma^{\mathrm{HF}}}(\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) &= \alpha\,(\tilde{\chi}(R_{\gamma^{\mathrm{HF}}}-K_{\gamma^{\mathrm{HF}}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) \\ &\quad + \alpha\,((1-\tilde{\chi})(R_{\gamma^{\mathrm{HF}}}-K_{\gamma^{\mathrm{HF}}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f)\,.\end{aligned} \tag{50}$$

By the induction hypothesis and Lemma 6 (see Appendix A) we have that $\tilde{\chi}R_{\gamma^{\mathrm{HF}}}\varphi$ and $\tilde{\chi}K_{\gamma^{\mathrm{HF}}}\varphi$ belong to $H^k(\mathbb{R}^3)$. Therefore there exists $w_5\in L^2(\mathbb{R}^3)$ such that

$$(\tilde{\chi}(R_{\gamma^{\mathrm{HF}}}-K_{\gamma^{\mathrm{HF}}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) = (w_5, f)\,.$$

For the second term in (50) we find, since $R_{\gamma^{\mathrm{HF}}}\varphi,\ K_{\gamma^{\mathrm{HF}}}\varphi\in L^2(\mathbb{R}^3)$, that

$$\begin{aligned}&((1-\tilde{\chi})(R_{\gamma^{\mathrm{HF}}}-K_{\gamma^{\mathrm{HF}}})\varphi, E(\mathbf{p})^{-1}\chi E(\mathbf{p})^{k+1}f) \\ &\qquad = (\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})(R_{\gamma^{\mathrm{HF}}}-K_{\gamma^{\mathrm{HF}}})\varphi, E(\mathbf{p})^{k+1}f)\,,\end{aligned}$$

and the result follows since $\chi E(\mathbf{p})^{-1}(1-\tilde{\chi})$ is a smoothing operator. □

2.3. **Exponential decay of the Hartree-Fock orbitals.** The pointwise exponential decay (30) will be a consequence of Proposition 1 and Lemma 4 below.

Proposition 1. *Let γ^{HF} be a Hartree-Fock minimizer, let $h_{\gamma^{\mathrm{HF}}}$ be the corresponding Hartree-Fock operator as defined in* (25)*, and let $\{\varphi_i\}_{i=1}^N$ be the Hartree-Fock orbitals, such that*

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

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

(i) *Let $\nu_{\varepsilon_N} := \sqrt{-\varepsilon_N(2\alpha^{-1}+\varepsilon_N)}$. Then $\varphi_i\in\mathcal{D}(e^{\beta|\cdot|})$ for every $\beta<\nu_{\varepsilon_N}$ and $i\in\{1,\ldots,N\}$.*

(ii) *Assume $h_{\gamma^{\mathrm{HF}}}\varphi=\varepsilon\varphi$ for some $\varepsilon\in[\varepsilon_N,0)$, and let $\nu_\varepsilon := \sqrt{-\varepsilon(2\alpha^{-1}+\varepsilon)}$. Then $\varphi\in\mathcal{D}(e^{\beta|\cdot|})$ for every $\beta<\nu_\varepsilon$.*

Lemma 4. *Let $E<0$ and $\nu_E := \sqrt{|-E(2\alpha^{-1}+E)|} = \sqrt{|\alpha^{-2}-(E+\alpha^{-1})^2|}$.*

Then the operator $T(-\mathrm{i}\nabla)-E = \sqrt{-\Delta+\alpha^{-2}}-\alpha^{-1}-E$ is invertible and the integral kernel of its inverse is given by

$$\begin{aligned}(T-E)^{-1}(\mathbf{x},\mathbf{y}) = G_E(\mathbf{x}-\mathbf{y}) &= \frac{(E+\alpha^{-1})e^{-\nu_E|\mathbf{x}-\mathbf{y}|}}{4\pi|\mathbf{x}-\mathbf{y}|} + \frac{\alpha^{-1}}{2\pi^2}\frac{K_1(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|} \\ &\quad + (\alpha^{-2}-\nu_E^2)\frac{\alpha^{-1}}{2\pi^2}\Big[\frac{K_1(\alpha^{-1}|\cdot|)}{|\cdot|} * \frac{e^{-\nu_E|\cdot|}}{4\pi|\cdot|}\Big](\mathbf{x}-\mathbf{y})\,,\end{aligned} \tag{51}$$

where K_1 is a modified Bessel function of the second kind [1].

Moreover,

$$0\leq G_E(\mathbf{x}) \leq C_{\alpha,E}\frac{e^{-\nu_E|\mathbf{x}|}}{4\pi|\mathbf{x}|} + \frac{\alpha^{-1}}{2\pi^2}\frac{K_1(\alpha^{-1}|\mathbf{x}|)}{|\mathbf{x}|}\,, \tag{52}$$

$$e^{\beta|\cdot|}G_E\in L^q(\mathbb{R}^3)\quad \textit{for all}\quad \beta<\nu_E \quad \textit{and}\quad q\in[1,3/2)\,. \tag{53}$$

Proof of Lemma 4: The formula (51) for the kernel of $(T-E)^{-1}$ can be found in [16, eq. (35)].

The estimate (52) is a consequence of the bound

$$\frac{K_1(\alpha^{-1}|\cdot|)}{|\cdot|} * \frac{e^{-\nu_E|\cdot|}}{4\pi|\cdot|}(\mathbf{x}) \le C_{\alpha,E}\frac{e^{-\nu_E|\mathbf{x}|}}{4\pi|\mathbf{x}|}\,.$$

This estimate, on the other hand, follows from Newton's theorem (see e. g. [12]),

$$\begin{aligned}&\int_{\mathbb{R}^3}\frac{K_1(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}\,\frac{e^{-\nu_E|\mathbf{y}|}}{4\pi|\mathbf{y}|}\,d\mathbf{y}\\ &\le e^{-\nu_E|\mathbf{x}|}\int_{\mathbb{R}^3}\frac{K_1(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}\,\frac{e^{\nu_E|\mathbf{x}-\mathbf{y}|}}{4\pi|\mathbf{y}|}\,d\mathbf{y} \le \frac{e^{-\nu_E|\mathbf{x}|}}{4\pi|\mathbf{x}|}\int_{\mathbb{R}^3}\frac{K_1(\alpha^{-1}|\mathbf{z}|)}{|\mathbf{z}|}\,e^{\nu_E|\mathbf{z}|}\,d\mathbf{z}\,.\end{aligned}$$

The last integral is finite since $\nu_E < \alpha^{-1}$, using the following properties of K_1 (see [6, 8.446, 8.451.6]):

$$K_1(t) \le \frac{1}{|t|} \quad \text{for all} \quad t>0\,, \tag{54}$$

and for every $r>0$ there exists c_r such that

$$K_1(t) \le c_r\frac{e^{-t}}{\sqrt{t}} \quad \text{for all} \quad t \ge r\,. \tag{55}$$

The estimate (53) is a consequence of (52), (54), and (55). □

Before proving Proposition 1, we apply it, and Lemma 4, to prove the pointwise exponential decay, i.e., the estimate in (30).

