Existence of a solution to Hartree-Fock equations with decreasing magnetic field

Mattias Enstedt
Uppsala University, mattias.enstedt@math.uu.se

Michael Melgaard
Dublin Institute of Technology, michael.melgaard@dit.ie

Existence of a solution to Hartree–Fock equations with decreasing magnetic fields

M. Enstedt, M. Melgaard*

Department of Mathematics, Uppsala University, SE-751 06 Uppsala, Sweden

Abstract

In the presence of an external magnetic field, we prove existence of a ground state within the Hartree–Fock theory of atoms and molecules. The ground state exists provided the magnetic field decreases at infinity and the total charge Z of K nuclei exceeds $N - 1$, where N is the number of electrons. In the opposite direction, no ground state exists if $N > 2Z + K$.
© 2007 Published by Elsevier Ltd

1. Introduction

In this paper, the existence of a solution in the form of a minimizer is established for the nonlinear coupled Hartree–Fock equations of Quantum Chemistry in the presence of an external magnetic field.

Within the Born–Oppenheimer approximation, the nonrelativistic quantum energy of N electrons interacting with K static nuclei with charges $\mathbf{Z} = (Z_1, \ldots, Z_K)$, $Z_k > 0$, and an external magnetic field $B = \nabla \times \mathcal{A}$, $\mathcal{A} = (A_1, A_2, A_3) : \mathbb{R}^3 \to \mathbb{R}^3$ being the vector potential, is given by

$$\mathcal{E}_N^{\mathrm{QM}}(\Psi_e) = \langle \Psi_e, H_{N,\mathbf{Z},\mathcal{A}} \Psi_e \rangle_{L^2(\mathbb{R}^{3N})}$$

$$= \sum_{n=1}^{N} \int_{\mathbb{R}^{3N}} \left(|\nabla_{\mathcal{A},x_n} \Psi_e(x)|^2 + V_{en}(x_n)|\Psi_e(x)|^2 \right) \mathrm{d}x + \sum_{1 \leq m < n \leq N} \int_{\mathbb{R}^{3N}} V_{ee}(x_m - x_n)|\Psi_e(x)|^2 \mathrm{d}x, \quad (1.1)$$

where $x = (x_1, \ldots, x_N) \in \mathbb{R}^{3N}$, $x_n = (x_n^{(1)}, x_n^{(2)}, x_n^{(3)}) \in \mathbb{R}^3$ being the position of the nth electron, the components of the magnetic gradient $\nabla_{\mathcal{A},x_n} = (P_{x_n}^{(1)}, P_{x_n}^{(2)}, P_{x_n}^{(3)})$ are $P_{x_n}^{(m)} = P_{\mathcal{A},x_n}^{(m)} = \partial_{x_n^{(m)}} + \mathrm{i}A_m(x_n)$, V_{en} is the Coulomb potential

$$V_{en}(y) = -\sum_{k=1}^{K} \frac{Z_k}{|y - R_k|}$$

Q1 * Corresponding author. Tel.: +46 18 158817; fax: +46 0 18 471 32 01.
   E-mail addresses: mattias.enstedt@math.uu.se (M. Enstedt), michael.melgaard@math.uu.se (M. Melgaard).

1 with $R_k \in \mathbb{R}^3$ being the position of the kth nucleus, $V_{ee}(x) = 1/|x|$, and $H_{N,\mathbf{Z},\mathcal{A}}$ is the N-particle electronic
2 Schrödinger operator

$$H_{N,\mathbf{Z},\mathcal{A}} = \sum_{n=1}^{N} \left(-\Delta_{\mathcal{A},x_n} + V_{en}(x_n) \right) + \sum_{1 \le m < n \le N} V_{ee}(x_m - x_n)$$

4 with $\Delta_{\mathcal{A},x_n} = \sum_{m=1}^{3} (P_{x_n}^{(m)})^2$ being the magnetic Laplacian. The interpretation of this Hamiltonian[1] is as follows: the
5 first term corresponds to the kinetic energy of the electrons, the second term is the one-particle attractive interaction
6 between the electrons and the nuclei, and the third term is the standard two-particle repulsive interaction between the
7 electrons.
8   The wave function Ψ_e in (1.1) belongs to $\mathcal{H}_e := \bigwedge^N \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3; \mathbb{C}^2)$, i.e., the N-particle Hilbert space consisting of
9 antisymmetric functions (expressing the Pauli exclusion principle)

$$\Psi_e(x_1, \ldots, x_N) = \text{sign}(\sigma)\, \Psi_e(x_{\sigma(1)}, \ldots, x_{\sigma(N)}) \text{ a.e.}, \quad \forall \sigma \in S_N,$$

11 where S_N is the group of permutations of $\{1, \ldots, N\}$, with the signature of a permutation σ being denoted by $\text{sign}(\sigma)$.
12 The space $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$ is the "magnetic" analogue of the standard Sobolev space $\mathbf{H}^1(\mathbb{R}^3)$; see Section 2 for its definition.
13   Poincaré's Lemma (see, e.g., [10]) asserts that the magnetic field strength B is described by a 2-form

$$B(x) = \sum_{l,m=1,l<m}^{3} \mathcal{F}_{lm}(x)\mathrm{d}x_l \wedge \mathrm{d}x_m \tag{1.2}$$

15 satisfying $\mathrm{d}B = 0$ (exterior derivative) and, consequently, $B = \mathrm{d}A$, or

$$\mathcal{F}_{lm}(x) = \frac{\partial A_l(x)}{\partial x_m} - \frac{\partial A_m(x)}{\partial x_l} \tag{1.3}$$

17 with the magnetic vector potential (1-form) $\mathcal{A}(x) = \sum_{m=1}^{3} A_m \mathrm{d}x_m$. Since the vector potential is not directly
18 observable, we should impose conditions on the field strengths.
19   We choose the Poincaré gauge, $x \cdot \mathcal{A}(x) = \mathcal{A}(x) \cdot x = 0$. It is well-known that

$$A_m(x) := \sum_{l=1}^{3} \int_0^1 \xi \mathcal{F}_{lm}(\xi x)\mathrm{d}\xi\, x_l, \quad m = 1, 2, 3, \tag{1.4}$$

21 defines a vector potential which satisfies the Poincaré gauge. For this choice, $\text{div}\,\mathcal{A} = \sum_{m=1}^{3} \partial_m A_m(x)$ is a physical
22 quantity and we shall impose the following conditions on it; in a different context, rather similar requirements are
23 imposed in [5,2].

24 **Assumption 1.1.**   (i) $\text{div}\,\mathcal{A} \in L_{\text{loc}}^2(\mathbb{R}^3)$.
25   (ii) $\text{div}\,\mathcal{A}$ is $-\Delta$-bounded with relative bound less than one.
26   (See, e.g., [4, Definition III.7.1].)
27 (iii) Smallness at infinity:

$$\left\| \text{div}\,\mathcal{A}(-\Delta + 1)^{-1}\widetilde{\chi}(|x| > R) \right\|_{\mathcal{B}(L^2)} \in L^1(\mathbb{R}_+, \mathrm{d}R).$$

29   (See Section 2 for the meaning of $\widetilde{\chi}$.)
30 (iv) $\mathcal{A}$ is homogeneous of degree -1.

31   The hypotheses on the field strength $\mathcal{F}_{lm}$ and $\sum_{l=1}^{3} \mathcal{F}_{lm}(x)\, x_m$ are summarized in the following, where we set
32 $\mathcal{F}_{lm} = \mathcal{F}_{lm}^b + \mathcal{F}_{lm}^s$, with $\mathcal{F}_{lm}^b$, resp., $\mathcal{F}_{lm}^s$ being associated with a bounded, resp. singular, part of $\mathcal{F}_{lm}$.

---

[1] Expressed in Rydberg units.

Assumption 1.2. (i) Let $\mathcal{F}_{lm}^b \in L^\infty(\mathbb{R}^3)$ such that, for some $\nu \in (0, 1)$,

$$|\mathcal{F}_{lm}^b(x)| \le c(1 + |x|)^{-(1+\nu)}.$$

(ii) Let $\mathcal{F}_{lm}^s \in L_{\text{loc}}^4(\mathbb{R}^3)$ such that, for some positive R and $\mu \in (2, \infty)$,

$$\int_{B(0,R)} \left| \sum_{l=1}^3 \mathcal{F}_{lm}^s(x)x_l \right|^4 \mathrm{d}x \le cR^\mu.$$

(iii) For some positive r_0, let

$$\operatorname{supp} \mathcal{F}_{lm}^s \subset B(0, r_0).$$

(iv) For $\nu \in (0, 1)$ and $\kappa > \max\{3/(1 - \nu), 6\}$, let

$$\mathcal{F}_{lm}^s \in L_{\text{loc}}^\kappa(\mathbb{R}^3).$$

The N-particle *quantum mechanical ground state energy* is the minimum of the spectrum of $H_{N,\mathbf{Z},\mathcal{A}}$ or, equivalently,

$$E^{\text{QM}}(N, \mathbf{Z}, \mathcal{A}) = \inf\{\mathcal{E}_N^{\text{QM}}(\Psi_e) : \Psi_e \in \mathcal{H}_e, \|\Psi_e\|_{L^2(\mathbb{R}^{3N})} = 1\}. \tag{1.5}$$

