J. Differential Equations 253 (2012) 1729–1743

Contents lists available at SciVerse ScienceDirect

Journal of Differential Equations

www.elsevier.com/locate/jde

Abstract criteria for multiple solutions to nonlinear coupled equations involving magnetic Schrödinger operators

M. Enstedt [a,1], M. Melgaard [b,*,2]

[a] Department of Mathematics, Uppsala University, SE-751 06 Uppsala, Sweden
[b] School of Mathematical Sciences, Dublin Institute of Technology, Dublin 8, Ireland

ARTICLE INFO

Article history:
Received 2 February 2011
Available online 15 June 2012

MSC:
primary 35J60
secondary 47J10, 58E05, 81Q10, 81V55

Keywords:
Nonlinear equations
Hartree–Fock model
Magnetic fields
Excited states
Ground state
Critical point theory

ABSTRACT

We consider a system of nonlinear coupled equations involving magnetic Schrödinger operators and general potentials. We provide the criteria for the existence of multiple solutions to these equations. As special cases we get the classical results on existence of infinitely many distinct solutions within Hartree and Hartree–Fock theory of atoms and molecules subject to an external magnetic fields. We also extend recent results within this theory, including Coulomb system with a constant magnetic field, a decreasing magnetic field and a "physically measurable" magnetic field.

Contents

* Corresponding author.
E-mail address: mmelgaard@dit.ie (M. Melgaard).

1 The first author acknowledges support of a Liljewalchs Travel Grant.
2 The research of the second author is supported by a Stokes Award (SFI), grant 07/SK/M1208.

0022-0396/$ – see front matter
http://dx.doi.org/10.1016/j.jde.2012.05.025

1. Introduction

Quantum mechanics has its origin in an effort to understand the properties of atoms and molecules. Its first achievement was to establish the Schrödinger equation by explaining the stability of the hydrogen atom. When we proceed to a molecule, the full quantum mechanical problem cannot be solved. Within the Born–Oppenheimer approximation, a molecule consisting of N electrons interacting with K static nuclei in an external magnetic field B, defined via a vector potential $\mathcal{A} = (A_1, A_2, A_3)$, is in quantum theory described by the following Hamiltonian, acting on the space $\bigwedge^N L^2(\mathbb{R}^3)$ of antisymmetric functions, $H_{N,\boldsymbol{Z},\mathcal{A}} = \sum_{n=1}^N -\Delta_{\mathcal{A},x_n} + V_C$, where $\Delta_{\mathcal{A},x_n}$ is the square of $\nabla_{\mathcal{A},x_n} = (P_{x_n}^{(1)}, P_{x_n}^{(2)}, P_{x_n}^{(3)})$, $P_{x_n}^{(m)} = \partial_{x_n^{(m)}} + iA_m(x_n)$, and the Coulomb potential V_C is given by

$$V_C = -\sum_{k=1}^{K}\sum_{n=1}^{N} Z_k|x_n - R_k|^{-1} + \sum_{m<n}|x_m - x_n|^{-1}$$

with x_n, R_k denoting the coordinates of the nth electron and kth nucleus respectively, and $Z_k > 0$ the charge of the kth nucleus.

The "must" of 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 $H_{N,\boldsymbol{Z},\mathcal{A}}$ or, equivalently,

$$E^{\mathrm{QM}} = \inf\bigl\{\mathcal{E}^{\mathrm{QM}}(\Psi_e)\colon \Psi_e \in \mathcal{H}_e,\ \|\Psi_e\|_{L^2(\mathbb{R}^{3N})} = 1\bigr\},$$

where

$$\mathcal{E}^{\mathrm{QM}}(\Psi_e) := \langle \Psi_e, H_{N,\boldsymbol{Z},\mathcal{A}}\Psi_e\rangle_{L^2(\mathbb{R}^{3N})}, \quad \Psi_e \in \mathcal{H}_e := \bigwedge^N \mathbf{H}^1_{\mathcal{A}}\bigl(\mathbb{R}^3\bigr);$$

$\mathbf{H}^1_{\mathcal{A}}$ being the "magnetic" analogue of the standard Sobolev space $\mathbf{H}^1$; see Section 2. If the minimum is attained, then the minimizer Ψ_e is called a *ground state*.

Quantum theory, in particular determining E^{QM}, is however too complicated for both theoretical and numerical studies. One of the classical approximation methods for determining E^{QM} is the *Hartree–Fock* (*HF*) *theory*, introduced by Hartree [16] and improved by Fock [13] and Slater [27] in the late 1920s, which consists of restricting attention to simple wedge products $\Psi_e \in \mathcal{S}$, where

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

with

$$\mathcal{C} := \bigl\{\phi \in \mathbf{H}^1_{\mathcal{A}}\bigl(\mathbb{R}^3\bigr)^N\colon \langle\phi_n, \phi_m\rangle_{L^2(\mathbb{R}^3)} = \delta_{nm}\bigr\}. \tag{1.1}$$

If $\Psi_e \in \mathcal{S}$ then the *magnetic Hartree–Fock* (*MHF*) *functional* $\mathcal{E}^{\mathrm{MHF}}(\cdot)$ is defined by

$$\mathcal{E}^{\mathrm{MHF}}(\phi_1, \dots, \phi_N) := \mathcal{E}^{\mathrm{QM}}(\Psi_e) = \sum_{n=1}^{N}\int_{\mathbb{R}^3}\bigl|\nabla_{\mathcal{A}}\phi_n(x)\bigr|^2\,\mathrm{d}x + \int_{\mathbb{R}^3} V_{\mathrm{en}}(x)\rho(x)\,\mathrm{d}x + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho(x)\rho(x') - |\tau(x,x')|^2}{|x-x'|}\,\mathrm{d}x\,\mathrm{d}x', \tag{1.2}$$

where $V_{\text{en}}(y) = -\sum_{k=1}^{K} Z_k/|y - R_k|$, $\rho(x) = \sum_{n=1}^{N} |\phi_n(x)|^2$, and $\tau(x, x') = \sum_{n=1}^{N} \phi_n(x)\phi_n(x')$. In contrast to the *linear* Schrödinger theory finding the *Hartree–Fock energy*, defined as

$$E^{\text{MHF}} := \inf\{\mathcal{E}^{\text{MHF}}(\Psi_{\text{e}}):\ \Psi_{\text{e}} \in \mathcal{S}\}, \tag{1.3}$$

is a nonlinear variational problem; a possible minimizer is called a *magnetic Hartree–Fock ground state*.

When no magnetic field is present, the Hartree–Fock minimization problem was studied by Lieb and Simon in [22]. 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 a 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 [22], the Hartree–Fock equations were studied by more direct approaches yielding less general results; see, e.g., the references in [5]. Later, Lions [23] studied both minimal and nonminimal "excited states" solutions to the nonrelativistic Hartree–Fock equations by using critical point theory in conjunction with Morse data. For the standard Hartree–Fock model, Lions verifies a Palais–Smale type (compactness) condition which, roughly speaking, amounts to "being away from the continuous spectrum" or, equivalently, when the Morse information is taken into account, showing that certain Schrödinger operators with Coulomb type potentials have enough negative eigenvalues. Below we elaborate on Lions's method.

