Unique Solutions to Hartree-Fock Equations for Closed Shell Atoms

Marcel Griesemer and Fabian Hantsch
Universität Stuttgart, Fachbereich Mathematik
70550 Stuttgart, Germany

Abstract

In this paper we study the problem of uniqueness of solutions to the Hartree and Hartree-Fock equations of atoms. We show, for example, that the Hartree-Fock ground state of a closed shell atom is unique provided the atomic number Z is sufficiently large compared to the number N of electrons. More specifically, a two-electron atom with atomic number $Z \geq 35$ has a unique Hartree-Fock ground state given by two orbitals with opposite spins and identical spatial wave functions. This statement is wrong for some $Z > 1$, which exhibits a phase segregation.

1 Introduction

The Hartree-Fock method is widely used in quantum chemistry for approximate electronic structure computations [11]. In the simplest case the state of the electrons is described by a single Slater determinant and one seeks to minimize the energy by variation of the one-electron orbitals. This is done by some self-consistent field algorithm such as the Roothaan, or the level-shift algorithm [5]. While there has been remarkable progress recently in the analysis of convergence properties of these algorithms [5, 4], it is still poorly understood what is actually being approximated. To some extent this is due to our ignorance about the set of critical points of the Hartree-Fock functional: we know that the Hartree-Fock functional for a neutral atom has a minimizer and infinitely many other critical points [16, 17], but uniqueness of the minimizer, e.g., is not known even in cases where it is expected. Neither is it known whether distinct methods for finding critical points lead to distinct critical points. Our goal is to give answers to such questions.

In this paper we establish existence and uniqueness of solutions to the Hartree-Fock equations for positively charged atoms with prescribed filled shells. We consider both restricted and unrestricted Hartree-Fock theory. In the unrestricted case a filled shell refers to a set of qn^2 electrons which means that we take the number of all electrons, N, of the form $N = q\sum_{k=1}^{s} n_k^2$ where $1 \leq n_1 < n_2 \ldots < n_s$ and where q denotes the number of spin states. In the restricted case our notion of a shell is the usual one and hence all values of N that occur in noble gas atoms are admissible. For atoms with partially filled shells our uniqueness results will not hold. Our method is based

on a perturbation argument which exploits the fact that in the limit of large atomic numbers, $Z \to \infty$, the electron-electron interaction energy is negligible compared to the total energy. This forces us to choose Z much larger than N, but thanks to a novel technique for comparing spectral projections, values of Z as small as 35 can be handled in the case of two-electron atoms. Also, we provide an example which shows that $Z > N-1$ is not sufficient for our results to hold in general. As a byproduct of our methods we obtain uniqueness of the minimizer of the N-electron Hartree functional for sufficiently large Z.

The Hartree-Fock equations for an atom with atomic number $Z > 0$ and N electrons are the set of equations

$$\left(-\Delta - \frac{2Z}{|x|}\right)\varphi_i(x) + 2\sum_{k=1}^{N}\int \frac{|\varphi_k(y)|^2\varphi_i(x) - \varphi_k(x)\overline{\varphi_k(y)}\varphi_i(y)}{|x-y|}dy = \varepsilon_i\varphi_i(x) \qquad (1)$$

for N functions $\varphi_1, \ldots, \varphi_N \in L^2(\mathbb{R}^3 \times \{1, \ldots, q\})$ subject to the constraints

$$\int \overline{\varphi_i(x)}\varphi_j(x)dx = \delta_{ij} \qquad (2)$$

and real numbers $\varepsilon_1, \ldots, \varepsilon_N$. Here and henceforth $x, y, \ldots$ denote elements $(\mathbf{x}, s)$ of $\mathbb{R}^3 \times \{1, \ldots, q\}$, $\int dx$ denotes integration with respect to the product of Lebesgue and counting measure, and $|x-y| = |\mathbf{x}-\mathbf{y}|$. Of course $q = 2$ for (spin-1/2) electrons but for later convenience we allow arbitrary $q \in \mathbb{N}$. We have chosen atomic units where $\hbar = 1$, the mass m of the electron equals $1/2$ and the Rydberg energy equals 1.

The following theorem is our main result on critical points of the unrestricted Hartree-Fock functional. An analog result on a restricted Hartree-Fock functional is given in Theorem 4.1.

Theorem 1.1. *Let q, N, s and $n_1, \ldots, n_s$ be positive integers with $1 \le n_1 < n_2 < \ldots < n_s$ and $N = q\sum_{k=1}^{s} n_k^2$. Suppose that*

$$Z > \frac{1}{\Delta_s}(20N + 8\sqrt{2N}), \qquad \Delta_s = n_s^{-2} - (n_s+1)^{-2}. \qquad (3)$$

Then the Hartree-Fock equations (1) *have a solution $\varphi_1, \ldots, \varphi_N$ with*

$$\varepsilon_1, \ldots, \varepsilon_N \in \cup_{k=1}^{s}\big[-Z^2/n_k^2, -Z^2/(n_k+1)^2\big), \qquad (4)$$

and the space spanned by $\varphi_1, \ldots, \varphi_N$ is uniquely determined by condition (4)*. The orbitals φ_i may be chosen in the form*

$$\varphi_{nlm\sigma}(\mathbf{x}, \mu) = \frac{f_{nl}(|\mathbf{x}|)}{|\mathbf{x}|}Y_{lm}(\mathbf{x})\delta_{\sigma,\mu} \qquad (5)$$

where $n \in \{n_1, \ldots, n_s\}$, $0 \le l \le n-1$, $-l \le m \le l$, $\sigma \in \{1, \ldots, q\}$, and each of these quadruples (n, l, m, σ) occurs exactly once.

The Hartree-Fock equations (1) are equivalent to the Euler-Lagrange equations of the Hartree-Fock functional

$$\mathcal{E}^{HF}(\varphi_1,\dots,\varphi_N) = \sum_{k=1}^{N}\int |\nabla\varphi_k(x)|^2 - \frac{2Z}{|x|}|\varphi_k(x)|^2\,dx + 2\sum_{i<k}\int \frac{|\varphi_i(x)|^2|\varphi_k(y)|^2 - \overline{\varphi_i(x)}\varphi_i(y)\varphi_k(x)\overline{\varphi_k(y)}}{|x-y|}dxdy \qquad (6)$$

where $\varphi_1,\dots,\varphi_N \in L^2(\mathbb{R}^3\times\{1,\dots,q\})$ are subject to the constraints (2). In fact, the Euler-Lagrange equations of (6) are equations of the form (1) with $\varepsilon_i\varphi_i$ replaced by the more general term $\sum_{j=1}^{N}\lambda_{ij}\varphi_j$, the coefficients λ_{ij} being Lagrange multipliers. These generalized Hartree-Fock equations, as well as the Hartree-Fock functional and the constraints (2) are invariant with respect to transformations $(\varphi_1,\dots,\varphi_N)\mapsto(\tilde\varphi_1,\dots,\tilde\varphi_N)$ of the form $\tilde\varphi_i = \sum_{j=1}^{N}U_{ij}\varphi_j$ where (U_{ij}) denotes any unitary $N\times N$ matrix. By choosing this matrix to diagonalize the self-adjoint matrix (λ_{ij}), the equations (1) emerge. This also means that the Hartree-Fock functional only depends on the N-dimensional subspace of $L^2(\mathbb{R}^3\times\{1,\dots,q\})$ spanned by $\varphi_1,\dots,\varphi_N$ or on the orthogonal projection

$$P = \sum_{k=1}^{N}|\varphi_k\rangle\langle\varphi_k| \qquad (7)$$

onto this space. As a function of P the Hartree-Fock functional is quadratic and its domain can be extended to a convex set without lowering the minimum [14, 3]. Nevertheless the Hartree-Fock functional is not convex due to the presence of the negative exchange term - the second term in the numerator of (6). The convex functional obtained by dropping the exchange term is called reduced Hartree-Fock functional.