In general, $E^{\text{QM}}(N, \mathbf{Z}, \mathcal{A})$ is inaccessible to direct calculation, due to the excessive dimension of the underlying Euclidean space $\mathbb{R}^{3N}$ on which wave functions are defined. For this reason, quantum chemists have introduced *ab initio* approximations which provide a simplified, but still quantum mechanical description of the electronic structure about the nuclei. Here we focus on one such approximation, namely the *Hartree–Fock approximation* [37,13,28]. Therein the main idea is to replace the Hilbert space $\mathcal{H}_e$ by a smaller space while maintaining the form of the energy $\mathcal{E}_N^{\text{QM}}(\Psi_e)$; see (1.1). Specifically, the Hartree–Fock approximation, introduced by Hartree [12] and improved by Fock [8] and Slater [35] in the late 1920s, consists in restricting in the minimization problem (1.5) the space $\mathcal{H}_e$ to that of functions of the variables $(x_1, \ldots, x_N) \in \mathbb{R}^{3N}$ that can be written as a *single* determinant (i.e. an antisymmetrized product) of N functions defined on $\mathbb{R}^3$. Bear in mind that, in its full generality, an arbitrary vector of $\mathcal{H}_e$ is only a converging infinite sum of such determinants [27]. The magnetic Hartree–Fock approximation is therefore defined as

$$\inf\{\langle \Psi_e, H_{N,\mathbf{Z},\mathcal{A}} \Psi_e \rangle : \Psi_e \in \mathcal{S}_N\}, \tag{1.6}$$

where

$$\mathcal{S}_N = \left\{ \Psi_e \in \mathcal{H}_e : \exists \Phi = \{\phi_n\}_{1 \le n \le N} \in \mathcal{C}_N, \ \Psi_e = \frac{1}{\sqrt{N!}} \det(\phi_n(x_m)) \right\}$$

with

$$\mathcal{C}_N = \{\Phi = \{\phi_n\}_{1 \le n \le N}, \phi_n \in \mathbf{H}_\mathcal{A}^1(\mathbb{R}^3), \langle \phi_m, \phi_n \rangle_{L^2} = \delta_{mn}, 1 \le m, n \le N\}. \tag{1.7}$$

This form of the wave function becomes more explicit if we write it out, viz.

$$\Psi_e(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \det(\phi_n(x_m)) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \cdots & \phi_1(x_N) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \phi_N(x_1) & \cdots & \phi_N(x_N) \end{vmatrix}. \tag{1.8}$$

In the language of Quantum Chemistry, a function of the form (1.8) is called a *Slater determinant*, and the ϕ_n are called *molecular orbitals*.

In fact, if $\Psi_e \in \mathcal{S}_N$ then, by simple algebraic calculations, $\langle \Psi_e, H_{N,\mathbf{Z},\mathcal{A}} \Psi_e \rangle = \mathcal{E}^{\text{MHF}}(\Psi_e)$, where the *magnetic Hartree–Fock functional* $\mathcal{E}_N^{\text{MHF}}(\cdot)$ is given by

$$\mathcal{E}^{\mathrm{MHF}}(\phi_1, \ldots, \phi_N) = \mathcal{E}_N^{\mathrm{MHF}}(\Psi_e) = \langle \Psi_e, H_{N,\mathbf{Z},\mathcal{A}} \Psi_e \rangle$$

$$= \sum_{n=1}^{N} \int_{\mathbb{R}^3} |\nabla_{\mathcal{A}} \phi_n(x)|^2 \mathrm{d}x + \int_{\mathbb{R}^3} V_{en}(x) \rho(x) \mathrm{d}x + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\,\rho(x')}{|x-x'|} \mathrm{d}x \mathrm{d}x'$$

$$- \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\tau(x,x')|^2}{|x-x'|} \mathrm{d}x \mathrm{d}x'. \tag{1.9}$$

Here $\tau(x,x') = \sum_{n=1}^{N} \phi_n(x)\,\phi_n(x')$ is the *density matrix*, and the *density associated to the state* Ψ_e is $\rho(x) = \sum_{n=1}^{N} |\phi_n(x)|^2$; ζ^* refers to the conjugate of the complex number ζ.

Definition 1.3 (*The Hartree–Fock Ground State*). Let $\mathbf{Z} = (Z_1, \ldots, Z_K)$, $Z_k > 0$, $k = 1, \ldots, K$, and let N be a nonnegative integer. The magnetic Hartree–Fock ground state energy is

$$E^{\mathrm{MHF}} \equiv E^{\mathrm{MHF}}(N, \mathbf{Z}, \mathcal{A}) := \inf\{\mathcal{E}^{\mathrm{MHF}}(\Psi_e) : \Psi_e \in \mathcal{S}_N\}. \tag{1.10}$$

If a minimizer exists, i.e., there exists some Ψ_e such that

$$\mathcal{E}^{\mathrm{MHF}}(\Psi_e) = E^{\mathrm{MHF}}, \tag{1.11}$$

then it is said that the atom has a magnetic Hartree–Fock ground state described by Ψ_e.

When no magnetic field is present, the Hartree–Fock minimization problem was studied by Lieb and Simon in [23] (see also [22,19]). Under the condition that the *total charge* $Z = \sum_{k=1}^{K} Z_k$ of the molecular system fulfills $Z + 1 > N$, they proved the existence of at least one minimizer, i.e., a Hartree–Fock ground state. The mathematical requirement $Z + 1 > N$ expresses that the total charge of the nuclei should be sufficiently positive to ensure that the N electrons are localized in their vicinity. Prior to [23], the Hartree–Fock equations were studied by more direct approaches [29,11,9,36,38,30], yielding less general results.

The proof in [23] relies on variational methods applied to the Hartree–Fock energy functional and, in particular, the weak lower semicontinuity of the functional in the Sobolev space $\mathbf{H}^1(\mathbb{R}^3)^N$. One property is instrumental in the proof: The infimum in (1.10) is unchanged if $\mathcal{C}_N$ is replaced by

$$\mathcal{C}_N^{\leq} = \{\Phi = \{\phi_n\}_{1 \leq n \leq N}, \phi_n \in \mathbf{H}^1(\mathbb{R}^3), \langle \phi_m, \phi_n \rangle_{L^2} \leq \delta_{mn}, 1 \leq m, n \leq N\}, \tag{1.12}$$

with the analogue of $\mathcal{S}_N$, denoted $\mathcal{S}_N^{\leq}$, being defined via $\mathcal{C}_N^{\leq}$. That is, if the orthonormality constraint in (1.7) is substituted by $\int_{\mathbb{R}^3} \phi_m \phi_n \mathrm{d}x \leq \delta_{mn}$; henceforth called the *relaxed constraint*. The property enables one to, first, prove the existence of a minimizer to the relaxed Hartree–Fock problem and, second, one proves that the latter minimizer does, indeed, satisfy the original orthonormality constraint.

The novelty of the present paper is to establish the existence of a Hartree–Fock ground state for a wide class of magnetic fields. The main theorem, valid for neutral molecules and positive ions, is:

Theorem 1.4. *Let Assumptions* 1.1 *and* 1.2 *hold. If the total nuclear charge* $Z = \sum_{k=1}^{K} Z_k$ *satisfies* $Z + 1 > N$, *then there exists a minimizer* $\boldsymbol{\varphi}$ *of* $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ *on the admissible set* $\mathcal{S}_N$.

The components of $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N)$ *satisfy the magnetic Hartree–Fock equations*

$$\begin{cases} H_{\mathcal{A}}^F \varphi_n = \epsilon_n \varphi_n, \\ \langle \varphi_m, \varphi_n \rangle_{L^2} = \delta_{mn}, \end{cases} \tag{1.13}$$

where $H_{\mathcal{A}}^F$ *is the magnetic Fock operator, defined in Proposition* 5.1. *Moreover, the numbers* ϵ_n *are the* N *lowest eigenvalues of the operator* $H_{\mathcal{A}}^F$.

If $\mathcal{A}$ is homogeneous of degree -1, bounded and tends to zero at infinity, then Assumptions 1.1 and 1.2 are satisfied. Assumptions 1.1 and 1.2 ensure that the (quantum) energy is monotonically decreasing in the numbers of electrons N which is crucial for the strategy of the proof. In particular, the proof will not apply to a constant magnetic field because if we add a particle at spatial infinity then it costs at least an energy of size $|B|$.

In the opposite direction, the following result on nonexistence holds under the same assumptions.

Theorem 1.5. *Let Assumptions 1.1 and 1.2 hold. If N is a positive integer such that $N > 2Z + K$ (Z being the total nuclear charge), there are no minimizers for the magnetic Hartree–Fock problem.*

For bounded vector potentials which tends to zero at infinity, the latter result was proven by Lieb [20]. The proof of Theorem 1.5 will appear elsewhere [6].

In the case of a constant magnetic field a result similar to Theorem 1.4 was established by Esteban and Lions [7] by a completely different approach, originally invented by Lions for the nonmagnetic case, based upon the construction of minimizing sequences which satisfy the "second minimality condition"; we refer to [26] for details.

2. Preliminaries

Let T be a self-adjoint operator on a Hilbert space $\mathcal{H}$ with domain $\mathfrak{D}(T)$. The spectrum and resolvent set are denoted by $\sigma(T)$ and $\rho(T)$, respectively. We use standard terminology for the various parts of the spectrum; see, e.g., [4,17]. The resolvent is $R(\zeta) = (T - \zeta)^{-1}$. The spectral family associated to T is denoted by $E_T(\lambda)$, $\lambda \in \mathbb{R}$. For a lower semi-bounded self-adjoint operator T, the counting function is defined by

$$\text{Coun}(\lambda; T) = \dim \text{Ran} \, E_T((-\infty, \lambda)).$$

Let $\mathbb{R}^3$ be the three-dimensional Euclidean space, wherein points are denoted by $x = (x^{(1)}, x^{(2)}, x^{(3)})$, and let $|x| = (\sum_{m=1}^3 (x^{(m)})^2)^{1/2}$. We set

$$B_R = \{x \in \mathbb{R}^3 : |x| < R\}, \qquad B(x, R) = \{y \in \mathbb{R}^3 : |x - y| < R\}.$$

For any set $\Omega \subset \mathbb{R}^3$ we denote by $\widetilde{\chi}(x \in \Omega)$ the operator of multiplication by the characteristic function of Ω. In the case $\Omega = \{x : |x| \leq R\}$ we write $\widetilde{\chi}(|x| \leq R)$ and the operator $1 - \widetilde{\chi}(|x| \leq R)$ will be designated $\widetilde{\chi}(|x| > R)$. For a self-adjoint operator T, we let $\widetilde{\chi}(|T| \leq E)$ be the spectral projection onto the subspace where $|T| \leq E$, defined by the functional calculus, and let $\widetilde{\chi}(|T| > E) = 1 - \widetilde{\chi}(|T| \leq E)$.