For the molecular system above, an initial investigation of MHF theory based upon the Hamiltonian $H_{N,\boldsymbol{Z},\mathcal{A}}$ is found in [5,6], wherein the objective is to establish existence, respectively non-existence, of an MHF ground state.

In the present paper we improve, complement and go beyond the results found in [5]. We consider general classes of vector potentials and scalar potentials and not just classical potentials such as the Coulomb potential. In addition to proving existence of a ground state, we establish existence of infinitely many distinct solutions of the magnetic Hartree–Fock type equations for the following three kinds of external magnetic fields:

- A constant magnetic field;
- Decreasing magnetic fields;
- "Physically measurable" magnetic fields.

Except for some spectral properties, which have to be established separately for each of these three applications, it turns out that it is possible to prove the existence results in a unified framework, wherein appropriate parameters and potentials are introduced in the Hartree–Fock functional. The main result, Theorem 3.2, is valid under fairly general conditions formulated in Assumption 3.1. The conditions correspond roughly speaking to a natural assumption on the structure of the spectrum of the Schrödinger operator involved in the equations. The results are analogues to the results obtained by Lions [23]; wherein no magnetic fields are present. Few results exist on the magnetic Hartree–Fock model. In the case of a constant magnetic field, Esteban and Lions [8] proved existence of a ground state by applying Lions's "second minimality condition" strategy. To be able to conclude existence of infinitely many solutions in this case there are several obstacles to overcome.

We proceed to sketch the proof of Theorem 3.2, starting with the existence of a ground state. We consider the C^2-functional $\mathcal{E}$ on a complete analytic Riemannian manifold $\mathcal{C}$ (see Chiumiento and Melgaard [2]) defined in (1.1). Since $\mathcal{E}$ is bounded from below, we may try to find a critical point at the level $l = \inf_{\mathcal{C}} \mathcal{E}$ by determining whether the infimum is achieved. As we shall see, it is easy to find an *almost critical sequence* at the level l, that is, a sequence $\{\boldsymbol{h}^{(j)}\}$ in $\mathcal{C}$ satisfying

$$\lim_{j\to\infty} \mathcal{E}(\boldsymbol{h}^{(j)}) = l, \quad \text{and} \quad \lim_{j\to\infty} \mathcal{E}|'_{\mathcal{C}}(\boldsymbol{h}^{(j)}) = 0. \tag{1.4}$$

The hard part is to prove existence of a converging subsequence of $\{\boldsymbol{h}^{(j)}\}$. To make sure that we can extract a convergent subsequence, we use second order information of $\mathcal{E}$.

We invoke a direct method developed by Fang and Ghoussoub [9,10] to address the existence of infinitely many *nonminimal solutions*. Since we are looking for nonminimal (or *unstable*) critical points, we consider a collection H of compact subsets of $\mathcal{C}$ which is stable under a specific class of homotopies and then we show that $\mathcal{E}$ has a critical point at the level

$$l = l_{\mathcal{E},\mathsf{H}} = \inf_{\mathsf{M}\in\mathsf{H}} \max_{\boldsymbol{h}\in\mathsf{M}} \mathcal{E}(\boldsymbol{h}).$$

As we shall see, the method by Fang and Ghoussoub gives us an almost critical sequence at the level l, that is, a sequence $\{\boldsymbol{h}^{(j)}\}$ in $\mathcal{C}$ satisfying (1.4), with additional Morse information (as mentioned above) which is crucial for proving that the sequence is convergent. Let us emphasize that this is the first time that the critical point theory by Fang and Ghoussoub is applied to the magnetic Hartree–Fock equations.

Related work on the application of critical point theory to semilinear elliptic equations includes: existence of solutions with finite Morse indices established by Dancer [4], de Figueiredo et al. [11], Flores et al. [12], and Tanaka [28], existence of multiple solutions established by Cingolani and Lazzo [3] and Ghoussoub and Yuan [15], "relaxed" Palais–Smale sequences as in Lazer and Solimini [19] and Jeanjean [17] and problems on noncompact Riemannian manifolds found in Mazepa [24], and Tanaka [29].

2. Preliminaries

Throughout the paper we denote by C (with or without indices) various constants whose precise value is of no importance.

Operators. Let $\mathcal{H}$ be a separable complex Hilbert space. We denote its scalar product and norm by $\langle\cdot,\cdot\rangle_{\mathcal{H}}$ and $\|\cdot\|_{\mathcal{H}}$, respectively. Let T be a linear operator on $\mathcal{H}$ with domain $\mathfrak{D}(T)$, range $\mathrm{Ran}(T)$ and kernel $\mathrm{Ker}(T)$. Its (Hilbert) adjoint (when it exists) is denoted by T^*. The spectrum and resolvent set are denoted by $\mathrm{spec}(T)$ and $\rho(T)$, respectively. Given a Hilbert space $\mathcal{H}$ we define $\mathcal{H}^N$ to be the N-fold (Cartesian) product of $\mathcal{H}$, equipped with the scalar product $\langle \boldsymbol{f}, \boldsymbol{g}\rangle = \sum_{n=1}^N \langle f_n, g_n\rangle_{\mathcal{H}}$. Given Banach spaces $\mathcal{X}$ and $\mathcal{Y}$, we say that $h \in \mathcal{X}+\mathcal{Y}$ if there exist $f\in\mathcal{X}$ and $g\in\mathcal{Y}$ such that $h = f+g$. This is a Banach space, e.g., when equipped with the norm $\|h\|_{\mathcal{X}+\mathcal{Y}} = \inf(\|f\|_{\mathcal{X}} + \|g\|_{\mathcal{Y}})$. We need the following abstract operator result by Lions [23, Lemma II.2].

Lemma 2.1. *Let T be a selfadjoint operator on a Hilbert space $\mathcal{H}$, and let $\mathcal{H}_1$, $\mathcal{H}_2$ be two subspaces of $\mathcal{H}$ such that $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$, $\dim \mathcal{H}_1 = \mathsf{h}_1 < \infty$ and $P_2 T P_2 \geqslant 0$, where P_2 is the orthogonal projection onto $\mathcal{H}_2$. Then T has at most h_1 negative eigenvalues.*

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

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

By $\mathbb{S}^{n-1}$ we will denote the unit sphere in the Euclidean space $\mathbb{R}^n$. For $1\leqslant p\leqslant\infty$, we let $L^p(\mathbb{R}^3)$ be the space of (equivalence classes of) complex valued functions ϕ which are μ-measurable and satisfy $\int_{\mathbb{R}^3} |\phi(x)|^p \,\mathrm{d}\mu < \infty$ if $p<\infty$ and $\|\phi\|_{L^\infty(\mathbb{R}^3)} = \operatorname{ess\,sup}|\phi| < \infty$ if $p=\infty$. When the measure is the standard Lebesgue measure and the underlying set is $\mathbb{R}^3$ we will sometimes simply write L^p. For any p the $L^p(\mathbb{R}^3)$ space is a Banach space with norm $\|\cdot\|_{L^p(\mathbb{R}^3)} = (\int_{\mathbb{R}^3} |\cdot|^p \,\mathrm{d}x)^{1/p}$. In the case $p=2$, $L^2(\mathbb{R}^3)$ is a separable Hilbert space with scalar product $\langle\phi,\psi\rangle_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} \phi\overline{\psi}\,\mathrm{d}x$ and corresponding norm $\|\phi\|_{L^2(\mathbb{R}^3)} = \langle\phi,\phi\rangle_{L^2(\mathbb{R}^3)}^{1/2}$. Similarly, $L^2(\mathbb{R}^3)^N$, the N-fold Cartesian product of $L^2(\mathbb{R}^3)$, is equipped with the scalar product $\langle\boldsymbol{\phi},\boldsymbol{\psi}\rangle = \sum_{n=1}^N \langle\phi_n,\psi_n\rangle_{L^2(\mathbb{R}^3)}$ and the norm defined by $\|\boldsymbol{\phi}\| = \langle\boldsymbol{\phi},\boldsymbol{\phi}\rangle^{1/2}$.

