Technological University Dublin
ARROW@TU Dublin

Articles School of Mathematics and Statistics

2008-01-01

Non-existence of a minimizer to the Hartree-Fock functional

Michael Melgaard
Technological University Dublin, michael.melgaard@dit.ie

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

Follow this and additional works at: https://arrow.tudublin.ie/scschmatart

Part of the Mathematics Commons

Recommended Citation
Melgaard, M. & Enstedt, M. (2008). Non-existence of a minimizer to the Hartree-Fock functional. *Positivity*, vol. 12, pg. 653-666. doi:10.21427/pbpd-j102

This Article is brought to you for free and open access by the School of Mathematics and Statistics at ARROW@TU Dublin. It has been accepted for inclusion in Articles by an authorized administrator of ARROW@TU Dublin. For more information, please contact arrow.admin@tudublin.ie, aisling.coyne@tudublin.ie, vera.kilshaw@tudublin.ie.

Positivity *Online First*
© 2008 Birkhäuser Verlag Basel/Switzerland
DOI 10.1007/s11117-008-2127-9

Positivity

Non-existence of a Minimizer to the Magnetic Hartree-Fock Functional

M. Enstedt and M. Melgaard*

Abstract. In the presence of an external magnetic field, we prove absence of a ground state within the Hartree-Fock theory of atoms and molecules. The result is established for a wide class of magnetic fields when the number of electrons is greater than or equal to $2Z + K$, where Z is the total charge of K nuclei. Positivity properties are instrumental in the proof of this bound for the maximal ionization.

Mathematics Subject Classification (2000). Primary 81V45; Secondary 35Q40, 47G20, 47N50.

Keywords. Magnetic Hartree-Fock equations, Ionization, Positivity.

Contents

1. Introduction

In a recent paper [3] we proved existence of a solution in the form of a minimizer for the nonlinear coupled Hartree-Fock equations of Quantum Chemistry in the presence of an external magnetic field described by a vector potential which is supposed to be homogeneous of degree -1 at infinity, roughly speaking. In the opposite direction, we herein study absence of a minimizer. It turns out that much weaker conditions on the magnetic field are needed to establish nonexistence.

* Corresponding author.

A molecule consisting of N electrons and K static nuclei with charges $\boldsymbol{Z} = (Z_1, \dots, Z_K)$, $Z_k > 0$, placed in an external magnetic field $B = \nabla \times \mathcal{A}$, $\mathcal{A} = (A_1, A_2, A_3) : \mathbb{R}^3 \to \mathbb{R}^3$ being the vector potential, is in quantum theory described by the Hamiltonian[1]

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

acting on the space $\bigwedge^N L^2(\mathbb{R}^3; \mathbb{C}^2)$ of antisymmetric spinor-valued functions. Above $x = (x_1, \dots, x_N) \in \mathbb{R}^{3N}$, $x_n = (x_n^{(1)}, x_n^{(2)}, x_n^{(3)}) \in \mathbb{R}^3$ being the position of the n^{th} electron, the components of the magnetic gradient $\nabla_{\mathcal{A},x_n} = (P_{x_n}^{(1)}, P_{x_n}^{(2)}, P_{x_n}^{(3)})$ are $P_{x_n}^{(m)} = P_{\mathcal{A},x_n}^{(m)} = \partial_{x_n^{(m)}} + iA_m(x_n)$, V_{en} is the Coulomb potential

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

with $R_k \in \mathbb{R}^3$ being the position of the k^{th} nucleus, $V_{\mathrm{ee}}(x) = 1/|x|$, and $\Delta_{\mathcal{A},x_n} = \sum_{m=1}^{3} (P_{x_n}^{(m)})^2$ is the magnetic Laplacian. The interpretation of this Hamiltonian is as follows: the first term corresponds to the kinetic energy of the electrons, the second term is the one-particle attractive interaction between the electrons and the nuclei, and the third term is the standard two-particle repulsive interaction between the electrons.

Within the Born-Oppenheimer approximation the **quantum mechanical ground state energy** of the molecule is the minimum of the spectrum of $H_{N,\boldsymbol{Z},\mathcal{A}}$ or, equivalently,

$$E^{\mathrm{QM}}(N, \boldsymbol{Z}, \mathcal{A}) = \inf \Big\{ \mathcal{E}_N^{\mathrm{QM}}(\Psi_{\mathrm{e}}) \,:\, \Psi_{\mathrm{e}} \in \mathcal{H}_{\mathrm{e}},\ \|\Psi_{\mathrm{e}}\|_{L^2(\mathbb{R}^{3N})} = 1 \Big\}.$$

where $\mathcal{E}_N^{\mathrm{QM}}(\Psi_{\mathrm{e}}) = \langle \Psi_{\mathrm{e}}, H_{N,\boldsymbol{Z},\mathcal{A}} \Psi_{\mathrm{e}} \rangle_{L^2(\mathbb{R}^{3N})}$ and $\mathcal{H}_{\mathrm{e}} := \bigwedge^N \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3; \mathbb{C}^2)$, i.e., the N-particle Hilbert space consisting of antisymmetric functions (expressing the Pauli exclusion principle)

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

where S_N is the group of permutations of $\{1, \dots, N\}$, with the signature of a permutation σ being denoted by $\mathrm{sign}\,(\sigma)$. The space $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ is the"magnetic" analogue of the standard Sobolev space $\mathbf{H}^1(\mathbb{R}^3)$; see Section 2 for its definition.