For $1 \leq p \leq \infty$, let $L^p(\mathbb{R}^3)$ be the space of (equivalence classes of) complex-valued functions ϕ which are measurable and satisfy $\int_{\mathbb{R}^3} |\phi(x)|^p dx < \infty$ if $p < \infty$ and $\|\phi\|_{L^\infty(\mathbb{R}^3)} = \text{ess sup} |\phi| < \infty$ if $p = \infty$. The measure dx is the Lebesgue measure. For any p the $L^p(\mathbb{R}^3)$ space is a Banach space with norm $\| \cdot \|_{L^p(\mathbb{R}^3)} = (\int_{\mathbb{R}^3} | \cdot |^p dx)^{1/p}$. In the case $p = 2$, $L^2(\mathbb{R}^3)$ is a complex and separable Hilbert space with scalar product $\langle \phi, \psi \rangle_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} \phi \psi^* dx$ and corresponding norm $\|\phi\|_{L^2(\mathbb{R}^3)} = \langle \phi, \phi \rangle_{L^2(\mathbb{R}^3)}^{1/2}$. Similarly, $L^2(\mathbb{R}^3)^N$, the N-fold Cartesian product of $L^2(\mathbb{R}^3)$, is equipped with the scalar product $\langle \phi, \psi \rangle = \sum_{n=1}^N \langle \phi_n, \psi_n \rangle_{L^2(\mathbb{R}^3)}$ and the norm $\|\phi\| = \langle \phi, \phi \rangle^{1/2}$.

The space of infinitely differentiable complex-valued functions with compact support will be denoted $C_0^\infty(\mathbb{R}^3)$ or $\mathscr{D}(\mathbb{R}^3)$, the space of test functions. The Schwarz space of rapidly decreasing functions and its adjoint space if tempered distributions are denoted by $\mathscr{S}(\mathbb{R}^3)$ and $\mathscr{S}'(\mathbb{R}^3)$, respectively.

Let p denote the momentum operator $-i\nabla$ and let $\langle p \rangle = (1 + p^2)^{1/2}$. For any $t \in \mathbb{R}$ the standard Sobolev space $\mathbf{H}^t(\mathbb{R}^3)$ is given by

$$\mathbf{H}^t(\mathbb{R}^3) = \{\phi \in \mathscr{S}'(\mathbb{R}^3) : \|\phi\|_{\mathbf{H}^t(\mathbb{R}^3)} = \|\langle p \rangle^t \phi\|_{L^2(\mathbb{R}^3)} < \infty\}. \tag{2.1}$$

2.1. The Sobolev space $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$

Define

$$\mathbf{H}_{\mathcal{A}}^1 \equiv \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3) := \left\{ \phi \in L^2(\mathbb{R}^3) : \nabla_{\mathcal{A}}\phi \in L^2(\mathbb{R}^3) \right\}$$

for $\nabla_{\mathcal{A}} := \nabla + i\mathcal{A}$, in which $\nabla\phi$ is taken in the distributional sense, endowed with norm

$$\|\phi\|_{\mathbf{H}_{\mathcal{A}}^1} := \left(\|\phi\|_{L^2}^2 + \|\nabla_{\mathcal{A}}\phi\|_{L^2}^2 \right)^{1/2}.$$

We do not suppose that $\nabla\phi$ or $\mathcal{A}\phi$ are separately in $L^2(\mathbb{R}^3)$. Consequently, in general, there is no relationship between the spaces $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$ and $\mathbf{H}^1(\mathbb{R}^3)$ on the whole of $\mathbb{R}^3$; more precisely, $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3) \not\subseteq \mathbf{H}^1(\mathbb{R}^3)$ and $\mathbf{H}^1(\mathbb{R}^3) \not\subseteq \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$.

If $\mathcal{A} \in L^2_{\text{loc}}(\mathbb{R}^3)^3$, then $\mathscr{D}(\mathbb{R}^3)$ is dense in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ (see [16,34,18]), and the following well-known *diamagnetic inequality* is valid.

Theorem 2.1. *Let* $\mathcal{A} \in L^2_{\text{loc}}(\mathbb{R}^3)^3$. *If* $\phi \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$, *then* $|\phi| \in \mathbf{H}^1(\mathbb{R}^3)$ *and*

$$|\nabla|\phi|| \leq |\nabla_{\mathcal{A}}\phi| \quad \text{for a.e. } x \in \mathbb{R}^3 \text{ and } \forall \phi \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3). \tag{2.2}$$

Proof. We sketch the argument; for more details we refer to [21]. Since $\mathcal{A}$ is real-valued, the relation (see, e.g., [14])

$$|\nabla|\phi|(x)| = \left| \text{Re}\left(\nabla\phi \frac{\phi^*}{|\phi|} \right) \right| = \left| \text{Re}\left((\nabla\phi + \mathrm{i}\mathcal{A}\phi)\frac{\phi^*}{|\phi|} \right) \right|$$

Q2 holds a.e., whence (2.2) follows for all $\phi \in \mathscr{D}(\mathbb{R}^3)$ and thus for all $\phi \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ because $\mathscr{D}(\mathbb{R}^3)$ is dense in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$.

As a consequence of Theorem 2.1 we have that $\phi \mapsto |\phi|$ maps $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ continuously into the Sobolev space $\mathbf{H}^1(\mathbb{R}^3)$, which implies the existence of a continuous embedding

$$\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) \hookrightarrow L^q(\mathbb{R}^3), \quad q \in [2, 6], \tag{2.3}$$

(see, e.g., [4, Theorem 3.7]). For the ball B_R centred at the origin with radius R, it follows from Rellich's embedding theorem [1, Theorem 3.8] that the embedding $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) \hookrightarrow L^2(B_R)$ is compact, i.e.,

$$\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) \hookrightarrow\hookrightarrow L^2(B_R). \tag{2.4}$$

2.2. Bound on kinetic energy of electrons

The following inequality was established by Lieb and Thirring [24,25] for the nonmagnetic case but it immediately carries over to our setting.

Theorem 2.2. *Let* $\mathcal{A} \in L^2_{\text{loc}}(\mathbb{R}^3)^3$ *and let* $\rho = \sum_{n=1}^N |\phi_n|^2$ *be the density associated to a vector in* $\mathcal{S}_N$. *Then there exists a positive constant* c *such that*

$$\int_{\mathbb{R}^3} \rho(x)^{5/3}\mathrm{d}x \leq c \sum_{n=1}^N \|\nabla_{\mathcal{A}}\phi_n\|^2_{L^2(\mathbb{R}^3)}. \tag{2.5}$$

2.3. Invariance under unitary transformations

The following property is fundamental:

Lemma 2.3. *The functional* $\mathcal{E}^{\text{MHF}}(\cdot)$ *is invariant under unitary transformations, i.e., if* $U = \{U_{mn}\}$ *is an unitary* $N \times N$ *matrix and* $\psi_m = \sum_n U_{mn}\phi_n$, *then* $\mathcal{E}^{\text{MHF}}(\Psi) = \mathcal{E}^{\text{MHF}}(\Phi)$, *where* $\Psi = (\psi_1, \ldots, \psi_N)$.

Proof. Recall that the set of admissible data is the Slater determinants, i.e. functions having the representation

$$\Psi_e(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \det\{\phi_m(x_n)\}_{m,n}$$

with $\phi_m \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ and $\langle\phi_m, \phi_n\rangle_{L^2} = \delta_{mn}$. Let U be a unitary transformation and set

$$(\phi'_1, \ldots, \phi'_N) := U(\phi_1, \ldots, U\phi_N),$$

then

$$\det\{\phi'_m(x_n)\}_{m,n} = \det U\{\phi_m(x_n)\}_{m,n} = \det\{\phi_m(x_n)\}_{m,n}$$

and hence $(\phi'_1, \ldots, \phi'_N)$ and $(\phi_1, \ldots, \phi_N)$ represent the same Ψ_e. Then clearly $\mathcal{E}^{\text{MHF}}$ is invariant under unitary transformations (If it was not invariant our original functional $\langle\Psi_e, H_{N,Z,\mathcal{A}}\Psi_e\rangle$ would not be well-defined since it could attain different values for the same Ψ_e and this is, of course, a contradiction). $\square$

2.4. Kato's space of potentials

To treat basic properties of the functional $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ we may consider potentials

$$V \in \mathcal{K}_3 := L^{\frac{3}{2}}(\mathbb{R}^3) + L^{\infty}_{\epsilon}(\mathbb{R}^3), \tag{2.6}$$

i.e., the standard Kato space consisting of real-valued functions on $\mathbb{R}^3$ belonging to the set

$$\{V : \forall \epsilon > 0 \, \exists V_1 \in L^{\frac{3}{2}}, V_2 \in L^{\infty}, \|V_2\|_{L^{\infty}} < \epsilon \text{ such that } V = V_1 + V_2\}$$

which is the closure of $\mathscr{D}(\mathbb{R}^3)$ in $L^{\frac{3}{2}}(\mathbb{R}^3) + L^{\infty}(\mathbb{R}^3)$. Equipped with the norm $\|V\|_{L^{3/2}+L^{\infty}} = \inf_{V=V_1+V_2}(\|V_1\|_{L^{3/2}}$ $+ \|V_2\|_{L^{\infty}})$, the space $\mathcal{K}_3$ has Banach structure and its dual space is $L^1 \cap L^3$; it emerges in a natural way as the largest $L^p + L^q$ space with the property that $\int V(x)|\phi(x)|^2 \mathrm{d}x$ is well-defined for all $\phi \in \mathbf{H}^1(\mathbb{R}^3)$.

3. Existence of minimizer for relaxed Hartree–Fock problem

In this section we establish the following result with $E^{\mathrm{MHF}}_{\leq}$ being defined analogously to E^{MHF} in (1.10) with $\mathcal{S}_N$ replaced by $\mathcal{S}^{\leq}_N$ therein.

Theorem 3.1. *Assume $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$. For any integer $N > 0$ there exists a minimizer (not necessarily unique) Ψ_e for the relaxed magnetic Hartree–Fock problem, i.e. $\exists \boldsymbol{\varphi} \in \mathcal{C}^{\leq}_N$ such that the corresponding $\Psi_e \in \mathcal{S}^{\leq}_N$ satisfies*

$$\mathcal{E}^{\mathrm{MHF}}(\Psi_e) = E^{\mathrm{MHF}}_{\leq}.$$

Moreover, the components of $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N)$ satisfy

$$\langle \varphi_m, \varphi_n \rangle = \gamma_m \delta_{mn} \tag{3.1}$$

for some $\gamma_m \in [0, 1]$.