Proof of Theorem 1 (iii): Fix $i \in \{1,\dots,N\}$. If $Z\alpha < 1/2$ we can rewrite the Hartree-Fock equation (28) as

$$\big(\sqrt{-\Delta+\alpha^{-2}}-\alpha^{-1}\big)\varphi_i = \varepsilon_i\varphi_i + \frac{Z\alpha}{|\mathbf{x}|}\,\varphi_i - \alpha R_{\gamma^{\mathrm{HF}}}\varphi_i + \alpha K_{\gamma^{\mathrm{HF}}}\varphi_i\,. \tag{56}$$

The idea of the proof is to study the elliptic regularity of the corresponding parametrix. By Lemma 4 we find that

$$\varphi_i(\mathbf{x}) = \int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big[(\varepsilon_i-\varepsilon_N)\varphi_i + \frac{Z\alpha}{|\cdot|}\,\varphi_i - \alpha R_{\gamma^{\mathrm{HF}}}\varphi_i + \alpha K_{\gamma^{\mathrm{HF}}}\varphi_i\big](\mathbf{y})\,d\mathbf{y}\,.$$

In the case $1/2 \le Z\alpha < 2/\pi$, on the other hand, the operator of which we are studying the eigenfunctions cannot be written as a sum of operators acting on $L^2(\mathbb{R}^3)$ and hence we cannot write directly the equation (28) as in (56). However, since the eigenfunctions are smooth away from the origin we are able to write a pointwise equation for a localized version of φ_i. In fact, let $\chi \in C^\infty(\mathbb{R}^3)$ be such that $0 \le \chi \le 1$ and

$$\chi(\mathbf{x}) = \begin{cases} 1 & \text{if } |\mathbf{x}| \ge 1,\\ 0 & \text{if } |\mathbf{x}| \le 1/2\,,\end{cases}$$

and let, for $R>0$, $\chi_R(\mathbf{x}) = \chi(\mathbf{x}/R)$. We will derive an equation (similar to (56)) for $T(-\mathrm{i}\nabla)(\chi_R\varphi_i)$. Indeed, for every $u \in H^{1/2}(\mathbb{R}^3)$ we have that

$$\begin{aligned}(u, h_{\gamma^{\mathrm{HF}}}(\chi_R\varphi_i)) &= \mathfrak{e}(u,\chi_R\varphi_i) - \alpha^{-1}(u,\chi_R\varphi_i) - \mathfrak{v}(u,\chi_R\varphi_i) + \mathfrak{b}_{\gamma^{\mathrm{HF}}}(u,\chi_R\varphi_i)\\ &= (\chi_R u, h_{\gamma^{\mathrm{HF}}}\varphi_i) + \mathfrak{e}(u,\chi_R\varphi_i) - \mathfrak{e}(\chi_R u,\varphi_i)\\ &\quad + \mathfrak{b}_{\gamma^{\mathrm{HF}}}(u,\chi_R\varphi_i) - \mathfrak{b}_{\gamma^{\mathrm{HF}}}(\chi_R u,\varphi_i)\,.\end{aligned}$$

Note that

$$\mathfrak{e}(u,\chi_R\varphi_i) - \mathfrak{e}(\chi_R u,\varphi_i) = (u,[E(\mathbf{p}),\chi_R]\varphi_i)\,,$$

where $[E(\mathbf{p}),\chi_R]$ is a bounded operator in $L^2(\mathbb{R}^3)$ (see Appendix B), and

$$\mathfrak{b}_{\gamma^{\rm HF}}(u,\chi_R\varphi_i)-\mathfrak{b}_{\gamma^{\rm HF}}(\chi_R u,\varphi_i)=(u,\mathcal{K}\varphi_i)\,,$$

with $\mathcal{K}$ the bounded operator on $L^2(\mathbb{R}^3)$ given by the kernel

$$\mathcal{K}(\mathbf{x},\mathbf{y})=\alpha\sum_{j=1}^{N}\varphi_j(\mathbf{x})\overline{\varphi_j(\mathbf{y})}\,\frac{\chi_R(\mathbf{x})-\chi_R(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,. \tag{57}$$

Therefore there exists $w\in L^2(\mathbb{R}^3)$ such that

$$\begin{aligned}\mathfrak{e}(u,\chi_R\varphi_i)=(\varepsilon_i+\alpha^{-1})(u,\chi_R\varphi_i)+\mathfrak{v}(u,\chi_R\varphi_i)-\mathfrak{b}_{\gamma^{\rm HF}}(u,\chi_R\varphi_i)\\ +(u,[E(\mathbf{p}),\chi_R]\varphi_i)+(u,\mathcal{K}\varphi_i)=(u,w)\,.\end{aligned}$$

Hence $\chi_R\varphi_i\in H^1(\mathbb{R}^3)$ and we can write the pointwise equation

$$\begin{aligned}(\sqrt{-\Delta+\alpha^{-2}}-\alpha^{-1})\chi_R\varphi_i=\varepsilon_i\chi_R\varphi_i+\frac{Z\alpha}{|\mathbf{x}|}\chi_R\varphi_i-\alpha R_{\gamma^{\rm HF}}\chi_R\varphi_i\\ +\alpha K_{\gamma^{\rm HF}}(\chi_R\varphi_i)+[E(\mathbf{p}),\chi_R]\varphi_i+\mathcal{K}\varphi_i\,.\end{aligned} \tag{58}$$

This is the substitute for (56) in the case $1/2\le Z\alpha<2/\pi$; if $Z\alpha<1/2$, the proof below simplifies somewhat, using (56) directly.

By Lemma 4, (58) implies that

$$\begin{aligned}\chi_R(\mathbf{x})\varphi_i(\mathbf{x})=\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big[\frac{Z\alpha}{|\cdot|}\chi_R\varphi_i-\alpha R_{\gamma^{\rm HF}}\chi_R\varphi_i+\alpha K_{\gamma^{\rm HF}}(\chi_R\varphi_i)\\ +(\varepsilon_i-\varepsilon_N)\chi_R\varphi_i+[E(\mathbf{p}),\chi_R]\varphi_i+\mathcal{K}\varphi_i\big](\mathbf{y})\,d\mathbf{y}\,.\end{aligned} \tag{59}$$

We will first show that, for all $R>0$ and $\beta<\nu_{\varepsilon_N}$,

$$\chi_R\varphi_i e^{\beta|\cdot|}\in L^p(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)\quad\text{for } p\in[2,6)\,, \tag{60}$$

and then, by a bootstrap argument, that $\chi_R\varphi_i e^{\beta|\cdot|}\in L^\infty(\mathbb{R}^3)$, which is the claim of Theorem 1 (iii).

We multiply (59) by $\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}$. Using that $|(Z\alpha/|\mathbf{y}|)\chi_R(\mathbf{y})|\le(Z\alpha)/R$ for all $\mathbf{y}\in\mathbb{R}^3$, (23), (24), and (57) (recall (27), that $\varphi_j\in H^{1/2}(\mathbb{R}^3)$, and (5)) we get, for some constant $C=C_{R,\alpha}>0$, that

$$\begin{aligned}\big|\chi_R(\mathbf{x})\varphi_i(\mathbf{x})e^{\beta|\mathbf{x}|}\big|\le C\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big[|\varphi_i(\mathbf{y})|+\sum_{j=1}^{N}|\varphi_j(\mathbf{y})|\big]\,d\mathbf{y}\\ +\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\Big|\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big([E(\mathbf{p}),\chi_R]\varphi_i\big)(\mathbf{y})\,d\mathbf{y}\Big|\,.\end{aligned} \tag{61}$$

We will show that the first term on the right side of (61) belongs to $L^p(\mathbb{R}^3)$ for $p\in[2,6)$, and that the second belongs to $L^\infty(\mathbb{R}^3)$. This will prove (60).