We are now in position to derive Theorem 1.2, below, on the uniqueness of the minimizer of the Hartree-Fock functional (6). Suppose we choose $n_1 = 1, n_2 = 2,\dots$ in Theorem 1.1. Then, by Proposition 2.2, for Z sufficiently large the condition (4) becomes equivalent to the statement that $\varepsilon_1,\dots,\varepsilon_N$ are the lowest N eigenvalues of the Fock operator, which is the linear operator acting on φ_i on the left hand side of (1). This condition on $\varepsilon_1,\dots,\varepsilon_N$ is satisfied for any solution of (1) associated with a minimizer of the Hartree-Fock functional [16]. Hence the Theorem 1.1 implies the following theorem with the exception of the bound on Z.

Theorem 1.2. *Let s, q and N be positive integers with $N = q\sum_{n=1}^{s}n^2$ and suppose that $Z > \Delta_s^{-1}(12N + 4\sqrt{2N} - 4)$ where $\Delta_s = s^{-2} - (s+1)^{-2}$. Then the minimizer of the Hartree-Fock functional is unique in the sense of a unique projection* (7)*. It may be represented by N orbitals $\varphi_1,\dots,\varphi_N$ of the form* (5) *satisfying the Hartree-Fock equations* (1)*. In particular, the density $\sum_{k=1}^{N}|\varphi_k(x)|^2$ is unique and spherically symmetric.*

For $N = q = 2$ and $Z \geq 35$ the Theorem 1.2 says that the Hartree-Fock functional has a unique minimizer given by two one-electron orbitals with opposite spins and equal spatial wave function $\varphi \in L^2(\mathbb{R}^3)$, φ being the unique minimizer of the restricted

Hartree functional $\varphi \mapsto \mathcal{E}^H(\varphi,\varphi)$, where $\mathcal{E}^H$ is defined in (8), below. In particular, if $q = 2$ and $Z \geq 35$ then $\inf \mathcal{E}^{HF}(\varphi_1,\varphi_2) \geq \inf \mathcal{E}^H(\varphi,\varphi)$. This statement is false for $Z < 1.0268$ (see the remark after Theorem 1.3), which proves the necessity of some lower bound on Z other than $Z > N-1$.

The (unrestricted) N-particle Hartree functional $\mathcal{E}^H$ is defined on arbitrary N tuples of functions $\varphi_k \in H^1(\mathbb{R}^3)$ with $\int |\varphi_k(x)|^2 dx = 1$, and it is given by

$$\begin{aligned}\mathcal{E}^H(\varphi_1,\ldots,\varphi_N) = &\sum_{k=1}^N \int |\varphi_k(x)|^2 - \frac{2Z}{|x|}|\varphi_k(x)|^2 dx \\ &+ 2\sum_{i<k} \int \frac{|\varphi_i(x)|^2|\varphi_k(y)|^2}{|x-y|} dxdy. \end{aligned} \tag{8}$$

No orthogonality is assumed on $\varphi_1,\ldots,\varphi_N$. It is well-known that $\mathcal{E}^H$ has a minimizer if $Z > N-1$ and that minimizing orbitals are pointwise positive by a suitable choice of their phase [16]. To establish uniqueness of the minimizer we consider $\mathcal{E}^H$ as a spin-restricted Hartree-Fock functional with $q = N$, the spin-restriction being that $\phi_k(\mathbf{x},s) = \varphi_k(\mathbf{x})\delta_{k,s}$. Then $\mathcal{E}^{HF}(\phi_1,\ldots,\phi_N) = \mathcal{E}^H(\varphi_1,\ldots,\varphi_N)$, and the following theorem, with the exception of the bound on Z, follows from Theorem 1.2 with $q = N$.

Theorem 1.3. *Let $N \in \mathbb{N}$ and suppose that $Z > 3^{-1}(40N + 16\sqrt{2N} - 8)$. Let $\varphi_1,\ldots,\varphi_N$ be any minimizer of the Hartree functional* (8)*. Then up to phases, $\varphi_k = \varphi$ for all k where φ is the unique, positive minimizer of the restricted Hartree functional $\varphi \mapsto \mathcal{E}^H(\varphi,\ldots,\varphi)$.*

N	2	3	4	5	6	7	8	9
Z_c	35	51	66	81	96	111	126	140

Figure 1: The Hartree minimizer is unique for $Z \geq Z_c$.

In general, the minimum of $\mathcal{E}^H$ is strictly below the minimum of the restricted Hartree functional $\mathcal{E}^H(\varphi,\varphi)$. In fact, Ruskai and Stillinger show that for $Z < 1.0268$ and $N = 2$ the restricted Hartree functional is bounded below by -1, while for $Z > 1$ it is straightforward to show that the unrestricted Hartree functional has its minimum below -1 [20]. A similar phenomenon of phase segregation is described in [2] for the two-electron Hartree functional with a confining external potential.

We now briefly sketch our strategy for proving Theorem 1.1. First, we use the well-known fact that N functions $Z^{3/2}\varphi_i(Z\mathbf{x},\sigma)$, $i = 1,\ldots,N$, $\varphi_i \in H^2(\mathbb{R}^3 \times \{1,\ldots,q\})$, form a solution to the Hartree-Fock equations (1) if and only if $\varphi_1,\ldots,\varphi_N$ is a solution to the new set of equations

$$\left(-\Delta - \frac{2}{|x|}\right)\varphi_i(x) + \frac{2}{Z}\sum_{k=1}^N \int \frac{|\varphi_k(y)|^2\varphi_i(x) - \varphi_k(x)\overline{\varphi_k(y)}\varphi_i(y)}{|x-y|} dy = Z^{-2}\varepsilon_i\varphi_i(x). \tag{9}$$

These rescaled Hartree-Fock equations clearly exhibit the perturbative nature of the electron-electron repulsion in the large Z limit. Let H_P denote the rescaled Fock

operator on the left hand side in (9), see (13), the index P being the projection onto $\mathrm{span}\{\varphi_1, \ldots, \varphi_N\}$. For Z sufficiently large, H_P has exactly N eigenvalues, counting multiplicities, near the eigenvalues $-n_k^{-2}$, $k = 1, \ldots, s$, of $-\Delta - 2/|x|$. More precisely, if d is smaller than the gap $n_s^{-2} - (n_s + 1)^{-2}$ and if Z is sufficiently large, then the spectrum of H_P in $\Omega := \cup_{k=1}^{s}[-n_k^{-2}, -n_k^{-2} + d]$ consists of N eigenvalues. The Hartree-Fock equations subject to (4) are therefore equivalent to

$$P = \chi_\Omega\big(H_P\big). \tag{10}$$

Here we use that all shells are filled. By making Z even larger, if necessary, we can achieve that $P \mapsto \chi_\Omega\big(H_P\big)$ becomes a contraction, and hence that (10) has a unique solution. This strategy obviously requires good eigenvalue estimates for H_P and good control of $\chi_\Omega\big(H_P\big) - \chi_\Omega\big(H_Q\big)$ in terms of $P - Q$. Concerning the second point we develop a novel method that yields much better bounds than, e.g., a resolvent integral for $\chi_\Omega\big(H_P\big)$ would give.