To make the exposition more pedagogical we divide the proof of this result into a few lemmas.

Lemma 3.2. *Assume that $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$. Then the functional $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ is well-defined on $\mathcal{S}^{\leq}_N$ and, furthermore, there exists a minimizing sequence in $\mathcal{S}^{\leq}_N$.*

Proof. We first show that $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ is bounded from below on $\mathcal{S}^{\leq}_N$, i.e.,

$$\inf\{\mathcal{E}^{\mathrm{MHF}}(\phi_1, \ldots, \phi_N) : \|\phi_n\|_{L^2} \leq 1, \phi_n \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)\} > -\infty. \tag{3.2}$$

The Cauchy–Schwarz inequality yields, for $x, y \in \mathbb{R}^3$,

$$|\tau(x, y)|^2 = \left| \sum_{n=1}^{N} \phi_n(x)\phi_n(y)^* \right|^2$$

$$\leq \left(\sum_{n=1}^{N} |\phi_n(x)|^2 \right) \left(\sum_{n=1}^{N} |\phi_n(y)^*|^2 \right) = \rho(x)\rho(y). \tag{3.3}$$

Hölder's inequality gives

$$\int_{\mathbb{R}^3} \frac{1}{|x-y|} |\phi(x)|^2 \mathrm{d}x \leq 2 \left(\int_{\mathbb{R}^3} \frac{1}{4} \frac{1}{|x-y|^2} |\phi(x)|^2 \mathrm{d}x \right)^{\frac{1}{2}} \left(\int_{\mathbb{R}^3} |\phi(x)|^2 \mathrm{d}x \right)^{\frac{1}{2}}. \tag{27}$$

An application of Hardy' inequality, i.e.,

$$\frac{1}{4} \int_{\mathbb{R}^3} \frac{1}{|x|^2} |\phi(x)|^2 \mathrm{d}x \leq \int_{\mathbb{R}^3} |\nabla\phi(x)|^2 \mathrm{d}x, \quad \forall \phi \in C^{\infty}_0(\mathbb{R}^3), \tag{3.4}$$

and the diamagnetic inequality (2.2) give us the *Coulomb uncertainty principle* expressed by the inequality

$$\int_{\mathbb{R}^3} \frac{1}{|x-y|} |\phi(x)|^2 \mathrm{d}x \le 2 \|\phi\|_{L^2(\mathbb{R}^3)} \|\nabla_{\mathcal{A}}\phi\|_{L^2(\mathbb{R}^3)}, \quad \forall \phi \in C_0^\infty(\mathbb{R}^3). \tag{3.5}$$

Since $C_0^\infty(\mathbb{R}^3)$ is dense in $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$, (3.5) holds for any $\phi \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$.

To verify (3.2), we consider the terms in $\mathcal{E}^{\mathrm{MHF}}(\cdot)$. Since, by hypothesis, $\phi_n \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$, we have that the first term is finite, i.e.,

$$\sum_{n=1}^{N} \int_{\mathbb{R}^3} |\nabla_{\mathcal{A}}\phi_n(x)|^2 \mathrm{d}x < \infty.$$

In view of (3.5), the second term is finite. The inequality (3.3) implies that the sum of the last two terms is nonnegative, i.e.,

$$\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\,\rho(x')}{|x-x'|} \mathrm{d}x \mathrm{d}x' - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\tau(x,x')|^2}{|x-x'|} \mathrm{d}x \mathrm{d}x' \ge 0. \tag{3.6}$$

Hence $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ is bounded from below on $\mathcal{S}_N^{\le}$. By the Sobolev inequality and the diamagnetic inequality Theorem 2.1 **Q3** it is a well-known fact that the sum of the first two terms in $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ is bounded from below *independently* of $\phi = (\phi_1, \ldots, \phi_N) \in \mathcal{S}_N^{\le}$ and, consequently, there exists a minimizing sequence in $\mathcal{S}_N^{\le}$.

Next we want to show that the magnetic Hartree–Fock functional is weakly lower semicontinuous on $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N$. We first consider the second term in $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ because it turns out to be weakly continuous.

Lemma 3.3. *Assume that $\mathcal{A} \in L_{\mathrm{loc}}^2(\mathbb{R}^3)^3$, and that $V \in \mathcal{K}_3$, where $\mathcal{K}_3$ is the Kato space defined in (2.6). Then the functional $\mathcal{V} : \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3) \to \mathbb{R}$ defined by*

$$\psi \mapsto \int_{\mathbb{R}^3} V(x) |\psi(x)|^2 \mathrm{d}x,$$

is weakly continuous on $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$.

Proof. Let $\psi_j \rightharpoonup \psi$ in $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$. Evidently the functional is well-defined on $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$; indeed the Hölder inequality, the Hardy inequality (3.4), and the diamagnetic inequality (2.2) imply that

$$\int_{\mathbb{R}^3} \frac{|\psi|^2}{|x|} \mathrm{d}x \le c \|\psi\|_{L^2} \|\nabla_{\mathcal{A}}\psi\|_{L^2}$$

for some positive constant c. The continuous embedding (2.3) implies that

$$\sup_j \|\psi_j\|_{L^6} < +\infty$$

and, since weak convergence implies strong convergence locally, we have that

$$\psi_j \to \psi \quad \text{in } L_{\mathrm{loc}}^2(\mathbb{R}^3).$$

Hence, after perhaps going to a subsequence, we have that

$$\psi_j \to \psi \quad \text{a.e. on } B,$$

where B is an open ball with some fix radius in $\mathbb{R}^3$ and by repeating this argument (every point in $\mathbb{R}^3$ belong to some open ball also contained in $\mathbb{R}^3$ and weak limits are unique) we may assume that

$$\psi_j \to \psi \quad \text{a.e. on } \mathbb{R}^3.$$

Since V belong to the Kato class we can, for all $\epsilon > 0$, write

$$V = V_1 + V_2,$$

where $V_1 \in L^{3/2}$, $V_2 \in L^\infty$ and $\|V_2\|_\infty < \epsilon$. By again invoking the Sobolev embedding theorem we have that

$$\sup_j \| |\psi_j|^2 \|_{L^3} < \infty.$$

Thus, $|\psi_j|^2 \rightharpoonup |\psi|^2$ in $L^3(\mathbb{R}^3)$ and we infer that (since $L^{3/2}(\mathbb{R}^3)$ has dual space $L^3(\mathbb{R}^3)$)

$$\int_{\mathbb{R}^3} V_1 |\psi_j|^2 \to \int_{\mathbb{R}^3} V_1 |\psi|^2.$$

This is of course also true for our original sequence. Indeed, assume that there exist a subsequence $\{\psi_{j_k}\}$, to $\{\psi_j\}$ such that

$$\psi \mapsto \int_{\mathbb{R}^3} V_1 |\psi|^2 \mathrm{d}x,$$

is not weakly sequentially continuous. Hence there exist some $\nu > 0$ such that

$$\left| \int_{\mathbb{R}^3} V_1 |\psi_{j_k}|^2 \mathrm{d}x - \int_{\mathbb{R}^3} V_1 |\psi|^2 \mathrm{d}x \right| > \nu \tag{3.7}$$

for all j_k. By the same argument as before we can create a subsequence to $\{\psi_{j_k}\}$ (still denoted by $\{\psi_{j_k}\}$) such that

$$\int_{\mathbb{R}^3} V_1 |\psi_{j_k}|^2 \mathrm{d}x \to \int_{\mathbb{R}^3} V_1 |\psi|^2 \mathrm{d}x$$

but this is an obvious contradiction to (3.7). Now, the assertion is a direct consequence of the fact that **Q4**

$$\int_{\mathbb{R}^3} |V_2| \, |\psi_j|^2 - |\psi|^2 \le \epsilon (\sup_j \|\psi_j\|_{L^2}^2 + \|\psi\|_{L^2}^2).$$

We show that the functional $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ is weakly lower semi-continuous in $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N$.

Lemma 3.4. *Assume that $\mathcal{A} \in L_{\mathrm{loc}}^2(\mathbb{R}^3)^3$. Then the functional $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ is weakly lower semicontinuous on $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N$.*

Proof. The first term is weakly lower semi-continuous because the $L^2(\mathbb{R}^3)^N$ norm of $\nabla \phi_n$ is weakly lower semi-continuous. In view of Lemma 3.3 the second term is weakly continuous. The two remaining terms of $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ are conveniently regarded as one single term having a nonnegative integrand; see (3.6). Then we may argue as in the proof of Lemma 3.3; briefly, the compact embedding in (2.4) on bounded subsets enable us to extract a subsequence so that $\phi_n^{(j)}$ converges to ϕ_n a.e. and an application of Fatou's lemma yields

$$\sum_{1 \le m < n \le N} \int_{\mathbb{R}^{3N}} V_{ee}(x_m - x_n) |\Psi(x)|^2 \mathrm{d}x \le \liminf_{j \to \infty} \sum_{1 \le m < n \le N} \int_{\mathbb{R}^{3N}} V_{ee}(x_m - x_n) |\Psi^{(j)}(x)|^2 \mathrm{d}x.$$

We are ready to complete the proof of Theorem 3.1.

