# Ground state solutions to Hartree–Fock equations with magnetic fields

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# GROUND STATE SOLUTIONS TO HARTREE-FOCK EQUATIONS WITH MAGNETIC FIELDS *

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Abstract. Within the Hartree-Fock theory of atoms and molecules we prove existence of a ground state in the presence of an external magnetic field when: (1) the diamagnetic effect is taken into account; (2) both the diamagnetic effect and the Zeeman effect are taken into account. For both cases the ground state exists provided the total charge $Z_{\rm tot}$ of the nuclei $K$ exceeds $N-1$, where $N$ is the number of electrons. For the first case, the Schrödinger case, we complement prior results [8, 7] by allowing a wide class of magnetic potentials. In the second case, the Pauli case, we include the magnetic field energy in order to obtain a stable problem and we assume $Z_{\rm tot}\alpha^2 \leq 0.041$, where $\alpha$ is the fine structure constant.

## Contents



## 1. Introduction

Within the Born-Oppenheimer approximation, a molecule consisting of $N$ electrons interacting with $K$ static nuclei in an external magnetic field $\mathcal{B} = \mathrm{curl}\ \mathcal{A}$, defined via a real-valued

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vector potential $\mathcal{A} = (A_1, A_2, A_3)$ is in Schrödinger's quantum theory described by the following molecular Hamiltonian (the so-called non-relativistic Schrödinger operator) acting on the space of antisymmetric functions $\bigwedge^N \mathfrak{H}^{\mathrm{s}}$ with $\mathfrak{H}^{\mathrm{s}} = L^2(\mathbb{R}^3; \mathbb{C})$,

$$\mathbb{H}_{N,\boldsymbol{Z},\mathcal{A}} = \frac{1}{2}\sum_{j=1}^{N} -\Delta_{\mathcal{A},\boldsymbol{r}_j} + V_{\mathrm{C}}, \tag{1.1}$$

where $-\Delta_{\mathcal{A},\boldsymbol{r}_j}$ is the square of $-i\nabla_{\mathcal{A},\boldsymbol{r}_j} = (P^{(1)}_{\boldsymbol{r}_j}, P^{(2)}_{\boldsymbol{r}_j}, P^{(3)}_{\boldsymbol{r}_j})$, $P^{(m)}_{\boldsymbol{r}_j} = P^{(m)}_{\mathcal{A},\boldsymbol{r}_j} = -i\partial_{\boldsymbol{r}^{(m)}_j} - A_m(\boldsymbol{r}_j)$, and the Coulomb potential $V_{\mathrm{C}}$ is given by

$$V_{\mathrm{C}} = \sum_{j=1}^{N} V_{\mathrm{en}}(\boldsymbol{r}_j) + \sum_{1\le j<k\le N} V_{\mathrm{ee}}(\boldsymbol{r}_j - \boldsymbol{r}_k). \tag{1.2}$$

where

$$V_{\mathrm{en}}(\boldsymbol{r}') = -\sum_{k=1}^{K} V_k(\boldsymbol{r}') := -\sum_{k=1}^{K} \frac{Z_k}{|\boldsymbol{r}' - \boldsymbol{R}_k|}, \quad V_{\mathrm{ee}}(\boldsymbol{r}') = 1/|\boldsymbol{r}'| \tag{1.3}$$

with $\boldsymbol{r}_j$, $\boldsymbol{R}_k$ denoting the coordinates of the $j$th electron and $k$th nucleus respectively, and $Z_k > 0$ the charge of the $k$th nucleus. The total charge of the nuclei is $Z_{\mathrm{tot}} = \sum_{k=1}^{K} Z_k$. A magnetic field has two effects on a system of electrons: (i) it tends to align their spins, and (ii) it alters their translational motion. The first effect appears when one adds a (*Zeeman*) term of the form $\boldsymbol{\sigma} \cdot \mathcal{B}$ to the Hamiltonian with $\boldsymbol{\sigma}$ being the angular momentum vector associated with the electron spin, while the second, *diamagnetic* effect arises from the usual kinetic energy $(-i\nabla)^2$ being replaced by $(-i\nabla - \mathcal{A})^2$. Above we have taken into account the second effect but we shall also consider the molecular Pauli operator, taking into account both (i) and (ii),

$$\mathbb{P}_{N,\boldsymbol{Z},\mathcal{A}} = \frac{1}{2}\sum_{j=1}^{N} \mathbb{P}^{(j)}_{\mathcal{A}} + \left( \sum_{1\le j<k\le N} V_{\mathrm{ee}}(\boldsymbol{r}_j - \boldsymbol{r}_k) + \sum_{j=1}^{N} V_{\mathrm{en}}(\boldsymbol{r}_j) \right) \mathbb{I}_2 \tag{1.4}$$

where the Pauli operator $\mathbb{P}^{(j)}_{\mathcal{A}}$ is given by

$$\mathbb{P}^{(j)}_{\mathcal{A}} = \left[\boldsymbol{\sigma}_j \cdot \left(-i\nabla_{\boldsymbol{r}_j} - \mathcal{A}(\boldsymbol{r}_j)\right)\right]^2 = \left(-i\nabla_{\boldsymbol{r}_j} - \mathcal{A}(\boldsymbol{r}_j)\right)^2 \mathbb{I}_2 - \boldsymbol{\sigma}_j \cdot \mathcal{B}(\boldsymbol{r}_j), \tag{1.5}$$

with $\boldsymbol{\sigma}_j = (\sigma_{xj}, \sigma_{yj}, \sigma_{zj})$ being the triple of Pauli spin matrices satisfying the anti-commutation relations. Specifically,

$$\boldsymbol{\sigma}_j = (\sigma_{xj}, \sigma_{yj}, \sigma_{zj}) = \left( \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_j, \quad \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_j, \quad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_j \right). \tag{1.6}$$

The Hamiltonian $\mathbb{P}_{N,\boldsymbol{Z},\mathcal{A}}$ operates on the Fermionic subspace of the Hilbert space $\otimes^N \mathfrak{H}_{\mathrm{p}}$ with $\mathfrak{H}_{\mathrm{p}} = L^2(\mathbb{R}^3; \mathbb{C}^2)$. The Fermionic subspace $\bigwedge^N \mathfrak{H}_{\mathrm{p}}$ consists of all antisymmetric functions.
For the reader's convenience we aim to make it easy to navigate in the paper, in particular distinguishing between the Schrödinger and Pauli cases throughout the paper (even within proofs) by using superscript, respectively, subscript for entities (spaces, operators, functions,

etc) related to the Schrödinger case, respectively, Pauli case; except for expressions related to energy, where superscript will be used throughout.
We impose the following conditions throughout the paper.

**Assumption 1.1.** Suppose
(i) *Schrödinger case.* $\mathcal{A} \in L^{\tau}(\mathbb{R}^3;\mathbb{R})^3 + L^{\omega}(\mathbb{R}^3;\mathbb{R})^3$, $2 \le \tau \le \omega < 6$.
(ii) *Pauli case.* $\mathcal{A} \in L^{6}(\mathbb{R}^3;\mathbb{R})^3$, $\nabla \cdot \mathcal{A} = 0$ and $\mathcal{B} \in L^{2}(\mathbb{R}^3;\mathbb{R})^3$.

The fundamental task in computational quantum chemistry, needed before addressing other questions, is to determine the ground state and the ground state energy, i.e., the minimum of the spectrum of $\mathbb{H}_{N,\boldsymbol{Z},\mathcal{A}}$ or, equivalently, $E^{\mathrm{QM}}_{\mathbb{H}}(N,\boldsymbol{Z},\mathcal{A}) = \inf\{\, \mathcal{E}^{\mathrm{QM}}_{\mathbb{H}}(\Psi_{\mathrm{e}}) \,:\, \Psi_{\mathrm{e}} \in \mathcal{H}_{\mathrm{e}}, \|\Psi_{\mathrm{e}}\|_{L^2(\mathbb{R}^{3N})} = 1 \,\}$, where $\mathcal{E}^{\mathrm{QM}}_{\mathbb{H}}(\Psi_{\mathrm{e}}) := \langle \Psi_{\mathrm{e}}, \mathbb{H}_{N,\boldsymbol{Z},\mathcal{A}}\Psi_{\mathrm{e}}\rangle_{L^2(\mathbb{R}^{3N})}$ and $\Psi_{\mathrm{e}} \in \mathcal{H}_{\mathrm{e}} := \bigwedge^N \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$; $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) := \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3;\mathbb{C})$ being the "magnetic" analogue of the standard Sobolev space $\mathbf{H}^1$; see Section 2. If the minimum is attained, then the minimizer $\Psi_{\mathrm{e}}$ is a *ground state.* Equivalently, the ground state energy of the system is defined by

$$E^{\mathrm{QM}}_{\mathrm{H}}(N,\boldsymbol{Z},\mathcal{A}) = \inf \operatorname{spec}(H_{N,\boldsymbol{Z},\mathcal{A}}), \qquad H = \mathbb{H}, \mathbb{P} \tag{1.7}$$

where $\operatorname{spec}(H_{N,\boldsymbol{Z},\mathcal{A}})$ denotes the spectrum of the Hamiltonian $H_{N,\boldsymbol{Z},\mathcal{A}}$. Quantum theory, in particular determining $E^{\mathrm{QM}}_{\mathbb{H}}(N,\boldsymbol{Z},\mathcal{A})$, is however too hard for both theoretical and numerical studies. One of the classical approximation methods for determining $E^{\mathrm{QM}}_{\mathbb{H}}(N,\boldsymbol{Z},\mathcal{A})$ is the *Hartree-Fock theory*, introduced by Hartree and improved by Fock and Slater in the late 1920s [25], which consists of restricting attention to simple wedge products $\Psi_{\mathrm{S}} \in \mathcal{W}^{\mathrm{Slater}}_N$, where

$$\mathcal{W}^{\mathrm{Slater}}_N = \left\{ \Psi_{\mathrm{S}} \in \mathcal{H}_{\mathrm{e}} \,:\, \exists \Phi = \{\phi_n\}_{1\le n\le N} \in \mathcal{C}_N \,, \Psi_{\mathrm{S}} = \frac{1}{\sqrt{N!}}\det\,(\phi_n(\boldsymbol{r}_m)) \right\} \tag{1.8}$$

with

$$\mathcal{C}_N = \left\{\, \Phi = \{\phi_n\}_{1\le n\le N},\ \ \phi_n \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3),\ \ \langle \phi_m, \phi_n\rangle_{\mathfrak{H}^{\mathrm{s}}} = \delta_{mn},\ \ 1 \le m,n \le N \,\right\}\,; \tag{1.9}$$

where the orthonormality constraint is understood in the sense of Hermitian matrices.The form of the wave function becomes apparent by writing it out in details, viz.

$$\Psi_e(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N) = \frac{1}{\sqrt{N!}}\det(\phi_n(\boldsymbol{r}_m)) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\boldsymbol{r}_1) & \cdots & \phi_1(\boldsymbol{r}_N) \\ . & & . \\ . & & . \\ . & & . \\ \phi_N(\boldsymbol{r}_1) & \cdots & \phi_N(\boldsymbol{r}_N) \end{vmatrix}. \tag{1.10}$$

In the wording of Quantum Chemistry, a function of the form (1.10) is known as a *Slater determinant*, and the $\phi_n$ are called *molecular orbitals.*

If $\Psi_{\rm S} \in \mathcal{W}_N^{\rm Slater}$ then $\langle \Psi_{\rm S}, \mathbb{H}_{N,\boldsymbol{Z},\mathcal{A}}\Psi_{\rm S}\rangle =: \mathcal{E}^{\rm s}(\Psi_{\rm S})$, where the (Schrödinger) *Hartree-Fock functional* $\mathcal{E}^{\rm s}(\cdot)$ is given by

$$\begin{aligned}\mathcal{E}^{\rm s}(\phi_1, ..., \phi_N) &= \mathcal{E}^{\rm s}(\Psi_{\rm S}) = \langle \Psi_{\rm S}, \mathbb{H}_{N,\boldsymbol{Z},\mathcal{A}}\Psi_{\rm S}\rangle \\ &= \frac{1}{2}\sum_{n=1}^{N}\int_{\mathbb{R}^3} |\nabla_{\mathcal{A}}\phi_n(\boldsymbol{r})|^2 \,\mathrm{d}\boldsymbol{r} + \int_{\mathbb{R}^3} V_{\rm en}(\boldsymbol{r})\rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} \\ &\quad + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(\boldsymbol{r})\,\rho(\boldsymbol{r}') - |\mathcal{D}(\boldsymbol{r},\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'. \end{aligned} \tag{1.11}$$

Here

$$\mathcal{D}(\boldsymbol{r},\boldsymbol{r}') = \sum_{n=1}^{N} \overline{\phi_n(\boldsymbol{r})}\,\phi_n(\boldsymbol{r}') \tag{1.12}$$

is the *density matrix*, and

$$\rho_{\mathcal{D}}(\boldsymbol{r}) = \sum_{n=1}^{N} |\phi_n(\boldsymbol{r})|^2 \tag{1.13}$$

is the *density* associated to the state $\Psi_{\rm S}$. In contrast to the *linear* Schrödinger theory finding the *Hartree-Fock energy* is a nonlinear variational problem:

**Definition 1.2** (*The Hartree-Fock ground state*)**.** Let $\boldsymbol{Z} = (Z_1, \ldots, Z_K)$, $Z_k > 0$, $k = 1, \ldots, K$, and let $N$ be a nonnegative integer. The magnetic Hartree-Fock ground state energy is

$$E^{\rm s} \equiv E^{\rm s}(N, \boldsymbol{Z}, \mathcal{A}) := \inf\left\{ \mathcal{E}^{\rm s}(\Psi_{\rm S}) \,:\, \Psi_{\rm S} \in \mathcal{W}_N^{\rm Slater} \right\}. \tag{1.14}$$

If a minimizer exists, i.e., there exists some $\Psi_{\rm S}$ such that

$$\mathcal{E}^{\rm s}(\Psi_{\rm S}) = E^{\rm s}, \tag{1.15}$$

then it is said that the molecule has a magnetic Hartree-Fock ground state described by $\Psi_{\rm S}$.