Our work was inspired by the paper of Huber and Siedentop on solutions of the Dirac-Fock equations [12]. Using the contraction principle, they solve an equation analog to (10) with the Laplacian replaced by the Dirac operator. We expect that our methods would allow to improve the results in [12]. Minimization problems for semi-bounded Dirac-Fock type functionals are studied in [10], and in the translation invariant case (no external potential) the minimizer is shown to be unique. When an external Coulomb potential is present the method of [10] does not seem to work. For results on absence of a Hartree-Fock minimizer see [15, 21]. Existence and uniqueness of radial solutions to Hartree equations are derived in [19]. Uniqueness results concerning Hartree equations with *attractive* Coulomb interactions are established, e.g., in [13, 1]. Several of the aforementioned results have been extended to pseudo-relativistic Hartree-Fock functionals and to Hartree-Fock functionals including a magnetic field [6, 7, 9, 8]. Last but not least we should mention the fundamental paper of Bach on the accuracy of the Hartree-Fock approximation to the quantum mechanical ground state energy [3].

This paper is organized as follows. In Section 2 we introduce all notations and we prove eigenvalue bounds for Fock operators. Section 3 contains the proofs of all theorem in this introduction. In Section 4 we establish a theorem analog to Theorem 1.1 in restricted HF-theory. Here, for proving existence of solutions we use the Schauder-Tychonoff theorem, which does not require as large values of Z as the contraction property does.

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2 Notations and Eigenvalue Estimates

In this section we collect the operator- and eigenvalue estimates needed in later sections. We also introduce the definitions and notations used throughout the paper.

The sets of bounded linear operators, of Hilbert-Schmidt operators, and of trace class operators in a separable Hilbert space $\mathcal{H}$ are denoted by $\mathcal{L}(\mathcal{H})$, $\mathcal{T}_2(\mathcal{H})$ and $\mathcal{T}_1(\mathcal{H})$, respectively. The corresponding norms are $\|\cdot\|$, $\|\cdot\|_2$, and $\|\cdot\|_1$. Recall that $\mathcal{T}_1(\mathcal{H}) \subset \mathcal{T}_2(\mathcal{H}) \subset \mathcal{L}(\mathcal{H})$ and that $\|K\| \leq \|K\|_2 \leq \|K\|_1$ for all $K \in \mathcal{T}_1(\mathcal{H})$. Let

$$S_{N,q} := \Big\{ P \in \mathcal{T}_1(L^2(\mathbb{R}^3 \times \{1,\dots,q\})) \Big| \, 0 \leq P \leq 1, \ \mathrm{tr}\, P = N \Big\}.$$

The only reason for working with $S_{N,q}$ rather than with the set of self-adjoint projections of rank N, is that we need $S_{N,q}$ to be convex in Section 4.

For each $P \in S_{N,q}$ there is a unique square-integrable kernel $\tau = \tau_P$ such that $P\varphi(x) = \int \tau(x,y)\varphi(y)dy$ and there is a unique way to associate a density $\rho = \rho_P \in L^1$ with P, see Lemma 5.1. If $P = \sum_n \lambda_n |\varphi_n\rangle\langle\varphi_n|$, then

$$\tau(x,y) = \sum_{n\geq 0} \lambda_n \varphi_n(x)\overline{\varphi_n(y)}, \tag{11}$$

$$\rho(x) = \sum_{n\geq 0} \lambda_n |\varphi_n(x)|^2. \tag{12}$$

For given $P \in S_{N,q}$ we define a Fock operator H_P in $L^2(\mathbb{R}^3 \times \{1,\dots,q\})$ by

$$H_P = -\Delta - V + \frac{1}{Z}(U_P - K_P), \tag{13}$$

where V, U_P are the multiplication operators associated with the real-valued functions $V(x) = 2/|x|$ and $U_P = \rho * V$, and for $\psi \in H^2$,

$$(K_P\psi)(x) := \int V(x-y)\tau(x,y)\psi(y)\, dy.$$

From the fact that V has a positive Fourier transform it is easy to see, using (11), that $K_P \geq 0$, and $U_P - K_P \geq 0$ by a straightforward computation. Hence $H_P \geq -\Delta - V \geq -1$. Moreover, by the Kato-Rellich theorem, H_P is self-adjoint on the Sobolev space $H^2(\mathbb{R}^3 \times \{1,\dots,q\})$.

By remarks in the introduction we may consider $\mathcal{E}^{HF}$ as a function on $S_{N,q} \cap \{P^2 = P\}$ given by $\mathcal{E}^{HF}(P) = \mathcal{E}^{HF}(\varphi_1,\dots,\varphi_N)$ where $(\varphi_1,\dots,\varphi_N)$ is any orthonormal basis of Ran$P$. Explicitely,

$$\mathcal{E}^{HF}(P) = \mathrm{tr}\left[(-\Delta - V)P\right] + \frac{1}{2Z}\int \big(\rho(x)\rho(y) - |P(x,y)|^2\big)V(x-y)\, dxdy.$$

Lemma 2.1. *Let $P \in S_{N,q}$. Then for all $\varepsilon > 0$*

(i) $V \leq -\varepsilon\Delta + \varepsilon^{-1}$,

(ii) $U_P \leq N\left(-\varepsilon\Delta + \varepsilon^{-1}\right)$,

(iii) $\frac{1}{Z}U_P \leq \varepsilon\,(-\Delta - V) + \frac{1}{\varepsilon}\left(\varepsilon + \frac{N}{Z}\right)^2$,

(iv) $-\Delta \leq \frac{1}{1-\varepsilon}H_P + \frac{1}{\varepsilon(1-\varepsilon)}$ *if* $\varepsilon \in (0,1)$.

Proof. Statement (i) follows from $-\Delta - V \geq -1$ and from the scaling properties of $-\Delta$ and V with respect to the unitary transformation $\varphi(\mathbf{x},\sigma) \mapsto \varepsilon^{-3/2}\varphi(\mathbf{x}/\varepsilon,\sigma)$. Statement (ii) follows from $U_P = \rho * V$, from (i) and from $\int \rho(x)dx = N$.