The first term on the right side of (61) is a sum of terms of the form

$$h_f(\mathbf{x}):=\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\,|f(\mathbf{y})|\,d\mathbf{y}\,, \tag{62}$$

with f such that, by Proposition 1, $fe^{\beta|\cdot|}\in L^2(\mathbb{R}^3)$. By Lemma 4 we have, using $e^{|\mathbf{x}|-|\mathbf{y}|}\le e^{|\mathbf{x}-\mathbf{y}|}$, that

$$|h_f(\mathbf{x})|\le C\int_{\mathbb{R}^3}e^{\beta|\mathbf{x}-\mathbf{y}|}G_{\varepsilon_N}(\mathbf{x}-\mathbf{y})e^{\beta|\mathbf{y}|}|f(\mathbf{y})|\,d\mathbf{y}\,.$$

From Young's inequality it follows that $h_f\in L^p(\mathbb{R}^3)$ for all $p\in[2,6)$, since $\beta<\nu_{\varepsilon_N}$, so (by Proposition 1) $fe^{\beta|\cdot|}\in L^2(\mathbb{R}^3)$ and (by Lemma 4) $e^{\beta|\cdot|}G_{\varepsilon_N}\in L^q(\mathbb{R}^3)$ for all $q\in[1,3/2)$.

We now prove that the second term on the right side of (61) is in $L^\infty(\mathbb{R}^3)$. This follows from Young's inequality once we have proved that

$$e^{\beta|\cdot|}[E(\mathbf{p}),\chi_R]\varphi_i \in L^p(\mathbb{R}^3) \quad \text{for } p\in[2,\infty)\,, \tag{63}$$

since

$$\begin{aligned} &e^{\beta|\mathbf{x}|}\Big|\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})\big([E(\mathbf{p}),\chi_R]\varphi_i\big)(\mathbf{y})\,d\mathbf{y}\Big| \\ &\quad\le \int_{\mathbb{R}^3} e^{\beta|\mathbf{x}-\mathbf{y}|}G_{\varepsilon_N}(\mathbf{x}-\mathbf{y})e^{\beta|\mathbf{y}|}\big|[E(\mathbf{p}),\chi_R]\varphi_i\big|(\mathbf{y})\,d\mathbf{y}\,,\end{aligned}$$

and $e^{\beta|\cdot|}G_{\varepsilon_N}\in L^q(\mathbb{R}^3)$ for $q\in[1,3/2)$.

To prove (60) it therefore remains to prove (63). To do so, we consider a new localization function. Let $\eta\in C_0^\infty(\mathbb{R}^3)$ be such that $0\le\eta\le 1$ and

$$\eta(\mathbf{x}) = \begin{cases} 1 & \text{if } R/4\le|\mathbf{x}|\le 3R/2\\ 0 & \text{if } |\mathbf{x}|\le R/8 \text{ or } |\mathbf{x}|\ge 2R\,,\end{cases}$$

and consider the following splitting

$$\begin{aligned} e^{\beta|\cdot|}[E(\mathbf{p}),\chi_R]\varphi_i &= e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R](\eta\varphi_i) + e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R]((1-\eta)\varphi_i)\\ &\quad + e^{\beta|\cdot|}(1-\eta)[E(\mathbf{p}),\chi_R](\eta\varphi_i) + e^{\beta|\cdot|}(1-\eta)[E(\mathbf{p}),\chi_R](1-\eta)\varphi_i\,. \end{aligned}\tag{64}$$

Since $\eta\varphi_i\in H^k(\mathbb{R}^3)$ for all $k\in\mathbb{N}$ (as proved earlier), $[E(\mathbf{p}),\chi_R](\eta\varphi_i)$ belongs to $H^k(\mathbb{R}^3)$ for all $k\in\mathbb{N}$. Hence, since η has compact support away from $\mathbf{x}=0$, the first term on the right side of (64) is in $L^p(\mathbb{R}^3)$ for $p\in[1,\infty]$ by Sobolev's imbedding theorem (the term is smooth).

For the second term in (64) we proceed by duality: We will prove that

$$\psi(\mathbf{x}) := \big(e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R]((1-\eta)\varphi_i)\big)(\mathbf{x})$$

defines a bounded linear functional on $L^q(\mathbb{R}^3)$ for any $q\in(1,2]$. It then follows that $\psi\in L^p(\mathbb{R}^3)$ for all $p\in[2,\infty)$.

Note that [12, 7.12 Theorem (iv)]

$$\begin{aligned} &(g,[\sqrt{-\Delta+\alpha^{-2}}-\alpha^{-1}]g)\\ &\quad= \frac{\alpha^{-2}}{4\pi^2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|g(\mathbf{x})-g(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|^2}K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)\,d\mathbf{x}d\mathbf{y} \quad \text{for } g\in\mathcal{S}(\mathbb{R}^3)\,,\end{aligned}\tag{65}$$

where K_2 is a modified Bessel function of the second kind (in fact, $K_2(t) = -t\frac{d}{dt}[t^{-1}K_1(t)]$), satisfying [1]

$$K_2(t)\le Ct^{-1}e^{-t} \quad \text{for}\quad t\ge 1\,. \tag{66}$$

Let $f\in C_0^\infty(\mathbb{R}^3)$. Using (65) and polarization, we have that

$$\begin{aligned} &\int_{\mathbb{R}^3}\overline{f(\mathbf{x})}\psi(\mathbf{x})\,d\mathbf{x} = (f, e^{\beta|\cdot|}\eta[E(\mathbf{p}),\chi_R]((1-\eta)\varphi_i))\\ &= \frac{\alpha^{-2}}{4\pi^2}\iint_{|\mathbf{x}-\mathbf{y}|\ge R/4}\frac{\chi_R(\mathbf{x})-\chi_R(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|^2}\,K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)\\ &\qquad\times\big[\,\overline{f(\mathbf{x})}e^{\beta|\mathbf{x}|}\eta(\mathbf{x})(1-\eta(\mathbf{y}))\varphi_i(\mathbf{y}) - \overline{f(\mathbf{y})}e^{\beta|\mathbf{y}|}\eta(\mathbf{y})(1-\eta(\mathbf{x}))\varphi_i(\mathbf{x})\big]\,d\mathbf{x}d\mathbf{y}\,,\end{aligned}$$

by the properties of χ and η. Hence,

$$\begin{aligned}\Big|\int_{\mathbb{R}^3}&\overline{f(\mathbf{x})}\psi(\mathbf{x})\,d\mathbf{x}\Big|\\&\le C_R\iint_{|\mathbf{x}-\mathbf{y}|\ge R/4}|f(\mathbf{x})|e^{\beta|\mathbf{x}-\mathbf{y}|}K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)e^{\beta|\mathbf{y}|}|\varphi_i(\mathbf{y})|\,d\mathbf{x}d\mathbf{y}\,,\\&\le C_R\iint|f(\mathbf{x})|e^{\beta|\mathbf{x}-\mathbf{y}|}K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)\chi_{R/4}(|\mathbf{x}-\mathbf{y}|)e^{\beta|\mathbf{y}|}|\varphi_i(\mathbf{y})|\,d\mathbf{x}d\mathbf{y}\,. \quad (67)\end{aligned}$$