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

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

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

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

When $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$, then $\mathscr{D}(\mathbb{R}^3)$ is dense in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$, and the following well-known *diamagnetic inequality* is valid (see [18,26,20]).

Theorem 2.2. *Let $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$. If $\phi \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$, then*

$$\big|\nabla|\phi|\big| \leqslant |\nabla_{\mathcal{A}}\phi|. \tag{2.1}$$

As a consequence of Theorem 2.2 we have that $\phi \mapsto |\phi|$ maps $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ continuously into the Sobolev space $\mathbf{H}^1(\mathbb{R}^3)$, which implies the existence of a continuous embedding

$$\mathbf{H}^1_{\mathcal{A}}\big(\mathbb{R}^3\big) \hookrightarrow L^q\big(\mathbb{R}^3\big), \quad q \in [2,6]. \tag{2.2}$$

Homotopic families. Let Ω be a compact subset of $\mathbb{R}^n$, $n \geqslant 1$, and let M be a complete C^2-Riemannian manifold. Assume that G is a compact Lie group acting freely and differentiably on M and Ω. A family $\mathcal{F}$ of the sets of the form

$$\big\{f(\Omega)\colon\ f \in C_G(\Omega, M)\big\}$$

is called a G-homotopic family of dimension n. Here $C_G(\Omega, M)$ is the set of all G-equivariant continuous $f : \Omega \to M$, that is, a continuous function such that $f(gx) = gf(x)$, $g \in G$ and $x \in \Omega$.

Kato space. We denote by $\mathcal{K}$ the Kato space

$$\mathcal{K} := \big\{V\colon\ \forall\epsilon > 0\ \exists V_1 \in L^{\frac{3}{2}} \wedge V_2 \in L^\infty\colon\ \|V_2\|_{L^\infty} < \epsilon \wedge V = V_1 + V_2\big\},$$

and we recall that this space has Banach structure with, e.g., the norm $\|\cdot\|_{L^{3/2}+L^\infty}$ introduced above.

The admissible set $\mathcal{C}$. To apply abstract critical point theory we need the following facts established in [2].

Theorem 2.3. *The admissible set $\mathcal{C}$ is a complete analytic Hilbert–Riemann manifold.*

3. General setting and main result

Henceforth we will consider a family of functionals, which will be defined on the Stiefel type manifold in (1.1). Throughout the paper we assume that $V \in L^2_{\mathrm{loc}}(\mathbb{R}^3, \mathbb{R})$, $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$, $\gamma \in [0, \infty)$ and $W \in L^p(\mathbb{R}^3) + L^q(\mathbb{R}^3)$, with $2 \leqslant p \leqslant q \leqslant 4$. We also assume that W is nonnegative, radial, and that it tends to 0 in the (weak) sense that $\mu(\{x\colon\ |W| > t\}) < \infty$ for all $t > 0$, where μ is the Lebesgue measure. The kinetic energy will be denoted by $\mathfrak{t}_0[\phi] := \|\nabla_{\mathcal{A}}\phi\|^2_{L^2}$. We introduce

$$\mathfrak{s}_V : \mathbf{H}^1_{\mathcal{A}}\big(\mathbb{R}^3\big) \to \mathbb{R} \quad \text{by } \phi \mapsto \int\limits_{\mathbb{R}^3} V(x)\big|\phi(x)\big|^2\,\mathrm{d}x, \tag{3.1}$$

along with (arising from the direct Coulomb energy)

$$\mathcal{J}_W(\psi, \phi) := \int\limits_{\mathbb{R}^3}\int\limits_{\mathbb{R}^3} \psi(x)\overline{\phi(y)}W(x-y)\,\mathrm{d}x\,\mathrm{d}y,$$

and (arising from the exchange energy)

$$\mathcal{K}_W(\psi,\phi) := \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \psi(x,y)\overline{\phi(x,y)}W(x-y)\,\mathrm{d}x\,\mathrm{d}y,$$

defined whenever it makes sense. We consider the following family of functionals $\mathcal{E}_m : \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N \to \mathbb{R}$ defined by

$$\begin{aligned}\boldsymbol{\phi} := (\phi_1,\dots,\phi_N) \mapsto \sum_{n=1}^{N}\big(\mathfrak{t}_0[\phi_n] + \mathfrak{s}_V[\phi_n]\big) + \frac{1}{2}\mathcal{J}_W(\rho_{\boldsymbol{\phi}},\rho_{\boldsymbol{\phi}})\\ - \frac{1}{2}\mathcal{K}_W\big(\big|\mathcal{D}_{\boldsymbol{\phi}}(x,x')\big|,\big|\mathcal{D}_{\boldsymbol{\phi}}(x,x')\big|\big) - \gamma\|\boldsymbol{\phi}\|^2_{L^2(\mathbb{R}^3)^N},\end{aligned}$$

where the subscript $m := m(\mathcal{A}, V, \gamma, W_1, W_2)$ indicates that the functional depends on $\mathcal{A}$, V, W and γ. Here $\mathcal{D}_{\boldsymbol{\phi}}(x,x') := \sum_{n=1}^N \phi_n(x)\overline{\phi_n(x')}$ and $\rho_{\boldsymbol{\phi}}(x) = \sum_{n=1}^N |\phi_n(x)|^2$. At the place we do not focus on whether the functionals are well defined or not, this will be discussed in detail in the sequel. Furthermore, given $\boldsymbol{\phi} \in \mathcal{C}$ we introduce

$$\mathfrak{f}^{\boldsymbol{\phi}}_m : \mathbf{H}^1_{\mathcal{A}}\big(\mathbb{R}^3\big) \times \mathbf{H}^1_{\mathcal{A}}\big(\mathbb{R}^3\big) \to \mathbb{R} \quad \text{by}$$

$$(\psi,\psi) \mapsto \mathfrak{t}_0[\psi] + \mathfrak{s}_V[\psi] + \mathcal{J}_W(\rho_{\boldsymbol{\phi}},\psi) - \mathcal{K}_W\big(\mathcal{D}_{\boldsymbol{\phi}}(x,y), \psi(y)\overline{\psi(x)}\big) - \gamma\langle\psi,\psi\rangle_{L^2}. \tag{3.2}$$

Standard arguments show that this form can be associated with a selfadjoint operator, which we denote by $F^{\boldsymbol{\phi}}_m$. We impose the following conditions:

Assumption 3.1. If the following two conditions hold, then we write $m \in \mathcal{N}_\gamma$. For any weakly convergent (with respect to the topology on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$) sequence $\{\phi^{(j)}\}_{j=1}^\infty \subset \mathcal{C}$ we have that:

(i) The quadratic form $\epsilon\mathfrak{t}_0 + \mathfrak{s}_V : \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) \to \mathbb{R}$ is uniformly bounded from below on $\mathcal{C}$ for some $\epsilon \in [0,1)$ and weakly lower semicontinuous for some $\epsilon \in [0,1]$.