To prove (iii), fix $\varepsilon > 0$. By (i) and (ii),

$$\varepsilon V + \frac{1}{Z}U_P \leq \left(\varepsilon + \frac{N}{Z}\right)\left(-\delta\Delta + \delta^{-1}\right)$$

for all $\delta > 0$. Upon subtracting εV from both sides and making the choice $\delta\left(\varepsilon + \frac{N}{Z}\right) = \varepsilon$ for δ, the desired estimate follows. Inequality (iv) follows from $-\Delta \leq H_P + V$ and from (i). □

Proposition 2.2. *Given $N \in \mathbb{N}$, $Z > 0$ and $P \in S_{N,q}$, let E_n^∞ and E_n^Z denote the n-th eigenvalue, counting multiplicities, of the Schrödinger operator $-\Delta - V$ and the Hartree-Fock operator H_P, respectively. Then:*

(a) For all $n \in \mathbb{N}$, $E_n^\infty \leq E_n^Z$ and

$$E_n^Z \leq E_n^\infty + 2\frac{N}{Z} + 2\frac{N}{Z}\sqrt{E_n^\infty + 1}.$$

(b) If P minimizes the Hartree-Fock functional, then E_N^Z obeys the following estimate:

$$E_N^Z \leq E_N^\infty + 2\frac{N-1}{Z} + 2\frac{N-1}{Z}\sqrt{E_N^\infty + 1}.$$

Proof. From $U_P - K_P \geq 0$, $K_P \geq 0$ and Lemma 2.1 (iii) we see that

$$-\Delta - V \leq H_P \leq -\Delta - V + \frac{1}{Z}U_P \leq (1+\varepsilon)\,(-\Delta - V) + \frac{1}{\varepsilon}\left(\varepsilon + \frac{N}{Z}\right)^2$$

for all $\varepsilon > 0$. By the min-max principle, this implies that

$$E_n^\infty \leq E_n^Z \leq (1+\varepsilon)\,E_n^\infty + \frac{1}{\varepsilon}\left(\varepsilon + \frac{N}{Z}\right)^2.$$

Optimizing with respect to ε yields the desired estimates of part (a).

To prove (b) let $\varphi_1, \ldots, \varphi_N$ be an orthonormal basis of $\mathrm{Ran}P$ with $H_P\varphi_k = E_k^Z\varphi_k$. Then the Hartree-Fock functional can be decomposed as

$$\begin{aligned}\mathcal{E}^{HF}(\varphi_1,\ldots,\varphi_N) &= \mathcal{E}_{N-1}^{HF}(\varphi_1,\ldots,\varphi_{N-1}) + \langle\varphi_N, H_{P,N-1}\varphi_N\rangle \\ &= \mathcal{E}_{N-1}^{HF}(\varphi_1,\ldots,\varphi_{N-1}) + E_N^Z,\end{aligned}$$

where $\mathcal{E}^{HF}_{N-1}$ and $H_{P,N-1}$ denote the Hartree-Fock functional and Fock operator belonging to the $(N-1)$-particle integral kernel $\tau_{N-1}(x,y) = \sum_{k=1}^{N-1} \varphi_k(x)\overline{\varphi_k(y)}$. Since $\psi \mapsto \mathcal{E}^{HF}(\varphi_1, \ldots, \varphi_{N-1}, \psi)$ is minimized by φ_N,

$$E_N^Z = \inf_{\substack{\psi \in D(H_{P,N-1});\ \|\psi\|=1 \\ \psi \in \mathrm{span}\{\varphi_1,\ldots,\varphi_{N-1}\}^\perp}} \langle \psi, H_{P,N-1}\psi \rangle.$$

Thus, using the min-max principle again, E_N^Z is bounded from above by the N-th eigenvalue of $H_{P,N-1}$. Part (a) applied to $H_{P,N-1}$ completes the proof of (b). □

3 Solving the Hartree-Fock Equations

This section contains the proofs of all the theorems given in the introduction. For restricted Hartree-Fock theory see the next section. Our main tool is the following abstract result comparing the spectral projections $\chi_\Omega(A)$ and $\chi_\Omega(B)$ of two self-adjoint operators A and B.

Proposition 3.1. *Let $A, B : D \subset \mathcal{H} \to \mathcal{H}$ be self-adjoint operators and let $\Omega \subset \mathbb{R}$ be a bounded Borel set for which the spectra of A and B satisfy the gap conditions*

$$\begin{aligned} \mathrm{dist}(\sigma(A) \cap \Omega, \sigma(B) \setminus \Omega) \geq \delta, \\ \mathrm{dist}(\sigma(B) \cap \Omega, \sigma(A) \setminus \Omega) \geq \delta, \end{aligned} \tag{14}$$

for some $\delta > 0$. Suppose A and B have only point spectrum in Ω. Then

$$\|\chi_\Omega(A) - \chi_\Omega(B)\|_2 \leq \delta^{-1} \left(\|(A-B)\chi_\Omega(A)\|_2^2 + \|(A-B)\chi_\Omega(B)\|_2^2 \right)^{1/2}.$$

Proof. We only prove the proposition in the case where $\chi_\Omega(A)$ and $\chi_\Omega(B)$ are finite rank projections. The more general case of infinite point spectrum in Ω is left as an exercise for the reader. Let $\chi(A) := \chi_\Omega(A)$ and $\chi(B) := \chi_\Omega(B)$ for short. Then $\chi(A)^2 = \chi(A) = \chi(A)^*$ and similarly for $\chi(B)$. It follows that

$$\begin{aligned} \|\chi(A) - \chi(B)\|_2^2 = &\,\mathrm{tr}(\chi(A)(1-\chi(B))\chi(A)) \\ &+ \mathrm{tr}(\chi(B)(1-\chi(A))\chi(B)) \end{aligned} \tag{15}$$

where we also used the cyclicity of the trace. To estimate the first term on the right hand side of (15) we choose an orthonormal basis $(\varphi_k)_{k=1}^n$ of $\chi(A)$ consisting of eigenfunctions of A:

$$A\varphi_k = \varepsilon_k \varphi_k, \quad \varepsilon_k \in \sigma(A) \cap \Omega,\ k = 1, \ldots, n.$$

By the gap assumption (14), $|\lambda - \varepsilon_k| \geq \delta$ for $\lambda \in \sigma(B) \setminus \Omega$ and hence, by the spectral theorem,

$$\frac{1}{\delta}|B - \varepsilon_k| \geq 1 - \chi_\Omega(B), \quad k = 1, \ldots, n.$$

We conclude that

$$\begin{aligned}\mathrm{tr}(\chi(A)(1-\chi(B))\chi(A)) &= \sum_{k=1}^{n}\langle\varphi_k,(1-\chi(B))\varphi_k\rangle \\ &\leq \delta^{-2}\sum_{k=1}^{n}\big\langle\varphi_k,(B-\varepsilon_k)^2\varphi_k\big\rangle \\ &= \delta^{-2}\sum_{k=1}^{n}\big\langle\varphi_k,(B-A)^2\varphi_k\big\rangle \\ &= \delta^{-2}\|(A-B)\chi(A)\|_2^2. \qquad (16)\end{aligned}$$

The proposition follows from (15), (16) and from an estimate similar to (16) with A and B interchanged. □

Lemma 3.2. *For all $\varphi\in H^1(\mathbb{R}^3\times\{1,\dots,q\})$ and $P,Q\in S_{N,q}$*

(i) $\|(U_P-U_Q)\varphi\|\leq 4\|P-Q\|_1\|\nabla\varphi\|$

(ii) $\|(K_P-K_Q)\varphi\|\leq 4\|P-Q\|_2\|\nabla\varphi\|$.