Note that, since $\beta<\nu_{\varepsilon_N}<\alpha^{-1}$, (66) implies that $e^{\beta|\cdot|}K_2(\alpha^{-1}|\cdot|)\chi_{R/4}$ is in $L^r(\mathbb{R}^3)$ for all $r\ge1$. Since (by Proposition 1) $e^{\beta|\cdot|}\varphi_i\in L^2(\mathbb{R}^3)$, Young's inequality therefore gives that

$$(e^{\beta|\cdot|}K_2(\alpha^{-1}|\cdot|)\chi_{R/4})*(e^{\beta|\cdot|}|\varphi_i|)\in L^s(\mathbb{R}^3)\quad\text{for all } s\in[2,\infty)\,.$$

This, (67), and Hölder's inequality (with $1/q+1/s=1$) imply that, for all $f\in C_0^\infty(\mathbb{R}^3)$ and all $q\in(1,2]$

$$\Big|\int_{\mathbb{R}^3}\overline{f(\mathbf{x})}\psi(\mathbf{x})\,d\mathbf{x}\Big|\le C_R\big\|(e^{\beta|\cdot|}K_2(\alpha^{-1}|\cdot|)\chi_{R/4})*(e^{\beta|\cdot|}|\varphi_i|)\big\|_s\,\|f\|_q\,.$$

By density of $C_0^\infty(\mathbb{R}^3)$ in $L^q(\mathbb{R}^3)$, it follows that ψ defines a bounded linear functional on $L^q(\mathbb{R}^3)$ for any $q\in(1,2]$, and therefore, that $\psi\in L^p(\mathbb{R}^3)$ for all $p\in[2,\infty)$.

Proceeding similarly one shows that the two remaining terms in (64) are also in $L^p(\mathbb{R}^3)$ for all $p\in[2,\infty)$.

This finishes the proof of (63), and therefore of (60).

Finally we prove that $\chi_R\varphi_i e^{\beta|\cdot|}\in L^\infty(\mathbb{R}^3)$. We start again from (61). We already know that the second term is in $L^\infty(\mathbb{R}^3)$. The first term is a sum of terms of the form (see also (62))

$$h_f(\mathbf{x})=\chi_{R/2}(\mathbf{x})e^{\beta|\mathbf{x}|}\int_{\mathbb{R}^3}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})|f(\mathbf{y})|\,d\mathbf{y}\,,$$

with $f\in L^2(\mathbb{R}^3)$ and $\chi_{R/4}e^{\beta|\cdot|}f\in L^p(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)$ for $p\in[2,6)$ by what just proved, replacing R by $R/4$ in (60). We find that

$$\begin{aligned}h_f(\mathbf{x})\le\chi_{R/2}(\mathbf{x})&\int_{\mathbb{R}^3}e^{\beta|\mathbf{x}-\mathbf{y}|}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})e^{\beta|\mathbf{y}|}\chi_{R/4}(\mathbf{y})|f(\mathbf{y})|\,d\mathbf{y}\\&+\chi_{R/2}(\mathbf{x})\int_{\mathbb{R}^3}e^{\beta|\mathbf{x}-\mathbf{y}|}(T-\varepsilon_N)^{-1}(\mathbf{x},\mathbf{y})e^{\beta|\mathbf{y}|}(1-\chi_{R/4})(\mathbf{y})|f(\mathbf{y})|\,d\mathbf{y}\,,\end{aligned}$$

and, again by Young's inequality, we see that both terms are in $L^\infty(\mathbb{R}^3)$. Notice that in the second integrand $|\mathbf{x}-\mathbf{y}|>R/4$.

This finishes the proof of Theorem 1 (iii). □

It therefore remains to prove Proposition 1.

Proof of Proposition 1: We start by proving (i). It will be convenient to write the Hartree-Fock equations $h_{\gamma^{\rm HF}}\varphi_i=\varepsilon_i\varphi_i$, $i=1,\dots,N$, (see (28)) as a system.

Let $\mathtt{t}$ be the quadratic form with domain $[H^{1/2}(\mathbb{R})]^N$ defined by

$$\mathtt{t}(\mathrm{u},\mathrm{v})=\sum_{i=1}^N\mathtt{t}(\mathrm{u}_i,\mathrm{v}_i)\text{ for all }\mathrm{u},\mathrm{v}\in[H^{1/2}(\mathbb{R}^3)]^N\,,$$

where u_i denotes the i-th component of $\mathrm{u}\in[H^{1/2}(\mathbb{R}^3)]^N$ and $\mathtt{t}$ is the quadratic form defined in (7). Similarly we define the quadratic forms $\mathtt{v}$, $\mathtt{r}_\gamma$ and $\mathtt{k}_\gamma$, all with domain $[H^{1/2}(\mathbb{R}^3)]^N$, by

$$\mathtt{v}(\mathrm{u},\mathrm{v}) = \sum_{i=1}^{N} \mathfrak{v}(\mathrm{u}_i,\mathrm{v}_i)\,, \quad \mathtt{r}_\gamma(\mathrm{u},\mathrm{v}) = \alpha \sum_{i=1}^{N} (\mathrm{u}_i, R_\gamma \mathrm{v}_i)\,, \quad \mathtt{k}_\gamma(\mathrm{u},\mathrm{v}) = \alpha\langle \mathrm{u}, \mathrm{K}_\gamma \mathrm{v}\rangle\,,$$

with $\mathfrak{v}$ defined in (6), R_γ defined in (22), and K_γ the $N\times N$-matrix given by

$$(\mathrm{K}_\gamma)_{i,j} = \int_{\mathbb{R}^3} \frac{\varphi_i(\mathbf{y})\overline{\varphi_j(\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y}\,.$$

The effect of writing the Hartree-Fock equations as a system is that K_γ is a (non-diagonal) multiplication operator. This idea was already used in [13]. Note that $(\mathrm{K}_\gamma)_{i,j} \in L^3(\mathbb{R}^3)\cap L^\infty(\mathbb{R}^3)$; the argument is the same as for (22).

Let finally $\mathtt{E}$ be the $N\times N$ matrix defined by $(\mathtt{E})_{i,j} = -\varepsilon_i\delta_{i,j}$.

We then define the quadratic form $\mathtt{q}$ by

$$\mathtt{q}(\mathrm{u},\mathrm{v}) = \mathtt{t}(\mathrm{u},\mathrm{v}) - \mathtt{v}(\mathrm{u},\mathrm{v}) + \mathtt{r}_\gamma(\mathrm{u},\mathrm{v}) - \mathtt{k}_\gamma(\mathrm{u},\mathrm{v}) + \langle \mathrm{u}, \mathtt{E}\mathrm{v}\rangle\,. \tag{68}$$

One sees that the quadratic form domain of $\mathtt{q}$ is $[H^{1/2}(\mathbb{R}^3)]^N$, that $\mathtt{q}$ is closed (since $\mathtt{t}$ is closed), and that there exists a unique selfadjoint operator $\mathtt{H}$ with $\mathcal{D}(\mathtt{H})\subset[H^{1/2}(\mathbb{R}^3)]^N$ such that

$$\langle \mathrm{u}, \mathtt{H}\mathrm{v}\rangle = \mathtt{q}(\mathrm{u},\mathrm{v}) \ \text{ for all } \ \mathrm{u}\in[H^{1/2}(\mathbb{R}^3)]^N\,,\ \mathrm{v}\in\mathcal{D}(\mathtt{H})\,.$$

Notice that the vector $\Phi = (\varphi_1,\dots,\varphi_N)$ satisfies $\mathtt{H}\Phi = 0$.