Proof (*Proof of Theorem* 3.1). Lemma 3.2 yields the existence of a minimizing sequence. Let $n \in \{1, \ldots, N\}$ and for each $j \in \mathbb{Z}_+$ choose a minimizing sequence $\phi_n^{(j)} \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$, with L^2-norm smaller than or equal to one, such that $\langle \phi_m^{(j)}, \phi_n^{(j)} \rangle_{L^2} = 0$ provided $m \ne n$ and

$$\mathcal{E}^{\mathrm{MHF}}(\phi_1^{(j)}, \ldots, \phi_N^{(j)}) \le E_{\le}^{\mathrm{MHF}} + \frac{1}{j}.$$

From the latter, together with $\|\phi_n^{(j)}\| \le 1$ for all j and all n, we get that $\|\nabla_{\mathcal{A}} \phi_n^{(j)}\|_{L^2} \le c$ for some positive constant c. Hence the minimizing sequence is contained in a fixed ball in the Hilbert space $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N$. Weak compactness of bounded sequences in the latter space implies that there exists a weakly convergent subsequence, i.e., there exists some $\widetilde{\varphi} \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N$ such that

$$\Phi^{(j_k)} \rightharpoonup \widetilde{\varphi} \quad \text{in } \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N.$$

The components of $\widetilde{\boldsymbol{\varphi}}$ are denoted $\tilde{\varphi}_n$. We have $\varphi_n^{(j)} \to \tilde{\varphi}_n$ weakly in $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$ with $\langle \varphi_m^{(j)}, \varphi_n^{(j)} \rangle \leq \delta_{mn}$. Then $\langle \tilde{\varphi}_m, \tilde{\varphi}_n \rangle = M_{mn}$ are the entries of an $N \times N$ matrix with $0 \leq M \leq 1$ (in the sense of matrices); the same argument as in [23, Lemma 2.2] applies.

At this stage we have a minimizer $\widetilde{\boldsymbol{\varphi}}$ satisfying

$$\mathcal{E}^{\mathrm{MHF}}(\widetilde{\boldsymbol{\varphi}}) = E_{\leq}^{\mathrm{MHF}}$$

and

$$0 \leq \left\{ \int \tilde{\varphi}_m \tilde{\varphi}_n^* \mathrm{d}x \right\} \leq 1.$$

We select an unitary matrix $U = \{u_{mn}\}$ which diagonalizes M. Setting $\varphi_n = \sum u_{mn} \tilde{\varphi}_m$ and $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N)$, Lemma 2.3 guarantees that $\mathcal{E}^{\mathrm{MHF}}(\boldsymbol{\varphi}) = E_{\leq}^{\mathrm{MHF}}$ and, by repeating the argument above, $\langle \varphi_m, \varphi_n \rangle = \gamma_m \delta_{mn}$ holds for some $\gamma_m \in [0, 1]$.

4. Magnetic Hartree–Fock equations

We show that the components of $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N)$ satisfy the magnetic Hartree–Fock equations (or Euler–Lagrange equations).

Lemma 4.1. *Suppose that* $\mathcal{A} \in L_{\mathrm{loc}}^2(\mathbb{R}^3)^3$. *Then the functional* $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ *belongs to* $C^1(\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N, \mathbb{R})$.

Proof. A straightforward computation show that the Gateaux derivative of $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ (in this proof we henceforth suppress the superscript) is given by

$$\mathcal{E}'(\Phi)\Psi = 2 \sum_{n=1}^{N} \mathrm{Re} \int_{\mathbb{R}^3} \nabla_{\mathcal{A}} \phi_n(x) \nabla_{\mathcal{A}} \psi_n^*(x) + V_{en}(x) \phi_n(x) \psi_n^*(x) \mathrm{d}x$$

$$+ 2\mathrm{Re} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\phi_n(y)\psi_n^*(y)}{|x-y|} \mathrm{d}x\mathrm{d}y - 2\mathrm{Re} \int_{R^3} \int_{R^3} \tau(x,y) \frac{\phi_n(y)\psi_n^*(x)}{|x-y|} \mathrm{d}y\mathrm{d}x.$$

It suffices to prove that $\mathcal{E}'(\Phi^{(j)}) \to \mathcal{E}'(\Phi)$ in the strong operator topology. Using the Hölder inequality and Hardy's inequality (3.4) we obtain, for some constant $c > 0$, the estimate

$$|\mathcal{E}'(\Phi)\Psi - \mathcal{E}'(\Phi^{(j)})\Psi| \leq c \left\{ \sum_{n=1}^{N} \|\nabla_{\mathcal{A}} \phi_n^{(j)} - \nabla_{\mathcal{A}} \phi_n\|_{L^2} \|\psi_n\|_{L^2} + \|\phi_n^{(j)} - \phi_n\|_{L^2} \|\nabla_{\mathcal{A}} \psi_n\|_{L^2} \right.$$

$$+ \|\rho\|_{L^1} \|\phi_n^{(j)} - \phi_n\|_{L^2} \|\nabla_{\mathcal{A}} \psi_n\|_{L^2} + \|\rho^{(j)} - \rho\|_{L^1} \sup_j \|\phi_n^{(j)}\|_{L^2} \|\nabla_{\mathcal{A}} \psi_n\|_{L^2}$$

$$\left. + \|\rho\|_{L^1} \|\phi_n^{(j)} - \phi_n\|_{L^2} \|\nabla_{\mathcal{A}} \psi_n\|_{L^2} + \Lambda(\tau^{(n)}, \phi_n^{(j)}, \tau, \phi_n, \psi_n) \right\},$$

where

$$\Lambda(\tau^{(j)}, \phi_n^{(j)}, \tau, \phi_n, \psi_n) := \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\tau^{(j)}\phi_n^{(j)} - \tau\phi_n||\psi_n|}{|x-y|} \mathrm{d}x\mathrm{d}y.$$

A direct application of the inequality

$$\left| |\lambda_n^{(j)}|^2 - |\lambda|^2 \right| \leq |\lambda_n - \lambda_n^{(j)}| \, |\lambda_n + \lambda_n^{(j)}|$$

yields

$$\|\rho^{(j)} - \rho\|_{L^1} \leq \sum_{n=1}^{N} \|\phi_n^{(j)} - \phi_n\|_{L^2} \sup_j \|\phi_n^{(j)} + \phi_n\|_{L^2}$$

and hence $\rho^{(j)} \to \rho$ in $L^1(\mathbb{R}^3)$. It remains to prove that $\Lambda \to 0$. The triangle inequality and the Cauchy–Schwarz inequality imply that

$$|\tau^{(j)}(x, y) - \tau(x, y)| \leq \sqrt{\rho^{(j)}(x) \sum_{n=1}^{N} |\phi_n^{(j)}(y) - \phi_n(y)|^2} + \sqrt{\rho(y) \sum_{n=1}^{N} |\phi_n^{(j)}(x) - \phi_n(x)|^2}. \qquad (4.1)$$

Writing $\tau^{(j)}\phi_n^{(j)} - \tau\phi_n = (\tau^{(j)} - \tau)\phi_n^{(j)} + \tau(\phi_n^{(j)} - \phi_n)$ we may argue as for the other terms above by applying (4.1), in conjunction with Hölder's inequality, Hardy's inequality and the diamagnetic inequality; for instance,

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\sqrt{\rho^{(j)}(x) \sum_{n=1}^{N} |\phi_n^{(j)}(y) - \phi_n(y)|^2} |\phi_n^{(j)}(y)\psi_n(x)^*|}{|x - y|} \mathrm{d}x\mathrm{d}y$$

$$\leq c\|\psi_n\|_{L^2} \left(\sum_{n=1}^{N} \|\phi_n^{(j)} - \phi_n\|_{L^2}^2 \right)^{1/2} \|\nabla_{\mathcal{A}}\psi_n\|_{L^2} \|\rho^{(j)}\|_{L^1}.$$

This yields the desired fact and we conclude that $\mathcal{E}^{\mathrm{MHF}}(\cdot) \in C^1(\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N, \mathbb{R})$.

Lemma 4.1 shows that the minimizer to the relaxed Hartree–Fock problem is a critical point to the functional $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ and Theorem 3.1 ensures that

$$\int_{\mathbb{R}^3} \varphi_m \varphi_n^* = \gamma_m \delta_{mn},$$

where $\gamma_m \in [0, 1]$.

Theorem 4.2. *Suppose that $\mathcal{A} \in L_{\mathrm{loc}}^2(\mathbb{R}^3)^3$. Then the components of the minimizer $\boldsymbol{\varphi}$ for the relaxed Hartree–Fock problem satisfy the magnetic Hartree–Fock equations*

$$-\Delta_{\mathcal{A}}\varphi_n + V_{en}\varphi_n + \left(\rho * \frac{1}{|x|}\right)\varphi_n - \left(\int_{\mathbb{R}^3} \tau(x, y)\frac{1}{|x - y|}\varphi_n(y)\mathrm{d}y\right) + \epsilon_n\varphi_n = 0, \quad in \ \mathbb{R}^3, \forall n$$

for some constants ϵ_n.

Proof. Define the functional $\mathcal{G}_n : \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N \to \mathbb{R}$ by

$$\Phi \mapsto \|\phi_n\|_{L^2}^2 - \gamma_n, \quad \Phi = (\phi_1, \ldots, \phi_N) \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N,$$

and note that clearly $\mathcal{G}_n' \in C(\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)^N, \mathbb{R})$ and, in particular, the Gateaux derivative at Φ equals

$$\mathcal{G}_n'(\Phi)(\Psi) = 2\mathrm{Re} \int_{\mathbb{R}^3} \phi_n \psi_n^* \mathrm{d}x.$$

According to the Lagrange multiplier rule [39, Section 4.14] there exists ϵ_n such that, for all n, the minimizer $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N)$ satisfies

$$\mathrm{Re}\, \mathfrak{h}_{\mathcal{A}}^F[\varphi_n, \psi_n] + \epsilon_n\mathrm{Re} \int_{\mathbb{R}^3} \varphi_n\psi_n^*\mathrm{d}x = 0 \quad \forall\psi_n \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3), \qquad (4.2)$$

where the sesquilinear form $\mathfrak{h}_{\mathcal{A}}^F[\varphi_n, \psi_n]$ is defined by

$$\mathfrak{h}_{\mathcal{A}}^F[\varphi_n, \psi_n] := \int_{\mathbb{R}^3} \nabla_{\mathcal{A}}\varphi_n(x)\nabla_{\mathcal{A}}\psi_n^*(x) + V_{en}(x)\varphi_n(x)\psi_n^*(x)\mathrm{d}x$$

$$+ \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\varphi_n(y)\psi_n^*(y)}{|x - y|}\mathrm{d}x\mathrm{d}y - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \tau(x, y)\frac{\varphi_n(y)\psi_n^*(x)}{|x - y|}\mathrm{d}y\mathrm{d}x.$$

Since both the terms in (4.2) are conjugate-linear in their second argument we can extend the equations to

$$\mathfrak{h}_{\mathcal{A}}^F[\varphi_n, \psi_n] + \epsilon_n \int_{\mathbb{R}^3} \varphi_n\psi_n^*\mathrm{d}x = 0 \quad \forall\psi_n \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3). \qquad (4.3)$$

5. The Fock mean-field operator

Herein we introduce the magnetic Fock operator and relate it to the minimizer for the relaxed Hartree–Fock problem.