Proof. For all $\psi\in L^2(\mathbb{R}^3\times\{1,\dots,q\})$

$$\begin{aligned}|\langle\psi,(U_P-U_Q)\varphi\rangle| &\leq 2\int dy|\rho_P(y)-\rho_Q(y)|\int|\psi(x)|\frac{|\varphi(x)|}{|x-y|}\,dx \\ &\leq 4\int dy|\rho_P(y)-\rho_Q(y)|\|\psi\|\|\nabla\varphi\| \\ &\leq 4\|P-Q\|_1\|\psi\|\|\nabla\varphi\|\end{aligned}$$

by Cauchy-Schwarz, the uncertainty principle lemma [18, section X.2] and by Lemma 5.1. This proves (i). The proof of (ii) is similar. □

Proposition 3.3. *Let $P,Q\in S_{N,q}\cap\{P^2=P\}$ and let $\Omega\subset(-\infty,0)$ be a bounded Borel set such that* $\mathrm{dist}(\Omega,\sigma(H_P)\setminus\Omega)\geq\delta$ *and* $\mathrm{dist}(\Omega,\sigma(H_Q)\setminus\Omega)\geq\delta$ *for some $\delta>0$. Suppose moreover that* $\mathrm{tr}(\chi_\Omega(H_P))=N=\mathrm{tr}(\chi_\Omega(H_Q))$. *Then*

$$\begin{aligned}&\|\chi_\Omega(H_P)-\chi_\Omega(H_Q)\|_2 \\ &\quad\leq\frac{4}{\delta Z}\left(1+\sqrt{2N}\right)\left(\left\|\sqrt{-\Delta}\chi_\Omega(H_P)\right\|_2^2+\left\|\sqrt{-\Delta}\chi_\Omega(H_Q)\right\|_2^2\right)^{1/2}\|P-Q\|_2 \\ &\quad\leq\frac{8}{\delta Z}\left(1+\sqrt{2N}\right)\sqrt{2N}\|P-Q\|_2.\end{aligned}$$

The factor 8 in the last line may be replaced by 4 if both P and Q satisfy the Hartree-Fock equation (10). *It may be replaced by $4\sqrt{2.5}$ if P or Q satisfies* (10).

Remark. The set $S_{N,q}\cap\{P^2=P\}$ is a closed subset of the Hilbert-Schmidt operators on $L^2(\mathbb{R}^3\times\{1,\dots,q\})$ and hence it is complete with respect to the metric $d(P,\tilde{P})=\|P-\tilde{P}\|_2$.

Proof. Applying Proposition 3.1 to H_P and H_Q we see that we need to estimate $\|(H_P - H_Q)\chi_\Omega(H_P)\|_2$ and the same expression with P and Q interchanged. By definition of H_P and H_Q,

$$H_P - H_Q = Z^{-1}(U_P - U_Q) - Z^{-1}(K_P - K_Q)$$

and by Lemma 3.2,

$$\begin{aligned}\|(U_P - U_Q)\chi_\Omega(H_P)\|_2 &\leq 4\|P-Q\|_1 \big\|\sqrt{-\Delta}\chi_\Omega(H_P)\big\|_2 \\ \|(K_P - K_Q)\chi_\Omega(H_P)\|_2 &\leq 4\|P-Q\|_2 \big\|\sqrt{-\Delta}\chi_\Omega(H_P)\big\|_2.\end{aligned}$$

The first inequality of the theorem now follows from $\|P-Q\|_1 \leq \sqrt{2N}\|P-Q\|_2$. Here we use that P and Q have rank N. From Lemma 2.1 (iv) with $\varepsilon = 1/2$ we see that $-\Delta \leq 2H_P + 4$. Therefore

$$\begin{aligned}\big\|\sqrt{-\Delta}\chi_\Omega(H_P)\big\|_2^2 &= \operatorname{tr}\left(\chi_\Omega(H_P)(-\Delta)\chi_\Omega(H_P)\right) \\ &\leq 4\operatorname{tr}\chi_\Omega(H_P) = 4N.\end{aligned}$$

If P solves the Hartree-Fock equation then $\big\|\sqrt{-\Delta}\chi_\Omega(H_P)\big\|_2^2 = |\mathcal{E}^{HF}(P)| \leq N$ by the virial theorem and because $-\Delta - V \geq -1$. □

For each $R \in \mathrm{SO}(3)$ we define a unitary operator $U(R)$ in $L^2(\mathbb{R}^3)$ by

$$[U(R)\psi](x) := \psi(R^{-1}x). \tag{17}$$

The following theorem describes the content of Theorem 1.1 in terms of rank N projections.

Theorem 3.4. *Under the assumptions of Theorem 1.1 the Hartree-Fock equation* (10) *has a unique solution $P \in S_{N,q}$ with the property that $Z^2\sigma(H_P\restriction P\mathcal{H})$ is given by* (4). *This P is of the form $P = P' \otimes 1$ with respect to $L^2(\mathbb{R}^3) \otimes \mathbb{C}^q$ where $P' \in S_{N/q,1}$ and moreover $P' = U(R)P'U(R)^*$ for all $R \in SO(3)$.*

Proof. We first prove existence and uniqueness of P using Proposition 3.3 with

$$\Omega := \bigcup_{k=1}^{s} \left[-n_k^{-2}, -n_k^{-2} + \frac{4N}{Z}\right].$$

By Proposition 2.2, for Z large enough and all $P \in S_{N,q}$

$$\operatorname{dist}(\Omega, \sigma(H_P) \setminus \Omega) \geq n_s^{-2} - (n_s+1)^{-2} - \frac{4N}{Z} =: \delta,$$

$\delta > 0$, and $\operatorname{tr}\chi_\Omega(H_P) = N$. Hence the Proposition 3.3, the remark thereafter, and the contraction principle imply that the equation $P = \chi_\Omega(H_P)$ has a unique solution P provided that

$$\frac{8}{Z}\left(1 + \sqrt{2N}\right)\sqrt{2N} < \delta. \tag{18}$$

This is satisfied for Z obeying (3).