Let $W(\kappa)$, $\kappa\in\mathbb{C}^3$, denote the multiplication operator from a subset of $[L^2(\mathbb{R}^3)]^N$ to $[L^2(\mathbb{R}^3)]^N$ given by $f(\mathbf{x})\mapsto e^{i\kappa\cdot\mathbf{x}}f(\mathbf{x})$. Instead of proving directly the claim of the proposition, we are going to prove the following statement, which implies the proposition:

$$\Phi\in\mathcal{D}(W(\kappa)) \ \text{ for } \ \|\mathrm{Im}(\kappa)\|_{\mathbb{R}^3} < \nu_{\varepsilon_N}\,, \tag{69}$$

where $\Phi = (\varphi_1,\dots,\varphi_N)$. Here, $\kappa = \mathrm{Re}(\kappa) + i\mathrm{Im}(\kappa)$ with $\mathrm{Re}(\kappa),\mathrm{Im}(\kappa)\in\mathbb{R}^3$.

We know that $W(\kappa)\Phi$ is well defined on $[L^2(\mathbb{R}^3)]^N$ for $\kappa\in\mathbb{R}^3$ and we need to show that it has a continuation into the 'strip' $\Sigma_{\nu_{\varepsilon_N}}$, where

$$\Sigma_t := \{\kappa\in\mathbb{C}^3 \mid \|\mathrm{Im}(\kappa)\|_{\mathbb{R}^3} < t\}\,.$$

We shall also need $\Sigma_{\alpha^{-1}}$; note that $\Sigma_{\alpha^{-1}}\supset\Sigma_{\nu_{\varepsilon_N}}$. The idea is to use O'Connor's Lemma (see Lemma 5 below).

Starting from the quadratic form $\mathtt{q}$ defined in (68) we define the following family of quadratic forms on $[H^{1/2}(\mathbb{R}^3)]^N$:

$$\mathtt{q}(\kappa)(\mathrm{u},\mathrm{u}) := \mathtt{q}(W(-\kappa)\mathrm{u}, W(-\kappa)\mathrm{u})\,,$$

depending on the *real* parameter $\kappa\in\mathbb{R}^3$. From the definition,

$$\mathtt{q}(\kappa)(\mathrm{u},\mathrm{u}) = \mathtt{t}(\kappa)(\mathrm{u},\mathrm{u}) - \mathtt{v}(\mathrm{u},\mathrm{u}) + \mathtt{r}_\gamma(\mathrm{u},\mathrm{u}) - \mathtt{k}_\gamma(\mathrm{u},\mathrm{u}) + \langle \mathrm{u}, \mathtt{E}\mathrm{u}\rangle\,,$$

where

$$\mathtt{t}(\kappa)(\mathrm{u},\mathrm{u}) = \sum_{i=1}^{N}\int_{\mathbb{R}^3}\Big(\alpha^{-2} + \sum_{j=1}^{3}(p_j-\kappa_j)^2\Big)^{1/2}|\hat{\mathrm{u}}_i(\mathbf{p})|^2\, d\mathbf{p} - \alpha^{-1}\langle \mathrm{u},\mathrm{u}\rangle\,. \tag{70}$$

One sees that $\mathtt{q}(\kappa)$ extends to a family of sectorial forms with angle $\theta<\frac{\pi}{4}$, and that $\mathtt{q}(\kappa)$ is holomorphic in the strip $\Sigma_{\alpha^{-1}}$ (indeed, $\|\mathrm{Im}(\kappa)\|_{\mathbb{R}^3} < \alpha^{-1}$ is needed to assure that the complex number under the square root in (70) has non-negative real part for all $\mathbf{p}\in\mathbb{R}^3$). Moreover, $\mathtt{q}(\kappa)$ is closed. Indeed, it is sufficient to prove that the real part of $\mathtt{q}(\kappa)$ is closed, which will follow from

$$\mathtt{v}(\mathrm{u},\mathrm{u}) + \mathtt{r}_\gamma(\mathrm{u},\mathrm{u}) + \mathtt{k}_\gamma(\mathrm{u},\mathrm{u}) + \langle \mathrm{u}, \mathtt{E}\mathrm{u}\rangle \le b\,\mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) + K\langle \mathrm{u},\mathrm{u}\rangle\,, \tag{71}$$

with $b<1$, $K>0$ and $\mathrm{Re}(\mathtt{t}(\kappa))$ closed. We now prove (71). We already know that

$$\mathtt{r}_\gamma(\mathrm{u},\mathrm{u}) + \mathtt{k}_\gamma(\mathrm{u},\mathrm{u}) + \langle \mathrm{u}, \mathtt{E}\mathrm{u}\rangle \le K'\langle \mathrm{u},\mathrm{u}\rangle \text{ for } K'>0\,. \tag{72}$$

By (8) we find

$$\begin{aligned}\mathtt{v}(\mathrm{u},\mathrm{u}) &\leq (Z\alpha)\frac{\pi}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|\mathbf{p}|\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\\ &\leq (Z\alpha)\frac{\pi}{2}R\sum_{i=1}^{N}\Big[\int_{|\mathbf{p}|\leq R}|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}+\int_{|\mathbf{p}|\geq R}|\mathbf{p}|\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\Big]\,. \qquad (73)\end{aligned}$$

Let $\delta > 0$ be such that $Z\alpha\frac{\pi}{2}(1-\delta)^{-1} < 1$. Since

$$\begin{aligned}\mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) = \sum_{i=1}^{N}\int_{\mathbb{R}^3}\Big|\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2\Big|^{1/2}\cos(\theta(\mathbf{p},\kappa))\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\\ -\alpha^{-1}\langle \mathrm{u},\mathrm{u}\rangle\,,\end{aligned}$$

with

$$2\cos^2(\theta(\mathbf{p},\kappa))-1 = \frac{\alpha^{-2}+\sum_{j=1}^{3}(p_j-\mathrm{Re}(\kappa_j))^2-(\mathrm{Im}(\kappa_j))^2)}{|\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2|}\,,$$

there exists $R > 0$ such that $\cos(\theta(\mathbf{p},\kappa)) \geq (1-\delta)$ for $|\mathbf{p}| > R$. Hence we find that

$$\begin{aligned}\mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) &\geq (1-\delta)\sum_{i=1}^{N}\int_{|\mathbf{p}|>R}\Big|\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2\Big|^{1/2}|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\\ &\quad-\alpha^{-1}\langle \mathrm{u},\mathrm{u}\rangle\\ &\geq (1-\delta)\sum_{i=1}^{N}\int_{|\mathbf{p}|>R}(|\mathbf{p}|-C)|\,\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}-\alpha^{-1}\langle \mathrm{u},\mathrm{u}\rangle\,, \qquad (74)\end{aligned}$$

with $C > \|\mathrm{Re}(\kappa)\|_{\mathbb{R}^3}$. The estimate in (71) follows combining (72) with (73) and (74).