Proposition 5.1. *Suppose $A_m \in L^4_{loc}(\mathbb{R}^3)$, $m = 1, 2, 3$, and $\operatorname{div} \mathcal{A} \in L^2_{loc}(\mathbb{R}^3)$. Let*

$$K^{xc}(x, y) = \frac{\tau(x, y)}{|x - y|}$$

be the integral kernel of the exchange operator K^{xc}. Then the operator

$$-\Delta_{\mathcal{A}}\phi + V_{en}\phi + \rho * \frac{1}{|x|}\phi - K^{xc}\phi \tag{5.1}$$

defined on $\mathscr{D}(\mathbb{R}^3)$ has a unique self-adjoint extension, denoted $H^F_{\mathcal{A}}$. The sesquilinear form associated with $H^F_{\mathcal{A}}$ is

$$\mathfrak{h}^F_{\mathcal{A}}[\phi, \psi] = \int_{\mathbb{R}^3} \nabla_{\mathcal{A}}\phi(x)\nabla_{\mathcal{A}}\psi^*(x) + V_{en}(x)\phi(x)\psi^*(x)\mathrm{d}x$$

$$+ \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\phi(y)\psi^*(y)}{|x - y|}\mathrm{d}x\mathrm{d}y - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \tau(x, y)\frac{\phi(y)\psi^*(x)}{|x - y|}\mathrm{d}y\mathrm{d}x \tag{5.2}$$

and the Lagrange multipliers (with changed sign) in (4.3) correspond to eigenvalues of the operator $H^F_{\mathcal{A}}$ with associated eigenfunctions φ_n provided the latter are nonzero.

Proof. Let us first prove that the operator in (5.1) is essentially self-adjoint and bounded from below on $\mathscr{D}(\mathbb{R}^3)$ and hence that there exists a unique self-adjoint extension, denote by $H^F_{\mathcal{A}}$. It is well-known that the magnetic Laplacian $-\Delta_{\mathcal{A}}$ is essentially self-adjoint on $\mathscr{D}(\mathbb{R}^3)$ provided $A_k \in L^4_{loc}(\mathbb{R}^3)$ and $\operatorname{div}\mathcal{A} \in L^2_{loc}(\mathbb{R}^2)$ holds [18]; in particular, the latter is ensured by Assumption 1.1(i) and Property A.1(i).

By invoking (3.3), the Hardy inequality (3.4) and the diamagnetic inequality (2.2), it follows that the kernel K^{xc} belongs to $L^2(\mathbb{R}^6)$ and, consequently, the exchange operator is a (bounded and self-adjoint) Hilbert–Schmidt operator.

We recall that V is infinitesimally $-\Delta$-bounded by Kato's theorem [15] and, due to [3, Theorem 2.4], V_{en} is thus infinitesimally $-\Delta_{\mathcal{A}}$-bounded. Now $\rho \in L^1(\mathbb{R}^3)$ and the bound (2.5) implies that $\rho \in L^{5/3}(\mathbb{R}^3)$. From this it follows that $\rho * \frac{1}{|x|}$ is a bounded function; in fact, it is continuous and tends to zero at infinity and, consequently, it belongs to the Kato class $\mathcal{K}_3$. An application of the Kato–Rellich theorem yields that $-\Delta_{\mathcal{A}} + V_{en} + \rho * \frac{1}{|x|}$ is an self-adjoint operator (and bounded from below) on $\mathscr{D}(\mathbb{R}^3)$.

Now, consider the following quadratic form:

$$\mathfrak{q}[\phi] = \int_{\mathbb{R}^3} |\nabla_{\mathcal{A}}\phi(x)|^2 + V_{en}(x)|\phi(x)|^2\mathrm{d}x + \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)|\phi(y)|^2}{|x - y|}\mathrm{d}x\mathrm{d}y.$$

We prove that this form is closed and semi-bounded from below on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ and therefore, according to the first representation theorem [4, Theorem VI.2.4], there exists a self-adjoint and bounded from below operator Q such that

$$\mathfrak{q}[\phi, \psi] = \langle Q\phi, \psi \rangle$$

for $\phi \in \mathfrak{D}(Q) \subset \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ and $\psi \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$, where $\mathfrak{q}[\phi, \psi]$ is the sesquilinear form associated with $\mathfrak{q}[\phi]$, i.e.,

$$\mathfrak{q}[\phi, \psi] = \int_{\mathbb{R}^3} \nabla_{\mathcal{A}}\phi(x)\nabla_{\mathcal{A}}\psi^*(x) + V_{en}(x)\phi(x)\psi^*(x)\mathrm{d}x + \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\phi(y)\psi^*(y)}{|x - y|}\mathrm{d}x\mathrm{d}y.$$

Invoking (3.5), in conjunction with $\rho * \frac{1}{|x|}$ being continuous and bounded on $\mathbb{R}^3$, we infer that

$$|\mathfrak{q}[\phi]| \le \|\nabla_{\mathcal{A}}\phi\|^2_{L^2} + c_2\|\phi\|_{L^2}\|\nabla_{\mathcal{A}}\phi\|_{L^2} + c_2\|\phi\|^2_{L^2} \le c_3\|\phi\|^2_{\mathbf{H}^1_{\mathcal{A}}},$$

which proves that the form is bounded on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. The form is closed if it is lower semi-continuous [33]. Since $V_{en}, \rho * \frac{1}{|x|} \in \mathcal{K}_3$, the result follows from Lemma 3.3. Now, evidently,

$$\mathfrak{h}^F_{\mathcal{A}}[\phi, \psi] = \mathfrak{q}[\phi, \psi] - \langle K^{xc}\phi, \psi \rangle$$

and $H_{\mathcal{A}}^F$ will be the operator associated with this sesquilinear form. Using (4.3) we conclude from [4, Theorem VI.2.4] that $-\epsilon_n$ corresponds to an eigenvalue of $H_{\mathcal{A}}^F$ with φ_n as its eigenfunction provided $\varphi_n \neq 0$.

Next we describe the components of $\boldsymbol{\varphi}$ by means of "complementary" minimization problems.

Theorem 5.2. *Suppose $A_m \in L_{\text{loc}}^4(\mathbb{R}^3)$, $m = 1, 2, 3$, and $\operatorname{div} \mathcal{A} \in L_{\text{loc}}^2(\mathbb{R}^3)$. Let $\mathfrak{h}_{\mathcal{A}}^F$ denote the sesquilinear form in (5.2). Then the nth component of $\boldsymbol{\varphi}$, i.e. φ_n, is a minimum to*

$$\inf \left\{ \mathfrak{h}_{\mathcal{A}}^F[\phi, \phi] : \phi \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3) \wedge \|\phi\|_{L^2} \leq 1 \wedge \int_{\mathbb{R}^3} \phi \phi_m^* \mathrm{d}x = 0, \forall m \neq n \right\}. \tag{5.3}$$

Moreover, the minimum is equal to $-\gamma_n \epsilon_n$.

Proof. First note that

$$\mathcal{E}^{\text{MHF}}(\phi_1, \ldots, \phi_{n-1}, \phi, \phi_{n+1}, \ldots, \phi_N) = \mathcal{E}^{\text{MHF}}(\phi_1, \ldots, \phi_{n-1}, 0, \phi_{n+1}, \ldots, \phi_N) + \mathfrak{h}_{\mathcal{A}}^F[\phi, \phi] + \mathfrak{r}[\phi, \phi_n], \tag{5.4}$$

where

$$\mathfrak{r}[\phi, \phi_n] = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \phi^*(x)\phi(y) \frac{1}{|x-y|} \phi_n(x)\phi_n^*(y) \, \mathrm{d}x \mathrm{d}y - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\phi(x)|^2 |\phi_n(y)|^2}{|x-y|} \mathrm{d}x \mathrm{d}y.$$

It is clear that $\mathfrak{r}[\phi_n, \phi_n] = 0$. The Cauchy–Schwartz inequality implies that

$$\left| \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \phi^*(x)\phi(y) \frac{1}{|x-y|} \phi_n(x)\phi_n^*(y) \mathrm{d}x \mathrm{d}y \right| \leq \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\phi(x)|^2 |\phi_n(y)|^2}{|x-y|} \mathrm{d}x \mathrm{d}y$$

and we conclude that

$$\mathfrak{r}[\phi, \phi_n] \leq 0.$$

We also note that according to (4.3) the minimum is $-\gamma_n \epsilon_n$. $\quad\blacksquare$

6. Lower spectral bound

Eventually we shall balance the electrostatic interaction. For this purpose we establish the following spectral result.