For several reasons quantum theory is too complicated for both theoretical and numerical studies. Much of theoretical and computational chemistry has thus been based on the Hartree-Fock approximation [25,8,17] introduced by Hartree [7] and improved by Fock [4] and Slater [21] in the late 1920s.

[1]Expressed in Rydberg units.

The **Hartree-Fock approximation** consists in restricting attention to functions of the form

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

with

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

By taking the infimum over all functions belonging to $\mathcal{S}_N$ while keeping the expression $\langle \Psi_{\mathrm{e}}, H_{N,\boldsymbol{Z},\mathcal{A}}\Psi_{\mathrm{e}}\rangle$ for the energy, one arrives at the Hartree-Fock energy which is an approximation to the full quantum mechanical energy $E^{\mathrm{QM}}(N,\boldsymbol{Z},\mathcal{A})$. If $\Psi_{\mathrm{e}} \in \mathcal{S}_N$, then simple algebraic calculations yields that $\langle \Psi_{\mathrm{e}}, H_{N,\boldsymbol{Z},\mathcal{A}}\Psi_{\mathrm{e}}\rangle = \mathcal{E}^{\mathrm{MHF}}(\Psi_{\mathrm{e}})$, where the **magnetic Hartree-Fock functional** $\mathcal{E}_N^{\mathrm{MHF}}(\cdot)$ is given by

$$\begin{aligned} \mathcal{E}^{\mathrm{MHF}}(\phi_1, ..., \phi_N) &= \mathcal{E}_N^{\mathrm{MHF}}(\Psi_{\mathrm{e}}) = \langle \Psi_{\mathrm{e}}, H_{N,\boldsymbol{Z},\mathcal{A}}\Psi_{\mathrm{e}}\rangle \\ &= \sum_{n=1}^{N} \int_{\mathbb{R}^3} |\nabla_{\mathcal{A}}\phi_n(x)|^2 \,\mathrm{d}x + \int_{\mathbb{R}^3} V_{\mathrm{en}}(x)\rho(x)\,\mathrm{d}x \\ &\quad + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\,\rho(x') - |\tau(x,x')|^2}{|x-x'|}\,\mathrm{d}x\,\mathrm{d}x' \end{aligned}$$

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

Definition 1.1. (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

$$E^{\mathrm{MHF}} \equiv E^{\mathrm{MHF}}(N,\boldsymbol{Z},\mathcal{A}) := \inf\left\{ \mathcal{E}^{\mathrm{MHF}}(\Psi_{\mathrm{e}}) \,:\, \Psi_{\mathrm{e}} \in \mathcal{S}_N \right\}. \tag{1.1}$$

If a minimizer exists, i.e., there exists some Ψ_{e} such that

$$\mathcal{E}^{\mathrm{MHF}}(\Psi_{\mathrm{e}}) = E^{\mathrm{MHF}}, \tag{1.2}$$

then it is said that the molecule has a magnetic Hartree-Fock ground state described by Ψ_{e}.

When no magnetic field is present, the Hartree-Fock minimization problem was studied by Lieb and Simon in [15] (see also [14,10,16]). Under the condition that the **total charge** $Z = \sum_{k=1}^K Z_k$ of the molecular system fulfills $Z+1 > N$, they proved the existence of at least one minimizer, i.e., a Hartree-Fock ground state. The mathematical requirement $Z+1 > N$ expresses that the total charge of the nuclei should be sufficiently positive to ensure that the N electrons are localized in their vicinity. Prior to [15], the Hartree-Fock equations were studied by more direct approaches[19,6,5,24,26,20], yielding less general results.

In [3] we established existence of a magnetic Hartree-Fock ground state for a wide class of magnetic fields under the condition $Z > N-1$. The latter condition is only a sufficient condition. No necessary condition is known for the existence.

The only result that is known in this direction is a result by Lieb [12] which states that for $N \geq 2Z+K$ there never exists a magnetic Hartree-Fock ground state; the result holds provided $\mathcal{A} \in L^\infty_\epsilon$, i.e., if $\mathcal{A}$ is bounded and $|A_j(x)| \to 0$ as $|x| \to \infty$. In the absence of a magnetic field, Solovej has improved Lieb's result by proving that there exists a universal constant $Q > 0$ such that $N \geq Z + Q$ ensures that there are no minimizers [23] (first announced in [22]).

Throughout this paper we impose the following conditions.

Assumption 1.2. (i) $\operatorname{div} \mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)$ and $\mathcal{A} \in L^4_{\mathrm{loc}}(\mathbb{R}^3, \mathbb{R}^3)$.
(ii) There exists some $R > 0$ such that $\mathcal{A}$ is dominated by a positively homogeneous function of degree $d \in (-\infty, 0)$ for $|x| > R$.

