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

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Abstract

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

MSC: 35Q20; 81G45; 81V45; 35Q40; 47G20; 81Q10

Keywords: Magnetic Hartree–Fock equations; Ground state; Variational method; Spectral bound

1. Introduction

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

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

$$\mathcal{E}_N^{\mathrm{QM}}(\Psi_e) = \langle \Psi_e, H_{N,\mathbf{Z},\mathcal{A}} \Psi_e \rangle_{L^2(\mathbb{R}^{3N})}$$
$$= \sum_{n=1}^{N} \int_{\mathbb{R}^{3N}} \left(|\nabla_{\mathcal{A},x_n} \Psi_e(x)|^2 + V_{en}(x_n)|\Psi_e(x)|^2 \right) \mathrm{d}x + \sum_{1 \le m < n \le N} \int_{\mathbb{R}^{3N}} V_{ee}(x_m - x_n)|\Psi_e(x)|^2 \mathrm{d}x, \quad (1.1)$$

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

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

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

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

with $\Delta_{\mathcal{A},x_n} = \sum_{m=1}^{3}(P_{x_n}^{(m)})^2$ being the magnetic Laplacian. The interpretation of this Hamiltonian[1] is as follows: the 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.

The wave function Ψ_e in (1.1) belongs to $\mathcal{H}_e := \bigwedge^N \mathbf{H}^1_{\mathcal{A}}(\mathbb{R}^3;\mathbb{C}^2)$, i.e., the N-particle Hilbert space consisting of antisymmetric functions (expressing the Pauli exclusion principle)

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

where S_N is the group of permutations of $\{1,\ldots,N\}$, with the signature of a permutation σ being denoted by $\operatorname{sign}(\sigma)$. 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.

Poincaré's Lemma (see, e.g., [10]) asserts that the magnetic field strength B is described by a 2-form

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

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

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

with the magnetic vector potential (1-form) $\mathcal{A}(x) = \sum_{m=1}^{3} A_m \mathrm{d}x_m$. Since the vector potential is not directly observable, we should impose conditions on the field strengths.

We choose the Poincaré gauge, $x\cdot\mathcal{A}(x) = \mathcal{A}(x)\cdot x = 0$. It is well-known that

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

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

Assumption 1.1. (i) $\operatorname{div}\mathcal{A} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)$.

(ii) $\operatorname{div}\mathcal{A}$ is $-\Delta$-bounded with relative bound less than one.
(See, e.g., [4, Definition III.7.1].)

(iii) Smallness at infinity:

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

(See Section 2 for the meaning of $\widetilde{\chi}$.)

(iv) $\mathcal{A}$ is homogeneous of degree -1.

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

[1] Expressed in Rydberg units.