The fact that $\mathrm{Re}(\mathtt{t}(\kappa))$ is closed follows from

$$\frac{1}{\sqrt{2}}\sum_{i=1}^{N}\int(|\mathbf{p}|-C)\,|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p} \leq \mathrm{Re}(\mathtt{t}(\kappa))(\mathrm{u},\mathrm{u}) \leq \sum_{i=1}^{N}\int(|\mathbf{p}|+C)|\hat{\mathrm{u}}_i(\mathbf{p})|^2\,d\mathbf{p}\,,$$

with $C \geq 2\alpha^{-1}+\mathrm{Re}(\kappa)$.

Hence, $\mathtt{q}(\kappa)$ is an analytic family of forms of type (a) ([9, p. 395]). The associated family $\mathtt{H}(\kappa)$ of sectorial operators is a holomorphic family of operators of type (B) and has domain in a subset of $[H^{1/2}(\mathbb{R}^3)]^N$.

We are interested now in locating the essential spectrum of $\mathtt{H}(\kappa)$. Since K_γ is a Hilbert-Schmidt operator, the essential spectrum of $\mathtt{H}(\kappa)$ coincides with the essential spectrum of the operator associated to

$$\mathtt{t}(\kappa)(\mathrm{u},\mathrm{u})-\mathtt{v}(\mathrm{u},\mathrm{u})+\alpha\,\mathtt{r}_\gamma(\mathrm{u},\mathrm{u})+\langle \mathrm{u},\mathtt{E}\mathrm{u}\rangle\,.$$

Notice that the operator associated to this quadratic form is diagonal. Proceeding as in the proof of $\sigma_{\mathrm{ess}}(h_\gamma) = [0,\infty)$ (Lemma 2), one sees that $\sigma_{\mathrm{ess}}(\mathtt{H}(\kappa)) \subset \sigma_{\mathrm{ess}}(T(\kappa)-\varepsilon_N)$ with $T(\kappa) := \sqrt{\alpha^{-2}+\sum_{j=1}^{3}(p_j-\kappa_j)^2}-\alpha^{-1}$. Hence we find that

$$\sigma_{\mathrm{ess}}(\mathtt{H}(\kappa)) \subset \big\{z\in\mathbb{C}\,\big|\,\mathrm{Re}(z)\geq\sqrt{\alpha^{-2}-\|\mathrm{Im}(\kappa)\|^2_{\mathbb{R}^3}}-\alpha^{-1}-\varepsilon_N\big\}\,.$$

Hence 0, eigenvalue of $\mathtt{H}(0)$, remains disjoint from the essential spectrum of $\mathtt{H}(\kappa)$ for all $\kappa\in\Sigma_{\nu_{\varepsilon_N}}$ (recall that $\Sigma_{\nu_{\varepsilon_N}}\subset\Sigma_{\alpha^{-1}}$) .

Since $\mathtt{H}(\kappa)$ is an analytic family of type (B) [20, p.20] in Σ_{ν_ε}, 0 is an eigenvalue of $\mathtt{H}(0)$ and moreover, 0 remains disjoint from the essential spectrum of $\mathtt{H}(\kappa)$, it follows that 0 is an eigenvalue in the pure point spectrum of $\mathtt{H}(\kappa)$ for all $\kappa\in\Sigma_{\nu_{\varepsilon_N}}$ (reasoning as in [20, page 187]). Let $\mathtt{P}(\kappa)$ be the projection onto the eigenspace corresponding to the eigenvalue 0 of the operator $\mathtt{H}(\kappa)$. Then $\mathtt{P}(\kappa)$ is an analytic function in $\Sigma_{\nu_{\varepsilon_N}}$ and for $\kappa \in \Sigma_{\nu_{\varepsilon_N}}$ and $\kappa_0 \in \mathbb{R}$ we have

$$\mathtt{P}(\kappa + \kappa_0) = W(\kappa_0)\mathtt{P}(\kappa)W(-\kappa_0)\,.$$

Here we used that $W(-\kappa_0)$ is a unitary operator. The result of the lemma follows by applying Lemma 5 below to $\tilde{W}(\theta) := e^{i\theta\kappa\cdot\mathbf{x}}$ with $\kappa \in \mathbb{R}^3$, $\|\kappa\|_{\mathbb{R}^3} = \nu_{\varepsilon_N}$, and $\theta \in \{z \in \mathbb{C}\,|\,|\mathrm{Im}(z)| < 1\}$. Notice that $\tilde{W}(\theta) = W(\theta\kappa)$ and that the projection $\tilde{\mathtt{P}}(\theta) := \mathtt{P}(\theta\kappa)$ is analytic and satisfies $\tilde{\mathtt{P}}(\theta + \theta_0) = \tilde{W}(\theta_0)\tilde{\mathtt{P}}(\theta)\tilde{W}(-\theta_0)$ for $\theta_0 \in \mathbb{R}$.

This finishes the proof of (i).

To prove (ii), we can work directly with the Hartree-Fock equation, since, from (i), the function $K_{\gamma^{\mathrm{HF}}}\varphi$ is exponentially decaying. Therefore, let

$$\mathfrak{q}[u,v] = (u, h_{\gamma^{\mathrm{HF}}}v) - \varepsilon(u,v) \quad \text{for} \quad u,v \in H^{1/2}(\mathbb{R}^3)\,, \tag{75}$$

and note that, by assumption, 0 is an eigenvalue for the corresponding operator (φ is an eigenfunction). Define, for $\kappa \in \mathbb{R}^3$,

$$\begin{aligned}\mathfrak{q}(\kappa)[u,v] &= \mathfrak{q}[W(-\kappa)u, W(-\kappa)v] \\ &= \mathfrak{t}(\kappa)[u,v] - \mathfrak{v}[u,v] + \mathfrak{b}_{\gamma^{\mathrm{HF}}}(\kappa)[u,v] - \varepsilon(u,v)\,,\end{aligned} \tag{76}$$

with $W(\kappa)$ and $\mathfrak{t}(\kappa)$ as before (but now on $H^{1/2}(\mathbb{R}^3)$), see (70), and

$$\mathfrak{b}_{\gamma^{\mathrm{HF}}}(\kappa)[u,v] = \alpha(u, R_{\gamma^{\mathrm{HF}}}v) - \alpha(u, K_{\gamma^{\mathrm{HF}}}(\kappa)v)\,, \tag{77}$$

where

$$K_{\gamma^{\mathrm{HF}}}(\kappa)(\mathbf{x},\mathbf{y}) = \sum_{j=1}^{N} \frac{\varphi_j(\mathbf{x})e^{i\kappa\mathbf{x}}e^{-i\kappa\mathbf{y}}\overline{\varphi_j(\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\,. \tag{78}$$

Using (i) of the proposition (exponential decay of the Hartree-Fock orbitals $\{\varphi_j\}_{j=1}^N$) one now proves that (78) extends to a holomorphic family of Hilberts-Schmidt operators in $\Sigma_{\nu_{\varepsilon_N}}$. One can now repeat the reasoning in the proof of (i) to obtain the stated exponential decay of φ.