Under Assumption 1.2 our main result, Theorem 4.1 asserts that there are no minimizers for the magnetic Hartree-Fock problem when $N \geq 2Z + K$, where N is a positive integer and Z is the total nuclear charge. This gives a bound for the maximal ionization. The proof of Theorem 4.1, given in Section 4, follows Lieb's approach in [12], written out for the full quantum mechanical problem. New auxiliary results, expressing positivity, are collected in Section 3. It is crucial for the proof that the energy is monotonically decreasing in the number of electrons. In particular, the proof does not apply to a constant magnetic field; indeed, placing a particle at spatial infinity costs at least an energy of size equal to the field strength. The required monotonicity is ensured by imposing that the magnetic field decays at infinity which is expressed by the "homogeneity at infinity" in Assumption 1.2(ii). The latter also suffices to carry over the main result in [3]; in other words, Assumption 1.1(iv) in [3] can be replaced by Assumption 1.2(ii) above.

2. Notation and preliminaries

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

Let $L^2(\mathbb{R}^3)$ be the space of (equivalence classes of) complex-valued functions ϕ which are measurable and satisfy $\int_{\mathbb{R}^3} |\phi(x)|^2 \, \mathrm{d}x < \infty$. The measure $\mathrm{d}x$ is the Lebesgue measure. The space $L^2(\mathbb{R}^3)$ is a complex and separable Hilbert space with scalar product $\langle \phi, \psi \rangle_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} \phi^* \psi \, \mathrm{d}x$ and corresponding norm $\|\phi\|_{L^2(\mathbb{R}^3)} = \langle \phi, \phi \rangle^{1/2}_{L^2(\mathbb{R}^3)}$. Let $L^2(\mathbb{R}^3)^N$, be the N-fold Cartesian product of $L^2(\mathbb{R}^3)$, 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 in $\mathbb{R}^3$ will be denoted $\mathscr{D}$ and the space of distributions by $\mathscr{D}'$. The Schwarz space of rapidly decreasing functions and its adjoint space if tempered distributions are denoted by $\mathscr{S}(\mathbb{R}^3)$ and $\mathscr{S}'(\mathbb{R}^3)$, respectively. Let p denote the momentum operator $-i\nabla$ and let $\langle p \rangle = (1 + p^2)^{1/2}$. For any $t \in \mathbb{R}$ the standard Sobolev space $\mathbf{H}^t(\mathbb{R}^3)$ is given by

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

Define the "magnetic" Sobolev space by

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

for $\nabla_{\mathcal{A}} := \nabla + i\mathcal{A}$, in which $\nabla\phi$ is taken in the distributional sense, endowed with 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 $L^2(\mathbb{R}^3)$. Thus there is usually no connection between the spaces $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ and $\mathbf{H}^1(\mathbb{R}^3)$ on the whole of $\mathbb{R}^3$, that is, in general $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) \not\subseteq \mathbf{H}^1(\mathbb{R}^3)$ or $\mathbf{H}^1(\mathbb{R}^3) \not\subseteq \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$.

3. Positivity properties

Positivity plays a key role at several places in our analysis. We begin with the following result:

Lemma 3.1. *Let Assumption 1.2 hold and suppose $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N) \in \mathcal{C}_N$ gives rise to a minimizer $\Psi_{\mathrm{e}} \in \mathcal{S}_N$ for the magnetic Hartree-Fock functional. Then the components of $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N)$ satisfy the magnetic Hartree-Fock equations for some nonnegative constants ϵ_n, i.e.,*

$$\begin{cases} H^F_{\mathcal{A}}\varphi_n + \epsilon_n\varphi_n = 0 \\ \langle \varphi_m, \varphi_n \rangle_{L^2} = \delta_{mn}, \end{cases}$$

where $H^F_{\mathcal{A}}$ is the magnetic Hartree-Fock operator, defined as the unique self-adjoint extension of

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

initially defined on $\mathscr{D}(\mathbb{R}^3)$, and with $K^{\mathrm{xc}}(x,y) := \tau(x,y)/|x-y|$ being the integral kernel of the exchange operator K^{xc}.

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

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

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

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

From the Lagrange multiplier rule [27, Section 4.14] we know that there exists ϵ_n such that, for all n, the components of $\boldsymbol{\varphi} = (\varphi_1, \ldots, \varphi_N)$ satisfy

$$\mathrm{Re}\,\mathfrak{h}^F_{\mathcal{A}}[\varphi_n, \psi_n] + \epsilon_n \mathrm{Re} \int_{\mathbb{R}^3} \varphi_n\psi^*_n \,\mathrm{d}x = 0 \quad \forall \psi_n \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3), \tag{3.1}$$

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

$$\begin{aligned}\mathfrak{h}_{\mathcal{A}}^F[\varphi_n, \psi_n] := &\int_{\mathbb{R}^3} \nabla_{\mathcal{A}}\varphi_n(x)\nabla_{\mathcal{A}}\psi_n^*(x) + V_{\mathrm{en}}(x)\varphi_n(x)\psi_n^*(x)\,\mathrm{d}x \\ &+ \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\varphi_n(y)\psi_n^*(y)}{|x-y|}\,\mathrm{d}x\mathrm{d}y - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \tau(x,y)\frac{\varphi_n(y)\psi_n^*(x)}{|x-y|}\,\mathrm{d}y\mathrm{d}x.\end{aligned}$$

Since both the terms in (3.1) are linear in their second argument we can extend the equations to

$$\mathfrak{h}_{\mathcal{A}}^F[\varphi_n, \psi_n] + \epsilon_n \int_{\mathbb{R}^3} \varphi_n\psi_n^*\,\mathrm{d}x = 0 \quad \forall \psi_n \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3). \tag{3.2}$$

In [3] it is verified that $\mathfrak{h}_{\mathcal{A}}^F$ is a closed semi-bounded sesquilinear form on $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$ and we infer from [2, Theorem IV.2.4] that $H_{\mathcal{A}}^F$ is the self-adjoint operator associated with this form and that $-\epsilon_n$ corresponds to eigenvalues of this operator.