For the molecular Pauli Hamiltonian $\mathbb{P}_{N,\boldsymbol{Z},\mathcal{A}}$ in (1.4) , the (Pauli) Hartree-Fock functional is

$$\begin{aligned}\mathcal{E}^{\rm p}(\Psi, \mathcal{A}) \;=\; & \frac{1}{2}\sum_{j=1}^{N}\int_{\mathbb{R}^{3N}} \|\boldsymbol{\sigma}_j\cdot(-i\nabla_j - \mathcal{A}(\boldsymbol{r}_j))\,\Psi_{\rm S}\|^2_{\mathbb{C}^2} \\ & + \left\langle \Psi_{\rm S}, \left(\sum_{j=1}^{N} V_{\rm en}(\boldsymbol{r}_j) + \sum_{1\le j<k\le N} V_{\rm ee}(\boldsymbol{r}_j - \boldsymbol{r}_k)\right)\Psi_{\rm S}\right\rangle_{L^2\left(\mathbb{R}^{3N};\mathbb{C}^{2^N}\right)} \\ & + \frac{1}{\alpha^2}\int_{\mathbb{R}^3} |\mathcal{B}(\boldsymbol{r})|^2 \mathrm{d}\boldsymbol{r}, \qquad \Psi_{\rm S} \in \mathcal{W}_N^{\rm Slater} \end{aligned} \tag{1.16}$$

where we have added the magnetic field energy ($\alpha$ being the fine structure constant) in the second line, a modification to be explained below, requiring $\mathcal{B} \in L^2(\mathbb{R}^3;\mathbb{R})^3$ and the admissible set $\mathcal{M}_{\rm p}$ of $(\Psi, \mathcal{A})$ consists of the Slater-state wave functions $\Psi_{\rm S} \in \mathcal{W}_N^{\rm Slater}$ (for precise definition in Pauli case, see Appendix A) and the unique class of vector potentials for which $\nabla \cdot \mathcal{A} = 0$, and $\mathcal{B} \in L^2(\mathbb{R}^3;\mathbb{R})^3$ [9], resulting in

$$\mathcal{M}_{\mathrm{p}} = \left\{ \begin{pmatrix} \Psi \\ \mathcal{A} \end{pmatrix} : \begin{array}{l} \Psi \in \mathcal{W}_N^{\mathrm{Slater}} \\ \mathcal{A} \in L^6(\mathbb{R}^3;\mathbb{R})^3, \quad \nabla \cdot \mathcal{A} = 0, \quad \mathcal{B} \in L^2(\mathbb{R}^3;\mathbb{R})^3 \end{array} \right\} \tag{1.17}$$

We add the field energy in order to obtain a stable physical model [17] (further explanations are provided at the end of Section 3). Note that the study of the Pauli operator is complicated by the fact that zero modes exist [21, 4]. When no magnetic field is present, the Hartree-Fock minimization problem (1.14) was studied by Lieb and Simon in [18] . Under the condition that the *total charge* $Z_{\mathrm{tot}} = \sum_{k=1}^{K} Z_k$ of the molecular system fulfills $Z_{\mathrm{tot}} + 1 > N$, 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 [18], the Hartree-Fock equations were studied by more direct approaches, yielding less general results (see the references in [7]).The proof in [18] 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 (1.14) is unchanged if $\mathcal{C}_N$ is replaced by

$$\mathcal{C}_N^{\leq} = \left\{ \Phi = \{\phi_n\}_{1\leq n\leq N}, \ \phi_n \in \mathbf{H}^1(\mathbb{R}^3), \ \langle \phi_m, \phi_n \rangle_{\mathfrak{H}^{\mathrm{s}}} \leq \delta_{mn}, \ 1 \leq m, n \leq N \right\}, \tag{1.18}$$

with the analogue of $\mathcal{W}_N^{\mathrm{Slater}}$, denoted $\mathcal{W}_{\leq N}^{\mathrm{Slater}}$, being defined via $\mathcal{C}_N^{\leq}$. That is, if the orthonormality constraint in (1.9) is substituted by $\int_{\mathbb{R}^3} \overline{\phi_m} \phi_n \, \mathrm{d}\boldsymbol{r} \leq \delta_{mn}$; 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 both within the Schrödinger theory and the Pauli theory. The main theorem, valid for neutral molecules and positive ions, is:

**Theorem 1.3.** *Let Assumption 1.1 be satisfied. Suppose the total nuclear charge* $Z_{\mathrm{tot}} = \sum_{k=1}^{K} Z_k$ *satisfies* $Z_{\mathrm{tot}} + 1 > N$. *Then:*
*1. Schrödinger case. There exists a minimizer* $\mathcal{D}^{(\infty)}$ *of* $\mathcal{E}^{\mathrm{s}}(\cdot)$ *on the admissible set* $\mathcal{M}^{\mathrm{s}}$*; see Definition 3.1. The density matrix* $\mathcal{D}^{(\infty)}$ *is a* $N$*-dimensional projection and one can write*

$$\mathcal{D}^{(\infty)}(\boldsymbol{r};\boldsymbol{r}') = \sum_{n=1}^{N} \overline{\phi_n(\boldsymbol{r})} \phi_n(\boldsymbol{r}') \tag{1.19}$$

*with* $\phi_n \in \mathbf{H}^1(\mathbb{R}^3;\mathbb{C})$, $n = 1, \ldots, N$, *orthonormal, such that the component orbitals* $\phi_n$ *satisfy the magnetic Hartree-Fock equations*

$$\begin{cases} F^{\mathrm{s}}_{\mathcal{D}^{(\infty)},\mathcal{A}} \phi_n = \epsilon_n^{\mathrm{s}} \phi_n, \\ \langle \phi_m, \phi_n \rangle_{\mathfrak{H}^{\mathrm{s}}} = \delta_{mn}, \end{cases} \tag{1.20}$$

*where* $F^{\mathrm{s}}_{\mathcal{D}^{(\infty)},\mathcal{A}}$ *is the diamagnetic Fock operator, defined in Proposition 5.1. Moreover, the numbers* $\epsilon_n^{\mathrm{s}}$ *are the* $N$ *lowest eigenvalues of the operator* $F^{\mathrm{s}}_{\mathcal{D}^{(\infty)},\mathcal{A}}$.

*2. Pauli case. Assuming that $Z_{\rm tot}\alpha^2 \leq 0.041$, then there exists a minimizer $(\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)})$ on the admissible set $\mathcal{M}_{\rm p}$, see (3.17). The density matrix $\mathcal{D}_{(\infty)}$ is a $N$-dimensional projection and one can write*

$$\mathcal{D}_{(\infty)}(\boldsymbol{r}, s; \boldsymbol{r}', t) = \sum_{n=1}^{N} \overline{\varphi_n(\boldsymbol{r}, s)}\varphi_n(\boldsymbol{r}', t) \tag{1.21}$$

*with $\varphi_n \in \mathbf{H}^1(\mathbb{R}^3; \mathbb{C}^2)$, $n = 1, \ldots, N$, orthonormal, such that the component orbitals $\varphi_n$ satisfy the magnetic (Pauli) Hartree-Fock equations*

$$\begin{cases} F^{\rm p}_{\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}} \varphi_n = \epsilon^{\rm p}_n \varphi_n, \\ \langle \varphi_m, \varphi_n \rangle_{\mathfrak{H}_{\rm p}} = \delta_{mn}, \end{cases} \tag{1.22}$$

*where $F^{\rm p}_{\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}}$ is the Fock-Pauli operator, defined in Proposition 5.1. Moreover, the numbers $\epsilon^{\rm p}_n$ are the $N$ lowest eigenvalues of the operator $F^{\rm p}_{\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}}$.*

Under very different conditions on the potentials, Theorem 1.3, assertion 1, was first established in a paper by Enstedt and Melgaard [7]. The aim of the present work is twofold: (1) To prove existence of a minimizer for the Schrödinger case under the (new) conditions on $\mathcal{A}$ in Assumption 1.1, and to give a proof within the *density operator formulation* (see Section 3); (2) To show existence of a minimizer for the Pauli case. To the best of our knowledge, the latter case has not been addressed before. We base our proof on the *relaxation* strategy by Lieb and Simon [18] but within the density operator formulation we minimize over density operators. The latter was first addressed by Solovej [24] within the reduced (non-magnetic) Hartree-Fock model (it is *reduced* because the exchange term is ignored) and we are strongly inspired by Solovej's arguments. In the case of a constant magnetic field a result similar to Theorem 1.3, assertion 2, was established by Esteban and Lions [8] by a completely different approach, originally invented by Lions for the non-magnetic case, based upon the construction of minimizing sequences which satisfy the "second minimality condition"; we refer to [20] for details.

## 2. Preliminaries

Henceforth function spaces consist of complex-valued functions unless otherwise specified. Let $\mathbb{R}^3$ be the three-dimensional Euclidean space, wherein points are denoted by $\boldsymbol{r} = (x^{(1)}, x^{(2)}, x^{(3)})$, and let $|\boldsymbol{r}| = (\sum_{m=1}^{3} (x^{(m)})^2)^{1/2}$. We set

$$B_R = \{ \boldsymbol{r} \in \mathbb{R}^3 \, : \, |\boldsymbol{r}| < R \}, \quad B(\boldsymbol{r}, R) = \{ \boldsymbol{r}' \in \mathbb{R}^3 \, : \, |\boldsymbol{r} - \boldsymbol{r}'| < R \}.$$

For $1 \leq p \leq \infty$, let $L^p(\mathbb{R}^3)$ be the space of (equivalence classes of) complex-valued functions $\phi$ which are measurable and satisfy $\int_{\mathbb{R}^3} |\phi(\boldsymbol{r})|^p \, {\rm d}\boldsymbol{r} < \infty$ if $p < \infty$ and $\|\phi\|_{L^\infty(\mathbb{R}^3)} = \text{ess sup}\, |\phi| < \infty$ if $p = \infty$. The measure ${\rm d}\boldsymbol{r}$ is the Lebesgue measure. For any $p$ the $L^p(\mathbb{R}^3)$ space is a Banach space with norm $\| \cdot \|_{L^p(\mathbb{R}^3)} = (\int_{\mathbb{R}^3} | \cdot |^p \, {\rm d}\boldsymbol{r})^{1/p}$. In the case $p = 2$, $L^2(\mathbb{R}^3)$ is a complex and separable Hilbert space with scalar product $\langle \phi, \psi \rangle_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} \overline{\phi} \psi {\rm d}\boldsymbol{r}$ and corresponding norm $\|\phi\|_{L^2(\mathbb{R}^3)} = \langle \phi, \phi \rangle^{1/2}_{L^2(\mathbb{R}^3)}$. 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 dual space of $\mathscr{D}(\mathbb{R}^3)$, the space of distributions, is denoted $\mathscr{D}'(\mathbb{R}^3)$. The Schwarz space of rapidly decreasing functions and its adjoint space of 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

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

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

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

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

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

We do not suppose that $\nabla\phi$ or $\mathcal{A}\phi$ are separately in $L^2(\mathbb{R}^3)$, whence, in general, there is no relationship between the spaces $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ and $\mathbf{H}^1(\mathbb{R}^3)$ on the whole of $\mathbb{R}^3$; specifically, $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) \not\subseteq \mathbf{H}^1(\mathbb{R}^3)$ and $\mathbf{H}^1(\mathbb{R}^3) \not\subseteq \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$.
If $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3;\mathbb{R})^3$, then $\mathscr{D}(\mathbb{R}^3)$ is dense in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ (see [12, 23]), and the following well-known *weak diamagnetic inequality* is valid.

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

$$|\nabla|\phi|| \le |\nabla_{\mathcal{A}}\phi| \ \text{ for a.e. } \boldsymbol{r} \in \mathbb{R}^3. \tag{2.2}$$

*Proof.* We sketch the argument; for more details we refer to [16]. Since $\mathcal{A}$ is real-valued, the relation

$$|\nabla|\phi|(\boldsymbol{r})| = \left|\mathrm{Re}\left(\nabla\phi\frac{\overline{\phi}}{|\phi|}\right)\right| = \left|\mathrm{Re}\left((\nabla\phi + i\mathcal{A}\phi)\frac{\overline{\phi}}{|\phi|}\right)\right|$$

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 $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. ☐

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., [6, 13]. 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

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

Let $\mathcal{S}(\mathcal{H})$ denote the set of self-adjoint, bounded operators on a Hilbert space $\mathcal{H}$. Furthermore, let $(\mathfrak{S}_1(\mathcal{H}), \mathrm{Tr}\,(|\cdot|))$ be the separable (non-reflexive) Banach space of trace class operators. We also need the Banach space

$$\mathfrak{K} = \{\, \mathcal{D} \in \mathcal{S}(\mathcal{H}) \,:\, \|\mathcal{D}\|_{\mathfrak{K}} = \mathrm{Tr}\,(|\mathcal{D}|) + \mathrm{Tr}\,(|\nabla|\mathcal{D}|\nabla|) < \infty \,\}, \tag{2.3}$$

where the choice of $\mathcal{H}$ will be specified in the sequel.

**Kato's space of potentials.** To treat basic properties of the functionals $\mathcal{E}^{\rm s}(\cdot), \mathcal{E}^{\rm p}(\cdot)$ we may consider potentials

$$V \in \mathcal{K}_3 := L^{\frac{3}{2}}(\mathbb{R}^3;\mathbb{R}) + L^{\infty}_{\epsilon}(\mathbb{R}^3;\mathbb{R}), \tag{2.4}$$

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 $L^{\frac{3}{2}}(\mathbb{R}^3;\mathbb{R}) + L^{\infty}(\mathbb{R}^3;\mathbb{R})$. 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 $\int V(\boldsymbol{r})|\phi(\boldsymbol{r})|^2 \, {\rm d}\boldsymbol{r}$ is well-defined for all $\phi \in \mathbf{H}^1(\mathbb{R}^3)$.

## 3. Density operator formulation

3.1. **Schrödinger case.** Introduce the first order density operator $\mathcal{D} = \mathcal{D}_\Phi = \sum_{n=1}^N \langle \phi_n, \cdot \rangle_{\mathfrak{H}^{\rm s}} \phi_n$ for some $\Phi = \{\phi_n\} \in \mathcal{C}_N$, i.e., the orthogonal projection from $\mathfrak{H}^{\rm s}$ onto the $N$-dimensional subspace of $\mathfrak{H}^{\rm s}$. We can re-write $\mathcal{E}^{\rm s}(\cdot)$ and the Hartree-Fock ground state energy via this one-to-one correspondence between Slater determinants and projections onto finite-dimensional subspaces of $\mathfrak{H}^{\rm s}$. Indeed, if $\Psi_{\rm e}$ is a Slater determinant, as in (1.10), with $\{\phi_n\}_{n=1}^N$, $\phi_n \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$, being orthonormal in $\mathfrak{H}^{\rm s}$, and $\mathcal{D}$ is the projection onto the subspace spanned by $\phi_1, \ldots, \phi_N$, then the kernel of $\mathcal{D}$ is given by (1.12) and the associated one-body density is given by (1.13). Furthermore, the Hartree-Fock functional can be re-written as

$$\mathcal{E}^{\rm s}(\mathcal{D}) = \frac{1}{2} \,{\rm Tr}\, [-\Delta_{\mathcal{A}} \mathcal{D}] + {\rm Tr}\, [V_{\rm en} \mathcal{D}] + \mathcal{J}(\mathcal{D}) - \mathcal{K}(\mathcal{D}), \tag{3.1}$$

where

$$\begin{aligned} {\rm Tr}\, [-\Delta_{\mathcal{A}} \mathcal{D}] &= \sum_{n=1}^N \mathfrak{h}[\phi_n, \phi_n] := \sum_{n=1}^N \int_{\mathbb{R}^3} |\nabla_{\mathcal{A}} \phi_n|^2 \, d\boldsymbol{r} & (3.2) \\ {\rm Tr}\, [V_{\rm en} \mathcal{D}] &= \sum_{n=1}^N \mathfrak{v}[\phi_n, \phi_n] := -\sum_{n=1}^N \sum_{k=1}^K \langle V_k^{1/2} \phi_n, V_k^{1/2} \phi_n \rangle. & (3.3) \end{aligned}$$

The **direct Coulomb energy** defined in terms of the Coulomb inner product

$$\mathcal{J}(\mathcal{D}) := \mathcal{J}(\rho_{\mathcal{D}}, \rho_{\mathcal{D}}) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho_{\mathcal{D}}(\boldsymbol{r}) |\boldsymbol{r} - \boldsymbol{r}'|^{-1} \rho_{\mathcal{D}}(\boldsymbol{r}') \, d\boldsymbol{r} d\boldsymbol{r}' \tag{3.4}$$

and the **exchange Coulomb energy** defined by

$$\mathcal{K}(\mathcal{D}) := \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} |\mathcal{D}(\boldsymbol{r}, \boldsymbol{r}')|^2 |\boldsymbol{r} - \boldsymbol{r}'|^{-1} \, d\boldsymbol{r} d\boldsymbol{r}'. \tag{3.5}$$

As a consequence, the Hartree-Fock ground state energy (1.14) can be expressed as

$$E^{\rm s}(N, \boldsymbol{Z}, \mathcal{A}) := \inf \{\, \mathcal{E}^{\rm s}(\mathcal{D}) \,:\, \mathcal{D} \in \mathcal{P}_N \,\} \tag{3.6}$$

where

$$\mathcal{P}_N = \{\, \mathcal{D} : \mathfrak{H}^{\mathrm{s}} \to \mathfrak{H}^{\mathrm{s}} \,:\, \mathcal{D} \text{ projection onto } \operatorname{span}\{\phi_1, \ldots, \phi_N\}, \\ \phi_n \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3),\ \langle \phi_m, \phi_n \rangle_{\mathfrak{H}^{\mathrm{s}}} = \delta_{mn} \,\} \tag{3.7}$$