(ii) The essential spectra of the following family of Schrödinger operators

$$-\Delta_{\mathcal{A}} + V + W * \rho_{\boldsymbol{\phi}^{(j)}}$$

equal the semi-axis $[\gamma,\infty)$ and that the operators has infinitely many eigenvalues strictly below γ.

The main result is the following theorem.

Theorem 3.2. *Suppose that $m \in \mathcal{N}_\gamma$.*

1. *Then every minimizing sequence of the functional $\mathcal{E}_m(\cdot)$ is relatively compact in $\mathcal{C}$. In particular, there exists a minimizer $\boldsymbol{\varphi}$ of $\mathcal{E}_m(\cdot)$ on $\mathcal{C}$ and (up to unitary transformations) the components of $\boldsymbol{\varphi} = (\varphi_1,\dots,\varphi_N)$ satisfy the Hartree–Fock type equations*

$$\begin{cases} F\varphi_n + \lambda_n\varphi_n = 0, \\ \langle\varphi_m,\varphi_n\rangle_{L^2(\mathbb{R}^3)} = \delta_{mn}, \end{cases} \tag{3.3}$$

where F is the Fock type operator defined via (3.2). Moreover, the numbers $-\lambda_n$ are the N lowest eigenvalues of F.

2. *There exists a sequence* $\{\boldsymbol{\varphi}^{(k)}\}_{k=1}^{\infty}$, *with entries* $\boldsymbol{\varphi}^{(k)} = (\varphi_1^{(k)}, \dots, \varphi_N^{(k)})$, *of solutions (on different levels of energy) of the Hartree–Fock type equations* (3.3) *which satisfy the constraints* $\langle \varphi_m^{(k)}, \varphi_n^{(k)} \rangle_{L^2(\mathbb{R}^3)} = \delta_{mn}$ *for all* $1 \leqslant m, n \leqslant N$ *and, furthermore, the Lagrange multipliers* $\lambda_n^{(k)}$ *are positive. Moreover, the following properties are valid as* $k \to \infty$:

$$\begin{cases} \lambda_n^{(k)} \to \lambda_n, \\ \mathcal{E}_m(\boldsymbol{\varphi}^{(k)}) \to 0, \\ \boldsymbol{\varphi}^{(k)} \to 0 \quad \text{weakly in } \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N. \end{cases}$$

4. Proof of main result

We are ready to prove the main theorem.

Proof of Theorem 3.2. The idea of the proof is to find levels of the functional on which we can find critical points. We will create infinitely many distinct levels with such properties. We will use the notation $\boldsymbol{\phi}^{(j)} := (\phi_1^{(j)}, \dots, \phi_N^{(j)})$ when there are no possibility of confusion and also drop the index on the functional.

For the first level we start out with the obvious global minimum, that is

$$l_0 := \inf \mathcal{E}|_{\mathcal{C}}.$$

Assumption 3.1 and the Cauchy–Schwarz inequality imply that $l_0 > -\infty$. We may therefore extract a minimizing sequence, say $\{\widetilde{\boldsymbol{\Phi}}^{(j)}\}_{j=1}^{\infty} \subset \mathcal{C}$. Given a complete metric space (X, d) we introduce $\mathcal{Q}$ as the set of functions that can be written as

$$q(x) = \frac{1}{2} \sum_{k=1}^{\infty} \alpha_k d(x, v_k)^2,$$

for some convergent sequence $\{v_k\}_{k=1}^{\infty}$ and $\alpha_k \geqslant 0$ such that $\sum_{k=1}^{\infty} \alpha_k = 1$. Now an application of the Borwein–Preiss smooth variational principle which can be found in [1, Theorem 2.6] provides us with a new minimization sequence $\{\boldsymbol{\Phi}^{(j)}\}_{j=1}^{\infty}$ corresponding to the same level and such that

$$\|\boldsymbol{\Phi}^{(j)} - \widetilde{\boldsymbol{\Phi}}^{(j)}\|_{\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N} \to 0.$$

We will also have that $\boldsymbol{\Phi}^{(j)}$ minimizes

$$\mathcal{E}(\cdot) + \mu^{(j)} q_j(\cdot),$$

on $\mathcal{C}$ with $\{q_j\}_{j=1}^{\infty} \subset \mathcal{Q}$ and $\mu^{(j)} \searrow 0$. From this we can, after some direct calculations, conclude that

$$\lim_{j \to \infty} \mathcal{E}(\boldsymbol{\phi}^{(j)}) = l_0,$$

for a sequence $\{\lambda^{(j)}\}_{j=1}^{\infty} \subset \mathbb{R}^N$ (the Lagrange multipliers) we get that

$$\|F_m^{\boldsymbol{\phi}^{(j)}} \boldsymbol{\phi}^{(j)} + \lambda^{(j)} \boldsymbol{\phi}^{(j)}\|_{L^2(\mathbb{R}^3)^N} \to 0, \tag{4.1}$$

and there exists a sequence $\delta^{(j)} > 0$, $\delta^{(j)} \to 0$, such that

$$\left(\sum_{n=1}^{N} \mathfrak{f}_m^{\phi^{(j)}}[\psi_n, \psi_n] + \left(\lambda_n^{(j)} + \delta^{(j)}\right)\|\psi_n\|_{L^2}^2\right) - \int_{\mathbb{R}^3\times\mathbb{R}^3} W\left(x-x'\right)\left|\nu\left(x,x'\right)\right|^2 - \nu(x,x)\nu\left(x',x'\right)W\left(\left|x-x'\right|\right)\mathrm{d}x\,\mathrm{d}x' \geqslant 0$$

holds on $(\psi_1,\ldots,\psi_N) \in M_{\phi^{(j)}}$. Here we define

$$\nu\left(x,x'\right) := \frac{1}{\sqrt{2}}\sum_{n=1}^{N}\phi_n^{(j)}(x)\overline{\psi_n\left(x'\right)} + \phi_n^{(j)}\left(x'\right)\overline{\psi_n(x)}$$

and $M_{\phi^{(j)}}$ is the set of all $(\psi_1,\ldots,\psi_N) \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$ such that

$$\left\langle\phi_k^{(j)}, \psi_l\right\rangle_{L^2} = 0 \quad \forall k, l,$$

and

$$\langle\psi_k, \psi_l\rangle_{L^2} = 0 \quad \forall k \neq l.$$

Therefore

$$\mathfrak{t}_0[\psi] + \mathfrak{s}_V[\psi] + \mathcal{J}_W\left(\rho_{\phi^{(j)}}, |\psi|^2\right) + \left(\lambda_n^{(j)} + \delta^{(j)} - \gamma\right)\|\psi\|_{L^2}^2 \geqslant 0$$

is satisfied on

$$\left\{\psi \in \mathbf{H}^1_{\mathcal{A}}\left(\mathbb{R}^3\right):\ \left\langle\phi_k^{(j)}, \psi\right\rangle_{L^2} = 0\ \forall k\right\}.$$