Let us show that the multipliers ϵ_n are non-negative. To do this we shall verify that φ_n is a minimizer to

$$\inf\left\{ \mathfrak{h}_{\mathcal{A}}^F[\phi, \phi] \,:\, \phi \in \mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3) \wedge \|\phi\|_{L^2} = 1 \wedge \int_{\mathbb{R}^3} \phi\varphi_m^*\,\mathrm{d}x = 0,\ \forall m \neq n \right\} \tag{3.3}$$

and the minimum is equal to $-\epsilon_n$. Postponing this verification momentarily, we proceed to show that $\epsilon_n \geq 0$.

The "complementary" minimization problem (3.3) gives us a relation between the multipliers and the properties of the magnetic field. Let $\mathfrak{l}_\mu$ denote the quadratic form defined by

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

on $\mathbf{H}_{\mathcal{A}}^1(\mathbb{R}^3)$ where, initially, we let μ be any finite positive Borel measure. Let B_R denote the open ball in $\mathbb{R}^3$ with radius $R > 0$. Select any normalized function $\phi \in \mathscr{D}(\mathbb{R}^3)$, with support in B_1, and let

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

Observe that

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

By Assumption 1.2(ii) we know that $\mathcal{A}(\lambda x)$ is dominated by a positively homogeneous function of degree $d \in (-\infty, 0)$ when $|\lambda x| \geq R$ for some $R > 0$. We have that

$$\begin{aligned}\mathfrak{l}_\mu[\phi_\lambda, \phi_\lambda] = &\frac{1}{\lambda^2}\int_{B_1} |\nabla\phi(x)|^2\,\mathrm{d}x \\ &-\frac{1}{\lambda}\int_{B_1} 2\,\mathrm{Im}\,\mathcal{A}(\lambda x)\phi(x)\cdot\nabla\phi^*(x)\,\mathrm{d}x + \int_{B_1} |\mathcal{A}(\lambda x)\phi(x)|^2\,\mathrm{d}x \\ &+\frac{1}{\lambda}\int_{B_1} V_\lambda(x)|\phi(x)|^2\,\mathrm{d}x + \frac{1}{\lambda}\int_{B_1}\left(\mu_\lambda * \frac{1}{|x|}\right)|\phi(x)|^2\,\mathrm{d}x.\end{aligned}$$

where

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

When $\lambda > R_1$ we note that

$$\begin{aligned}
&-\frac{1}{\lambda}\int_{B_1} 2\mathrm{Im}\mathcal{A}(\lambda x)\phi(x)\cdot\nabla\phi^*(x)\mathrm{d}x \\
&\quad\le \frac{\text{const}}{\lambda}\int_{B_{\frac{R}{\lambda}}} |\mathcal{A}(\lambda x)|\mathrm{d}x + \frac{\text{const}}{\lambda}\int_{B^C_{\frac{R}{\lambda}}\bigcap B_1} |\mathcal{A}(\lambda x)|\mathrm{d}x \le \frac{\text{const}}{\lambda^4} + \frac{\text{const}}{\lambda^{1-d}}
\end{aligned}$$

and mutatis mutandis we get that

$$\int_{B_1} |\mathcal{A}(\lambda x)\phi(x)|^2 \mathrm{d}x \le \frac{\text{const}}{\lambda^3}\int_{B_R} |\mathcal{A}(x)|^2\,\mathrm{d}x + \frac{\text{const}}{\lambda^{-2d}}\int_{B_1} |\mathcal{A}(x)|^2\,\mathrm{d}x.$$

By choosing ϕ as radially symmetric on $\mathbb{R}^3$, Newton's theorem for measures [13, Theorem 9.7] implies that

$$\begin{aligned}
\int_{\mathbb{R}^3}\left(\mu_\lambda * \frac{1}{|x|}\right)|\phi(x)|^2\,\mathrm{d}x &= \int_{\mathbb{R}^3}\left(|\phi(x)|^2 * \frac{1}{|x|}\right)\mathrm{d}\mu_\lambda \\
&= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{\max(|x|,|y|)}\,\mathrm{d}x\mathrm{d}\mu_\lambda \le \mu_\lambda(\mathbb{R}^3)\int_{\mathbb{R}^3}\frac{|\phi(x)|^2}{|x|}\,\mathrm{d}x,
\end{aligned}$$

where, evidently, $\mu_\lambda(\mathbb{R}^3) = \mu(\mathbb{R}^3)$. Now let

$$\mu = \rho\,\mathrm{d}x$$

that is, a weighted Lebesgue measure. It is clearly finite and positive. We note that

$$\mathfrak{h}^F_{\mathcal{A}} \le \mathfrak{l}_{\rho\,\mathrm{d}x}$$

on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. Therefore by choosing λ large enough we can conclude that $\epsilon_n \ge 0$.