We next show that P is of the form $P' \otimes 1$ in $L^2(\mathbb{R}^3) \otimes \mathbb{C}^q$ where $P' \in S_{N/q,1}$. To this end we consider the modified Hartree-Fock equation

$$P' = \chi_\Omega(H^{(q)}_{P'}) \tag{19}$$

where

$$H^{(q)}_{P'} := -\Delta - V + \frac{q}{Z} U_{P'} - \frac{1}{Z} K_{P'}$$

in $L^2(\mathbb{R}^3)$. The eigenvalues of $H^{(q)}_{P'}$ satisfy the estimate given by Proposition 2.2 a). Therefore, the arguments above show that (19) has a unique solution P' because (18) holds by assumption (3). From $H_{P' \otimes 1} = H^{(q)}_{P'} \otimes 1$ and (19) it follows that $P' \otimes 1$ solves the Hartree-Fock equation (10). Hence, $P = P' \otimes 1$ by the uniqueness of the solution to (10).

Finally we prove that P' commutes with $U(R)$. From the spherical symmetry of V it follows that $U(R) H^{(q)}_{P'} U(R)^* = H^{(q)}_{P'(R)}$ where $P'(R) = U(R) P' U(R)^*$. Using (19), we conclude that

$$P'(R) = U(R) \chi_\Omega(H^{(q)}_{P'}) U(R)^* = \chi_\Omega\Big(U(R) H^{(q)}_{P'} U(R)^*\Big) = \chi_\Omega\Big(H^{(q)}_{P'(R)}\Big)$$

which implies $P'(R) = P'$ because the solution to (19) is unique. □

Proof of Theorem 1.1. Theorem 3.4 tells us that $P = P' \otimes 1$ where P' commutes with all rotations. Moreover, $H_P = H^{(q)}_{P'} \otimes 1$, $P' = \chi_\Omega(H^{(q)}_{P'})$ and $H^{(q)}_{P'}$ commutes with all rotations as well. Let $\varepsilon_k \in \Omega$ be an eigenvalue of $H^{(q)}_{P'}$. The eigenspace associated with ε_k carries a representation of $SO(3)$ given by (17). Its irreducible subspaces are spanned by functions of the form

$$|\mathbf{x}|^{-1} f(|\mathbf{x}|) Y_{lm}(\mathbf{x}), \qquad f \in L^2(\mathbb{R}_+), \tag{20}$$

where Y_{lm} denotes a spherical harmonic. Now fix l and m and let $\mathcal{H}_{lm}$ denote the space of all functions of the form (20) with arbitrary f. This space is reducing for both $-\Delta - V$ and $H^{(q)}_{P'}$. Since the spectrum of $(-\Delta - V) \restriction \mathcal{H}_{lm}$ in $(-\infty, 0)$ consists of the simple eigenvalues $-1/n^2$, $n \geq l+1$, it follows from Proposition 2.2 and from the assumption on Z that $H^{(q)}_{P'} \restriction \mathcal{H}_{lm}$ has exactly one eigenvalue in each of the intervals $[-n_k^{-2}, -(n_k+1)^{-2})$ with $n_k \geq l+1$. This completes the proof of Theorem 1.1. □

Proof of Theorem 1.2. For $Z > N-1$ the Hartree-Fock functional is known to have a minimizer and any minimizer P is the spectral projection onto the spectral subspace of H_P associated with the lowest N eigenvalues [16]. If $N = q \sum_{n=1}^{s} n^2$ for some s, then, by Proposition 2.2 the lowest N eigenvalues of H_P belong to $[-1, -(s+1)^{-2})$ provided that $4(N-1)/Z < s^{-2} - (s+1)^{-2}$. Thus for sufficiently large Z Theorem 1.1 implies uniqueness of the minimizer of the Hartree-Fock functional as well as the assertions on the one-particle orbitals. The bound on Z is obtained by inspection of the proof of Theorem 1.1 keeping in mind that P is a minimizer which is given. Hence the improved bounds from Proposition 2.2 and Proposition 3.3 are available. □

Proof of Theorem 1.3. Given $\varphi_1, \dots, \varphi_N \in H^1(\mathbb{R}^3)$ with $\int |\varphi_k(x)|^2\, dx = 1$ let $\Phi_1, \dots, \Phi_N \in H^1(\mathbb{R}^3 \times \{1, \dots, N\})$ be defined by

$$\Phi_k(\mathbf{x}, s) := \varphi_k(\mathbf{x})\delta_{ks}, \quad k = 1, \dots, N. \tag{21}$$

Then $\Phi_1, \dots, \Phi_N$ are orthonormal in $L^2(\mathbb{R}^3 \times \{1, \dots, N\})$ and

$$\mathcal{E}^{HF}(\Phi_1, \dots, \Phi_N) = \mathcal{E}^H(\varphi_1, \dots, \varphi_N) \tag{22}$$

by the definitions of $\mathcal{E}^{HF}$ and $\mathcal{E}^H$. By (22), the minimization problem for $\mathcal{E}^H$ is equivalent to the minimization problem for $\mathcal{E}^{HF}$ with $q = N$ in the restricted class of orbitals of the form (21). By Theorem 1.2, the (unrestricted) Hartree-Fock functional for $q = N$ and Z sufficiently large has a unique minimizer $P \in S_{N,N}$, which is of the form $P = P' \otimes 1$ with respect to $L^2(\mathbb{R}^3 \times \{1, \dots, N\}) = L^2(\mathbb{R}^3) \otimes \mathbb{C}^N$. P' here is a rank one projection that commutes with rotations. Hence $(P'\psi) = \varphi\langle\varphi, \psi\rangle$ with a spherically symmetric function φ. It follows that $\mathcal{E}^{HF}(P) = \mathcal{E}^H(\varphi, \dots, \varphi)$. It remains to determine the condition on Z for uniqueness of the Hartree-Fock minimizer in the present case where $q = N$. To this end we use the improved eigenvalue estimate from Proposition 2.2 b). The gap condition becomes

$$\delta := \frac{3}{4} - 2\frac{N-1}{Z} > 0 \tag{23}$$

and the contraction condition reads

$$\frac{4}{Z}\left(1 + \sqrt{2N}\right)\sqrt{2N} < \delta. \tag{24}$$

Both, (23) and (24) are satisfied if

$$Z > \frac{40}{3}N + \frac{16}{3}\sqrt{2N} - \frac{8}{3}.$$

□

Corollary 3.5. *Under the assumptions of Theorem 3.4 let P_Z be the unique solution provided by this theorem. Then*

$$\lim_{Z\to\infty} P_Z = \sum_{k=1}^{s} \chi_{\{-n_k^{-2}\}}(-\Delta - V). \tag{25}$$

Proof. Let P_∞ denote the right hand side of (25). A copy of the proof of Proposition 3.3 with $P = P_Z$ and H_Q replaced by $H_\infty = -\Delta - V$ shows that

$$\|P_Z - P_\infty\|_2 \leq \frac{4}{\delta Z}\left(1 + \sqrt{2N}\right)\sqrt{2N}\|P_Z\|_2 = \frac{4\sqrt{2}}{\delta}\frac{N}{Z}\left(1 + \sqrt{2N}\right) \to 0 \quad (Z \to \infty).$$

Here, by Proposition 2.2, δ can be chosen independently of Z for Z sufficiently large. □

4 Restricted Hartree-Fock Theory

In this section the Hartree-Fock functional is restricted to one-particle orbitals of the special form (5). This will allow for all the electron configurations found in noble gas atoms. In this section we set $q = 1$ to simplify the presentation.