We will call these properties *level-information*, *first-order information* and *second-order information* of this Palais–Smale type property, respectively. We will now create more levels on which we can find this kind of information. We begin by making some observations concerning symmetry and structure. The functional $\mathcal{E}(\cdot)$ is obviously even and $\mathcal{C}$ is a complete C^2-Riemannian manifold according to Theorem 2.3. We note that $\mathbb{Z}_2 := \{-1, 1\}$ equipped with multiplication as binary operation and the discrete topology can be considered to be a compact Lie group. Choose $k \geqslant N$ and let $\mathbb{Z}_2$ act on the manifolds $\mathcal{C}$ and $\mathbb{R}^k$ by the actions

$$(\pm 1, \phi) \mapsto \pm\phi, \quad \phi \in \mathcal{C},$$

and

$$(\pm 1, x) \mapsto \pm x, \quad x \in \mathbb{R}^k.$$

Note that the Lie group is acting freely on $\mathcal{C}$ and $\mathbb{R}^k$. Under the previously stated Lie group actions on the manifolds $\mathcal{C}$ and $\mathbb{R}^k$ we define

$$\mathsf{H}_k := \left\{\mathsf{M} = f\left(\mathbb{S}^{k-1}\right):\ f \in C_{\mathbb{Z}_2}\left(\mathbb{S}^{k-1}, \mathcal{C}\right)\right\}$$

and observe that this is a $\mathbb{Z}_2$-homotopic family of dimension k (see Section 2 for the definition). We define

$$l_k := \inf_{\mathsf{M}\in\mathsf{H}_k} \max_{\boldsymbol{\phi}\in\mathsf{M}} \mathcal{E}(\boldsymbol{\phi}).$$

We note that from the definition of l_k above that $\{l_k\}_{k=1}^{\infty}$ will be a nondecreasing sequence. From Assumption 3.1 we infer that

$$\mathfrak{l}_0[\phi] + \mathfrak{s}_V[\phi] - \gamma \leqslant -\epsilon_k,$$

for some $\epsilon_k > 0$ on a k-dimensional subspace, say $\mathcal{H}_k$, of $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ such that $\|\phi\|_{L^2(\mathbb{R}^3)} = 1$ for all $\phi \in \mathcal{H}_k$ (the unit sphere in this subspace will be denoted by $\widetilde{\mathbb{S}}^{k-1}$). Now let $g_- : \mathcal{H}_n \to \mathbb{R}^k$ be a continuous and linear such that $g_-(\mathbb{S}^{k-1}) = \widetilde{\mathbb{S}}^{k-1}$. Let e be the natural embedding of $\widetilde{\mathbb{S}}^{k-1}$ into $\mathcal{C}$. Note that $g_- \circ e \in C_{\mathbb{Z}_2}(\mathbb{S}^{k-1}, \mathcal{C})$ and also note that since the global minimum is finite (proved above) we get that

$$\mathcal{E}|_{\mathcal{C}} \geqslant C. \tag{4.2}$$

Therefore $\{l_k\}_{k=1}^{\infty} \subset (-\infty, 0]$. Thus we may therefore find $\mathsf{M}_k \in \mathsf{H}_k$ such that

$$l_k \leqslant \max_{\mathsf{M}_k} \mathcal{E} < \frac{l_k}{2} < 0. \tag{4.3}$$

Let $\{\psi_m\}_{m=1}^{\infty}$ be a basis of $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$. Denote by $\mathcal{W}_k$ the linear hull of $\{\psi_m\}_{m=1}^{k}$. Define $\mathcal{V}_k$ as the orthogonal complement of $\mathcal{W}_{k-1}$ and assume that $\mathsf{M}_k \cap \mathcal{V}_k = \emptyset$. Let π_k be the orthogonal projection from $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$ onto $\mathcal{W}_k$. Then (note that $\mathcal{V}_{k+1} = \operatorname{Ker}(\pi_k) \subset \mathcal{V}_k$)

$$\pi_{k-1}(\mathsf{M}_k) \subset \mathcal{W}_{k-1} \setminus \{0\} \cong \mathbb{R}^{k-1} \setminus \{0\}.$$

Since $\mathsf{M}_k = f(\mathbb{S}^{k-1})$, for some $f \in C_{\mathbb{Z}_2}(\mathbb{S}^{k-1}, \mathcal{C})$ we have existence of a continuous and odd map from $\mathbb{S}^{k-1}$ to $\mathbb{R}^{k-1} \setminus \{0\}$. From the Borsuk–Ulam theorem we will now get existence of two antipodal points on $\mathbb{S}^{k-1}$ which maps (due to symmetry) to 0, a contradiction. For each k fix some $\boldsymbol{\varphi}^{(k)} \in \mathsf{M}_k \cap \mathcal{V}_k$ and extract an $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$-weakly convergent subsequence $\{\boldsymbol{\varphi}^{(k)}\}_{k=1}^{\infty}$. Note that $\mathcal{E}(\boldsymbol{\varphi}^{(k)}) \leqslant (l_k/2) < 0 = \mathcal{E}(\mathbf{0})$ and $\boldsymbol{\varphi}^{(k)} \to \mathbf{0}$ weakly in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$. In $\mathcal{E}(\cdot)$ the term $(1/2)\mathcal{J}_W(\cdot) - (1/2)\mathcal{K}_W(\cdot)$ is weakly lower semicontinuously (as a consequence of Fatou's lemma because $\varphi_n^{(j)} \to \varphi_n$ pointwise a.e. and, by hypothesis on W, the integrand is nonnegative) and, in conjunction with Assumption 3.1(i) we deduce that $\mathcal{E}(\cdot) + \gamma\|\cdot\|^2_{(L^2)^N}$ is weakly lower semicontinuous. Using this we obtain $0 = \mathcal{E}(\mathbf{0}) \leqslant \liminf_k(\mathcal{E}(\boldsymbol{\varphi}^{(k)}) + \gamma\|\boldsymbol{\varphi}^{(k)}\|^2_{(L^2)^N})$ which, in view of (4.3), implies that $\lim_k l_k = 0$.

We can now use abstract critical point theory results by Fang and Ghoussoub [10] (see also [14, Theorem 11.1 and Remark 11.13]) to extract a sequence on each level l_k with the same type of information as for the ground state (the second-order information will hold on a subspace of $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ with finite codimension which is independent of j). We proceed to prove relative compactness of such a sequence. We have that

$$\left(F_m^{\boldsymbol{\varphi}^{(j)}} \boldsymbol{I} + \Lambda^{(j)}\right)\boldsymbol{\varphi}^{(j)} \to 0 \tag{4.4}$$

in $L^2(\mathbb{R}^3)^N$. Here $F_m^{\boldsymbol{\varphi}^{(j)}}$ is the operator associated with the form in (3.2), $\boldsymbol{I}$ is the $N \times N$ identity matrix, and $\Lambda^{(j)}$ is a diagonal matrix with diagonal elements $\{\lambda_n^{(j)}\}_{n=1}^{N}$ (here we use that $\mathcal{E}_m$ is unitary invariant, see e.g. [22]). We will now prove existence of a $\lambda > 0$ such that $\lambda_n^{(j)} \geqslant \lambda > 0$. Assumption 3.1(i), the boundedness of $\mathcal{E}(\boldsymbol{\varphi}^{(j)})$ and the Cauchy–Schwarz inequality ensure that the Palais–Smale sequence $\{\boldsymbol{\varphi}^{(j)}\}$ is bounded in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$. The boundedness of $\mathcal{E}(\boldsymbol{\varphi}^{(j)})$, in combination with (4.4) and the Cauchy–Schwarz inequality, also implies that $\{\lambda_n^{(j)}\}$ is bounded, and hence we may assume – by extracting a subsequence if necessary – that $\varphi_n^{(j)}$ converges weakly in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ (and a.e. in $\mathbb{R}^3$) to some φ_n and (using the Bolzano–Weierstrass theorem) that $\lambda_n^{(j)}$ converges to some λ_n. Now, using Assumption 3.1, the level information and first-order information we conclude that we have an upper bound on $|\lambda_n^{(j)}| \leqslant C$ independent of (j and n) and we may therefore assume, perhaps after going to a subsequence, that $\lambda_n^{(j)}$ converge for each n to some λ_n. Passing to the limit in (4.1) we deduce