Now we return to the minimization problem in (3.3). First note that

$$\begin{aligned}
&\mathcal{E}^{\mathrm{MHF}}(\varphi_1,\ldots,\varphi_{n-1},\phi,\varphi_{n+1},\ldots,\varphi_N) \\
&\quad= \mathcal{E}^{\mathrm{MHF}}(\varphi_1,\ldots,\varphi_{n-1},0,\varphi_{n+1},\ldots,\varphi_N) + \mathfrak{h}^F_{\mathcal{A}}[\phi,\phi] + \mathfrak{r}[\phi,\varphi_n],
\end{aligned} \tag{3.4}$$

where

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

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

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

and we conclude that

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

We also note that according to (3.2) the minimum equals $-\epsilon_n$. □

Next we establish an inequality for the magnetic Laplacian.

Lemma 3.2. (Benguria-Lieb-Baumgartner type inequality). *Let Assumption 1.2(i) hold. Suppose that $-\Delta_{\mathcal{A}}\phi, \phi\eta_\delta^{-1} \in L^2(\mathbb{R}^3)$ for all $\delta > 0$, where η_δ is defined by*

$$\eta_\delta := \int_{\mathbb{R}^3} |x-y|^{-1} \,\mathrm{d}\mu(y) + \delta$$

for some positive finite Borel measure μ. Then

$$\operatorname{Re} \int_{\mathbb{R}^3} -\eta_\delta^{-1}\phi^* \Delta_{\mathcal{A}}\phi \,\mathrm{d}x \geq 0. \tag{3.5}$$

Proof. We claim that, without loss of generality, we may prove the statement for $\mu \in C^\infty(\mathbb{R}^3)$ and $\phi \in \mathscr{D}$. Take $\mathscr{D} \ni \phi_n \to \phi$ in $L^2(\mathbb{R}^3)$, then since, $-\Delta_{\mathcal{A}}$ is self-adjoint (see [9]) and hence closed we know that $-\Delta_{\mathcal{A}}\phi_n \to -\Delta_{\mathcal{A}}\phi$. Let k_l be an approximate identity in $\mathscr{D}$. Put $\mu_l := k_l * \mu$, then $\mu_l \in C^\infty(\mathbb{R}^3)$ because a finite measure is a distribution of order zero. We note that $\eta_{\delta,l} = \mu_l * \eta_\delta$ and hence that $\eta_{\delta,l} \in C^\infty(\mathbb{R}^3)$. Since $L^2(\mathbb{R}^3)$ is a homogeneous Banach space we know that $\eta_{\delta,l} \to \eta_\delta$ in L^2_{loc}. Then, if nesessary going to subsequence, we can assume that $\eta_{\delta,l} \to \eta_\delta$ a.e. and since $\eta_{\delta,l} \leq \text{const}$, we get, by dominated convergence, that

$$\lim_{l\to\infty} \int_{\mathbb{R}^3} -\phi_n^* \eta_{\delta,l}^{-1} \Delta_{\mathcal{A}}\phi_n(x) \,\mathrm{d}x = \int_{\mathbb{R}^3} -\phi_n^* \eta_\delta^{-1} \Delta_{\mathcal{A}}\phi_n(x) \,\mathrm{d}x.$$

This prove our claim.

Next let $\gamma > 0$ and introduce

$$u_\gamma := (|u|^2 + \gamma^2)^{1/2}.$$

Then the Kato type inequality

$$\operatorname{Re} u(-\Delta_{\mathcal{A}}u)^* \geq u_\gamma(-\Delta u_\gamma) \tag{3.6}$$

holds pointwise a.e. on $\mathscr{D}$; its proof is a variant of the one in [18, Theorem X.33]. Thus, if we let $u\eta_\delta := \phi$ we get from (3.6) that

$$\operatorname{Re}\langle -\Delta_{\mathcal{A}}u\eta_\delta, u\rangle = \operatorname{Re}\langle u\eta_\delta, -\Delta_{\mathcal{A}}u\rangle \geq \langle -\Delta u_\gamma, u_\gamma\eta_\delta\rangle = \langle -\Delta v, \eta_\delta v\rangle + \gamma\langle -\Delta v, \eta_\delta\rangle$$

where $v := u_\gamma - \gamma \geq 0$. With repeated use of the Fourier transform we can prove that

$$\langle -\Delta v, \eta_\delta v\rangle = \int_{\mathbb{R}^3} \eta_\delta |\nabla v|^2 \,\mathrm{d}x + 2\pi \int_{\mathbb{R}^3} |v|^2 \,\mathrm{d}\mu$$

and

$$\langle -\Delta v, \eta_\delta\rangle = 4\pi \int_{\mathbb{R}^3} v \,\mathrm{d}\mu.$$

This completes the proof. □

For the usual (negative) Laplacian, Benguria proved the strict version of (3.5) provided ϕ is real-valued and spherically symmetric, and Lieb managed to prove it for any real-valued ϕ; see [11, Lemma 7.21]. A more direct approach enabled Baumgartner [1] to prove it for complex-valued ϕ. In [12] Lieb carried it over to the magnetic Laplacian provided $\mathcal{A} \in L^\infty_\epsilon$. For our purpose the strict inequality is not necessary although it *is* valid under our hypotheses.