An *(admissible) density operator* $\mathcal{D}$ is a trace class operator $\mathcal{D} : \mathfrak{H}^{\mathrm{s}} \to \mathfrak{H}^{\mathrm{s}}$, i.e. $\mathcal{D} \in \mathfrak{S}_1(\mathfrak{H}^{\mathrm{s}})$, which satisfies the operator inequality

$$0 \le \mathcal{D} \le I. \tag{3.8}$$

Such an operator can be expressed as $\mathcal{D} = \sum_j \nu_j \overline{f_j} \otimes f_j$, where $(f_j)_j$ is an orthonormal family in $\mathfrak{H}^{\mathrm{s}}$ and $\nu_j \in [0,1]$. The *density* corresponding to $\mathcal{D}$ is then defined by

$$\rho_{\mathcal{D}}(\boldsymbol{r}) := \sum_j \nu_j |f_j(\boldsymbol{r})|^2. \tag{3.9}$$

Suppose

$$\mathrm{Tr}\ [-\Delta_{\mathcal{A}} \mathcal{D}] := \sum_j \nu_j \mathfrak{h}_0[f_j, f_j] < +\infty \tag{3.10}$$

Then all terms in $\mathcal{E}^{\mathrm{s}}(\cdot)$ are finite. Indeed, since Kato's theorem asserts that $V_{\mathrm{en}}$ is infinitesimally $-\Delta$- (and thus $-\Delta_{\mathcal{A}}$-) operator bounded [1], we infer that

$$\mathrm{Tr}\ [V_{\mathrm{en}} \mathcal{D}] := \sum_{j=1}^{N} \nu_j \mathfrak{v}[f_j, f_j] = -\int_{\mathbb{R}^3} \sum_{k=1}^{K} V_k(\boldsymbol{r}) \rho_{\mathcal{D}}(\boldsymbol{r})\, d\boldsymbol{r} \tag{3.11}$$

is finite, whence $f_j \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. Moreover, the diamagnetic Lieb-Thirring inequality (3.3) implies that $\rho_{\mathcal{D}} \in L^{5/3}(\mathbb{R}^3;\mathbb{R})$. The latter, together with $\rho_{\mathcal{D}} \in L^1(\mathbb{R}^3;\mathbb{R})$ (by hypothesis) and standard interpolation for $L^p$ spaces implies that $\rho_{\mathcal{D}} \in L^{6/5}(\mathbb{R}^3;\mathbb{R})$. Then the Hardy-Littlewood-Sobolev inequality [16, Theorem 4.3] immediately informs us that $\mathcal{J}(\mathcal{D})$ is finite. From the explicit representation

$$\mathcal{J}(\mathcal{D}) - \mathcal{K}(\mathcal{D}) \\ = \frac{1}{4} \sum \nu_i \nu_j \int\!\!\int \frac{|f_i(\boldsymbol{r}) f_j(\boldsymbol{r}') - f_j(\boldsymbol{r}) f_i(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r} d\boldsymbol{r}' \ge 0 \tag{3.12}$$

we see that $\mathcal{J}(\mathcal{D}) \ge \mathcal{K}(\mathcal{D})$. Hence we conclude that $\mathcal{E}^{\mathrm{s}}(\cdot)$ is bounded from below provided $\mathrm{Tr}\,[-\Delta_{\mathcal{A}} \mathcal{D}] < \infty$. The minimization problem (3.6) is thus equivalent to

$$E^{\mathrm{s}}(N, \boldsymbol{Z}, \mathcal{A}) := \inf \left\{ \mathcal{E}^{\mathrm{s}}(\mathcal{D}) \,:\, \mathcal{D}^* = \mathcal{D},\ \mathcal{D} = \mathcal{D}^2,\ \mathrm{Tr}[\mathcal{D}] = N,\ \mathrm{Tr}\,(-\Delta_{\mathcal{A}} \mathcal{D}) < \infty \right\}. \tag{3.13}$$

but the discussion above also motivates the following definition:

**Definition 3.1.** Admissible set of density operators:

$$\mathcal{M}^{\mathrm{s}} := \mathcal{M}_{\mathcal{A}} := \{\, \mathcal{D} \text{ admissible} \,:\, \mathrm{Tr}\,(\mathcal{D}) = N,\ \mathrm{Tr}\,(-\Delta_{\mathcal{A}} \mathcal{D}) < +\infty \,\}.$$

We use the notation $\mathcal{M}^{\mathrm{s}}$ (a variational space of one variable) to distinguish the Schrödinger case from the Pauli case. The analogue for the Pauli case (introduced below) will be denoted $\mathcal{M}_{\mathrm{p}}$; a variational space of two variables. If $\mathcal{A} \equiv \mathbf{0}$ in the Schrödinger case, then we use the notation $\mathcal{M}$ (see also Appendix A) .
In [15] Lieb proved that minimizing $\mathcal{E}^{\mathrm{s}}(\cdot)$ over admissible density operators yields the same result as minimizing over projections only.

**Theorem 3.2** (Lieb's variational principle)**.** *For all non-negative integers $N$ the following equality holds:*

$$\inf\{\mathcal{E}^{\mathrm{s}}(\mathcal{D}) \,:\, \mathcal{D}^* = \mathcal{D},\, \mathcal{D} = \mathcal{D}^2,\, \mathrm{Tr}[\mathcal{D}] = N\} = \inf\{\mathcal{E}^{\mathrm{s}}(\mathcal{D}) \,:\, \mathcal{D} \in \mathcal{M}_{\mathcal{A}}\} \tag{3.14}$$

**Bound on kinetic energy of electrons.** The following inequality was established by Lieb and Thirring [19] for the non-magnetic case but it immediately carries over to our setting.

**Theorem 3.3.** *Let $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3;\mathbb{R})^3$ and let $\rho_{\mathcal{D}}$ be the density associated to a density operator in $\mathcal{M}_{\mathcal{A}}$. Then there exists a positive constant $C$ such that*

$$\int_{\mathbb{R}^3} \rho_{\mathcal{D}}(\boldsymbol{r})^{5/3}\,\mathrm{d}\boldsymbol{r} \le C\,\mathrm{Tr}\,[-\Delta_{\mathcal{A}}\mathcal{D}]$$

To distinguish the Schrödinger case from the Pauli case, we henceforth let $\mathcal{M}^{\mathrm{s}} := \mathcal{M}_{\mathcal{A}}$; a variational space of one variable. The analogue for the Pauli case (introduced below) will be denoted $\mathcal{M}_{\mathrm{p}}$; a variational space of two variables.

3.2. **Pauli case.** The Pauli Hamiltonian (1.4) acts on the Hilbert space

$$\begin{aligned}\bigwedge_{n=1}^{N} \mathfrak{H}_{\mathrm{p}} := \Big\{ &\Psi(\boldsymbol{r}_1, s_1, \ldots, \boldsymbol{r}_N, s_N),\ \boldsymbol{r}_j \in \mathbb{R}^3, \sigma_j \in \{\uparrow,\downarrow\},\\ &\sum_{s_1,\ldots,s_N \in \{\uparrow,\downarrow\}^N} \int_{\mathbb{R}^{3N}} |\Psi\left(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right)|^2 \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N < \infty\\ &\forall p \in S_N,\ \Psi\left(\boldsymbol{r}_{p(1)}, s_{p(1)}, \boldsymbol{r}_{p(2)}, s_{p(2)}, \ldots, \boldsymbol{r}_{p(N)}, s_{p(N)}\right)\\ &= \epsilon(p)\Psi\left(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right) \Big\}.\end{aligned} \tag{3.15}$$

Here $S_N$ is the set of all permutations of $(1, \ldots, N)$, and $\epsilon(p)$ denotes the parity of the permutation $p$. The space $\bigwedge_{n=1}^{N} \mathfrak{H}_{\mathrm{p}}$ is equipped with the scalar product

$$\langle \Psi_1, \Psi_2 \rangle = \sum_{s_1,\ldots,s_N \in \{\uparrow,\downarrow\}^N} \int_{\mathbb{R}^{3N}} \overline{\Psi_1\left(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right)}\Psi_2\left(\boldsymbol{r}_1, s_1, \boldsymbol{r}_2, s_2, \ldots, \boldsymbol{r}_N, s_N\right) \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N$$

The ground state energy of the system is obtained by solving the minimization problem

$$E^{\mathrm{QM}}_{\mathbb{P}} = \inf\left\{ \mathrm{Tr}\left(\mathbb{P}_{N,\boldsymbol{Z},\mathcal{A}}\mathsf{D}\right) \,:\, \mathsf{D} \in \mathcal{M}^{\mathrm{pure}}_N \right\} = \inf\left\{ \mathrm{Tr}\left(\mathbb{P}_{N,\boldsymbol{Z},\mathcal{A}}\mathsf{D}\right) \,:\, \mathsf{D} \in \mathcal{M}^{\mathrm{mix}}_N \right\},$$

where $\mathcal{M}_N^{\mathrm{pure}}$, respectively, $\mathcal{M}_N^{\mathrm{mix}}$ is the set of spin-polarised pure-states, respectively mixed states, $N$-particle density matrices defined in (A.4), respectively (A.5); see Appendix A. The analogue of the Hartree-Fock minimization problem (3.13) for the Schrödinger case is, except for one modification to be explained, as follows in the Pauli case:

$$E^{\mathrm{p}} \equiv E^{\mathrm{p}}(N, \boldsymbol{Z}) := \inf \{ \mathcal{E}^{\mathrm{p}}(\mathcal{D}, \mathcal{A}) \,:\, (\mathcal{D}, \mathcal{A}) \in \mathcal{M}_{\mathrm{p}} \} . \tag{3.16}$$

where the admissible set is

$$\mathcal{M}_{\mathrm{p}} = \left\{ \begin{pmatrix} \mathcal{D} \\ \mathcal{A} \end{pmatrix} \,:\, \begin{matrix} \mathcal{D} \in \mathcal{M} \\ \mathcal{A} \in L^6(\mathbb{R}^3;\mathbb{R})^3, \quad \nabla \cdot \mathcal{A} = 0, \quad \mathcal{B} \in L^2(\mathbb{R}^3;\mathbb{R})^3 \end{matrix} \right\} \tag{3.17}$$

and the (Pauli) Hartree-Fock functional is

$$\begin{aligned} \mathcal{E}^{\mathrm{p}}(\mathcal{D}, \mathcal{A}) \;=\; & \frac{1}{2} \mathrm{Tr} \left( \mathbb{P}_{\mathcal{A}}^{(j)} \mathcal{D} \right) + \mathrm{Tr} \left( V_{\mathrm{en}} \mathcal{D} \right) \\ & + \mathcal{J}(\mathcal{D}) - \mathcal{K}(\mathcal{D}) + \frac{1}{\alpha^2} \int_{\mathbb{R}^3} |\mathcal{B}(\boldsymbol{r})|^2 \, \mathrm{d}\boldsymbol{r} \end{aligned} \tag{3.18}$$

where (and this is the modification mentioned above) we have added the magnetic field energy in the last term, $\alpha$ is the fine structure constant, $\mathcal{J}(\cdot)$ is defined in (3.4) and

$$\mathcal{K}(\mathcal{D}) := \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{Tr}_{\mathbb{C}^2} \left[ |\mathcal{D}(\boldsymbol{r}, \boldsymbol{r}')|^2 \right] |\boldsymbol{r} - \boldsymbol{r}'|^{-1} \, d\boldsymbol{r} d\boldsymbol{r}'. \tag{3.19}$$

In the Schrödinger setting, the inclusion of a magnetic field $\mathcal{B}$ changes the energy but the lower bound on the energy is independent of $\mathcal{B}$ (so no minimization over $\mathcal{A}$ is needed). For the Pauli case, the term $\boldsymbol{\sigma} \cdot \mathcal{B}$ changes everything because the Pauli operator is much weaker than $(\boldsymbol{p} + \mathcal{A})^2$. One of the most important features in the spectral theory of Pauli operators is the presence of zero modes [22, Section 10], i.e., for suitable $\mathcal{A}$, the existence of eigenfunctions corresponding to a zero eigenvalue, which causes instability for large $Z^2\alpha$. It is known that without adding the field energy term arbitrarily large $\mathcal{B}$ may give rise to arbitrarily negative energy [17]. By adding the field energy – as we did in (1.16) – we ensure that the resulting Hartree-Fock functional becomes bounded from below and, in this sense, it is physically "stable"; in fact, this addition ensures that stability of matter holds for the model [17].

## 4. Existence of a minimizer for the relaxed problem

We shall apply the *relaxation* method by Lieb and Simon [18]. For this purpose we define, for the Schrödinger case,

$$\mathcal{M}_{\leq}^{\mathrm{s}} = \{ \mathcal{D} \in \mathcal{S}(\mathfrak{H}^{\mathrm{s}}) \,:\, 0 \leq \mathcal{D} \leq 1, \, \mathrm{Tr}\,(\mathcal{D}) \leq N, \, \mathrm{Tr}\,(-\Delta_{\mathcal{A}} \mathcal{D}) < \infty \} \tag{4.1}$$

and the corresponding energy

$$E_{\leq}^{\mathrm{s}}(N, \boldsymbol{Z}, \mathcal{A}) := \inf \left\{ \mathcal{E}^{\mathrm{s}}(\mathcal{D}) \,:\, \mathcal{D} \in \mathcal{M}_{\leq}^{\mathrm{s}} \right\} . \tag{4.2}$$

Similarly, in the Pauli case, we define

$$\mathcal{M}_{\mathrm{p}}^{\leq} = \left\{ \begin{pmatrix} \mathcal{D} \\ \mathcal{A} \end{pmatrix} \,:\, \begin{matrix} \mathcal{D} \in \mathcal{S}(\mathfrak{H}_{\mathrm{p}}) & 0 \leq \mathcal{D} \leq 1, \, \mathrm{Tr}\,(\mathcal{D}) \leq N, \, \mathrm{Tr}\,(-\Delta \mathcal{D}) < \infty \\ \mathcal{A} \in L^6(\mathbb{R}^3;\mathbb{R})^3, \quad \nabla \cdot \mathcal{A} = 0, \quad \mathcal{B} \in L^2(\mathbb{R}^3;\mathbb{R})^3 & \end{matrix} \right\} \tag{4.3}$$

and the corresponding energy

$$E^{\mathrm{p}}_{\leq}(N,\boldsymbol{Z}) := \inf\left\{\,\mathcal{E}^{\mathrm{p}}(\mathcal{D},\mathcal{A})\;:\;(\mathcal{D},\mathcal{A})\in\mathcal{M}^{\leq}_{\mathrm{p}}\,\right\}. \tag{4.4}$$

We first prove that the relaxed problem (4.2), respectively, (4.4), has a minimizer. Unless otherwise stated, we impose Assumption 1.1 and the additional conditions in Theorem 1.3 throughout this section.