□

Lemma 5. ([20, p. 196]) *Let $W(\kappa) = e^{i\kappa A}$ be a one-parameter unitary group (in particular, A is self-adjoint) and let D be a connected region in $\mathbb{C}$ with $0 \in D$. Suppose that a projection-valued analytic function $P(\kappa)$ is given on D with $P(0)$ of finite rank and so that*

$$W(\kappa_0)P(\kappa)W(\kappa_0)^{-1} = P(\kappa+\kappa_0) \text{ for } \kappa_0 \in \mathbb{R} \text{ and } \kappa, \kappa+\kappa_0 \in D\,.$$

Let $\psi \in \mathrm{Ran}(P(0))$. Then the function $\psi(\kappa) = W(\kappa)\psi$ has an analytic continuation from $D \cap \mathbb{R}$ to D.

Appendix A. Some useful lemmata

Lemma 6. *Let Ω be an open subset of $\mathbb{R}^3 \setminus \{0\}$ with smooth boundary and let $f_1, f_2 \in H^k(\Omega)$ for some $k \geq 1$.*

Then the function

$$F(\mathbf{x}) := \int_{\mathbb{R}^3} \frac{f_1(\mathbf{y})f_2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y}$$

belongs to $C^k(\Omega)$ if $k \geq 2$, while if $k = 1$, it belongs to $W^{1,p}(\Omega)$ for all $p \geq 1$, and hence to $C(\Omega)$.

Proof. We are going to prove the following equivalent statement. If $k \geq 2$, $\chi F \in C^k(\mathbb{R}^3)$ for all $\chi \in C_0^\infty(\Omega)$, while if $k = 1$, $\chi F \in W^{1,p}(\mathbb{R}^3)$ for all $p \geq 1$ and $\chi \in C_0^\infty(\Omega)$.

Fix $\chi \in C_0^\infty(\Omega)$ and take $\tilde{\chi} \in C_0^\infty(\Omega)$ verifying $\tilde{\chi} \equiv 1$ on $\operatorname{supp}\chi$ and such that there is a strictly positive distance between $\operatorname{supp}\chi$ and $\operatorname{supp}(1-\tilde{\chi})$. We write $\chi F(\mathbf{x}) = \chi F_1(\mathbf{x}) + \chi F_2(\mathbf{x})$ with

$$F_1(\mathbf{x}) = \int_{\mathbb{R}^3} \frac{\tilde{\chi}(\mathbf{y}) f_1(\mathbf{y}) f_2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} \quad \text{and} \quad F_2(\mathbf{x}) = \int_{\mathbb{R}^3} (1-\tilde{\chi}(\mathbf{y})) \frac{f_1(\mathbf{y}) f_2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y}\,.$$

The term χF_2 is clearly in $C^\infty(\mathbb{R}^3)$. For the other term we use Young's inequality: if $f \in L^p(\mathbb{R}^3)$ and $g \in L^q(\mathbb{R}^3)$ then

$$\|f * g\|_r \leq C \|f\|_p \|g\|_q \quad \text{with } 1 + \frac{1}{r} = \frac{1}{p} + \frac{1}{q}\,. \tag{79}$$

Moreover, if $1/p + 1/q = 1$ then $f * g$ is continuous (see [24, Lemma 2.1]). Let $\alpha \in \mathbb{N}_0^3$ with $|\alpha| \leq k$. Then

$$|D^\alpha(\chi F_1)(\mathbf{x})| \leq \sum_{\substack{\beta_1+\beta_2=\alpha,\\ \beta_1,\beta_2\in\mathbb{N}_0^3}} |D^{\beta_1}\chi(\mathbf{x})| \Big| \int_{\mathbb{R}^3} \frac{1}{|\mathbf{x}-\mathbf{y}|} D^{\beta_2}(\tilde{\chi} f_1 f_2)(\mathbf{y}) d\mathbf{y} \Big|\,. \tag{80}$$

If $f_1, f_2 \in H^k(\Omega)$, $k \geq 2$, then $D^{\beta_2}(\tilde{\chi} f_1 f_2) \in L^{5/3}(\mathbb{R}^3)$ for all β_2 as in (80). From (79), (80) and $\tilde{\chi}/|\cdot| \in L^{5/2}(\mathbb{R}^3)$ it follows that $D^\alpha(\chi F_1)$ is continuous and, since α is arbitrary, that $\chi F \in C^k(\mathbb{R}^3)$.

If $f_1, f_2 \in H^1(\Omega)$ then $\partial(\tilde{\chi} f_1 f_2) \in L^{3/2}(\mathbb{R}^3)$ and from (79) we get (only) that $\partial(\chi F) \in L^p(\mathbb{R}^3)$ for all $p \geq 1$. It then follows that $F \in W^{1,p}(\Omega)$ for all $p \geq 1$ and therefore (by the Sobolev imbedding theorem) $F \in C(\Omega)$. $\square$

Lemma 7. *Let, for $Z\alpha < 2/\pi$, h_0 be the self-adjoint operator defined in (9), and let $\Lambda_-(\alpha)$ be the projection onto the pure point spectrum of h_0.*

Then the operator $\Lambda_-(\alpha) h_0 \Lambda_-(\alpha)$ is Hilbert-Schmidt.

Proof. Let $\epsilon > 0$ be such that $Z\alpha(1+\epsilon) \leq 2/\pi(1-\epsilon)$. We are going to prove that there exists a constant $M = M(\epsilon)$ such that

$$h_0 \geq \frac{1}{M + 2\alpha^{-1}} P(-\Delta - \frac{C}{|\cdot|})P\,, \tag{81}$$

with $C = Z\alpha(M + 2\alpha^{-1})(1 + 1/\epsilon)$ and $P = \chi_{[0,M]}(T(\mathbf{p}))$. The claim will then follow from (81) since

$$\operatorname{Tr}\big([h_0]_-\big)^2 \leq \frac{1}{(M+2\alpha^{-1})^2} \operatorname{Tr}\big([-\Delta - \frac{C}{|\cdot|}]_-\big)^2 < \infty\,.$$

The last inequality follows since the eigenvalues of $-\Delta - C/|\cdot|$ are $-C^2/4n^2, n \in \mathbb{N}$, with multiblicity n^2.

We now prove (81). For $\epsilon > 0$ and any projection P (with $P^\perp = \mathbf{1} - P$), we have that

$$\begin{aligned} h_0 &= P h_0 P + P^\perp h_0 P^\perp - P\frac{Z\alpha}{|\cdot|}P^\perp - P^\perp \frac{Z\alpha}{|\cdot|} P \\ &\geq P(h_0 - \frac{1}{\epsilon}\frac{Z\alpha}{|\cdot|})P + P^\perp(h_0 - \epsilon \frac{Z\alpha}{|\cdot|})P^\perp\,. \end{aligned} \tag{82}$$

By a direct computation one sees that there exists a constant $M = M(\epsilon)$ such that $T(\mathbf{p}) \geq M$ implies $T(\mathbf{p}) \geq (1-\epsilon)|\mathbf{p}|$ and $T(\mathbf{p}) \leq M$ implies $T(\mathbf{p}) \geq \frac{1}{M+2\alpha^{-1}}(-\Delta)$. Hence, with this choice of M and $P = \chi_{[0,M]}(T(\mathbf{p}))$, (82) implies that

$$h_0 \geq P\big[\frac{1}{M+2\alpha^{-1}}(-\Delta) - (1+\epsilon^{-1})\frac{Z\alpha}{|\cdot|}\big]P + P^\perp\big[(1-\epsilon)\sqrt{-\Delta} - (1+\epsilon)\frac{Z\alpha}{|\cdot|}\big]P^\perp\,.$$

The inequality (81) follows directly by the choice of ϵ. □

Appendix B. Pseudodifferential operators

In this appendix we collect facts needed from the calculus of pseudodifferential operators (ψdo's) (for references, see e.g. [8] or [21]).