By a shell index we mean a pair of integers (n, ℓ) with $n \geq 1$ and $0 \leq \ell \leq n-1$.

Theorem 4.1. *Let $(n_1, \ell_1), \ldots, (n_s, \ell_s)$ be given, pairwise distinct shell indices with $n_1 \leq n_2 \leq \ldots \leq n_s$. Suppose $N = \sum_{j=1}^{s}(2\ell_j + 1)$ and let $\Delta_s := n_s^{-2} - (n_s + 1)^{-2}$.*

(i) If $Z > 4N/\Delta_s$ then there exist normalized functions $f_1, \ldots, f_s \in L^2(\mathbb{R}_+)$ such that the N functions

$$\varphi_{jm}(x) := \frac{1}{|x|} f_j(|x|) Y_{\ell_j m}(x), \qquad j = 1, \ldots, s,\ m = -\ell_j \ldots \ell_j,$$

solve the Hartree-Fock equations (1) with eigenvalues ε_j satisfying

$$-\frac{1}{n_j^2} \leq \varepsilon_j \leq -\frac{1}{n_j^2} + \frac{4N}{Z}. \tag{26}$$

(ii) If Z satisfies (3) then the functions f_j in (i) are unique up to global phases.

Remark: A result similar to part (i) of this theorem with the weaker assumption $Z \geq N$ is described in Section III.3 of [17]. However, Lions' argument is based on the unproven assertion that all eigenvalues of a radial Hartree-Fock operator are simple.

To prove Theorem 4.1 we solve the fixed point equation

$$P = F(P) := \sum_{j=1}^{s} \chi_{\Omega_j}(H_P)\pi_{\ell_j} \tag{27}$$

where π_ℓ denotes the orthogonal projection associated with the eigenvalue $\ell(\ell+1)$ of the square of the total angular momentum operator, and

$$\Omega_j := \Big[-\frac{1}{n_j^2}, -\frac{1}{n_j^2} + \frac{4N}{Z} \Big].$$

The spherical symmetry will be imposed by restricting F to the subset

$$S_N^{sym} := \big\{ P \in S_{N,1} \big| U(R) P U(R)^* = P, \text{ for all } R \in SO(3) \big\}$$

of $S_{N,1}$. To find a solution of (27) we use the Schauder-Tychonoff theorem. Its uniqueness will follow from the contraction principle.

Lemma 4.2. *Suppose the hypotheses of Theorem 4.1 are satisfied and that $\delta := \Delta_s - 4N/Z > 0$. Then $F(S_N^{sym}) \subset S_N^{sym}$ and for all $P, Q \in S_N^{sym}$,*

$$\|F(P) - F(Q)\|_1 \leq 32 \frac{N}{\delta Z} \|P - Q\|_1. \tag{28}$$

If $P, Q \in S_N^{sym} \cap \{P^2 = P\}$ then

$$\|F(P) - F(Q)\|_2 \leq \frac{8}{\delta Z} \sqrt{2N}(1 + \sqrt{2N}) \|P - Q\|_2. \tag{29}$$

Remark. The Lipshitz constant in (29) agrees with the one in Proposition 3.3.

Proof. We first show that $F(S_N^{sym}) \subset S_N^{sym}$. For $P \in S_N^{sym}$, the Fock operator H_P commutes with all rotations $U(R)$ and hence so does its spectral projection $\chi_{\Omega_j}(H_P)$. It follows that $F_j(P) := \chi_{\Omega_j}(H_P)\pi_{\ell_j} = \pi_{\ell_j}\chi_{\Omega_j}(H_P)$ is an orthogonal projection and that

$$F_j(P)F_k(P) = \delta_{jk}F_j(P) \tag{30}$$

because $(n_j, \ell_j) \neq (n_k, \ell_k)$ for $j \neq k$. Hence $F(P) = \sum_{j=1}^s F_j(P)$ is an orthogonal projection that commutes with all rotations. As for the trace of $F(P)$, we note that $H_P \restriction \pi_{\ell_j}\mathcal{H}$ has exactly $2\ell_j + 1$ eigenvalues in Ω_j, counted with multiplicities. This shows that $\operatorname{tr} F(P) = \sum_{j=1}^s \operatorname{tr} F_j(P) = \sum_{j=1}^s (2\ell_j + 1) = N$.

By inspection of the proof of Proposition 3.1, using (30) we see that

$$\|F(P) - F(Q)\|_2^2 = \operatorname{tr} F(P)(1 - F(Q))F(P) + \operatorname{tr} F(Q)(1 - F(P))F(Q) \tag{31}$$

where

$$\begin{aligned} \operatorname{tr} F(P)(1 - F(Q))F(P) &= \sum_{j=1}^s \operatorname{tr} F_j(P)(1 - F(Q))F_j(P) \\ &\leq \delta^{-2} \sum_{j=1}^s \|(H_P - H_Q)F_j(P)\|_2^2. \end{aligned} \tag{32}$$

Here it is important that H_P and H_Q are considered as operators on $\pi_{\ell_j} L^2(\mathbb{R}^3)$, which have $2\ell_j + 1$ eigenvalues in Ω_j separated by a gap of size δ from the rest of the spectrum. To bound $\|(H_P - H_Q)F_j(P)\|_2$ we use estimates from the proof of Proposition 3.3 as well as $\|P - Q\|_2 \leq \|P - Q\|_1$. We find

$$\|(H_P - H_Q)F_j(P)\|_2 \leq \frac{16}{Z}\sqrt{2\ell_j + 1}\|P - Q\|_1. \tag{33}$$

The proof of (28) is now completed by combining (31), (32), (33) with

$$\|F(P) - F(Q)\|_1 \leq \sqrt{2N}\|F(P) - F(Q)\|_2 \tag{34}$$

and with estimates similar to (32), (33) where the roles of P and Q are interchanged. (34) follows from the fact that $F(P)$ and $F(Q)$ have rank N. For proving (29) we use $\|P - Q\|_1 \leq \sqrt{2N}\|P - Q\|_2$ instead of (34). The rest is similar to the proof of (28). □