$$F_m^{\boldsymbol{\varphi}}\varphi_n = -\lambda_n\varphi_n.$$

From the second-order information and an application of Lemma 2.1 we get that $-\Delta_{\mathcal{A}} + V + W * \rho_{\boldsymbol{\phi}^{(j)}} - \gamma$ has at most a finite number of eigenvalues below $-\lambda_n^{(j)} - \delta_n^{(j)}$. On the contrary we know by Assumption 3.1 that these operators have infinitely many eigenvalues, with the only possible cluster point located at 0. We may therefore conclude, perhaps after going to a subsequence, the existence of a $\lambda > 0$, independent of j and n (recall that $\delta_n^{(j)} \to 0$ in the standard Euclidean metric for each n) such that

$$\lambda_n^{(j)} \geqslant \lambda > 0$$

and, consequently, $\lambda_n > 0$. Using the weak lower semicontinuity of the functional $\mathcal{E}(\cdot) + \gamma\|\cdot\|^2_{(L^2)^N}$ (and $(1/2)\mathcal{J}_W - (1/2)\mathcal{K}_W$) we have that

$$\begin{aligned}
\limsup_j \sum_{n=1}^N \big(\gamma + \lambda_n^{(j)}\big)\big\|\varphi_n^{(j)}\big\|^2_{L^2} &= -\liminf_j \Bigg\{ \sum_{n=1}^N \mathfrak{t}_0\big[\varphi_n^{(j)}\big] + \mathfrak{s}_V\big[\varphi_n^{(j)}\big] \\
&\quad + \mathcal{J}_W(\rho_{\boldsymbol{\varphi}^{(j)}}, \rho_{\boldsymbol{\varphi}^{(j)}}) - \mathcal{K}_W\big(\big|\mathcal{D}_{\boldsymbol{\varphi}^{(j)}}(x,x')\big|, \big|\mathcal{D}_{\boldsymbol{\varphi}^{(j)}}(x,x')\big|\big) \\
&\quad - \gamma \sum_{n=1}^N \big\|\varphi_n^{(j)}\big\|^2_{L^2} + \gamma \sum_{n=1}^N \big\|\varphi_n^{(j)}\big\|^2_{L^2} \Bigg\} \\
&= -\liminf_j \Bigg\{ \mathcal{E}\big(\boldsymbol{\varphi}^{(j)}\big) + \gamma \sum_{n=1}^N \big\|\varphi_n^{(j)}\big\|^2_{L^2} \\
&\quad + \frac{1}{2}\mathcal{J}_W(\rho_{\boldsymbol{\varphi}^{(j)}}, \rho_{\boldsymbol{\varphi}^{(j)}}) - \frac{1}{2}\mathcal{K}_W\big(\big|\mathcal{D}_{\boldsymbol{\varphi}^{(j)}}(x,x')\big|, \big|\mathcal{D}_{\boldsymbol{\varphi}^{(j)}}(x,x')\big|\big) \Bigg\} \\
&\leqslant -\Bigg\{ \mathcal{E}(\boldsymbol{\varphi}) + \gamma \sum_{n=1}^N \|\varphi_n\|^2_{L^2} \\
&\quad + \frac{1}{2}\mathcal{J}_W(\rho_{\boldsymbol{\varphi}}, \rho_{\boldsymbol{\varphi}}) - \frac{1}{2}\mathcal{K}_W\big(\big|\mathcal{D}_{\boldsymbol{\varphi}}(x,x')\big|, \big|\mathcal{D}_{\boldsymbol{\varphi}}(x,x')\big|\big) \Bigg\} \\
&= \sum_{n=1}^N (\gamma + \lambda_n)\|\varphi_n\|^2_{L^2} \leqslant \liminf_j \sum_{n=1}^N \big(\gamma + \lambda_n^{(j)}\big)\big\|\varphi_n^{(j)}\big\|^2_{L^2}.
\end{aligned}$$

We conclude that $\|\varphi_n^{(j)}\|_{L^2} \to \|\varphi_n\|_{L^2}$ and, consequently, $\varphi_n^{(j)}$ converges strongly to φ_n in $L^2(\mathbb{R}^3)$.

We have already seen when we made the construction of the levels that we may, without loss of generality, assume that $-\infty < l_k < l_{k+1} < 0$ and therefore that

$$-\infty < l_{k-1} < l_k = \mathcal{E}\big(\boldsymbol{\varphi}^{(k)}\big) < l_{k+1} < 0. \tag{4.5}$$

Here $\boldsymbol{\varphi}^{(k)}$ corresponds of course to the critical point on level l_k. We conclude that $\mathcal{E}(\boldsymbol{\varphi}^{(k)}) \to 0$. □

5. Applications

We give several applications of Theorem 3.2. We will use $W = \frac{1}{|x|}$. We need a few auxiliary facts before we proceed to our examples.

Lemma 5.1. *Assume that $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$ and $V \in \mathcal{K}$. Then, given $\epsilon > 0$, there exists a constant $C_\epsilon > 0$ such that*

$$\mathcal{E}(\boldsymbol{\varphi}) \geqslant (1-\epsilon)\sum_{n=1}^{N} \|\nabla_{\mathcal{A}}\varphi_n\|^2_{L^2} - C_\epsilon \sum_{n=1}^{N} \|\varphi_n\|^2_{L^2}$$

for all $\boldsymbol{\varphi} \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$. In particular, $\mathcal{E}$ is bounded from below on $\mathcal{C}$, and minimizing sequences are bounded in $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$.

We refer to [5] for details. Next we establish weak continuity of the electron–nuclei potential.

Lemma 5.2. *Let $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$ and $V \in \mathcal{K}$. Then the functional $\mathfrak{s}_V : \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3) \to \mathbb{R}$, defined in (3.1), is weakly continuous on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$. Moreover, the estimate*

$$\mathfrak{s}_V[\phi] \geqslant -\frac{1}{2}\int_{\mathbb{R}^3} \big|\nabla_{\mathcal{A}}\phi(x)\big|^2\,\mathrm{d}x + C\|\phi\|^2_{L^2}$$

holds on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)$ for some constant C.