In the Schrödinger case, it is convenient to introduce, for any $\Psi\in\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$,

$$\begin{aligned} T(\Psi) &:= \sum_{n=1}^{N}\int_{\mathbb{R}^{3N}}|\nabla_{\mathcal{A},\boldsymbol{r}_n}\Psi(\boldsymbol{R})|^2\,d\boldsymbol{R} \\ W_{\mathrm{en}}(\Psi) &:= \sum_{n=1}^{N}\langle V_{\mathrm{en}}(\boldsymbol{r}_n)\Psi,\Psi\rangle_{\mathcal{H}} \\ W_{\mathrm{ee}}(\Psi) &:= \frac{1}{2}\sum_{1\leq m<n\leq N}\langle V_{\mathrm{ee}}(\boldsymbol{r}_m-\boldsymbol{r}_n)\Psi,\Psi\rangle_{\mathcal{H}}. \end{aligned}$$

so that $\mathcal{E}^{\mathrm{s}}(\Psi)=T(\Psi)+W_{\mathrm{en}}(\Psi)+W_{\mathrm{ee}}(\Psi)$

**Lemma 4.1.**

*1. Assuming $\mathcal{A}\in L^2_{\mathrm{loc}}(\mathbb{R}^3;\mathbb{R})^3$ and $V_{\mathrm{en}},V_{\mathrm{ee}}\in L^{3/2}(\mathbb{R}^3;\mathbb{R})+L^\infty(\mathbb{R}^3;\mathbb{R})_\epsilon$, the functional $\mathcal{E}^{\mathrm{s}}(\cdot)$ is well-defined on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$ and, in particular, $\mathcal{E}^{\mathrm{s}}(\cdot)$ is bounded from below on $\mathcal{M}^{\mathrm{s}}_{\leq}$.*

*2. Assuming $Z_{\mathrm{tot}}\alpha^2\leq 0.041$, the functional $\mathcal{E}^{\mathrm{p}}(\cdot,\cdot)$ is well-defined on $\mathcal{M}_{\mathrm{p}}$ and, in particular, $\mathcal{E}^{\mathrm{p}}(\cdot,\cdot)$ is bounded from below on $\mathcal{M}^{\leq}_{\mathrm{p}}$.*

*Proof.*

1. *Schrödinger case.* It suffices to prove that, for any $\epsilon>0$, there exists $C_\epsilon>0$ such that

$$\mathcal{E}^{\mathrm{s}}(\Psi)\geq(1-\epsilon)T(\Psi)-C_\epsilon\|\Psi\|^2_{\mathcal{H}} \tag{4.5}$$

for all $\Psi\in\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$. Since $V_{\mathrm{en}},V_{\mathrm{ee}}\in L^{3/2}(\mathbb{R}^3;\mathbb{R})+L^\infty(\mathbb{R}^3;\mathbb{R})_\epsilon$, we make the decompositions $V_{\mathrm{en}}=V_1+V_2$ and $V_{\mathrm{ee}}=W_1+W_2$ such that $\|V_1\|_{L^{3/2}}<\epsilon$, $\|W_1\|_{L^{3/2}}<\epsilon$ and $V_2,W_2\in L^\infty(\mathbb{R}^3;\mathbb{R})$. Now,

$$\begin{aligned} &\left|\int_{\mathbb{R}^3}V_{\mathrm{ee}}(\boldsymbol{r}_1-\boldsymbol{r}_2)|\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)|^2\,\mathrm{d}\boldsymbol{r}_1\right| \\ &\leq\;\|W_1\|_{L^{3/2}}\int_{\mathbb{R}^3}|\Psi(\boldsymbol{R})|^6\,\mathrm{d}\boldsymbol{r}_1+\|W_2\|_{L^\infty}\int_{\mathbb{R}^3}|\Psi(\boldsymbol{R})|^2\,\mathrm{d}\boldsymbol{r}_1 \\ &\leq\;\|W_1\|_{L^{3/2}}c_{\mathrm{sob}}\int|\nabla_{\boldsymbol{r}_1}\Psi|^2\,d\boldsymbol{r}_1+\|W_2\|_{L^\infty}\int_{\mathbb{R}^3}|\Psi(\boldsymbol{R})|^2\,\mathrm{d}\boldsymbol{r}_1 \\ &\leq\;\|W_1\|_{L^{3/2}}c_{\mathrm{sob}}\int|\nabla_{\mathcal{A},\boldsymbol{r}_1}\Psi|^2\,d\boldsymbol{r}_1+\|W_2\|_{L^\infty}\int_{\mathbb{R}^3}|\Psi(\boldsymbol{R})|^2\,\mathrm{d}\boldsymbol{r}_1 \end{aligned}$$

where we used Hölder's inequality in conjunction with the Sobolev inequality and the diamagnetic inequality (2.2). Next we integrate over $\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N$, replacing $\boldsymbol{r}_1,\boldsymbol{r}_2$ by $\boldsymbol{r}_m,\boldsymbol{r}_n$, and then we sum over $m, n$. In this way we obtain

$$|W_{\rm ee}(\Psi)| \leq \frac{N-1}{2}\|W_1\|_{L^{3/2}} c_{\rm sob} T(\Psi) + \frac{N(N-1)}{2}\|W_2\|_{L^\infty}\|\Psi\|_{\mathcal{H}}^2.$$

Similarly, when we address $W_{\rm en}$, we find that

$$|W_{\rm en}(\Psi)| \leq \|V_1\|_{L^{3/2}} c_{\rm sob} T(\Psi) + N\|V_2\|_{L^\infty}\|\Psi\|_{\mathcal{H}}^2.$$

The inequality (4.5) now follows.
2. *Pauli case.* Under the hypotheses, Lieb, Loss and Solovej [17] proved stability of matter in this context, viz.,

$$E_{\mathbb{P}}^{\rm QM} \geq -C_{\boldsymbol{Z}}(N+K);$$

bear in mind that $K$ is the number of nuclei. As a consequence, $\mathcal{E}^{\rm p}(\cdot,\cdot)$ is well-defined and it is bounded from below on $\mathcal{M}_{\rm p}^{\leq}$. □

**Proposition 4.2.**
*1. Schrödinger case. Assuming $\mathcal{A} \in L^2_{\rm loc}(\mathbb{R}^3;\mathbb{R})^3$ and $V_{\rm en}, V_{\rm ee} \in L^{3/2}(\mathbb{R}^3;\mathbb{R}) + L^\infty(\mathbb{R}^3;\mathbb{R})_\epsilon$, there exists a density matrix $\mathcal{D}^{(\infty)}$ minimizing the relaxed problem, i.e.,*

$$\exists \mathcal{D}^{(\infty)} \in \mathcal{M}^{\rm s}_{\leq} \text{ s.t. } \mathcal{E}^{\rm s}(\mathcal{D}^{(\infty)}) = E^{\rm s}_{\leq}(N, \boldsymbol{Z}, \mathcal{A}). \tag{4.6}$$

*2. Pauli case. Suppose $Z_{\rm tot}\alpha^2 \leq 0.041$, then there exists a minimizer $(\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)})$ for the relaxed problem, i.e.,*

$$\exists (\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}) \in \mathcal{M}_{\rm p}^{\leq} \text{ s.t. } \mathcal{E}^{\rm p}(\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}) = E^{\rm p}_{\leq}(N, \boldsymbol{Z}). \tag{4.7}$$

To make the exposition more pedagogical we divide the proof of this result into a few lemmas. First, however, we note that Lemma 4.1 enables us to construct a minimizing sequence. Indeed, since $\mathcal{E}^{\rm s}(\mathcal{D}) > -\infty$ for $\mathcal{D} \in \mathcal{M}^{\rm s}$ we can select $\mathcal{D}^{(n)} \in \mathcal{M}^{\rm s}_{\leq}$ such that

$$\mathcal{E}^{\rm s}(\mathcal{D}^{(n)}) \leq E_{\leq}(N, \boldsymbol{Z}, \mathcal{A}) + \frac{1}{n}$$

Hence

$$\lim_{n\to\infty} \mathcal{E}^{\rm s}(\mathcal{D}^{(n)}) = E^{\rm s}_{\leq}(N, \boldsymbol{Z}, \mathcal{A}).$$

Likewise, in the Pauli case, there exists $(\mathcal{D}_{(n)}, \mathcal{A}_{(n)}) \in \mathcal{M}_{\rm p}^{\leq}$ such that

$$\mathcal{E}^{\rm p}(\mathcal{D}_{(n)}, \mathcal{A}_{(n)}) \leq E^{\rm p}_{\leq} + \frac{1}{n} \text{ and } \lim_{n\to\infty} \mathcal{E}^{\rm p}(\mathcal{D}_{(n)}, \mathcal{A}_{(n)}) = E^{\rm p}_{\leq}(N, \boldsymbol{Z}).$$

**Lemma 4.3.**
*1. Schrödinger case. The sequences $\operatorname{Tr}(\mathcal{D}^{(n)})$ and $\operatorname{Tr}(-\Delta_{\mathcal{A}}\mathcal{D}^{(n)})$ are uniformly bounded.*
*2. Pauli case. The sequences $(\|\mathcal{A}_n\|_{L^6})_n$, $(\|\mathcal{B}_{(n)}\|_{L^2})_n$ are uniformly bounded and $(\mathcal{D}_{(n)})_n$ is*

*uniformly bounded in $\mathfrak{K}$ (see its definition in (2.3) where $\mathcal{H}$ is chosen as $\mathfrak{H}_{\rm p}$).*
*In particular, there exist $\mathcal{A}_{(\infty)} \in L^6(\mathbb{R}^3;\mathbb{R})^3$, $\mathcal{B}_{(\infty)} \in L^2(\mathbb{R}^3;\mathbb{R})^3$ and $\mathcal{D}_{(\infty)} \in \mathfrak{K}$ such that*

$$\begin{aligned} \|\mathcal{A}_{(\infty)}\|_{L^6} &\leq \liminf_{n\to\infty} \|\mathcal{A}_{(n)}\|_{L^6}, \\ \|\mathcal{B}_{(\infty)}\|_{L^2} &\leq \liminf_{n\to\infty} \|\mathcal{B}_{(n)}\|_{L^2}, \\ \mathcal{D}_{(n)} &\rightharpoonup \mathcal{D}_{(\infty)} \ \textit{weakly-}* \textit{ in } \mathfrak{K}. \end{aligned}$$

*Moreover, $(\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}) \in \mathcal{M}_{\rm p}^{\leq}$.*

*Proof.*
1. *Schrödinger case.* We have

$$\mathrm{Tr}\,\left[\left(-\frac{1}{2}\Delta_{\mathcal{A}} - V_{\rm en}\right)\mathcal{D}^{(n)}\right]$$

is bounded uniformly. Indeed, for any $n \in \mathbb{N}$, using $\mathcal{J}(\mathcal{D}) \geq \mathcal{K}(\mathcal{D})$, we have that

$$E^{\rm s}_{\leq}(N, \boldsymbol{Z}, \mathcal{A}) + 1 \geq \mathcal{E}^{\rm s}(\mathcal{D}^n) \geq \mathrm{Tr}\,\left[\left(-\frac{1}{2}\Delta_{\mathcal{A}} - V_{\rm en}\right)\mathcal{D}^{(n)}\right]$$

Kato's inequality, i.e., for any $\epsilon > 0$ there exists $C_\epsilon > 0$ so that

$$\mathrm{Tr}\,\left[V_{\rm en}\mathcal{D}^{(n)}\right] \leq \epsilon\,\mathrm{Tr}\,\left[-\frac{1}{2}\Delta_{\mathcal{A}}\mathcal{D}^{(n)}\right] + C_\epsilon\,\mathrm{Tr}\,\left[\mathcal{D}^{(n)}\right],$$

then implies that

$$\begin{aligned} E^{\rm s}_{\leq}(N, \boldsymbol{Z}, \mathcal{A}) + 1 &\geq \mathrm{Tr}\,\left[-\frac{1}{2}\Delta_{\mathcal{A}}\mathcal{D}^{(n)}\right] - \mathrm{Tr}\,\left[V_{\rm en}\mathcal{D}^{(n)}\right] \\ &\geq (1-\epsilon)\,\mathrm{Tr}\,\left[-\frac{1}{2}\Delta_{\mathcal{A}}\mathcal{D}^{(n)}\right] - C_\epsilon\,\mathrm{Tr}\,[\mathcal{D}^{(n)}] \end{aligned}$$

whence $\mathrm{Tr}\,[-\Delta_{\mathcal{A}}\mathcal{D}^{(n)}]$ is uniformly bounded.
2. *Pauli case.* From Lieb-Loss-Solovej [17] we extract the inequality

$$1 + E^{\rm p}_{\leq} \geq \mathcal{E}^{\rm p}(\mathcal{D}_n, \mathcal{A}_n) \geq c_{\rm LLS}\int_{\mathbb{R}^3} |\mathcal{B}_{(n)}(\boldsymbol{r})|^2 {\rm d}\,\boldsymbol{r} - C_{\rm LLS}$$

for constants $c_{\rm LLS}, C_{\rm LLS} > 0$. As a consequence, the sequence $(\mathcal{B}_{(n)})_n$ is a bounded sequence in $L^2(\mathbb{R}^3;\mathbb{R})^3$. Moreover, in view of Fröhlich-Lieb-Loss [9] and the Sobolev inequality we have that

$$\|\mathcal{B}_{(n)}\|^2_{L^2} = \|\nabla\mathcal{A}_{(n)}\|^2_{L^2} \geq C^2_{\rm Sob}\|\mathcal{A}_n\|^2_{L^6},$$

which implies that $(\mathcal{A}_{(n)})_n$ is a bounded sequence in $L^6(\mathbb{R}^3;\mathbb{R})^3$. Furthermore, from Fröhlich-Lieb-Loss [9, Theorem A.2] and the Kato-inequality for $V_{\rm en}$ we deduce that there exist constants $\tilde{c}, \widetilde{C} > 0$

$$\widetilde{C}\,\mathrm{Tr}\,(\mathcal{D}_{(n)}) + \mathcal{E}^{\rm p}(\mathcal{D}_{(n)}, \mathcal{A}_{(n)}) \geq \widetilde{c}\,\mathrm{Tr}\,(-\Delta\mathcal{D}_{(n)}),$$

whence $(-\Delta\mathcal{D}_n)_n$ is a bounded sequence and, as therefore, $(\mathcal{D}_n)_n$ is a bounded sequence in the Banach space $\mathfrak{K}$. Note that, furthermore, $(\mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)})_n$ is bounded as a sequence in $\mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}})$,

$$\mathcal{E}^{\mathrm{p}}(\mathcal{D}_{(n)},\mathcal{A}_{(n)}) \geq \frac{1}{2}\operatorname{Tr}(\mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)}) - \epsilon\operatorname{Tr}(-\Delta\mathcal{D}_{(n)}) - C_\epsilon\operatorname{Tr}(\mathcal{D}_{(n)})$$

as a consequence of the Kato-inequality for $V_{\mathrm{en}}$ and the boundedness of $\operatorname{Tr}(\mathcal{D}_{(n)})$ and $\operatorname{Tr}(-\Delta\mathcal{D}_{(n)})$.

The claims in the last paragraph follow from the Banach-Alaoglu theorem, in conjunction with $\operatorname{div}\mathcal{A}_{(\infty)} = 0$ and $\operatorname{Tr}(\mathcal{D}_{(\infty)}) \leq N$. □

**Lemma 4.4.**

*1. Schrödinger case. There exists $\mathcal{D}^{(\infty)} \in \mathcal{M}^{\mathrm{s}}_{\leq}$ such that*

$$\operatorname{Tr}(-\Delta_{\mathcal{A}}\mathcal{D}^{(\infty)}) \leq \liminf_{n\to\infty}\operatorname{Tr}(-\Delta_{\mathcal{A}}\mathcal{D}^{(n)}). \tag{4.8}$$

*2. Pauli case. There exists $(\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}) \in \mathcal{M}_{\mathrm{p}}$ such that*

$$\operatorname{Tr}(\mathbb{P}_{\mathcal{A}_{(\infty)}}\mathcal{D}_{(\infty)}) \leq \liminf_{n\to\infty}\operatorname{Tr}(\mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)}) \tag{4.9}$$

*Proof.* We divide the proof into the two cases we consider.

1. *Schrödinger case.* Since $\{\mathcal{D}^{(n)}\}$ is a minimizing sequence, we have that the sequences

$$\operatorname{Tr}[\mathcal{D}^{(n)}] \text{ and } \operatorname{Tr}\left[-\frac{1}{2}\Delta_{\mathcal{A}}\mathcal{D}^{(n)}\right]$$

are bounded. Next we extract a weakly convergent subsequence. Since the Banach space $\mathfrak{S}_1(\mathfrak{H}^{\mathrm{s}})$ is non-reflexive (so no weak compactness is available), we switch momentarily from $\mathfrak{S}_1(\mathfrak{H}^{\mathrm{s}})$ to the Hilbert space $\mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$ consisting of Hilbert-Schmidt operators defined on $\mathfrak{H}^{\mathrm{s}}$. We do this by defining an auxiliary sequence of operators

$$\tilde{\mathcal{D}}^{(n)} = (1-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(n)}(1-\Delta_{\mathcal{A}})^{\frac{1}{2}} \tag{4.10}$$

Sequence of positive trace operators with bounded trace norms

$$\operatorname{Tr}\left[\tilde{\mathcal{D}}^{(n)}\right] = \operatorname{Tr}\left[(1-\Delta_{\mathcal{A}})\mathcal{D}^{(n)}\right]$$

In fact, $\{\tilde{\mathcal{D}}^{(n)}\}$ is a sequence of Hilbert-Schmidt operator with bounded Hilbert-Schmidt norm.