Finally, we note:

Lemma 3.3. *Assume that $u \in L^1(\mathbb{R}^{2d})$ is positive on a set of positive measure. Then*

$$\int_{\mathbb{R}^{2d}} u(x,y)((|x|+|y|)|x-y|^{-1}-1)\mathrm{d}x\mathrm{d}y > 0.$$

Proof. We note that $(|x|+|y|)|x-y|^{-1}-1$ is non-negative by the triangle inequality. The latter function equals zero if and only if $y=-ax$ for a non-positive a and since $\{x,-ax\}$ has zero $2d$-dimensional Lebesgue measure we are done. □

4. Absence of minimizer

In this section we prove the main theorem of this paper, a non-existence theorem on a minimizer to the magnetic Hartree-Fock functional along with a nondecreasing property (in the number of particles) of the functional.

Theorem 4.1. (Bound on maximal ionization)*. Let Assumption 1.2 hold. If N is a positive integer such that $N \geq 2Z+K$ (Z being the total nuclear charge), there are no minimizers for the magnetic Hartree-Fock problem.*

Proof. We argue by contradiction, whence we assume that $\boldsymbol{\varphi} = (\varphi_1,\ldots,\varphi_N) \in \mathcal{C}_N$ gives rise to a minimizer $\Psi_\mathrm{e} \in \mathcal{S}_N$ for the magnetic Hartree-Fock problem (1.1).

In view of Lemma 3.1, the components of $\boldsymbol{\varphi}$ satisfy the magnetic Hartree-Fock equations

$$\begin{cases} H^F_{\mathcal{A}}\varphi_n + \epsilon_n\varphi_n = 0 \\ \langle \varphi_m, \varphi_n\rangle_{L^2} = \delta_{mn}, \end{cases}$$

Introduce the function

$$\eta_\delta(x) = \sum_{k=1}^K \frac{\alpha_k}{|x-R_k|} + \delta, \tag{4.1}$$

where $\alpha_k > 0$ and $\delta \geq 0$. Note that $\inf_\delta \eta_\delta = \eta_0 =: \eta$ and that, for any fixed $\delta > 0$, the function $\varphi_n\eta_\delta^{-1}$ belongs to $L^2(\mathbb{R}^3)$. Take the scalar product of $H^F_{\mathcal{A}}\varphi_n + \epsilon_n\varphi_n$ and $\varphi_n\eta_\delta^{-1}$ and sum over all n. This yields

$$\sum_{n=1}^N \langle \varphi_n\eta_\delta^{-1}, H^F_{\mathcal{A}}\varphi_n\rangle = \sum_{n=1}^N -\epsilon_n\langle\varphi_n\eta_\delta^{-1},\varphi_n\rangle. \tag{4.2}$$

Now, the right-hand side is clearly well-defined and it will have a well-defined non-positive limit (possibly equal to $-\infty$). Invoking Lemma 3.1 we infer that $\epsilon_n \geq 0$.

Therefore, if we show that the left-hand side is positive and well-defined (for $\delta = 0$) we arrive at a contradiction.

By straightforward algebraic calculations we can write the left-hand side of (4.2) as

$$\sum_{n=1}^{N} \int_{\mathbb{R}^3} -\varphi_n^* \eta_\delta^{-1} \Delta_{\mathcal{A}} \varphi_n(x)\, \mathrm{d}x + \sum_{n=1}^{N} \int_{\mathbb{R}^3} V_{\mathrm{en}}(x) |\varphi_n|^2 \eta_\delta^{-1}\, \mathrm{d}x$$
$$+ \frac{1}{2} \sum_{n=1}^{N} \int_{\mathbb{R}^6} \left(\rho(x)\rho(x') - |\tau(x,x')|^2\right) |x - x'|^{-1} \left(\eta_\delta(x)^{-1} + \eta_\delta(x')^{-1}\right) \mathrm{d}x\mathrm{d}x',$$

where we used symmetry to obtain the last sum. Now, if we assume that the limit of the last two sums are finite we have that the first sum has a well-defined limit. Lemma 3.2 informs us that the first sum is non-negative (possibly equal to $+\infty$), therefore we can conclude that we have a contradiction if we can prove that the last two sums are positive. To do this recall that $\langle \varphi_m, \varphi_n \rangle_{L^2} = \delta_{mn}$, therefore we may repeat the idea we used to arrive at the magnetic Hartree-Fock functional, to re-write these sums as

$$\sum_{n=1}^{N} \int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2 \eta_\delta^{-1}(x_n) V_{\mathrm{en}}(x_n)\, \mathrm{d}x$$
$$+ \sum_{1 \le m < n \le N} \int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2 |x_m - x_n|^{-1} (\eta_\delta^{-1}(x_m) + \eta_\delta^{-1}(x_n))\, \mathrm{d}x.$$