Lemma 6.1. *Let Assumptions 1.1 and 1.2 hold, and let μ be any bounded nonnegative measure on $\mathbb{R}^3$ obeying $\mu(\mathbb{R}^3) \leq \vartheta$. Define the magnetic Schrödinger operator*

$$L_\mu = -\Delta_{\mathcal{A}} + V_{en} + \mu * \frac{1}{|x|}.$$

Then, for any $j \geq 1$ and any $0 \leq \vartheta < Z$, there exists $\epsilon_{j,\vartheta} > 0$ such that

$$\operatorname{Coun}(-\epsilon_{j,\vartheta}; L_\mu) \geq j.$$

Proof. Under Assumptions 1.1 and 1.2 the essential spectrum of the magnetic Laplacian $-\Delta_{\mathcal{A}}$ equals the semiaxis $[0, \infty)$, as stated in Proposition A.2. Let $\mathfrak{l}_\mu$ denote the quadratic form defined by

$$\int_{\mathbb{R}^3} |\nabla_{\mathcal{A}} \phi(x)|^2 + \left(V_{en} + \mu * \frac{1}{|x|} \right) |\phi(x)|^2 \mathrm{d}x. \tag{6.1}$$

For any $j \geq 1$ and any $0 \leq \vartheta \leq Z$ we construct a j-dimensional subspace $\mathcal{H}_{j,\vartheta}$ in $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$ such that

$$\mathfrak{l}_\mu[\phi, \phi] < -\epsilon_{j,\vartheta} < 0 \tag{6.2}$$

for all L^2-normalized $\phi \in \mathcal{H}_{j,\vartheta}$. We pick any normalized function $\phi \in \mathscr{D}(\mathbb{R}^3)$ and then we let

$$\phi_\lambda := \lambda^{-3/2} \phi(\cdot/\lambda), \quad \lambda > 0.$$

Observe that

$$|\nabla_{\mathcal{A}} \phi|^2 = |\nabla \phi|^2 - 2\operatorname{Im} \mathcal{A}\phi \cdot \nabla \phi^* + |\mathcal{A}\phi|^2.$$

1 Since $\mathcal{A}$ is homogeneous of degree -1, we thus find that

$$\mathfrak{l}_\mu[\phi_\lambda, \phi_\lambda] = \frac{1}{\lambda^2} \int_{\mathbb{R}^3} |\nabla\phi(x)|^2 \mathrm{d}x - \frac{1}{\lambda^2} \int_{\mathbb{R}^3} 2\mathrm{Im}\,\mathcal{A}\phi \cdot \nabla\phi^* + |\mathcal{A}\phi|^2 \mathrm{d}x$$

$$+ \frac{1}{\lambda} \int_{\mathbb{R}^3} V_\lambda(x)|\phi(x)|^2 \mathrm{d}x + \frac{1}{\lambda} \int_{\mathbb{R}^3} \left(\mu_\lambda * \frac{1}{|x|}\right)|\phi(x)|^2 \mathrm{d}x, \tag{6.3}$$

4 where

$$V_\lambda(x) := -\sum_{k=1}^{K} \frac{Z_k}{|x - R_k/\lambda|}, \quad \text{and} \quad \mu_\lambda = \lambda^3 \mu(\lambda\cdot).$$

6 By choosing ϕ as radially symmetric on $\mathbb{R}^3$, Newton's Theorem for measures [21, Theorem 9.7] enables us to re-write
7 the last term in (6.3):

$$\int_{\mathbb{R}^3} \left(\mu_\lambda * \frac{1}{|x|}\right)|\phi(x)|^2 \mathrm{d}x = \int_{\mathbb{R}^3} \left(|\phi(x)|^2 * \frac{1}{|x|}\right) \mathrm{d}\mu_\lambda$$

$$= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{\max(|x|, |y|)} \mathrm{d}x \mathrm{d}\mu_\lambda \le \mu_\lambda(\mathbb{R}^3) \int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x|} \mathrm{d}x,$$

10 where, obviously, $\mu_\lambda(\mathbb{R}^3) = \mu(\mathbb{R}^3)$. We observe that, as $\lambda \to \infty$,

$$\int_{\mathbb{R}^3} V_\lambda(x)|\phi(x)|^2 \mathrm{d}x \longrightarrow -Z \int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x|} \mathrm{d}x < -\mu(\mathbb{R}^3) \int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x|} \mathrm{d}x.$$

12 As a consequence, by selecting a j-dimensional subspace of normalized, radially symmetric functions in $\mathscr{D}(\mathbb{R}^3)$ and
13 then dilate them as above, we can construct a subspace $\mathcal{H}_{j,\vartheta}$ of functions satisfying (6.2) provided λ is large enough.
14 Then the assertion follows by an application of Glazman's Lemma (see, e.g., [31]).

15 For $\mathcal{A} \equiv 0$ a similar result was established in [26].

7. Completion of proof of Theorem 1.4

17 We are ready to complete the proof of Theorem 1.4:

18 **Proof** (*Proof of Theorem* 1.4: *Final Arguments*). If the measure μ in Lemma 6.1 is chosen as $\rho\mathrm{d}x$ with ρ being the
19 density $\rho(x) = \sum_{n=1}^{N} |\varphi_n(x)|^2$ $(x \in \mathbb{R}^3)$, then the resulting Schrödinger operator $L_{\rho\mathrm{d}x}$ satisfies the operator inequality

$$H_\mathcal{A}^F \le L_{\rho\mathrm{d}x}, \tag{7.1}$$

21 where $H_\mathcal{A}^F$ is the magnetic Fock mean-field operator introduced in Proposition 5.1.

22 We first claim that all components of $\boldsymbol{\varphi}$ are nonzero. Suppose one of the orbitals vanishes, say φ_1; i.e. $\rho(x) = \sum_{n=2}^{N}$
23 $|\varphi_n(x)|^2$. Then

$$\mu(\mathbb{R}^3) = \sum_{n=2}^{N} \int_{\mathbb{R}^3} |\varphi_n(x)|^2 \mathrm{d}x \le N - 1.$$

25 By hypothesis, $N - 1 < Z$ so an application of Lemma 6.1, in conjunction with (7.1), informs us that $H_\mathcal{A}^F$ has at least
26 N *negative* eigenvalues. The eigenvalues of $H_\mathcal{A}^F$ are related to the "complementary" minimization problems (5.3) in
27 the following way. Let Π_{N-1} be the subspace spanned by the $N - 1$ orbitals $\varphi_2, \ldots, \varphi_N$, and let $\mathcal{M}_{N-1}$ be any linear
28 subspace of $\mathbf{H}_\mathcal{A}^1(\mathbb{R}^3)$ of dimension at most $N - 1$. If the Nth eigenvalue of $H_\mathcal{A}^F$ is denoted by ν_N, then the min–max
29 principle yields

$$0 > \nu_N(H_\mathcal{A}^F) = \sup_{\mathcal{M}_{N-1}} \inf_{\psi \in \mathfrak{D}(H_\mathcal{A}^F) \cap \mathcal{M}_{N-1}^\perp, \|\psi\|=1} \langle H_\mathcal{A}^F \psi, \psi \rangle$$

$$= \inf_{\psi \in \mathfrak{D}(H_\mathcal{A}^F) \cap \Pi_{N-1}^\perp, \|\psi\|=1} \langle H_\mathcal{A}^F \psi, \psi \rangle$$

$$\ge -\epsilon_1 \gamma_1.$$

Since the infimum in (5.3) is negative, φ_1 cannot vanish (if $\varphi_1 \equiv 0$, then the infimum in (5.3) equals zero when φ_1 is inserted). Hence all orbitals $\varphi_1, \ldots, \varphi_N$ are nonzero. In particular, we have thus shown that $\gamma_1, \ldots, \gamma_N > 0$.

Next we show that $\gamma_1 = \gamma_2 = \cdots = \gamma_N = 1$. Generally, the infimum in (5.3) is nonpositive; this is easily shown by a scaling argument. In particular, this implies that $\epsilon_n \geq 0$. To prove that $\epsilon_n > 0$ for all n, we argue by contradiction. Suppose ϵ_1 vanishes. Then Theorem 5.2 implies that

$$\langle H_{\mathcal{A}}^F \varphi_1, \varphi_1 \rangle = 0, \quad \varphi_1 \neq 0.$$

In view of (5.4), we infer that

$$\mathcal{E}^{\mathrm{MHF}}(\varphi_1, \ldots, \varphi_N) = \mathcal{E}^{\mathrm{MHF}}(0, \varphi_2, \ldots, \varphi_N).$$

In other words, $(0, \varphi_2, \ldots, \varphi_N)$ is a minimizer in $\mathcal{S}_N^{\leq}$ and thus $\gamma_1 = 0$ which contradicts γ_n for all n (shown above). We conclude that $\epsilon_1, \ldots, \epsilon_N > 0$, i.e. $H_{\mathcal{A}}^F$ has at least N negative eigenvalues, namely $-\epsilon_1, \ldots, -\epsilon_N$. The latter implies that $\gamma_n = 1$ for all n.

Uncited references

Q5   [32].

Appendix. Essential spectrum of magnetic Laplacian

The following properties of the vector potential are straightforward to verify from (1.4) and Assumption 1.2 (cf. [2]).

Property A.1. *Let Assumption* 1.2 *be satisfied. Then, for $m = 1, 2, 3$,*

  (i)

$$A_m \in L^4_{\mathrm{loc}}(\mathbb{R}^3).$$

  (ii)

$$\left\| A_m(x)(-\Delta + \mathrm{i})^{-\frac{1}{2}} \right\|_{\mathcal{B}(L^2)} < \infty.$$

(iii) *$|A_m(x)|^2$ and $A_m(x)\nabla$ are $-\Delta$-bounded with relative bound less than one.*
(iv) *Smallness at infinity: For $\nu \in (0, 1)$,*

$$\left\| A_m(x)\widetilde{\chi}(|x| > R)(-\Delta + 1)^{-\frac{1}{2}} \right\|_{\mathcal{B}(L^2)} \leq c\, R^{-\nu} \quad and$$

$$\left\| |A_m(x)|^2 \widetilde{\chi}(|x| > R)(-\Delta + 1)^{-1} \right\|_{\mathcal{B}(L^2)} \leq c\, R^{-2\nu}.$$

Let Assumptions 1.1 and 1.2 be satisfied. Then $-\Delta_{\mathcal{A}} = (\mathrm{i}\nabla - \mathcal{A}(x))^2$ is a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $\mathfrak{D}(-\Delta_{\mathcal{A}}) = \mathfrak{D}(-\Delta) = \mathbf{H}^2(\mathbb{R}^3)$. Moreover, $-\Delta_{\mathcal{A}}$ is essentially self-adjoint on $C_0^\infty(\mathbb{R}^3)$. Indeed, in view of Assumption 1.1(ii) and Property A.1(ii), the operators div $\mathcal{A}(x)$, $\mathcal{A}(x)\nabla$, and $|\mathcal{A}(x)|^2$ are $-\Delta$-bounded with bound less than one, and thus the Kato–Rellich theorem asserts that $-\Delta_{\mathcal{A}}$ is a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $\mathfrak{D}(-\Delta_{\mathcal{A}}) = \mathfrak{D}(-\Delta) = \mathbf{H}^2(\mathbb{R}^3)$. Assumption 1.1(i) and Property A.1(i) ensure that $-\Delta_{\mathcal{A}}$ is essentially self-adjoint on $C_0^\infty(\mathbb{R}^3)$ [18]. We proceed to determining the essential spectrum of $-\Delta_{\mathcal{A}}$:

Proposition A.2. *Let Assumptions 1.1 and 1.2 be satisfied. Then $f(-\Delta_{\mathcal{A}}) - f(-\Delta)$ is compact for any $f \in C_\infty(\mathbb{R})$; the continuous functions vanishing at infinity. In particular, $\sigma_{\mathrm{ess}}(-\Delta_{\mathcal{A}}) = \sigma_{\mathrm{ess}}(-\Delta) = [0, \infty)$.*

Proof. We make a few introductory observations. Now

$$\widetilde{\chi}(|x| \leq R)(-\Delta + 1)^{-\frac{1}{2}} \tag{A.1}$$

is Hilbert–Schmidt and thus compact because the kernel of (A.1), namely

$$\chi_R(x)(-\Delta + 1)^{-\frac{1}{2}}(x, y)$$

belongs to $L^2(\mathbb{R}^6)$. In view of Assumption 1.1(ii) and Property A.1(iii), the operator

$$(-\Delta + 1)^{-1}(-\Delta_{\mathcal{A}} - \zeta)^{-\frac{1}{2}}$$

is bounded and, consequently,

$$\widetilde{\chi}(|x| \leq R)(-\Delta_{\mathcal{A}} - \zeta)^{-\frac{1}{2}} = \widetilde{\chi}(|x| \leq R)(-\Delta + 1)^{-\frac{1}{2}}(-\Delta + 1)^{\frac{1}{2}}(-\Delta_{\mathcal{A}} - \zeta)^{-\frac{1}{2}}$$

is compact. It follows that

$$\widetilde{\chi}(|x| \leq R)\widetilde{\chi}(-\Delta_{\mathcal{A}} \leq E)$$

is compact. Next we set $V_{\mathcal{A}} := 2i\mathcal{A}\nabla + i\operatorname{div}\mathcal{A} + |\mathcal{A}|^2$. To prove the first assertion, it suffices to prove that

$$(-\Delta_{\mathcal{A}} - \zeta)^{-1} - (-\Delta - \zeta)^{-1} = (-\Delta_{\mathcal{A}} - \zeta)^{-1}\widetilde{\chi}(|x| \leq R) - (-\Delta - \zeta)^{-1}\widetilde{\chi}(|x| \leq R)$$

$$+ (-\Delta_{\mathcal{A}} - \zeta)^{-1}V_{\mathcal{A}}(-\Delta - \zeta)^{-1}\widetilde{\chi}(|x| \geq R). \tag{A.2}$$

The first two terms are compact for any (finite) R because, as we demonstrated above, $\widetilde{\chi}(|x| \leq R)\widetilde{\chi}(-\Delta_{\mathcal{A}} \leq E)$ is compact. According to Assumption 1.1(iii) and Property A.1(iv), the third term in (A.2) has arbitrary small norm provided R is large enough. Hence $(-\Delta_{\mathcal{A}} - \zeta)^{-1} - (-\Delta - \zeta)^{-1}$ is compact by the norm-closure of the compact operators. This proves the first assertion. The second follows directly from Weyl's essential spectrum theorem.

References

[1] Sh. Agmon, Lectures on elliptic boundary value problems, in: Nostrand Mathematical Studies, vol. 2, D. Van Nostrand Co., Inc., Princeton, NJ, Toronto, London, 1965.

[2] S. Arians, Eine neue phasenraumlokalisierung im vollständigkeitsbeweis für Hamiltonoperatoren mit magnetfeld, Berlin, Logos-Verl, 1996.

[3] J. Avron, I. Herbst, B. Simon, Schrödinger operators with magnetic fields: I. General interactions, Duke Math. J. 45 (1978) 847–883.

[4] D.E. Edmunds, W.D. Evans, Spectral Theory and Differential Operators, Clarendon Press, Oxford University Press, New York, 1987.

[5] V. Enss, Quantum scattering with long-range magnetic fields, in: Operator Calculus and Spectral Theory (Lambrecht, 1991), in: Oper. Theory Adv. Appl., vol. 57, Birkhäuser, Basel, 1992, pp. 61–70.

Q6 [6] M. Enstedt, M. Melgaard, On the non-existence of a minimizer to the magnetic Hartree–Fock functional, 2007, 16 pages (submitted for publication).

[7] M.J. Esteban, P.-L. Lions, Stationary solutions of nonlinear Schrödinger equations with an external magnetic field, in: Partial Differential Equations and the Calculus of Variations, in: Progr. Nonlinear Differential Equations Appl., vol. I, Birkhäuser Boston, Boston, MA, 1989, pp. 401–449.

[8] V. Fock, Näherungsmethode zur lösung des quantenmechanischen Mehrkörperproblems, Z. Phys. 61 (1930) 126–148.

[9] G. Fonte, R. Mignani, G. Schiffrer, Solution of the Hartree–Fock equations, Comm. Math. Phys. 33 (1973) 293–304.

[10] T. Frankel, The Geometry of Physics. An Introduction, 2nd ed., Cambridge University Press, Cambridge, 2004.

Q7 [11] K. Gustafson, D. Sather, A branching analysis of the Hartree equation, Rend. Mat. 4 (6) (1971) 723–734.

[12] D.R. Hartree, The wave mechanics of an atom with the non-Coulomb central field, I. Theory and methods, Proc. Cambridge Philos. Soc. 24 (1928) 89–132.

[13] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, 1986.

[14] A. Jaffe, C. Taubes, Vortices and Monopoles. Structure of Static Gauge Theories, in: Progress in Physics, vol. 2, Birkhäuser, Boston, Mass., 1980.

[15] T. Kato, Fundamental properties of Hamiltonian operators of Schrödinger type, Trans. Amer. Math. Soc. 70 (1951) 195–211.

[16] T. Kato, Remarks on Schrödinger operators with vector potentials, Integral Equations Oper. Theory 1 (1) (1978) 103–113.

[17] T. Kato, Perturbation Theory for Linear Operators, in: Classics in Mathematics, Springer-Verlag, Berlin, 1995. Reprint of the 1980 edition.

[18] H. Leinfelder, C.G. Simader, Schrödinger operators with singular magnetic vector potentials, Math. Z. 176 (1) (1981) 1–19.

[19] E.H. Lieb, Thomas–Fermi and Hartree–Fock theory, in: Proceedings of the International Congress of Mathematicians (Vancouver, B.C., 1974), in: Canad. Math. Congress, vol. 2, Montreal, Que., 1975, pp. 383–386.

[20] E.H. Lieb, Bound on the maximum negative ionization of atoms and molecules, Phys. Rev. A 29 (1984) 3018–3028.

Q8 [21] E.H. Lieb, M. Loss, Analysis, American Mathematical Society, Providence, RI, 1997.

[22] E.H. Lieb, B. Simon, On solutions to the Hartree–Fock problem for atoms and molecules, J. Chem. Phys. 61 (1974) 735–736.

[23] E.H. Lieb, B. Simon, The Hartree–Fock theory for Coulomb systems, Comm. Math. Phys. 53 (3) (1977) 185–194.

[24] E.H. Lieb, W. Thirring, Bound for the kinetic energy of fermions which proves the stability of matter, Phys. Rev. Lett. 35 (1975) 687–689. Errata Phys. Rev. Lett. 35 (1975) 1116.

[25] E.H. Lieb, W. Thirring, Inequalities for the moment of the eigenvalues of the Schrödinger Hamiltonian and their relation to Sobolev inequalities, in: E.H. Lieb, B. Simon, A. Wightman (Eds.), in: Studies in Mathematical Physics, Princeton Univ. Press, 1976, pp. 269–303.

[26] P.-L. Lions, Solutions of Hartree–Fock equations for Coulomb systems, Comm. Math. Phys. 109 (1) (1987) 33–97.

[27] P.-O. Löwdin, Quantum theory of many-particle systems. I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction, Phys. Rev. 97 (2) (1955) 1474–1489.

[28] R. McWeeny, Methods of Molecular Quantum Mechanics, 2nd ed., Academic Press, 1992.

[29] M. Reeken, General theorem on bifurcation and its application to the Hartree equation of the helium atom, J. Math. Phys. 11 (1970) 2505–2512.

[30] M. Reeken, Existence of solutions to the Hartree–Fock equations, in: Eigenvalues of Non-Linear Problems (Centro Internaz. Mat. Estivo (C.I.M.E.), III Ciclo, Varenna, 1974), Edizioni Cremonese, Rome, 1974, pp. 197–209.

[31] G. Rozenblum, M. Melgaard, Schrödinger operators with singular potentials, in: Stationary Partial Differential Equations, in: Handb. Differ. Equ., vol. II, Elsevier/North-Holland, Amsterdam, 2005, pp. 407–517.

[32] B. Simon, Universal diamagnetism of spinless Boson systems, Phys. Rev. Lett. 36 (1976) 1083–1084.

[33] B. Simon, Lower semicontinuity of positive quadratic forms, Proc. Roy. Soc. Edinburgh 79 (1977) 267–273.

[34] B. Simon, Maximal and minimal Schrödinger forms, J. Oper. Theory 1 (1) (1979) 37–47.

[35] J.C. Slater, Note on Hartree's method, Phys. Rev. 35 (1930) 210–211.

[36] C.A. Stuart, Existence theory for the Hartree equation, Arch. Ration. Mech. Anal. 51 (1973) 60–69.

[37] A. Szabo, N.S. Ostlund, Modern Quantum Chemistry: An Introduction to Advanced Electronic Structure Theory, MacMillan, 1982.

[38] J.H. Wolkowisky, Existence of solutions of the Hartree equations for *N* electrons. An application of the Schauder–Tychonoff theorem, Indiana Univ. Math. J. 22 (1972–1973) 551–568.

[39] E. Zeidler, Applied Functional Analysis. Main Principles and their Applications, in: Applied Mathematical Sciences, vol. 109, Springer-Verlag, New York, 1995.