Extracting if necessary a subsequence, we may assume that $\tilde{\mathcal{D}}^{(n)}$ converges weakly in $\mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$, i.e., there exists some $\tilde{\mathcal{D}}^{(\infty)} \in \mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$ such that, as $n\to\infty$,

$$\operatorname{Tr}\left[S\tilde{\mathcal{D}}^{(n)}\right] \longrightarrow \operatorname{Tr}\left[S\tilde{\mathcal{D}}^{(\infty)}\right], \quad \forall S \in \mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}}).$$

We next select an orthonormal basis $\{\psi_k\}$ in $\mathfrak{H}^{\mathrm{s}}$ such that $\psi_k \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3;\mathbb{C}^2)$. If $\langle\cdot,\cdot\rangle$ denotes the scalar product in $\mathfrak{H}^{\mathrm{s}}$, then the weak convergence in $\mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$ implies that

$$\begin{aligned}\lim_{n\to\infty}\langle\psi_k,\mathcal{D}^{(n)}\psi_k\rangle &= \lim_{n\to\infty}\langle(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}}\psi_k,\tilde{\mathcal{D}}^{(n)}(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}}\psi_k\rangle \\ &= \langle\psi_k,\mathcal{D}^{(\infty)}\psi_k\rangle.\end{aligned}$$

Since $\mathcal{D}^{(n)}$ is nonnegative, an application of Fatou's lemma yields

$$\mathrm{Tr}\,\left[\mathcal{D}^{(\infty)}\right] = \sum_k \langle \psi_k, \mathcal{D}^{(\infty)}\psi_k\rangle \leq \liminf_{n\to\infty} \mathrm{Tr}\,\left[\mathcal{D}^{(n)}\right] \leq N \tag{4.11}$$

Analogously, we have that

$$\lim_{n\to\infty} \langle \psi_k, (-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(n)}(-\Delta_{\mathcal{A}})^{\frac{1}{2}}\psi_k\rangle = \langle \psi_k, (-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(\infty)}(-\Delta_{\mathcal{A}})^{\frac{1}{2}}\psi_k\rangle.$$

and the nonnegativity of $(-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(n)}(-\Delta_{\mathcal{A}})^{\frac{1}{2}}$, in conjunction with Fatou's lemma, yields

$$\mathrm{Tr}\,\left[-\Delta_{\mathcal{A}}\mathcal{D}^{(\infty)}\right] \leq \liminf_{n\to\infty} \mathrm{Tr}\,\left[-\Delta_{\mathcal{A}}\mathcal{D}^{(n)}\right] \tag{4.12}$$

Furthermore, we see that $0 \leq \mathcal{D}^{(\infty)} \leq I$.
2. *Pauli case.* We know that $(\mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)})_n$ has a weak-$*$ limit in $\mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}})$. As above let $-\Delta_{\mathcal{A}}$ denote the magnetic Schrödinger operator with vector potential $\mathcal{A}$. Define $T_{(n)} = (-\Delta_{\mathcal{A}_{(n)}}+1)^{-1/2}$ and $T_{(\infty)} = (-\Delta_{\mathcal{A}_{(\infty)}}+1)^{-1/2}$. We have that, using standard arguments [1],

$$T_{(n)} \longrightarrow T_{(\infty)} \text{ strongly in } \mathfrak{H}_{\mathrm{p}}.$$

Now, let $S_{(n)} = (-\Delta_{\mathcal{A}_{(n)}}+1)^{1/2}\mathcal{D}_{(n)}(-\Delta_{\mathcal{A}_{(n)}}+1)^{1/2}$. Then $(S_{(n)})_n$ is bounded in $\mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}})$ because $(\mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)})_n$ is bounded therein. Hence $S_{(n)}$ has a weak-$*$ limit $S_{(\infty)}$ in $\mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}})$. Now, using the above,

$$\mathcal{D}_{(n)} = T_{(n)}S_{(n)}T_{(n)}^* \rightharpoonup T_{(\infty)}S_{(\infty)}T_{(\infty)}^* \text{ weak-}* \text{ in } \mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}})$$

and

$$\mathcal{D}_{(n)} \rightharpoonup \mathcal{D}_{(\infty)} \text{ weak-}* \text{ in } \mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}}).$$

Hence $S_{(\infty)} = T_{(\infty)}\mathcal{D}_{(\infty)}(T_{(\infty)}^*)^{-1}$ and we deduce

$$-\Delta_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)} \rightharpoonup -\Delta_{\mathcal{A}_{(\infty)}}\mathcal{D}_{(\infty)} \text{ weak-}* \text{ in } \mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}}),$$

and, therefore, we have that

$$\mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)} \rightharpoonup \mathbb{P}_{\mathcal{A}_{(\infty)}}\mathcal{D}_{(\infty)} \text{ weak-}* \text{ in } \mathfrak{S}_1(\mathfrak{H}_{\mathrm{p}}).$$

Then, by arguing as in the Schrödinger case, the latter implies that

$$\langle \phi, \mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)}\psi\rangle_{\mathfrak{H}_{\mathrm{p}}} \longrightarrow \langle \phi, \mathbb{P}_{\mathcal{A}_{(\infty)}}\mathcal{D}_{(\infty)}\psi\rangle_{\mathfrak{H}_{\mathrm{p}}}, \qquad \phi,\psi \in C_0^\infty(\mathbb{R}^3;\mathbb{C}^2).$$

and we deduce that, for any orthonormal basis $(\psi_k)$ in $\mathfrak{H}_{\mathrm{p}}$ such that $\psi_k \in \mathbf{H}^1(\mathbb{R}^3;\mathbb{C}^2)$,

$$\lim_{n\to\infty} \langle \psi_k, \mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)}\psi_k\rangle_{\mathfrak{H}_{\mathrm{p}}} = \langle \psi_k, \mathbb{P}_{\mathcal{A}_{(\infty)}}\mathcal{D}_{(\infty)}\psi_k\rangle_{\mathfrak{H}_{\mathrm{p}}}$$

which, together with Fatou's lemma gives us that

$$\mathrm{Tr}\,(\mathbb{P}_{\mathcal{A}_{(\infty)}}\mathcal{D}_{(\infty)}) \leq \liminf_{n\to\infty} \mathrm{Tr}\,(\mathbb{P}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)}).$$

Since $0 \leq \mathcal{D}^{(\infty)} \leq I$, we conclude that $\mathcal{D}_{(\infty)} \in \mathcal{M}_{\mathrm{p}}^{\leq}$. □

With these preparations we are ready to establish weakly lower semicontinuity.

**Lemma 4.5.**
*1. Schrödinger case.*
$$\mathcal{E}^{\mathrm{s}}(\mathcal{D}^{(\infty)}) \leq \liminf_{n\to\infty} \mathcal{E}^{\mathrm{s}}(\mathcal{D}^{(n)})$$

*2. Pauli case.*
$$\mathcal{E}^{\mathrm{p}}(\mathcal{D}_{\infty}, \mathcal{A}_{(\infty)}) \leq \liminf_{n\to\infty} \mathcal{E}^{\mathrm{p}}(\mathcal{D}_{(n)}, \mathcal{A}_{(n)})$$

*Proof.* We divide the proof into the two cases we consider.
1. *Schrödinger case.* To simplify the notation, henceforth we write $\rho^{(n)}$, resp. $\rho^{(\infty)}$, instead of $\rho_{\mathcal{D}^{(n)}}$, resp. $\rho_{\mathcal{D}^{(\infty)}}$. We already know that $\mathcal{D} \mapsto \mathrm{Tr}\,[-(1/2)\Delta_{\mathcal{A}}\mathcal{D}]$ is weakly lower semicontinuous, i.e.
$$\mathrm{Tr}\,\left[-\Delta_{\mathcal{A}}\mathcal{D}^{(\infty)}\right] \leq \liminf_{n\to\infty} \mathrm{Tr}\,\left[-\Delta_{\mathcal{A}}\mathcal{D}^{(n)}\right]$$
In particular,
$$\mathrm{Tr}\,\left[-\Delta_{\mathcal{A}}\mathcal{D}^{(\infty)}\right] < \infty.$$
Then
$$\mathcal{J}(\mathcal{D}^{(\infty)}) = \mathcal{J}(\rho^{(\infty)}, \rho^{(\infty)}) < \infty \tag{4.13}$$
because, due to the Hardy-Littlewood-Sobolev inequality, $\rho^{(\infty)} \in L^1(\mathbb{R}^3;\mathbb{R}) \cap L^{\frac{5}{3}}(\mathbb{R}^3;\mathbb{R}) \subset L^{\frac{6}{5}}(\mathbb{R}^3;\mathbb{R})$. By means of (4.13) we now show that the second term in $\mathcal{E}^{\mathrm{s}}(\cdot)$ is weakly lower semicontinuous, i.e.,
$$\mathrm{Tr}\,\left[V_{\mathrm{en}}\mathcal{D}^{(\infty)}\right] \leq \liminf \mathrm{Tr}\,\left[V_{\mathrm{en}}\mathcal{D}^{(n)}\right] \tag{4.14}$$
It suffices to prove that, for $k = 1, \ldots, K$ and $v_k(\boldsymbol{r}) = Z_k/|\boldsymbol{r}|$,
$$\int v_k(\boldsymbol{r})\rho^{(\infty)}(\boldsymbol{r})\, d\boldsymbol{r} = \lim_{n\to\infty} \int v_k(\boldsymbol{r})\rho^{(n)}(\boldsymbol{r})\, d\boldsymbol{r} \tag{4.15}$$
We make the decomposition
$$v_k(\boldsymbol{r}) = v_k\chi_R + v_k(1-\chi_R)$$
where $\chi_R$ is the characteristic function for the set $\{\,|\boldsymbol{r}| \leq R\,\}$. Let $Z_R$ denote the uniform charge distribution over $\{\,|\boldsymbol{r}| \leq r\,\}$ with total charge equal to $Z_k$. Then
$$v_k(1-\chi_R)(\boldsymbol{r}) = Z_R * |\boldsymbol{r}|^{-1} \text{ for } |\boldsymbol{r}| \geq R. \tag{4.16}$$
Then, by using (4.13) and by invoking the Schwarz inequality for the Coulomb inner product, we have that
$$\begin{aligned}
&\left|\int v_k(1-\chi_R)(\rho^{(n)} - \rho^{(\infty)})\, d\boldsymbol{r}\right| \\
&\leq\; 2\mathcal{J}(|\rho^{(n)} - \rho^{(\infty)}|, Z_R) \\
&\leq\; 2\mathcal{J}(\rho^{(n)} + \rho^{(\infty)}, \rho^{(n)} + \rho^{(\infty)})^{\frac{1}{2}} \cdot \mathcal{J}(Z_R, Z_R)^{\frac{1}{2}} \\
&\leq\; 2\left(\mathcal{J}(\rho^{(n)}, \rho^{(n)})^{\frac{1}{2}} + \mathcal{J}(\rho^{(\infty)}, \rho^{(\infty)})^{\frac{1}{2}}\right)\mathcal{J}(Z_R, Z_R)^{\frac{1}{2}} \\
&\leq\; C\mathcal{J}(Z_R, Z_R)^{\frac{1}{2}} \longrightarrow 0 \text{ as } R \to \infty.
\end{aligned} \tag{4.17}$$

where $\mathcal{J}(\rho^{(n)},\rho^{(n)})$ is bounded because $\mathcal{D}^{(n)}$ is minimizing. Furthermore, since $(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}}v_k\chi_R(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}} \in \mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$, we also have

$$\begin{aligned}\int v_k(\boldsymbol{r})\chi_R(\boldsymbol{r})\rho^{(n)}(\boldsymbol{r})\,d\boldsymbol{r} &= \mathrm{Tr}\,\left[\mathcal{D}^{(n)}v_k\chi_R\right]\\ &= \mathrm{Tr}\,\left[\tilde{\mathcal{D}}^{(n)}(1-\Delta)^{-\frac{1}{2}}v_k\chi_R(1-\Delta)^{-\frac{1}{2}}\right]\\ &\longrightarrow \mathrm{Tr}\,\left[\mathcal{D}^{(\infty)}(1-\Delta)^{-\frac{1}{2}}v_k\chi_R(1-\Delta)^{-\frac{1}{2}}\right]\end{aligned}$$

which, in conjunction with (4.16), proves (4.15).
*Third term.* Let

$$\mathcal{L}(\mathcal{D}^{(j)},\mathcal{D}^{(j)}) = \mathcal{J}(\mathcal{D}^{(j)},\mathcal{D}^{(j)}) - \mathcal{K}(\mathcal{D}^{(j)},\mathcal{D}^{(j)})$$

We need to show that

$$\mathcal{L}(\mathcal{D}^{(\infty)},\mathcal{D}^{(\infty)}) \le \lim_{j\to\infty}\inf \mathcal{L}(\mathcal{D}^{(j)},\mathcal{D}^{(j)}) \tag{4.18}$$

when $\mathcal{D}^{(j)} \to \mathcal{D}^{(\infty)}$ weakly; the latter means that

$$\mathrm{Tr}\,\left[S\tilde{\mathcal{D}}^{(j)}\right] \longrightarrow \mathrm{Tr}\,\left[S\tilde{\mathcal{D}}^{(\infty)}\right], \quad \forall S \in \mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}}),$$

where $\tilde{\mathcal{D}}^{(j)}$ is defined as in (4.10) and, analogously,

$$\tilde{\mathcal{D}}^{(\infty)} = (1-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(\infty)}(1-\Delta_{\mathcal{A}})^{\frac{1}{2}}$$

We proceed to prove first that

$$\lim_{j\to\infty}\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r}') = \mathcal{D}^{(\infty)}(\boldsymbol{r},\boldsymbol{r}') \text{ for a.e. } (\boldsymbol{r},\boldsymbol{r}') \in \mathbb{R}^3\times\mathbb{R}^3, \tag{4.19}$$

and, in addition,

$$\lim_{j\to\infty}\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r}) = \mathcal{D}^{(\infty)}(\boldsymbol{r},\boldsymbol{r}) \text{ for a.e. } \boldsymbol{r} \in \mathbb{R}^3. \tag{4.20}$$

As above we switch to $\tilde{\mathcal{D}}^{(j)} = (1-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(j)}(1-\Delta_{\mathcal{A}})^{\frac{1}{2}}$. Since $\{\tilde{\mathcal{D}}^{(j)}\}$ is a bounded sequence in $\mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$ we may extract a subsequence, which converges weakly to some $\hat{\mathcal{D}}^{(\infty)}$ in $\mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$, i.e., for any $S \in \mathfrak{S}_2(\mathfrak{H}^{\mathrm{s}})$ we have that

$$\mathrm{Tr}\,\left[S\tilde{\mathcal{D}}^{(j)}\right] \longrightarrow \mathrm{Tr}\,\left[S\hat{\mathcal{D}}^{(\infty)}\right],$$

whence

$$\begin{aligned}\mathrm{Tr}\,\left[S\hat{\mathcal{D}}^{(\infty)}\right] &= \lim_{j\to\infty}\mathrm{Tr}\,\left[S\tilde{\mathcal{D}}^{(j)}\right]\\ &= \lim_{j\to\infty}\mathrm{Tr}\,\left[(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}}S(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}}(1-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(j)}(1-\Delta_{\mathcal{A}})^{\frac{1}{2}}\right]\\ &= \mathrm{Tr}\,\left[(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}}S(1-\Delta_{\mathcal{A}})^{-\frac{1}{2}}(1-\Delta_{\mathcal{A}})^{\frac{1}{2}}\mathcal{D}^{(\infty)}(1-\Delta_{\mathcal{A}})^{\frac{1}{2}}\right]\\ &= \mathrm{Tr}\,\left[S\tilde{\mathcal{D}}^{(\infty)}\right],\end{aligned}$$

which shows that $\hat{\mathcal{D}}^{(\infty)} = \tilde{\mathcal{D}}^{(\infty)}$ and thus

$$\mathcal{D}^{(j)}(\cdot,\cdot) \longrightarrow \mathcal{D}^{(\infty)}(\cdot,\cdot) \tag{4.21}$$

weakly in $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$. The spectral decomposition of the $\mathcal{D}^{(j)}$ enables us to express $\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r}')$ as

$$\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r}') = \sum_{i=1}^{I} \overline{f_i^{(j)}(\boldsymbol{r})} f_i^{(j)}(\boldsymbol{r}')$$

with each sequence $\{f_i^{(j)}\}_{j\in\mathbb{N}}$, $i = 1,\ldots,I$, being orthonormal in $L^2(\mathbb{R}^2)$ with elements in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. Invoking the compact embedding $\mathbf{H}^1(\mathbb{R}^3) \hookrightarrow \mathbf{H}^{1-\epsilon}(\mathbb{R}^3)$ we may for every $g \in C_0^\infty(\mathbb{R}^3)$ and $i = 1,2,\ldots,I$ extract a subsequence $\{f_i^{(j)}\}_{j\in\mathbb{N}}$, also denoted $\{f_i^{(j)}\}_{j\in\mathbb{N}}$, such that $\{g f_i^{(j)}\}_{j\in\mathbb{N}}$ converges strongly in $L^2(\mathbb{R}^3)$. The latter allows us to extract a subsequence of $(f_1^{(j)},\ldots,f_I^{(j)})$, denoted again by $(f_1^{(j)},\ldots,f_I^{(j)})$, such that

$$f_i^{(j)}(\boldsymbol{r}) \longrightarrow f_i^{(\infty)}(\boldsymbol{r}) \text{ for a.e. } \boldsymbol{r} \in \mathbb{R}^3 \text{ and } \forall i = 1,\ldots,I, \tag{4.22}$$

and thus

$$\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r}') \longrightarrow \mathcal{D}(\boldsymbol{r},\boldsymbol{r}') := \sum_{i=1}^{I} \overline{f_i^{(\infty)}(\boldsymbol{r})} f_i^{(\infty)}(\boldsymbol{r}') \tag{4.23}$$