By a straightforward estimate we can easily prove that both of these terms are finite for $\delta = 0$ and by monotone convergence, the limit and integral operations commute. Let us now derive a condition for

$$\sum_{n=1}^{N} \int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2 \eta^{-1}(x_n) V_{\mathrm{en}}(x_n)\, \mathrm{d}x_n$$
$$+ \sum_{1 \le m < n \le N} \int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2 |x_m - x_n|^{-1} (\eta^{-1}(x_m) + \eta^{-1}(x_n))\, \mathrm{d}x$$

to be positive. For this purpose we introduce

$$\psi_n(y) := \int_{\mathbb{R}^{3(N-1)}} |\Psi_{\mathrm{e}}(x_1, \ldots, x_{n-1}, y, x_{n+1}, \ldots, x_n)|^2\, \mathrm{d}x_1 \cdots \mathrm{d}x_{n-1} \mathrm{d}x_{n+1} \cdots \mathrm{d}x_n$$

along with

$$\beta_k := \int_{\mathbb{R}^3} \psi'(y) \eta(y)^{-1} |y - R_k|^{-1}\, \mathrm{d}y,$$

where

$$\psi'(y) := \sum_{n=1}^{N} \psi_n(y).$$

Then we can write

$$
\begin{aligned}
&-\sum_{n=1}^{N}\int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2\eta^{-1}(x_n)V_{\mathrm{en}}(x_n)\,\mathrm{d}x_n\\
&\qquad\qquad= \sum_{k=1}^{K} Z_k \sum_{n=1}^{N}\int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2\eta^{-1}(x_n)|x_n-R_k|^{-1}\,\mathrm{d}x\\
&\qquad\qquad= \sum_{k=1}^{K} Z_k \sum_{n=1}^{N}\int_{\mathbb{R}^{3}} \psi_n(y)\eta^{-1}(y)|y-R_k|^{-1}\,\mathrm{d}y = \sum_{k=1}^{K}\beta_k Z_k.
\end{aligned}
$$

Making the same rewriting as in [1], in conjunction with an application of Lemma 3.3 yields

$$
\begin{aligned}
R :=& \sum_{1\le m<n\le N}\int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2|x_m-x_n|^{-1}(\eta^{-1}(x_m)+\eta^{-1}(x_n))\,\mathrm{d}x\\
=& \sum_{1\le m<n\le N}\int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2|x_m-x_n|^{-1}(\eta(x_m)+\eta(x_n))(\eta^{-1}(x_n)\eta^{-1}(x_m))\,\mathrm{d}x\\
=& \sum_{1\le m<n\le N}\sum_{k=1}^{K}\int_{\mathbb{R}^{3N}} \alpha_k|\Psi_{\mathrm{e}}(x)|^2|x_m-x_n|^{-1}\\
&\times(|x_n-R_k|^{-1}+|x_m-R_k|^{-1})(\eta^{-1}(x_n)\eta^{-1}(x_m))\,\mathrm{d}x\\
=& \sum_{1\le m<n\le N}\sum_{k=1}^{K}\int_{\mathbb{R}^{3N}} \alpha_k|\Psi_{\mathrm{e}}(x)|^2|x_m-x_n|^{-1}\\
&\times(|x_n-R_k|+|x_m-R_k|)(\eta(x_n)|x_n-R_k|)^{-1}(\eta(x_m)|x_m-R_k|)^{-1}\,\mathrm{d}x\\
>& \sum_{k=1}^{K}\int_{\mathbb{R}^{3N}} \alpha_k|\Psi_{\mathrm{e}}(x)|^2\\
&\times\sum_{1\le m<n\le N}(\eta(x_n)|x_n-R_k|)^{-1}(\eta(x_m)|x_m-R_k|)^{-1}\,\mathrm{d}x.
\end{aligned}
$$

Since

$$
\begin{aligned}
&2\sum_{1\le m<n\le N}(\eta(x_n)|x_n-R_k|)^{-1}(\eta(x_m)|x_m-R_k|)^{-1}\\
&\quad= \left|\sum_{n=1}^{N}(\eta(x_n)|x_n-R_k|)^{-1}\right|^2-\sum_{n=1}^{N}|(\eta(x_n)|x_n-R_k|)^{-1}|^2,
\end{aligned}
$$

we have from Hölder's inequality and the property $\|\Psi_{\mathrm{e}}\|_{L^2} = 1$ that

$$2R > \sum_{k=1}^{K} \left(\alpha_k \left(\int_{\mathbb{R}^3} \psi'(y)(\eta(y)|y - R_k|)^{-1}\,\mathrm{d}y \right)^2 - \int_{\mathbb{R}^3} \alpha_k \psi'(y)(\eta(y)|y - R_k|)^{-2}\,\mathrm{d}y \right).$$

We note that $\eta(y)|y - R_k| \geq \alpha_k$, hence $\alpha_k(\eta(y)|y - R_k|)^{-1} \leq 1$ and we conclude that

$$2R > \sum_{k=1}^{K} \left(\alpha_k \left(\sum_{n=1}^{N} \int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2 \eta(x_n)|x_n - R_k|)^{-1}\,\mathrm{d}x \right)^2 - \sum_{n=1}^{N} \int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2 (\eta(x_n)|x_n - R_k|)^{-1} \right) = \sum_{k=1}^{K} \alpha_k \beta_k^2 - \beta_k.$$