Define the standard (Hörmander) symbol class $S^\mu(\mathbb{R}^n)$, $\mu \in \mathbb{R}$, to be the set of functions $a \in C^\infty(\mathbb{R}^n_x \times \mathbb{R}^n_\xi)$ satisfying

$$\left|\partial_x^\alpha \partial_\xi^\beta a(x,\xi)\right| \le C_{\alpha,\beta}(1+|\xi|^2)^{(\mu-|\beta|)/2} \text{ for all } (x,\xi) \in \mathbb{R}^n_x \times \mathbb{R}^n_\xi \,. \tag{83}$$

Here, $\alpha, \beta \in \mathbb{N}^n$ and $|\alpha| = \alpha_1 + \cdots + \alpha_n$. Furthermore, $S^\mu(\mathbb{R}^n) \subset S^{\mu'}(\mathbb{R}^n)$ for $\mu \le \mu'$. We denote $S^\infty(\mathbb{R}^n) = \cup_{\mu\in\mathbb{R}} S^\mu(\mathbb{R}^n)$ and $S^{-\infty}(\mathbb{R}^n) = \cap_{\mu\in\mathbb{R}} S^\mu(\mathbb{R}^n)$. Finally, note that $ab \in S^{\mu_1+\mu_2}(\mathbb{R}^n)$, $\partial_x^\alpha \partial_\xi^\beta a \in S^{\mu_1-|\beta|}(\mathbb{R}^n)$ when $a \in S^{\mu_1}(\mathbb{R}^n), b \in S^{\mu_2}(\mathbb{R}^n)$.

A symbol $a \in S^\mu(\mathbb{R}^n)$ defines a linear operator $A = \mathrm{Op}(a) \in: \Psi^\mu$ ('pseudodifferential operator of order μ') by

$$[\mathrm{Op}(a)u](x) = (2\pi)^{-n} \int_{\mathbb{R}^n} e^{ix\cdot\xi} a(x,\xi)\hat{u}(\xi)\, d\xi \,, \tag{84}$$

where $\hat{u}$ is the Fourier-transform of u. The operator A is well-defined on the space $\mathcal{S}(\mathbb{R}^n)$ of Schwartz-functions; it extends by duality to $\mathcal{S}'(\mathbb{R}^n)$, the space of tempered distributions. Note that for

$$a(x,\xi) = \sum_{0\le|\alpha|\le\mu} a_\alpha(x)\xi^\alpha \tag{85}$$

(with a_α smooth and with all derivatives bounded, i.e., $a_\alpha \in \mathcal{B}(\mathbb{R}^n)$), $A = \mathrm{Op}(a) \in \Psi^\mu$ is the partial differential operator given by

$$[\mathrm{Op}(a)u](x) = \sum_{0\le|\alpha|\le\mu} a_\alpha(x) D^\alpha u(x) \,. \tag{86}$$

Note also that, with $a = a(x)$ and $b = b(\xi)$,

$$[\mathrm{Op}(a)u](x) = a(x)u(x) \quad\text{and}\quad [\widehat{\mathrm{Op}(b)u}](\xi) = b(\xi)\hat{u}(\xi)\,.$$

If $a \in S^\mu(\mathbb{R}^n)$, then $\mathrm{Op}(a)$, defined this way, maps $H^k(\mathbb{R}^n)$ continuously into $H^{k-\mu}(\mathbb{R}^n)$ for all $k \in \mathbb{R}$. Here, $H^k(\mathbb{R}^n)$ is the Sobolev-space of order k, consisting of $u \in \mathcal{S}'(\mathbb{R}^n)$ for which

$$\|u\|^2_{H^k(\mathbb{R}^n)} := \int_{\mathbb{R}^n} |\hat{u}(\xi)|^2 (1+|\xi|^2)^k \, d\xi \tag{87}$$

is finite; this defines the norm on $H^k(\mathbb{R}^n)$. We denote

$$H^\infty(\mathbb{R}^n) = \bigcap_{k\in\mathbb{R}} H^k(\mathbb{R}^n)\,, \quad H^{-\infty}(\mathbb{R}^n) = \bigcup_{k\in\mathbb{R}} H^k(\mathbb{R}^n)\,.$$

In particular, symbols in $S^0(\mathbb{R}^n)$ define bounded operators on $L^2(\mathbb{R}^n) = H^0(\mathbb{R}^n)$. Furthermore, operators defined by symbols in $S^{-\infty}(\mathbb{R}^n)$ maps any $H^k(\mathbb{R}^n)$ into $H^\infty(\mathbb{R}^n)$; such operators are called 'smoothing'.

We need to compose ψdo's. There exists a composition # of symbols,

$$\# : S^{\mu_1}(\mathbb{R}^n) \times S^{\mu_2}(\mathbb{R}^n) \to S^{\mu_1+\mu_2}(\mathbb{R}^n) \tag{88}$$

$$(a,b) \mapsto a\#b\,, \tag{89}$$

such that $\mathrm{Op}(a)\mathrm{Op}(b) = \mathrm{Op}(a\#b)$. It is given by

$$(a\#b)(x,\xi) = \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n\times\mathbb{R}^n} e^{-iy\cdot\xi} a(x,\xi-\eta) b(x-y,\eta)\, dy d\eta\,. \tag{90}$$

Here, the integral is to be understood as an oscillating integral.

The symbol $a\#b$ has the expansion

$$a\#b \sim \sum_{\alpha} \frac{i^{-|\alpha|}}{\alpha!} (\partial_x^\alpha a)(\partial_\xi^\alpha b)\,. \tag{91}$$

Here, '$\sim$' means that for all $j \in \mathbb{N}$,

$$a\#b - \sum_{|\alpha|<j} \frac{i^{-|\alpha|}}{\alpha!} (\partial_x^\alpha a)(\partial_\xi^\alpha b) \in S^{\mu_1+\mu_2-j}(\mathbb{R}^n) \tag{92}$$

(recall that $(\partial_x^\alpha a)(\partial_\xi^\alpha b) \in S^{\mu_1+\mu_2-|\alpha|}$). One easily sees that the composition is associative.

Proposition 2. *If $a \in S^{m_1}(\mathbb{R}^n)$, $b \in S^{m_2}(\mathbb{R}^n)$ then the symbol associated to $[\mathrm{Op}(a), \mathrm{Op}(b)]$ belongs to $S^{m_1+m_2-1}(\mathbb{R}^n)$.*

In particular, if $\phi_1, \phi_2 \in \mathcal{B}^\infty(\mathbb{R}^n)$ (the smooth functions with bounded derivatives) with $\operatorname{supp}\phi_1 \cap \operatorname{supp}\phi_2 = \emptyset$ and $a \in S^\mu(\mathbb{R}^n)$, $a(x,\xi) = a(\xi)$, then $\phi_1\#a\#\phi_2 \sim 0$, and so, with $A := \mathrm{Op}(a)$,

$$\phi_1 A \phi_2 = \mathrm{Op}(\phi_1)\mathrm{Op}(a)\mathrm{Op}(\phi_2)$$

is smoothing.

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