In particular, (4.21) and (4.23) imply that

$$\mathcal{D}^{(\infty)}(\boldsymbol{r},\boldsymbol{r}') = \mathcal{D}(\boldsymbol{r},\boldsymbol{r}') \text{ for a.e. } (\boldsymbol{r},\boldsymbol{r}') \in \mathbb{R}^3 \times \mathbb{R}^3$$

As a consequence, $\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r}')$ converges to $\mathcal{D}^{(\infty)}(\boldsymbol{r},\boldsymbol{r}')$ almost everywhere on $\mathbb{R}^3 \times \mathbb{R}^3$ which, together with (4.23), yields (4.19). The latter immediately implies that

$$\mathcal{D}^{(\infty)} = \sum_{i=1}^{I} \langle f_i^{(\infty)}, \cdot\rangle_{L^2} f_i^{(\infty)}$$

which proves (4.20).
An application of Fatou's lemma in conjunction with (4.19) and (4.20) yields

$$\begin{aligned}
&\liminf_{j\to\infty} \mathcal{L}(\mathcal{D}^{(j)},\mathcal{D}^{(j)}) \\
&\qquad \geq \int_{\mathbb{R}^6} \lim_{j\to\infty} \frac{\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r})\mathcal{D}^{(j)}(y,y) - |\mathcal{D}^{(j)}(\boldsymbol{r},\boldsymbol{r}')|^2}{|\boldsymbol{x}-\boldsymbol{r}'|}\, d\boldsymbol{r} d\boldsymbol{r}' \\
&\qquad = \int_{\mathbb{R}^6} \frac{\mathcal{D}^{(\infty)}(\boldsymbol{r},\boldsymbol{r})\mathcal{D}^{(\infty)}(\boldsymbol{r}',\boldsymbol{r}') - |\mathcal{D}^{(\infty)}(\boldsymbol{x},\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r} d\boldsymbol{r}' \\
&\qquad = \mathcal{L}(\mathcal{D}^{(\infty)},\mathcal{D}^{(\infty)})
\end{aligned} \tag{4.24}$$

This proves the assertion.

2. *Pauli case.* Now,

$$\begin{aligned}
\mathcal{E}^{\mathrm{p}}(\mathcal{D}_{(n)},\mathcal{A}_{(n)}) &= \underbrace{\frac{1}{2}\operatorname{Tr}\left(\mathbb{P}^{(j)}_{\mathcal{A}_{(n)}}\mathcal{D}_{(n)}\right)}_{\text{Term 1}} + \underbrace{\int_{\mathbb{R}^3} V\rho_{\mathcal{D}_{(n)}}}_{\text{Term 2}} \\
&\quad \underbrace{+\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_{\mathcal{D}_{(n)}}(\boldsymbol{r})\rho_{\mathcal{D}_{(n)}}(\boldsymbol{r}') - \operatorname{Tr}_{\mathbb{C}^2}\left(|\mathcal{D}_{(n)}(\boldsymbol{r},\boldsymbol{r}')|^2\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'}_{\text{Term 3}} \\
&\quad \underbrace{+\frac{1}{\alpha^2}\int_{\mathbb{R}^3}|\mathcal{B}_{(n)}(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r}}_{\text{Term 4}}
\end{aligned}$$

We treat them in reverse order:

*Term 4.* The weakly lower semicontinuity

$$\liminf_{n\to\infty}\|\mathcal{B}_{(n)}\|^2_{L^2} \geq \|\mathcal{B}_{(\infty)}\|^2_{L^2}$$

follows immediately from weak lower semicontinuity of the $L^2$-norm.

*Term 3.* To handle terms 3 and 2, we bear in mind that, in view of Lemma A.1, one has

$$\begin{aligned}
\rho_{\mathcal{D}_{(n)}} &\longrightarrow \rho_{\mathcal{D}_{(\infty)}} && \text{strongly in } L^p_{\mathrm{loc}}(\mathbb{R}^3;\mathbb{R}),\ p\in[1,3)\,; \\
\rho_{\mathcal{D}_{(n)}} &\longrightarrow \rho_{\mathcal{D}_{(\infty)}} && \text{weakly in } L^p(\mathbb{R}^3;\mathbb{R}),\ p\in[1,3], \\
& && \text{and almost everywhere.}
\end{aligned} \tag{4.25}$$

From the Cauchy-Schwarz inequality, Fatou's lemma and the convergence a.e. mentioned above, we obtain

$$\begin{aligned}
\liminf_{n\to\infty}\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}&\frac{\rho_{\mathcal{D}_{(n)}}(\boldsymbol{r})\rho_{\mathcal{D}_{(n)}}(\boldsymbol{r}') - \operatorname{Tr}_{\mathbb{C}^2}\left(|\mathcal{D}_{(n)}(\boldsymbol{r},\boldsymbol{r}')|^2\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \\
&\geq \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_{\mathcal{D}_{(\infty)}}(\boldsymbol{r})\rho_{\mathcal{D}_{(\infty)}}(\boldsymbol{r}') - \operatorname{Tr}_{\mathbb{C}^2}\left(|\mathcal{D}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}')|^2\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'
\end{aligned}$$

Term 2. Once again using (4.25) we deduce that

$$\lim_{n\to\infty}\int_{\mathbb{R}^3} V_{\mathrm{en}}\rho_{\mathcal{D}_n}\,\mathrm{d}\boldsymbol{r} = \int_{\mathbb{R}^3} V_{\mathrm{en}}\rho_{\mathcal{D}_{(\infty)}}\,\mathrm{d}\boldsymbol{r}$$

for any $V \in (L^{3/2}+L^\infty)(\mathbb{R}^3;\mathbb{R})$.

Term 1. Treated in Lemma 4.4. □

To summarize we conclude that

$$\begin{aligned}
\mathcal{E}^{\mathrm{s}}(\mathcal{D}^{(\infty)}) &= E^{\mathrm{s}}_{\leq}(N,\boldsymbol{Z},\mathcal{A}) \text{ and} \\
\mathcal{E}^{\mathrm{p}}(\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}) &= E^{\mathrm{p}}_{\leq}(N,\boldsymbol{Z}).
\end{aligned}$$

## 5. The Fock operator and the Fock-Pauli operator

Herein we introduce the Fock operator, respectively the Fock-Pauli operator.

**Proposition 5.1.** *Let*

$$K^{\mathrm{xc}}(\boldsymbol{r},\boldsymbol{r}') = \frac{\mathcal{D}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

*be the integral kernel of the exchange operator* $K^{\mathrm{xc}}$.
*1. Schrödinger case. The form generated by the differential expression*

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

*is closed on its form domain* $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$*. The closed form gives rise to a unique self-adjoint operator* $F^{\mathrm{s}}_{\mathcal{D},\mathcal{A}}$*, the diamagnetic Fock operator.*
*2. Pauli case. The form generated by the differential expression*

$$\left[\boldsymbol{\sigma}\cdot\left(i\nabla - \mathcal{A}_{(\infty)}\right)\right]^2 + \left(V_{\mathrm{en}} + \rho_{\mathcal{D}} * \frac{1}{|\boldsymbol{r}|}\right)\mathbb{I}_2 - K^{\mathrm{xc}}_{\mathcal{D}} \tag{5.2}$$

*is closed on its form domain* $\mathbf{H}^1(\mathbb{R}^3)$*. The closed form gives rise to a unique self-adjoint operator* $F^{\mathrm{p}}_{\mathcal{D},\mathcal{A}_{(\infty)}}$*, the Fock-Pauli operator.*

*Proof.* We divide the proof into the two cases:
1. *Schrödinger case.* When $\mathcal{A}\in L^2_{\mathrm{loc}}(\mathbb{R}^3;\mathbb{R})^3$, the quadratic form $\int_{\mathbb{R}^3}|\nabla_{\mathcal{A}}u|^2\,d\boldsymbol{r}$ is closed and nonnegative on the form domain $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. Hence it generates a unique self-adjoint operator $-\Delta_{\mathcal{A}}$ (the magnetic Laplacian). Proposition 4.2 yields the existence of a minimizer $\mathcal{D}^{\mathrm{s}}\in\mathcal{M}^{\mathrm{s}}_{\leq}$ of the form

$$\mathcal{D}^{\mathrm{s}}(x,\boldsymbol{r}') = \sum \nu_n\overline{\phi_n(\boldsymbol{r})}\phi_n(\boldsymbol{r}'), \tag{5.3}$$

where $1\geq\nu_1\geq\nu_2\geq\cdots\geq 0$ and $\{\phi_n\}_n$, $\phi_n\in\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$, is an orthonormal system in $\mathfrak{H}^{\mathrm{s}}$. The Cauchy-Schwarz inequality yields, for $\boldsymbol{r},\boldsymbol{r}'\in\mathbb{R}^3$,

$$\begin{aligned}|\mathcal{D}^{\mathrm{s}}(\boldsymbol{r},\boldsymbol{r}')|^2 &= \left|\sum_n \nu_n\overline{\phi_n(\boldsymbol{r})}\phi_n(\boldsymbol{r}')\right|^2\\ &\leq \left(\sum_n\nu_n|\phi_n(\boldsymbol{r})|^2\right)\left(\sum_n\nu_n|\phi_n(\boldsymbol{r}')|^2\right) = \rho_{\mathcal{D}^{\mathrm{s}}}(\boldsymbol{r})\rho_{\mathcal{D}^{\mathrm{s}}}(\boldsymbol{r}'). \end{aligned}\tag{5.4}$$

Hölder's inequality gives

$$\int_{\mathbb{R}^3}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}|\phi(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r} \;\leq\; 2\left(\int_{\mathbb{R}^3}\frac{1}{4}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|^2}|\phi(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r}\right)^{\frac{1}{2}}\left(\int_{\mathbb{R}^3}|\phi(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r}\right)^{\frac{1}{2}}.$$

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

$$\frac{1}{4}\int_{\mathbb{R}^3}\frac{1}{|\boldsymbol{r}|^2}|\phi(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r} \leq \int_{\mathbb{R}^3}|\nabla\phi(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r},\quad \forall\phi\in C^\infty_0(\mathbb{R}^3), \tag{5.5}$$

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

$$\int_{\mathbb{R}^3} \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}|\phi(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r} \leq 2\|\phi\|_{L^2(\mathbb{R}^3)}\|\nabla_{\mathcal{A}}\phi\|_{L^2(\mathbb{R}^3)}, \quad \forall\phi\in C_0^\infty(\mathbb{R}^3). \tag{5.6}$$

Since $C_0^\infty(\mathbb{R}^3)$ is dense in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$, (5.6) holds for any $\phi\in\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. By invoking (5.4), the Hardy inequality (5.5) and the diamagnetic inequality (2.2), it follows that the kernel $K^{\mathrm{xc}}$ 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 [11] and, due to [1, Theorem 2.4], $V_{\mathrm{en}}$ is thus infinitesimally $-\Delta_{\mathcal{A}}$-bounded. Now $\rho\in L^1(\mathbb{R}^3;\mathbb{R})$ and the bound (3.3) implies that $\rho\in L^{5/3}(\mathbb{R}^3)$. From this it follows that $\rho*\frac{1}{|\boldsymbol{r}|}$ 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 KLMN theorem yields that $-\Delta_{\mathcal{A}}+V_{\mathrm{en}}+\rho*\frac{1}{|\boldsymbol{r}|}+K^{\mathrm{xc}}$ is an self-adjoint operator (and bounded from below) with form domain $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$.

2. *Pauli case.* The reasoning is very similar to the previous case. □

## 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 hold, and let $\mu$ be any bounded non-negative measure on $\mathbb{R}^3$ obeying $\mu(\mathbb{R}^3)\leq\vartheta$.*

*1. Schrödinger case. Define the magnetic Schrödinger operator*

$$L_{\mathcal{A},\mu} = -\Delta_{\mathcal{A}} + V_{\mathrm{en}} + \mu * \frac{1}{|\boldsymbol{r}|}.$$

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

$$\mathrm{Coun}\left(-\epsilon_{j,\vartheta}; L_{\mathcal{A},\mu}\right)\geq j.$$

*2. Pauli case. Define the Pauli operator*

$$\mathbb{P}_{\mathcal{A}_{(\infty)},\mu} = \left[\boldsymbol{\sigma}\cdot\left(i\nabla-\mathcal{A}_{(\infty)}\right)\right]^2 + \left(V_{\mathrm{en}}+\mu*\frac{1}{|\boldsymbol{r}|}\right)\mathbb{I}_2.$$

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

$$\mathrm{Coun}\left(-\epsilon_{j,\vartheta}; \mathbb{P}_{\mathcal{A}_{(\infty)},\mu}\right)\geq j.$$

*Proof.*

1. *Schrödinger operator.* We note that $\mu*\frac{1}{|\boldsymbol{r}|}\in\mathcal{K}_3$. Indeed, note that $\frac{1}{|\boldsymbol{r}|}\in\mathcal{K}_3$ and by the generalized Minkowski inequality (see e.g. [16, Theorem 2.4]),

$$\|g*\mu\|_{L^p}\leq\vartheta\|g\|_{L^p}.$$

holds for any $g \in L^p(\mathbb{R}^3)$, $p \in [1,\infty]$. From this we conclude that the quadratic form

$$\mathfrak{l} : \mathbf{H}^1_{\mathcal{A}} \to \mathbb{R} : \phi \mapsto \int_{\mathbb{R}^3} |\nabla_{\mathcal{A}}\phi(\boldsymbol{r})|^2 + \left(V_{\rm en}(\boldsymbol{r}) + \mu * \frac{1}{|\boldsymbol{r}|}\right) |\phi(\boldsymbol{r})|^2 {\rm d}\boldsymbol{r},$$

is lower semi-continuous and thus closed. Indeed, the form is weakly lower semi-continuous in view of [7, Lemma 3.3] and the weakly lower semi-continuity of $\phi \mapsto \|\nabla_{\mathcal{A}}\phi\|_{L^2}$. Moreover, the form is evidently semi-bounded from below. Hence, there is a self-adjoint operator, $L_{\mathcal{A},\mu}$ (which is also bounded from below) with $\mathfrak{D}(L_{\mathcal{A},\mu}) \subset \mathbf{H}^1_{\mathcal{A}}$ according to the first representation theorem [6, Theorem VI.2.4]. As mentioned above, the assumptions on $V_{\rm f}$ implies that it is infinitesimally form-bounded with respect to the Dirichlet form, see e.g. [22].