Hence we have a contradiction if

$$\sum_{k=1}^{K} \beta_k(\alpha_k \beta_k - 1 - 2Z_k) \geq 0. \tag{4.3}$$

Let $N\gamma_k := \alpha_k \beta_k$ along with $(2Z + K)\lambda_k := 2Z_k + 1$ and note that

$$\sum_{k=1}^{K} \gamma_k = \sum_{k=1}^{K} \lambda_k = 1,$$

the first equality is true since

$$\sum_{k=1}^{K} \alpha_k \beta_k = \int_{\mathbb{R}^3} \psi'(y)\,\mathrm{d}y = \sum_{n=1}^{N} \int_{\mathbb{R}^{3N}} |\Psi_{\mathrm{e}}(x)|^2\,\mathrm{d}x = N.$$

and the second one is obvious. Thus we can write (4.3) as

$$\sum_{k=1}^{K} \beta_k(N\gamma_k - (K + 2Z)\lambda_k) \geq 0.$$

An application of the Perron-Frobenius theorem (see [12, Appendix B] for details) implies that we can choose α_k such that $\gamma_k = \lambda_k$ and, therefore, we arrive at

$$\sum_{k=1}^{K} \beta_k \lambda_k (N - K - 2Z) \geq 0$$

and thus since $\beta_k \lambda_k \geq 0$ a condition is

$$N - K - 2Z \geq 0$$

so we are done. $\square$

As a spin-off, the analysis above gives us the following monotonity property:

Theorem 4.2. *Under Assumption 1.2, the function*

$$N \mapsto \mathcal{E}^{\mathrm{MHF}} = \mathcal{E}^{\mathrm{MHF}}(N, \boldsymbol{Z}, \mathcal{A})$$

is non-increasing.

In particular, the latter result holds for $\mathcal{A} = 0$. This property is well-known but the derivation herein is, to the best of the authors' knowledge, new.

References

[1] B. Baumgartner, *On the degree of ionization in the TFW theory,* Lett. Math. Phys., **7**(5) (1983), 439–441.

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

[3] M. Enstedt, M. Melgaard, *Existence of solution to Hartree–Fock equations with decreasing magnetic fields* (27 pages, 2007), Nonlinear Anal Theory Methods Appl., (2008 in press).

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

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

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

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

[8] W. J. Hehre, L. Radom, L., P.v.R. Schleyer, J. A. Pople, *Ab initio molecular orbital theory*, Wiley, Chichester (1986).

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

[10] E.H. Lieb, Thomas–Fermi and Hartree-Fock theory, In: Proceedings of the International Congress of Mathematicians (Vancouver, 1974), Vol. 2, pp. 383–386. Canad. Math. Congress, Montreal (1975).

[11] E. H. Lieb, Thomas–Fermi and related theories of atoms and molecules, Rev. Mod. Phys., **53** (1981), 603-641 (Errata **54** (1982), 311).

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

[13] E. H. Lieb, E. H., M. Loss, *Analysis.* American Mathematical Society, Providence (1997)

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

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

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

[17] R. McWeeny, *Methods of Molecular Quantum Mechanics,* 2nd edn. Academic Press (1992).

[18] M. Reed, B Simon, *Methods of Modern Mathematical Physics. II. Fourier Analysis, Self-adjointness*, Academic Press, New York (1975).

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

[20] M. Reeken, Existence of solutions to the Hartree-Fock equations. In: *Eigenvalues of non-linear problems* (*Centro Internaz. Mat. Estivo C.I. M. E.*)*, III Ciclo, Varenna, 1974*, pp. 197–209. Edizioni Cremonese, Rome (1974).

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

[22] J. P. Solovej, The size of atoms in Hartree–Fock theory.In: L. Hörmander et al (eds), *Partial differential equations and mathematical physics,*Prog. Nonlinear Differ. Equ. Appl. The Danish-Swedish analysis seminar,Proceedings, Birkhäuser, Vol. 21, pp. 321–332 (1995).

[23] J. P. Solovej, *The ionization conjecture in Hartree–Fock theory.* Ann. of Math. **158**(2) (2003), 509–576.

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

[25] A. Szabo, N. S. Ostlund, *Modern quantum chemistry: an introduction to advanced electronic structure theory*, MacMillan,Basingstoke (1982).

[26] J. H. Wolkowisky, *Existence of solutions of the Hartree equations for N electrons. An application of the Schauder–Tychonoff theorem.* Indiana Univ. Math. J. **22** (1972/73), 551–568.

[27] E. Zeidler, *Applied functional analysis. Main principles and their applications.* Applied Mathematical Sciences, Vol. 109. Springer-Verlag, New York (1995).

M. Enstedt and M. Melgaard
Department of Mathematics
Uppsala University
Box 480, SE-751 06 Uppsala
Sweden
e-mail: `mattias.enstedt@math.uu.se`
`melgaard@math.uu.se`

Received 20 May 2007; accepted 27 December 2007

To access this journal online:
www.birkhauser.ch/pos