Proof of Theorem 4.1. To prove (i) we check that the map $F : S_N^{sym} \to S_N^{sym}$ satisfies the hypotheses of the Schauder-Tychonoff theorem. By construction, S_N^{sym} is convex and closed in $\mathcal{T}_1(L^2(\mathbb{R}^3))$, and $F : S_N^{sym} \to S_N^{sym}$ is continuous by Lemma 4.2. To prove compactness of the map F let (P_n) be any sequence in S_N^{sym}. Then $F(P_n)$ may be written in the form

$$F(P_n) = \sum_{k=1}^N |\varphi_k^{(n)}\rangle\langle\varphi_k^{(n)}|, \qquad H_{P_n}\varphi_k^{(n)} = \varepsilon_k^{(n)}\varphi_k^{(n)}$$

with eigenvalues $\varepsilon_k^{(n)} < -(n_s+1)^{-2}$ for all k, n. By Lemma 2.1, the sequences $(\varphi_k^{(n)})_n$ are bounded in $H^1(\mathbb{R}^3)$. We may assume they are weakly convergent in H^1 and hence locally convergent after passing to a subsequence of (P_n). Hence $F(P_n)$ will be convergent provided that $\varphi_k^{(n)}(x) \to 0$ as $|x| \to \infty$ uniformly in n. To prove this uniform decay we pick a function $\chi \in C^\infty(\mathbb{R}; [0,1])$ with $\chi(t) = 0$ for $t \leq 1$ and $\chi(t) = 1$ for $t \geq 2$. Let $\chi_R(x) = \chi(|x|/R)$ for $R > 0$. The IMS-formula tells us that

$$2\chi_R(H_{P_n} - \varepsilon_k^{(n)})\chi_R = \chi_R^2(H_{P_n} - \varepsilon_k^{(n)}) + (H_{P_n} - \varepsilon_k^{(n)})\chi_R^2 - [[H_{P_n}, \chi_R], \chi_R],$$

where $[[H_{P_n}, \chi_R], \chi_R] = 2|\nabla\chi_R|^2 - Z^{-1}[[K_{P_n}, \chi_R], \chi_R]$ and

$$\chi_R(H_{P_n} - \varepsilon_k^{(n)})\chi_R \geq (-2R^{-1} - \varepsilon_k^{(n)})\chi_R^2 \geq c\chi_R^2$$

for some $c > 0$ if $R \geq R_0$ and R_0 is large enough. It follows that

$$\begin{aligned} c\|\chi_R\varphi_k^{(n)}\|^2 &\leq \frac{1}{2Z}\left|\left\langle \varphi_k^{(n)}, [\chi_R, [\chi_R, K_{P_n}]]\varphi_k^{(n)}\right\rangle\right| + O(R^{-2}) \\ &= O(R^{-1}), \qquad (R \to \infty), \end{aligned}$$

uniformly in n. In the last step we expanded the double commutator, we used $|\tau^{(n)}(x,y)| \leq \rho^{(n)}(x)^{1/2}\rho^{(n)}(y)^{1/2}$, Cauchy-Schwarz, the spherical symmetry of $\rho^{(n)}$ and Newton's theorem to replace $|x-y|^{-1}$ by $\min(|x|^{-1}, |y|^{-1})$. Here $\tau^{(n)}$ and $\rho^{(n)}$ denote the kernel and density of P_n. Statement (ii) in Theorem 4.1 follows from (29) and the remark following Lemma 4.2. □

5 Appendix

The following lemma seems to be well-known, but we have not found it in the literature.

Lemma 5.1. *There exists a bounded linear mapping*

$$\begin{aligned} \rho : \mathcal{T}_1(L^2(\mathbb{R}^n)) &\to L^1(\mathbb{R}^n) \\ K &\mapsto \rho_K \end{aligned}$$

which is uniquely determined by

$$|\psi\rangle\langle\varphi| \mapsto \psi(x)\overline{\varphi(x)}.$$

Furthermore, ρ has the following properties:

(i) $\int \rho_K(x)\,dx = \operatorname{tr}(K)$

(ii) $\int |\rho_K(x)|\,dx \leq \operatorname{tr}|K|$

Proof. The map ρ is unique because, by linearity and continuity, it is completely determined by its action on operators of rank one. For the proof of existence let $J \in C_0^\infty(\mathbb{R}^n)$ be a real, non-negative and even function with $\int J(x)\,dx = 1$. Let $J_\varepsilon(y) := \varepsilon^{-n}J(y/\varepsilon)$ and $J_{\varepsilon,x}(y) := J_\varepsilon(y-x)$. Then

$$\langle J_{\varepsilon,x}, \varphi\rangle = \int J_\varepsilon(x-y)\varphi(y)\,dy = (J_\varepsilon * \varphi)(x). \tag{35}$$

For given $K \in \mathcal{T}_1(L^2(\mathbb{R}^n))$ we define $\rho_K \in L^1(\mathbb{R}^n)$ by

$$\begin{aligned} \rho_K &:= L^1 - \lim_{\varepsilon \to 0} \rho_{K,\varepsilon} \\ \rho_{K,\varepsilon}(x) &:= \langle J_{\varepsilon,x}, K J_{\varepsilon,x} \rangle. \end{aligned} \tag{36}$$

We claim that the limit (36) exists and that

$$\begin{aligned} \rho_K(x) &= \sum_{n \geq 0} \lambda_n \varphi_n(x) \overline{\psi_n(x)} \\ \text{if} \quad K &= \sum_{n \geq 0} \lambda_n |\varphi_n\rangle\langle\psi_n| \end{aligned} \tag{37}$$

denotes the singular value decomposition of K, that is $\lambda_n \geq 0$ and φ_n, ψ_n are orthonormal bases. Using (35), (37), $\|J_\varepsilon * \varphi\| \leq \|J_\varepsilon\|_1 \|\varphi\| = \|\varphi\|$ and $\sum_n \lambda_n = \operatorname{tr}|K|$, we see that

$$\|\rho_{K,\varepsilon}\|_1 \leq \operatorname{tr}|K|, \qquad \text{for all } \varepsilon > 0. \tag{38}$$

Hence if the limit (36) exists, then (ii) holds and $K \mapsto \rho_K$ is a continuous linear map. Moreover, if K_N denotes the N-th partial sum of (37), then, by (38),

$$\|\rho_{(K-K_N),\varepsilon}\|_1 \leq \operatorname{tr}|K - K_N| \to 0, \qquad (N \to \infty),$$

uniformly in $\varepsilon > 0$. Therefore it suffices to prove the existence of ρ_{K_N}, which follows if we prove that ρ maps the rank one operator $|\varphi\rangle\langle\psi|$ to $\varphi(x)\overline{\psi(x)}$. Indeed,

$$\begin{aligned} &\left\| (J_\varepsilon * \varphi)\overline{(J_\varepsilon * \psi)} - \varphi\overline{\psi} \right\|_1 \\ &= \left\| (J_\varepsilon * \varphi - \varphi)\overline{\psi} + (J_\varepsilon * \varphi)\left(\overline{(J_\varepsilon * \psi)} - \overline{\psi}\right) \right\|_1 \\ &\leq \|J_\varepsilon * \varphi - \varphi\|\|\psi\| + \|J_\varepsilon * \varphi\|\|J_\varepsilon * \psi - \psi\| \to 0 \quad (\varepsilon \to 0) \end{aligned}$$

where we used that $J_\varepsilon * \varphi \to \varphi$ in $L^2(\mathbb{R}^n)$. It now remains to prove (i). This follows from

$$\int \rho_K(x)\,dx = \sum_{n \geq 0} \lambda_n \int \varphi_n(x)\overline{\psi_n(x)}\,dx = \sum_{n \geq 0} \lambda_n \langle \psi_n, \varphi_n \rangle$$

$$\operatorname{tr} K = \sum_{n \geq 0} \langle \psi_n, K\psi_n \rangle = \sum_{n \geq 0} \lambda_n \langle \psi_n, \varphi_n \rangle.$$

□

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