Write $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$, where $\mathcal{A}_1 \in L^\tau(\mathbb{R}^3)$ and $\mathcal{A}_2 \in L^\omega$. An application of Hölder's inequality shows that

$$\lim_{|\boldsymbol{q}|\to\infty} \int_{B_1(\boldsymbol{q})} \mathcal{A}^2 + V_{\rm en} + \mu * \frac{1}{|\boldsymbol{r}|} {\rm d}\boldsymbol{r} = 0,$$

and, in view of [14, Theorem 2.5], the latter implies that $\mathrm{spec}_{\rm ess}(L_{\mathcal{A},\mu}) = [0,\infty)$.

Define $\phi(\boldsymbol{r}) := \frac{g(1-|\boldsymbol{r}|^2)}{\|g(1-|\boldsymbol{r}|^2)\|_{L^2}}$, where $g(t) = e^{-1/t}$ for $t > 0$ and $g(t) = 0$ otherwise, and the rescaled family

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

Furthermore, define

$$V_\lambda(\boldsymbol{r}) := -\sum_{k=1}^{K} \frac{Z_k}{|\boldsymbol{r} - R_k/\lambda|}$$

and $\mu_\lambda := \lambda^3\mu(\lambda\cdot)$. Then, for $\lambda$ sufficiently large, we have that

$$\begin{aligned}\mathfrak{l}[\phi_\lambda] \le \frac{1}{\lambda^2}\int_{B_1} |\nabla\phi(\boldsymbol{r})|^2 {\rm d}\boldsymbol{r} + \mathrm{const}\bigg(\frac{1}{\lambda^{6/\omega}}\big(\|\mathcal{A}_1\|^2_{L^\tau} + \|\mathcal{A}_2\|^2_{L^\omega} \\ + \|\mathcal{A}_1\|_{L^\tau}\|\mathcal{A}_2\|_{L^\omega}\big) + \frac{1}{\lambda^{1+\tau}}\big(\|\mathcal{A}_1\|_{L^\tau} + \|\mathcal{A}_2\|_{L^\omega}\big)\bigg) \\ + \frac{1}{\lambda}\int_{B_1}\left(V_\lambda(\boldsymbol{r}) + \mu_\lambda * \frac{1}{|\boldsymbol{r}|}\right)|\phi(\boldsymbol{r})|^2{\rm d}\boldsymbol{r}.\end{aligned}$$

It is also easy to prove that

$$\int_{B_1}\left(V_\lambda(\boldsymbol{r}) + \mu_\lambda * \frac{1}{|\boldsymbol{r}|}\right)|\phi(\boldsymbol{r})|^2{\rm d}\boldsymbol{r} < 0$$

uniformly in $\lambda$ perhaps after increasing $\lambda$ further. Thus we have constructed a subspace with infinite dimension (again we might have to increase $\lambda$ further) such that $\mathfrak{l}[\cdot] < 0$ holds (on this subspace). Thus, we are done by a direct application of Glazman's Lemma (see, e.g., [22, Lemma A.3]).

2. *Pauli case.* The reasoning is similar to the previous case. Let $\mathfrak{p}[\phi,\phi]$ be the form associated

with $\mathbb{P}_{\mathcal{A}_{(\infty)},V,\mu}$ and let $\phi = (\phi^{\uparrow}, \phi^{\downarrow})^{\mathrm{T}} \in C_0^\infty(\mathbb{R}^3;\mathbb{C}^2)$ be radial with support in $\{1 < |\boldsymbol{r}| < 3\}$. Then rescale in the usual way,

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

Furthermore, define

$$V_\lambda(\boldsymbol{r}) := -\sum_{k=1}^{K} \frac{Z_k}{|\boldsymbol{r} - \boldsymbol{R}_k/\lambda|}$$

and $\mu_\lambda := \lambda^3\mu(\lambda\cdot)$. Then, for $\lambda$ sufficiently large, we have that

$$\mathfrak{p}[\phi_\lambda] = \frac{1}{\lambda}\int_{B_1}\left(V_\lambda(\boldsymbol{r}) + \mu_\lambda * \frac{1}{|\boldsymbol{r}|}\right)|\phi(\boldsymbol{r})|^2 \mathrm{d}\boldsymbol{r} + \mathrm{o}(1/|\lambda|)$$

It is also easy to prove that

$$\int_{B_1}\left(V_\lambda(x) + \mu_\lambda * \frac{1}{|x|}\right)|\phi(x)|^2 \mathrm{d}x < 0$$

uniformly in $\lambda$ perhaps after increasing $\lambda$ further. Thus we have constructed a subspace with infinite dimension (again we might have to increase $\lambda$ further) such that $\mathfrak{l}[\cdot] < 0$ holds (on this subspace). Thus, we are done by a direct application of Glazman's Lemma (see, e.g., [22, Lemma A.3]). ☐

## 7. Completion of proof of Theorem 1.3

We are ready to finish the proof of Theorem 1.3 by proving that

**P1** $\mathcal{D}_{(\infty)}$ is a projection,
**P2** $\mathrm{Tr}\,(\mathcal{D}_{(\infty)}) = N$, and
**P3** $\{\varphi_n\}_{n=1}^N$ are eigenfunctions associated to the lowest eigenvalues of $F^{\mathrm{p}}_{\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}}$.

We only write out the details for the Pauli case; the Schrödinger case can be treated in a similar way). We define, for any $\mu_1, \mu_2 \in \mathbb{R}$ and any $\phi_1, \phi_2 \in \mathbf{H}^1(\mathbb{R}^3;\mathbb{C}^2)$,

$$\mathcal{D}_{\boldsymbol{\Phi}}^{\boldsymbol{\mu}} := \mathcal{D}_{\phi_1,\phi_2}^{\mu_1,\mu_2} = \mu_1\overline{\phi_1} \otimes \phi_1 + \mu_2\overline{\phi_2} \otimes \phi_2 \tag{7.1}$$

and

$$R_{\boldsymbol{\Phi}} := R_{\phi_1,\phi_2} = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\|\phi_1(\boldsymbol{r}) \otimes \phi_2(\boldsymbol{r}') - \phi_2(\boldsymbol{r}) \otimes \phi_1(\boldsymbol{r}')\|^2_{\mathbb{C}^2\otimes\mathbb{C}^2}}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d\boldsymbol{r} d\boldsymbol{r}'. \tag{7.2}$$

We shall repeatedly use the follow fact: If $\mu_1, \mu_2 \in \mathbb{R}$ are chosen to ensure that

$$\widetilde{\mathcal{D}}(\boldsymbol{r}, \boldsymbol{r}') := \mathcal{D}(\boldsymbol{r}, \boldsymbol{r}') + \mathcal{D}_\Phi(\boldsymbol{r}, \boldsymbol{r}') \in \mathcal{M}_{\mathrm{p}}, \quad \mathcal{D} \in \mathcal{M}_{\mathrm{p}}$$

then a straightforward computation yields

$$\mathcal{E}^{\mathrm{p}}(\widetilde{\mathcal{D}}, \mathcal{A}_{(\infty)}) = \mathcal{E}^{\mathrm{p}}(\mathcal{D}, \mathcal{A}_{(\infty)}) + \mu_1\langle\phi_1, F^{\mathrm{p}}_{\mathcal{D},\mathcal{A}_{(\infty)}}\phi_1\rangle + \mu_2\langle\phi_2, F^{\mathrm{p}}_{\mathcal{D},\mathcal{A}_{(\infty)}}\phi_2\rangle + \mu_1\mu_2 R_{\boldsymbol{\Phi}}. \tag{7.3}$$

where $R_{\boldsymbol{\Phi}}$ is defined in (7.2). The formula (7.3) is a two-component/function version of a one-component/function formula found in [24, page 309, line 12 from above]. It can also be compared with [2, Equation (32)] and [3, Equation (35)] . As a tool it plays much the same role as the complementary minimizing formula in [7, Equation (5.3)].

It is convenient to divide the proofs of properties **P1-P2** into two lemmas wherein, by hypothesis, $N < Z_{\rm tot}$, respectively, $Z_{\rm tot} \le N < Z_{\rm tot} + 1$.

**Lemma 7.1.** *Suppose $N < Z_{\rm tot}$. Then **P1** and **P2** hold.*

*Proof.* As a first application of (7.3) we show that the eigenvalues $\epsilon_{m_n}$ of $F^{\rm p}_{\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}}$ associated to eigenfunctions $\varphi_n$ are non-positive. Indeed, if $\epsilon_{m_n} > 0$ then an application of (7.3) to $\widetilde{\mathcal{D}}(\boldsymbol{r},\boldsymbol{r}') = \mathcal{D}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') - \nu_n \overline{\varphi_n(\boldsymbol{r})}\varphi_n(\boldsymbol{r}')$ yields

$$\mathcal{E}^{\rm p}(\widetilde{\mathcal{D}},\mathcal{A}_{(\infty)}) = \mathcal{E}^{\rm p}(\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}) - \nu_n\epsilon_{m_n} < \mathcal{E}^{\rm p}(\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}),$$

so the energy has been made smaller which is a contradiction. To show **P1**, we argue by contradiction. Thus, suppose there exist $l, m$ such that $0 < \nu_l, \nu_m < 1$. Set $\widetilde{\mathcal{D}}(\boldsymbol{r},\boldsymbol{r}') := \mathcal{D}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') + \epsilon\varphi_l(x)\varphi_l(\boldsymbol{r}') - \epsilon\overline{\varphi_m(\boldsymbol{r})}\varphi_m(\boldsymbol{r}')$ with $\epsilon$ such that $0 \le \widetilde{\mathcal{D}} \le I$; letting $\epsilon > 0$ if $\epsilon_{n_l} < \epsilon_{n_m}$ and $\epsilon < 0$ if $\epsilon_{n_l} \ge \epsilon_{n_m}$. An application of (7.3) yields $\mathcal{E}^{\rm p}(\widetilde{\mathcal{D}},\mathcal{A}_{(\infty)}) < \mathcal{E}^{\rm p}(\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)})$ which is a contradiction. Likewise, to show **P2**, we argue by contradiction, so suppose that $\mathrm{Tr}\,(\mathcal{D}_{(\infty)}) < N$. If the measure $\mu$ in Lemma 6.1 is chosen as $\rho\,\mathrm{d}\boldsymbol{r}$ with $\rho$ being the density $\rho(\boldsymbol{r}) = \sum_{n=1}^N |\varphi_n(\boldsymbol{r})|^2$ ($\boldsymbol{r} \in \mathbb{R}^3$), then the resulting Pauli operator $\mathbb{P}_{\mathcal{A},V_{\rm en},\rho\,\mathrm{d}\boldsymbol{r}}$ satisfies the operator inequality

$$F^{\rm p}_{\mathcal{D},\mathcal{A}_{(\infty)}} \le \mathbb{P}_{\mathcal{A},V_{\rm en},\rho\,\mathrm{d}\,\boldsymbol{r}}, \tag{7.4}$$

where $F^{\rm p}_{\mathcal{D},\mathcal{A}_{(\infty)}}$ is the Fock-Pauli operator introduced in Proposition 5.1. We first claim that all components of $\boldsymbol{\varphi}$ are nonzero. Suppose one of the orbitals vanishes, say $\varphi_1$; i.e. $\rho(\boldsymbol{r}) = \sum_{n=2}^N |\varphi_n(\boldsymbol{r})|^2$. Then

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

By hypothesis, $N - 1 < N < Z_{\rm tot}$ so an application of Lemma 6.1, in conjunction with (7.4), informs us that $F^{\rm p}_{\mathcal{D},\mathcal{A}_{(\infty)}}$ has at least $N$ *negative* eigenvalues. In particular, there exists an eigenfunction $\psi$ associated with a negative eigenvalue of $F^{\rm p}_{\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}}$ so that $\psi \perp \{\varphi_1, \ldots, \varphi_L\}$, where $L$ denotes the multiplicity of the eigenvalue one in (5.3). Introduce the density operator $\mathcal{D}$ with integral kernel given by

$$\mathcal{D}(\boldsymbol{r},\boldsymbol{r}') := \mathcal{D}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') + \epsilon\overline{\psi(\boldsymbol{r})}\psi(\boldsymbol{r}')$$

with $\epsilon$ chosen small enough to ensure that $\mathrm{Tr}\,(\mathcal{D}) \le N$. Invoking (7.3), taking $\varphi_1 = \psi$, $\mu_1 = \epsilon$, and $\mu_2 = 0$ therein, gives the contradiction

$$\mathcal{E}^{\rm p}(\mathcal{D},\mathcal{A}_{(\infty)}) = \mathcal{E}^{\rm p}(\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}) + \epsilon\langle\psi, F^{\rm p}_{\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}}\psi\rangle < \mathcal{E}^{\rm p}(\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}).$$

□

**Lemma 7.2.** *Suppose $Z_{\rm tot} \le N < Z_{\rm tot} + 1$. Then **P1** and **P2** hold.*

*Proof.* Let $\mathcal{D}^{N-1}_{(\infty)}$ be the minimizer associated with $E^{\leq}_{N-1}$. From Lemma 7.1 we know that $\mathcal{D}^{N-1}_{(\infty)}$ is a projection and $\operatorname{Tr}(\mathcal{D}^{N-1}_{(\infty)}) = N-1$. In particular, the integral kernel of $\mathcal{D}^{N-1}_{(\infty)}$ takes the form

$$\mathcal{D}^{N-1}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') = \sum_{m=1}^{N-1} \overline{\varphi_m(\boldsymbol{r})}\varphi_m(\boldsymbol{r}')$$

with the $\varphi_m$'s being eigenfunctions of $F^{\mathrm{p}}_{\mathcal{D}^{N-1}_{(\infty)},\mathcal{A}_{(\infty)}}$. Arguing as in the proof of Lemma 7.1 there exists an eigenfunction $\psi$ of $F^{\mathrm{p}}_{\mathcal{D}^{N-1}_{(\infty)},\mathcal{A}_{(\infty)}}$ associated to a negative eigenvalue such that $\psi \perp \{\phi_1,\ldots,\phi_{N-1}\}$. Then

$$\widetilde{\mathcal{D}}(\boldsymbol{r},\boldsymbol{r}') := \mathcal{D}^{N-1}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') + \overline{\psi(\boldsymbol{r})}\psi(\boldsymbol{r}')$$

satisfies $\operatorname{Tr}(\widetilde{\mathcal{D}}) = N$ and

$$\mathcal{E}^{\mathrm{p}}(\widetilde{\mathcal{D}},\mathcal{A}_{(\infty)}) = \mathcal{E}^{\mathrm{p}}(\mathcal{D}^{N-1}_{(\infty)},\mathcal{A}_{(\infty)}) + \langle \psi, F^{\mathrm{p}}_{\mathcal{D}^{N-1}_{(\infty)},\mathcal{A}_{(\infty)}}\psi\rangle < \mathcal{E}^{\mathrm{p}}(\mathcal{D}^{N-1}_{(\infty)},\mathcal{A}_{(\infty)}).$$

Thus $E^{\leq}_{N} < E^{\leq}_{N-1}$. In other words, $E^{\leq}_{N}$ is not attained at $\mathcal{D}^{N-1}_{(\infty)}$. Next, suppose $E^{\leq}_{N}$ is attained at some $\mathcal{D}^{N}_{(\infty)}$; its existence is guaranteed by Proposition 4.2. A priori, $N-1 < \operatorname{Tr}(\mathcal{D}^{N}_{(\infty)}) \leq N$. We proceed to prove that there exists a minimizer, denoted $\mathcal{D}_{(\infty)}$, satisfying $\operatorname{Tr}(\mathcal{D}_{(\infty)}) = N$.
If $\{\varphi_l\}$ are the orthonormal eigenfunctions of $F^{\mathrm{p}}_{\mathcal{D}^{N}_{(\infty)},\mathcal{A}_{(\infty)}}$ and $1 \geq \nu_1 \geq \cdots \geq 0$, then the integral kernel of $\mathcal{D}^{N}_{(\infty)}$ is

$$\mathcal{D}^{N}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') = \sum_{l} \nu_l\overline{\varphi_l(\boldsymbol{r})}\varphi_l(\boldsymbol{r}').$$