Proof. Let $\psi_n \to \psi$ in the weak topology on $\mathbf{H}^1_{\mathcal{A}}$. By a combination of Sobolev's embedding theorem and the diamagnetic inequality we conclude that

$$\|\psi_n\|_{L^p} \leqslant C\|\psi_n\|_{\mathbf{H}^1_{\mathcal{A}}}, \quad p \in [2,6]. \tag{5.1}$$

Hence, we may assume strong convergence locally in e.g. L^2 and therefore without loss of generality that

$$\psi_n \to \psi \quad \text{a.e.}$$

Thus, using (5.1) again, it is standard that

$$|\psi_n|^2 \rightharpoonup |\psi|^2$$

in L^p, where $p \in (1,3]$. It remains to show weak continuity for $\mathfrak{s}_{V'}$, where $V' \in \mathcal{K}$. For any $\epsilon > 0$, we may choose V'' (here $V'' := V' - g$, for some $g \in L^{\frac{3}{2}}$) such that $\|V''\|_{L^\infty} < \epsilon$. We note that

$$\int_{\mathbb{R}^3} |V_{f''}| \big| |\psi_n|^2 - |\psi|^2 \big| \leqslant \epsilon \Big(\sup_n \|\psi_n\|_{L^2}^2 + \|\psi\|_{L^2}^2 \Big),$$

and we are done. It is well-known (cf. [25]) that

$$\int_{\mathbb{R}^3} V(x)|\phi|^2 \, dx \geqslant -\frac{1}{2} \int_{\mathbb{R}^3} \big|\nabla_{\mathcal{A}}\phi(x)\big|^2 \, dx + C\|\phi\|_{L^2}^2$$

holds for $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$, $V_- \in L^{3/2}(\mathbb{R}^3)$ and $V \in L^1_{\mathrm{loc}}(\mathbb{R}^3)$. $\square$

The following fact is also well-known (see, e.g., [5]).

Lemma 5.3. *Assume that $\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)^3$ and $V \in \mathcal{K}$. Then $\mathcal{E}(\cdot)$ is weakly lower semicontinuous on $\mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$.*

With these preparations we are ready to give examples. Lemma 5.1, Lemma 5.2, and Lemma 5.3 are all necessary in order to apply Theorem 3.2.

Example 5.4. In the first application we consider the Hartree–Fock model of N electrons and K nuclei in a constant magnetic field. We establish existence of infinitely many solutions to the Hartree–Fock equations for this system provided the total nuclear charge $Z_{\mathrm{tot}} = \sum_{k=1}^{K} Z_k$ satisfies $Z_{\mathrm{tot}} > N$; cf. [23, 7]. To the best of our knowledge this result is new.

Corollary 5.5 *(Constant magnetic field). Let $\mathbf{B} := (b_1, b_2, b_3)$, with $b_j \in \mathbb{R}$ and V_{en} as in Section 1. Note that, without loss of generality, we may after suitable rotations, assume that $b_1 = b_2 = 0$ and $b_3 = 1$. Then $m \in \mathcal{N}_1$ and assertion* 1 *of Theorem* 3.2 *along with assertion* 2 *of Theorem* 3.2 *hold.*

Proof. We may choose the Coulomb gauge, i.e. $\mathcal{A} := \frac{1}{2}(-x_2, x_1, 0)$. In view of Assumption 3.1 and Lemma 5.2 we only need to prove existence of infinitely many eigenvalues of the corresponding magnetic Fock operator below 1. This spectral property was proved by Esteban and Lions [8, Theorem 5.1]. Therefore, $m \in \mathcal{N}_1$ and the corresponding assertions 1 and 2 of Theorem 3.2 hold. $\square$

The condition $Z_{\mathrm{tot}} \geqslant N$ and $Z_{\mathrm{tot}} > N - 1$ are *identical* for the relevant applications in Physics.

Example 5.6. Next we consider the Hartree–Fock model with N electrons and K nuclei in the presence of an external magnetic field which belongs to a class of fields which decrease at infinity.

Corollary 5.7 *(Decreasing magnetic fields). Suppose that $\mathcal{A} \in L^p + L^q$, $2 \leqslant p \leqslant q < 6$ and that $V' \in L^a + L^b$, $1 \leqslant a \leqslant b < 3$ with $V'_- \in L^{3/2}$. Write $V = V_{\mathrm{en}} + V'$. Then $m \in \mathcal{N}_0$ and the assertions* 1 *and* 2 *of Theorem* 3.2 *hold.*

Proof. We need to prove that $m \in \mathcal{N}_0$. In view of Lemma 5.2 it is evident that Assumption 3.1(i) holds and, therefore, it remains to be shown that Assumption 3.1(ii) is satisfied. Take $f \in \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3)^N$, put $\mu := |f|^2 dx$, where dx is the Lebesgue measure. Assume that $\mu(\mathbb{R}^3) \leqslant N$. Then we claim that the operator

$$L_{\mathcal{A},V,\mu} = -\Delta_{\mathcal{A}} + V + \mu * \frac{1}{|x|}$$

has infinitely many negative eigenvalues. The operator $L_{\mathcal{A},V,\mu}$ is associated with the canonical quadratic form $\mathfrak{l}$ which is to be defined below. We note that $\mu * \frac{1}{|x|} \in \mathcal{K}$. Indeed, $\frac{1}{|x|} \in \mathcal{K}$ and by the generalized Minkowski inequality

$$\|g * \mu\|_{L^r} \leqslant Z_{\mathrm{tot}} \|g\|_{L^r}$$

holds for any $g \in L^r(\mathbb{R}^3)$, $r \in [1, \infty]$.

Write $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$, where $\mathcal{A}_1 \in L^p(\mathbb{R}^3)$ and $\mathcal{A}_2 \in L^q$. We claim that

$$\lim_{|y| \to \infty} \int_{B_1(y)} \mathcal{A}^2 + V + \mu * \frac{1}{|x|} \, \mathrm{d}x = 0.$$

We note that it is enough to prove that

$$\lim_{|y| \to \infty} \int_{B_1(y)} g \, \mathrm{d}x = 0$$

for $g \in L^p$, $1 \leqslant p < 3$. Let $\epsilon > 0$ and take h as a smooth function with compact support such that $\|g - h\|_{L^p} \leqslant \epsilon$. Using this we get that

$$\lim_{|y| \to \infty} \int_{B_1(y)} |g| \, \mathrm{d}x \leqslant C\epsilon.$$

Hence we conclude that $\mathrm{spec}_{\mathrm{ess}}(L_{\mathcal{A},V,\mu}) = [0, \infty)$ by [21, Theorem 2.5]. Write $V' = W_1 + W_2$, where $W_1 \in L^a$ and $W_2 \in L^b$. Define $\phi(x) := \frac{g(1-|x|^2)}{\|g(1-|x|^2)\|_{L^2}}$, 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

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

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

$$\begin{aligned}
\mathfrak{l}[\phi_\lambda] \leqslant{}& \frac{1}{\lambda^2} \int_{B_1} \left|\nabla \phi(x)\right|^2 \mathrm{d}x + C\bigg(\frac{1}{\lambda^{6/\beta}} \left(\|\mathcal{A}_1\|_{L^p}^2 + \|\mathcal{A}_2\|_{L^q}^2 + \|\mathcal{A}_1\|_{L^p} \|\mathcal{A}_2\|_{L^q}\right) \\
&+ \frac{1}{\lambda^{1+p}} \left(\|\mathcal{A}_1\|_{L^p} + \|\mathcal{A}_2\|_{L^q}\right) + \frac{1}{\lambda^{3/q}} \left(\|W_1\|_{L^\alpha} + \|W_2\|_{L^\beta}\right)\bigg) \\
&+ \frac{1}{\lambda} \int_{B_1} \left(V_{\mathrm{en}}^\lambda(x) + \mu_\lambda * \frac{1}{|x|}\right) \left|\phi(x)\right|^2 \mathrm{d}x.
\end{aligned}$$