In the case $\operatorname{Tr}(\mathcal{D}^{N}_{(\infty)}) < N$, a new density operator $\widetilde{\mathcal{D}}$ with $\operatorname{Tr}(\widetilde{\mathcal{D}}) \leq N$ and $\mathcal{E}^{\mathrm{p}}(\widetilde{\mathcal{D}},\mathcal{A}_{(\infty)}) \leq \mathcal{E}^{\mathrm{p}}(\mathcal{D}^{N}_{(\infty)},\mathcal{A}_{(\infty)})$ can be constructed as follows: The assumption implies that there exists a $l_0$ such that $0 < \nu_{l_0} < 1$. Thus, setting $\kappa := \min\{N - \operatorname{Tr}(\mathcal{D}^{N}_{(\infty)}), 1-\nu_{l_0}\} > 0$, we may define

$$\widetilde{\mathcal{D}}(\boldsymbol{r},\boldsymbol{r}') = \mathcal{D}^{N}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') + \kappa\overline{\varphi_{l_0}(\boldsymbol{r})}\varphi_{l_0}(\boldsymbol{r}')$$

Applying (7.3) yields

$$\mathcal{E}^{\mathrm{p}}(\widetilde{\mathcal{D}}) = \mathcal{E}^{\mathrm{p}}(\mathcal{D}^{N}_{(\infty)},\mathcal{A}_{(\infty)}) + \kappa\epsilon_{n_{l_0}};$$

here we used $F^{\mathrm{p}}_{\mathcal{D}^{N}_{(\infty)},\mathcal{A}_{(\infty)}}\varphi_l = \epsilon_{n_l}\varphi_l$, $\epsilon_{n_l} \leq 0$, for all $l$. Now, if $\epsilon_{n_{l_0}} < 0$ then $\mathcal{E}^{\mathrm{p}}(\widetilde{\mathcal{D}},\mathcal{A}_{(\infty)}) < \mathcal{E}^{\mathrm{p}}(\mathcal{D}^{N}_{(\infty)},\mathcal{A}_{(\infty)})$ follows. Otherwise, if $\epsilon_{n_{l_0}} = 0$, then $\mathcal{E}^{\mathrm{p}}(\widetilde{\mathcal{D}},\mathcal{A}_{(\infty)}) = \mathcal{E}^{\mathrm{p}}(\mathcal{D}^{N}_{(\infty)},\mathcal{A}_{(\infty)})$ and $\operatorname{Tr}(\mathcal{D}^{N}_{(\infty)}) < \operatorname{Tr}(\widetilde{\mathcal{D}}) \leq N$. If $\operatorname{Tr}(\widetilde{\mathcal{D}}) = N$ then we set $\mathcal{D}_{(\infty)} := \widetilde{\mathcal{D}}$ and, as above, this proves the statement. If, on the other hand, $\operatorname{Tr}(\widetilde{\mathcal{D}}) < N$, then the arguments above are applied to

$$\widetilde{\mathcal{D}}(\boldsymbol{r},\boldsymbol{r}') = \sum_{l=1}^{l_0} \overline{\varphi_l(\boldsymbol{r})}\varphi_l(\boldsymbol{r}') + \sum_{l>l_0} \nu_l\overline{\varphi_l(\boldsymbol{r})}\varphi_l(\boldsymbol{r}')$$

and this procedure is repeated until it terminates which it will do because the trace is bounded above by $N$. Therefore, letting $\mathcal{D}_{(\infty)}$ be the resulting density operator, we have $\mathrm{Tr}\,(\mathcal{D}_{(\infty)}) = N$ and, by an argument as in the proof of Lemma 7.1, we deduce that $\mathcal{D}_{(\infty)}$ is a projection. □

We complete the proof of Theorem 1.3 by establishing **P3**:

**Lemma 7.3.** *Let Assumption 1.1 be satisfied. If the total nuclear charge* $Z_{\mathrm{tot}} = \sum_{k=1}^{K} Z_k$ *satisfies* $Z_{\mathrm{tot}} + 1 > N$*, then property* ***P3*** *holds.*

*Proof.* As above, let $\{\varphi_l\}$ be the eigenfunctions of $F^{\mathrm{p}}_{\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}}$ ordered according to the eigenvalues $\epsilon_1 \le \epsilon_2 \le \cdots$, where $\epsilon_1$ is the lowest eigenvalue of $F^{\mathrm{p}}_{\mathcal{D}_{(\infty)},\mathcal{A}_{(\infty)}}$. For some $l_1, \ldots, l_N$ we have

$$\mathcal{D}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') = \sum_{m=1}^{N} \overline{\varphi_{l_m}(\boldsymbol{r})}\varphi_{l_m}(\boldsymbol{r}')$$

We show by contradiction that $\{\epsilon_{l_1}, \ldots, \epsilon_{l_N}\} = \{\epsilon_1, \ldots, \epsilon_N\}$. If the latter is not true, then there exists $m \in \{1, \ldots, , N\}$ with $\epsilon_{l_m} > \epsilon_m$. Again imitating [24, page 309], we define, for $\delta \in (0, 1)$,

$$\widetilde{\mathcal{D}}(\boldsymbol{r},\boldsymbol{r}') = \mathcal{D}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') + \delta\overline{\varphi_m(\boldsymbol{r})}\varphi_m(\boldsymbol{r}') - \delta\overline{\varphi_{l_m}(\boldsymbol{r})}\varphi_{l_m}(\boldsymbol{r}')$$

An application of (7.3) gives us that

$$\begin{aligned} \mathcal{E}^{\mathrm{p}} &= \mathcal{E}^{\mathrm{p}}(\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}) + \delta(\epsilon_m - \epsilon_{l_m}) - \delta^2 R_{\varphi_m,\varphi_{l_m}} \\ &< \mathcal{E}^{\mathrm{p}}(\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)}), \end{aligned}$$

where the last inequality holds provided $\delta$ is chosen sufficiently small.
We finish the proof by showing that $\epsilon_n < 0$ for all $n$. If $N < Z_{\mathrm{tot}}$, then Lemma 6.1 gives us this immediately. If $Z_{\mathrm{tot}} \le N < Z_{\mathrm{tot}} + 1$, then we argue by contradiction. So suppose $\epsilon_N = 0$, say. Applying (7.3) to

$$\widetilde{\mathcal{D}}(\boldsymbol{r},\boldsymbol{r}') := \mathcal{D}_{(\infty)}(\boldsymbol{r},\boldsymbol{r}') - \overline{\varphi_N(\boldsymbol{r})}\varphi_N(\boldsymbol{r}')$$

yields $\mathcal{E}^{\mathrm{p}}(\widetilde{\mathcal{D}}, \mathcal{A}_{(\infty)}) = \mathcal{E}^{\mathrm{p}}(\mathcal{D}_{(\infty)}, \mathcal{A}_{(\infty)})$ and, moreover, $\mathrm{Tr}\,(\widetilde{\mathcal{D}}) = N - 1$. This contradicts $E^{\infty}_{\le} < E^{N-1}_{\le}$. □

## Appendix A. Pure states, mixed states and density matrices

Let $\mathfrak{H}_{\mathrm{p}} = L^2(\mathbb{R}^3; \mathbb{C}^2)$ be the usual one-electron state-space given by

$$\mathfrak{H}_{\mathrm{p}} = \Big\{\, \Phi = (\phi^{\uparrow}, \phi^{\downarrow})^T \,:\, \|\Phi\|_2^2 := \int_{\mathbb{R}^3} |\phi^{\uparrow}|^2 + |\phi^{\downarrow}|^2 < \infty \Big\}. \tag{A.1}$$

Then the set of admissible antisymmetric wave functions is

$$\mathcal{W}^{\mathrm{pure}}_N := \Big\{\, \Psi \in \bigwedge^N \mathfrak{H}_{\mathrm{p}} \,:\, \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1,\ \|\nabla\Psi\|_{L^2(\mathbb{R}^{3N})} < \infty \Big\}. \tag{A.2}$$

Henceforth we let $\boldsymbol{x}_j = (\boldsymbol{r}_j, s_j)$ denote the $j$-th spatial-spin component. If $\Phi_1, \Phi_2, \dots, \Phi_N$ is a set of orthonormal functions in $\mathfrak{H}_{\rm p}$, then the Slater determinant $\Psi_{\rm S}$ arising from $(\Phi_1, \Phi_2, \dots, \Phi_N)$ is defined by

$$\Psi_{\rm S}[\Phi_1, \Phi_2, \dots, \Phi_N](\boldsymbol{x}_1, \dots, \boldsymbol{x}_N) := \frac{1}{\sqrt{N!}} \det\left(\Phi_i(\boldsymbol{x}_j)\right)_{1\le i,j\le N}. \tag{A.3}$$

The subset of $\mathcal{W}_N^{\rm pure}$ consisting of all finite energy Slater determinants is denoted by $\mathcal{W}_N^{\rm Slater}$. One has $\mathcal{W}_1^{\rm Slater} = \mathcal{W}_1^{\rm pure}$ and $\mathcal{W}_N^{\rm Slater} \subsetneq \mathcal{W}_N^{\rm pure}$ for $N \ge 2$.
For a wave function $\Psi \in \mathcal{W}_N^{\rm pure}$, one defines the associated $N$-particle density matrix $\mathsf{D}_\Psi := |\Psi\rangle\langle\Psi|$, which corresponds to the projection $\{\mathbb{C}\Psi\}$ in $\bigwedge^N \mathfrak{H}_{\rm p}$. The set of pure-state and Slater-state $N$-particle density matrices are respectively

$$\mathcal{M}_N^{\rm pure} := \{\, \mathsf{D}_\Psi \,:\, \Psi \in \mathcal{W}_N^{\rm pure} \,\} \text{ and } \mathcal{M}_N^{\rm Slater} := \{\, \mathsf{D}_\Psi \,:\, \Psi \in \mathcal{W}_N^{\rm Slater} \,\} \tag{A.4}$$

One has $\mathcal{M}_1^{\rm Slater} = \mathcal{M}_1^{\rm pure}$ and $\mathcal{M}_N^{\rm Slater} \subsetneq \mathcal{M}_N^{\rm pure}$ for $N \ge 2$. Using the notation CH for the convex hull, the set of mixed-state $N$-particle density matrices is defined as $\mathcal{M}_N^{\rm mix} = \overline{{\rm CH}\,(\mathcal{M}_N^{\rm pure})}$, i.e.,

$$\mathcal{M}_N^{\rm mix} = \Big\{ \sum_{j=1}^{\infty} \nu_j \langle \cdot, \Psi_j\rangle \Psi_j \,:\, 0 \le \nu_j \le 1,\, \sum_{j=1}^{\infty} \nu_j = 1,\, \Psi_j \in \mathcal{W}_N^{\rm pure} \Big\}. \tag{A.5}$$

It also coincides with the convex hull of $\mathcal{M}_N^{\rm Slater}$. For a mixed state $\mathsf{D} \in \mathcal{M}_N^{\rm mix}$, the spin-polarized one-particle spin-density matrix is defined by

$$\mathcal{D}_{\mathsf{D}} = \begin{pmatrix} \mathcal{D}_{\mathsf{D}}^{\uparrow\uparrow} & \mathcal{D}_{\mathsf{D}}^{\uparrow\downarrow} \\ \mathcal{D}_{\mathsf{D}}^{\downarrow\uparrow} & \mathcal{D}_{\mathsf{D}}^{\downarrow\downarrow} \end{pmatrix} \in \mathcal{S}(\mathfrak{H}_{\rm p})$$

with

$$\mathcal{D}_{\mathsf{D}}^{\mu\nu}(\boldsymbol{r}, \boldsymbol{r}') = N \sum_{s_2,\dots,s_N \in \{\downarrow,\uparrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \mathsf{D}(\boldsymbol{r}, \mu, \boldsymbol{r}_2, s_2, \dots, \boldsymbol{r}_N, s_N; \boldsymbol{r}', \nu, \boldsymbol{r}_2, s_2 \dots, \boldsymbol{r}_N, s_N) {\rm d}\boldsymbol{r}_2 \dots {\rm d}\boldsymbol{r}_N. \tag{A.6}$$

Hence, the set of one-particle spin-density matrices, denoted by $\mathcal{M}$, is

$$\mathcal{M} = \{\, \mathcal{D}_{\mathsf{D}} \,:\, \mathsf{D} \in \mathcal{M}_N^{\rm mix} \,\}. \tag{A.7}$$

Coleman [5] proved, by associating the kernel $\mathcal{D}(\boldsymbol{r}, \boldsymbol{r}')$ with the corresponding operator in $\mathcal{S}(\mathfrak{H}_{\rm p})$, the space of self-adjoint, bounded operators on $\mathfrak{H}_{\rm p}$, that

$$\mathcal{M} = \{\, \mathcal{D} \in \mathcal{S}(\mathfrak{H}_{\rm p}) \,:\, 0 \le \mathcal{D} \le 1,\ {\rm Tr}\,(\mathcal{D}) = N,\ {\rm Tr}\,(-\Delta\mathcal{D}) < \infty \,\}. \tag{A.8}$$

We also define the density by

$$\rho_{\mathsf{D}}(\boldsymbol{r}) := {\rm Tr}_{\mathbb{C}^2}\left(\mathcal{D}_{\mathsf{D}}(\boldsymbol{r}, \boldsymbol{r})\right). \tag{A.9}$$

we will use the notation $\rho_{\mathcal{D}} := \rho_{\mathsf{D}}$.
The Banach space $\mathfrak{K}$ (with $\mathcal{H}$ chosen as $\mathfrak{H}_{\rm p}$ in its definition, see (2.3)), and its weak-$*$ topology plays a key role in the following result for $\rho_{\mathcal{D}}$ [10, Lemma 3]:

**Lemma A.1.** *Let $(\mathcal{D}_{(n)})$ be a bounded sequence of $\mathfrak{K}$. Then, extracting a subsequence if necessary, there exists $\mathcal{D}_{(\infty)}$ such that $\mathcal{D}_{(n)} \overset{*}{\rightharpoonup} \mathcal{D}_{(\infty)}$ in $\mathfrak{K}$ and $\rho_{\mathcal{D}_{(n)}}$ converges to $\rho_{\mathcal{D}_{(\infty)}}$ strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3;\mathbb{R})$ for $1 \le p < 3$, weakly in $L^p(\mathbb{R}^3)$ for $1 \le p \le 3$ and almost everywhere.*

## Appendix B. Auxiliary results for the Pauli case

We record the following results from [9, Theorem A.1 and Theorem A.2].

**Lemma B.1.** *Let $\mathcal{B} \in L^2(\mathbb{R}^3;\mathbb{R})^3$ be a given vector field and let $\operatorname{div}\mathcal{B} = 0$ in $\mathscr{D}'(\mathbb{R}^3)$. Let the vector potential $\mathcal{A}$ be given by*

$$\mathcal{A}(\boldsymbol{r}) = \int_{\mathbb{R}^3} |\boldsymbol{r} - \boldsymbol{r}'|^{-1}(\boldsymbol{r} - \boldsymbol{r}) \times \mathcal{B}(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'. \tag{B.1}$$

*Then:*
*(i) $\mathcal{A} \in L^6(\mathbb{R}^3;\mathbb{R})^3$, $\operatorname{curl}\mathcal{A} = \mathcal{B}$, and $\operatorname{div}\mathcal{A} = 0$ in $\mathscr{D}'(\mathbb{R}^3)$.*
*(ii) The distribution $\partial_i A_j$ is an $L^2$ function and*

$$\sum_i \int |\nabla A_i|^2\,dx = \int B^2\,dx.$$

*(iii) The vector potential $\mathcal{A}$ given by (B.1) is the only vector field which fulfill the three properties in (i).*

**Lemma B.2.** *For any $\mathcal{A} \in L^6(\mathbb{R}^3;\mathbb{R})^3$ and $\psi \in \mathfrak{H}_{\mathrm{p}}$, $\|\boldsymbol{\sigma}(-i\nabla - \mathcal{A})\psi\| < \infty$ implies $\psi \in \mathbf{H}^1(\mathbb{R}^3;\mathbb{C}^2)$.*

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