It is also easy to prove that

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

uniformly in λ perhaps after increasing λ further. Thus we have constructed a subspace with infinite dimension (again we might have to increase λ further) such that $\mathfrak{l}[\cdot] < 0$ holds on this subspace (except at 0 of course). Thus, we are done by a direct application of Glazman's lemma which can be found in e.g., [25, Lemma A.3]. □

Example 5.8. In a paper by Enstedt and Melgaard [5] existence of a ground state was established for the Hartree–Fock model in the presence of a wide class of physically measurable magnetic fields which, roughly speaking, decrease at infinitely. We refer to the paper for the full characterization of the fields. Here we merely point out that an application of Theorem 3.2 allows us to conclude the existence of infinitely many solutions to the Hartree–Fock equations (in the case $Z_{\text{tot}} > N$ with the same remark as above concerning extensions) for the class of magnetic fields considered in [5].

Corollary 5.9 *(Physically measurable fields). If Assumptions* 1.1 *in* [5] *are fulfilled, then* $m \in \mathcal{N}_0$ *and the assertions* 1 *and* 2 *of Theorem* 3.2 *hold true.*

It is worth to mention that one of the assumptions in [5] can be relaxed; the proofs in [5] still apply and the main theorems, Theorem 1.4 and Theorem 1.5, remain true. More specifically, Assumption 1.1(iv) can be replaced by, for instance, the existence of some $R > 0$ such that $\mathcal{A}$ is dominated by a positively homogeneous function of degree $d \in (-\infty, 0)$ for $|x| > R$ (i.e., *at infinity*).

References

[1] J. Borwein, D. Preiss, A smooth variational principle with applications to subdifferentiability and to differentiability of convex functions, Trans. Amer. Math. Soc. 303 (1987) 517–527.
[2] E. Chiumiento, M. Melgaard, Stiefel and Grassmann manifolds in quantum chemistry, J. Geom. Phys. 62 (8) (2012) 1866–1881.
[3] S. Cingolani, M. Lazzo, Multiple semiclassical standing waves for a class of nonlinear Schrödinger equations, Topol. Methods Nonlinear Anal. 10 (1) (1997) 1–13.
[4] E.N. Dancer, Finite Morse index solutions of exponential problems, Ann. Inst. H. Poincaré Anal. Non Linéaire 25 (2008) 173–179.
[5] M. Enstedt, M. Melgaard, Existence of solution to the Hartree–Fock equations with decreasing magnetic fields, Nonlinear Anal. 69 (7) (2008) 2125–2141.
[6] M. Enstedt, M. Melgaard, On the non-existence of a minimizer to the magnetic Hartree–Fock functional, Positivity 12 (4) (2008) 653–666.
[7] M. Enstedt, M. Melgaard, Existence of infinitely many distinct solutions to the quasirelativistic Hartree–Fock equations, Int. J. Math. Math. Sci. 2009 (2009), Article ID 651871.
[8] M.J. Esteban, P.-L. Lions, Stationary solutions of nonlinear Schrödinger equations with an external magnetic field, in: Partial Differential Equations and the Calculus of Variations, vol. I, in: Progr. Nonlinear Differential Equations Appl., vol. 1, Birkhäuser Boston, Boston, MA, 1989, pp. 401–449.
[9] G. Fang, N. Ghoussoub, Second order information on Palais–Smale sequences in the mountain pass theorem, Manuscripta Math. 75 (1992) 81–95.
[10] G. Fang, N. Ghoussoub, Morse-type information on Palais–Smale sequences obtained by min–max principles, Comm. Pure Appl. Math. 47 (12) (1994) 1595–1653.
[11] D.G. de Figueiredo, P.N. Srikanth, S. Santra, Non-radially symmetric solutions for a superlinear Ambrosetti–Prodi type problem in a ball, Commun. Contemp. Math. 7 (6) (2005) 849–866.
[12] G. Flores, P. Padilla, Y. Tonegawa, Higher energy solutions in the theory of phase transitions: a variational approach, J. Differential Equations 169 (1) (2001) 190–207.
[13] V. Fock, Näherungsmethode zur lösung des quantenmechanischen Mehrkörperproblems, Z. Physik 61 (1930) 126–148.
[14] N. Ghoussoub, Duality and Perturbation Methods in Critical Point Theory, Cambridge University Press, 1993.
[15] N. Ghoussoub, C. Yuan, Multiple solutions for quasi-linear PDEs involving the critical Sobolev and Hardy exponents, Trans. Amer. Math. Soc. 352 (12) (2000) 5703–5743.
[16] D.R. Hartree, The wave mechanics of an atom with the non-Coulomb central field, I. Theory and methods, Proc. Cambridge Philos. Soc. 24 (1928) 89–132.
[17] L. Jeanjean, On the existence of bounded Palais–Smale sequences and application to a Landesman–Lazer type problem set on $\mathbb{R}^N$, Proc. Roy. Soc. Edinburgh Sect. A 129 (1999) 787–809.
[18] T. Kato, Remarks on Schrödinger operators with vector potentials, Integral Equations Operator Theory 1 (1) (1978) 103–113.
[19] A.C. Lazer, S. Solimini, Nontrivial solutions of operator equations and Morse indices of critical points of min–max type, Nonlinear Anal. 12 (8) (1988) 761–775.
[20] H. Leinfelder, C.G. Simader, Schrödinger operators with singular magnetic vector potentials, Math. Z. 176 (1) (1981) 1–19.
[21] H. Leinfelder, Gauge invariance of Schrödinger operators and related spectral properties, J. Operator Theory 9 (1) (1983) 163–179.

[22] E.H. Lieb, B. Simon, The Hartree–Fock theory for Coulomb systems, Comm. Math. Phys. 53 (3) (1977) 185–194.
[23] P.-L. Lions, Solutions of Hartree–Fock equations for Coulomb systems, Comm. Math. Phys. 109 (1) (1987) 33–97.
[24] E.A. Mazepa, On the existence of entire solutions of a semilinear elliptic equation on noncompact Riemannian manifolds, Mat. Zametki 81 (1) (2007) 153–156 (in Russian); translation in: Math. Notes 81 (1–2) (2007) 135–139.
[25] G. Rozenblum, M. Melgaard, Schrödinger operators with singular potentials, in: Stationary Partial Differential Equations, vol. II, in: Handb. Differ. Equ., Elsevier/North-Holland, Amsterdam, 2005, pp. 407–517.
[26] B. Simon, Maximal and minimal Schrödinger forms, J. Operator Theory 1 (1) (1979) 37–47.
[27] J.C. Slater, Note on Hartree's method, Phys. Rev. 35 (1930) 210–211.
[28] K. Tanaka, Morse indices at critical points related to the symmetric mountain pass theorem and applications, Comm. Partial Differential Equations 14 (1) (1989) 99–128.
[29] K. Tanaka, Periodic solutions for singular Hamiltonian systems and closed geodesics on noncompact Riemannian manifolds, Ann. Inst. H. Poincaré Anal. Non Linéaire 17 (1) (2000) 1–33.