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Existence of minimizers for Kohn-Sham within the Local Spin Density Approximation

David Gontier,
Université Paris Est, CERMICS (ENPC), INRIA
F-77455 Marne-la-Vallée, France
david.gontier@cermics.enpc.fr

Abstract

The purpose of this article is to extend the work by Anantharaman and Cancès [1], and prove the existence of minimizers for the spin-polarized Kohn-Sham model in the presence of a magnetic field within the local spin density approximation. We show that for any magnetic field that vanishes at infinity, the existence of minimizers is ensured for neutral or positively charged systems. The proof relies on classical concentration-compactness techniques.

1 Introduction

The density functional theory (DFT) introduced in 1964 by Hohenberg and Kohn [2] is a very popular tool in modern quantum chemistry. This theory transforms the high-dimensional Schrödinger problem into a low-dimensional one, hence computationally solvable. The price to pay is the introduction of the so-called exchange-correlation (xc) energy term, which is unknown. Throughout the literature, several different approximations of this energy can be found. The first successful one, and still broadly used nowadays, was proposed by Kohn and Sham [3], and is called the local density approximation (LDA). The mathematical properties resulting of the Kohn-Sham LDA are still not fully understood. Proving the existence of minimizers is made difficult by the non-convexity of the problem due to the LDA term. Using concentration-compactness techniques introduced by Lions [4], it has been possible to prove the existence of minimizers in several cases. Le Bris [5] proved that for a neutral or positively charged system, the Kohn-Sham problem with LDA exchange-correlation energy admits a minimizer. A similar result was proved by Anantharaman and Cancès [1] for the so-called extended-Kohn-Sham model with LDA exchange-correlation energy.

The purpose of the present article is to extend the result by Anantharaman and Cancès to spin-polarized systems, the electrons of the molecular system into consideration being subjected to the electric potential V created by the nuclei, and to an arbitrary external magnetic field \mathbf{B} that vanishes at infinity. In order to take into account spin effects, we have to resort to spin density functional theory (SDFT). In this theory, all magnetic contributions coming from orbital magnetism (paramagnetic current, spin-orbit coupling,...) are neglected. Historically, while Kohn and Sham briefly discussed the inclusion of spin effects in their model, the general theory was pioneered by von Barth and Hedin [6] and is known as the local spin density approximation (LSDA). These authors proposed the following ansatz to transform a spin-unpolarized exchange-correlation energy to a spin-polarized version of it:

$$E_{xc}^{\text{LSDA}}(\rho^+, \rho^-) := \frac{1}{2} [E_{xc}^{\text{LDA}}(2\rho^+) + E_{xc}^{\text{LDA}}(2\rho^-)],$$

where E_{xc}^{LDA} is the spinless exchange-correlation energy, and $\rho^{+/-}$ are the eigenvalues of the 2×2 spin density matrix (see Sec. 2 for details). There are two other major differences between spin-polarized and spin-unpolarized models. First, the ground state of spin-unpolarized models is given

by a minimization problem onto the set of electronic densities, while in spin-polarized models, it is given by a minimization problem onto the set of spin density matrices, consisting of 2×2 hermitian matrices. Second, the magnetic field adds a Zeeman-type term $-\mu \int \mathbf{B} \cdot \mathbf{m}$ to the energy functional, where \mathbf{m} is the spin angular momentum density.

Due to all those additional difficulties with respect to the spinless case, the fully polarized SDFT has not been very popular until recently. Chemists generally prefer its collinear version (collinear-SDFT), where all the spins are constrained to be orientated along a fixed direction on the whole space. This allows one to work with two scalar fields (one for spin-up, and one for spin-down), instead of fields of hermitian matrices. While this simplification provides very good results, it misses some physical properties (spin dynamics [7], frustrated solids [8], ...). The implementation of the unconstrained (fully polarizable) model appeared with the work of Sandratskii and Guletskii [9], and Kübler *et al.* [10, 11], and this model is becoming a standard tool nowadays. To the best of our knowledge, no rigorous proof of the existence of solutions has yet been provided for this case.

Our result is that, under the same hypotheses as in [1], plus some mild conditions on \mathbf{B} , the existence of minimizers is still ensured for neutral or positively charged systems. Whereas the main tools of the proof are similar to those used in [1], namely concentration-compactness techniques, some adaptations are necessary, in particular to handle the Zeeman term. The structure of the article is as follows. We first recall how to derive the LSDA models, and formulate the main theorem. Then, we break the proof of the theorem into several lemmas, that we prove at the end of the paper.

2 Derivation of the local spin density approximation models

We recall how the extended Kohn-Sham models are derived in the spin setting. We start from the Schrödinger-Pauli Hamiltonian for N -electrons in the Born-Oppenheimer approximation. In atomic units, this operator reads

$$H^{\text{SP}}(V, \mathbf{A}) = \sum_{i=1}^N \frac{1}{2} (-i\nabla_i + \mathbf{A}(\mathbf{r}_i))^2 \mathbb{I}_2 + \sum_{i=1}^N V(\mathbf{r}_i) \mathbb{I}_2 - \mu \sum_{i=1}^N \mathbf{B}(\mathbf{r}_i) \cdot \sigma_i + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \mathbb{I}_2,$$

where \mathbb{I}_2 is the 2×2 identity matrix,

$$V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|} \quad (1)$$

is the electric potential generated by the M nuclei, \mathbf{A} is the external magnetic vector potential, and $\mathbf{B} := \nabla \times \mathbf{A}$ is the external magnetic field. We denote by \mathbf{r}_i (resp. \mathbf{R}_k) the positions of the electrons (resp. nuclei). The charge of the k -th nucleus is $z_k \in \mathbb{N}^*$ and $Z := \sum_{k=1}^M z_k$ is the total nuclear charge. We can assume without loss of generality that $\mathbf{R}_1 = \mathbf{0}$. The constant μ is the Bohr magneton. Its value is $1/2$ in atomic units, but we prefer to keep the notation μ in the rest of the paper. The term σ_i appearing in the Hamiltonian contains the Pauli matrices acting on the i -th spin variable:

$$\sigma_i := (\sigma_{xi}, \sigma_{yi}, \sigma_{zi}) = \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_i, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_i \right).$$

Although the magnetic field \mathbf{B} and magnetic vector potential \mathbf{A} are linked by the relation $\mathbf{B} = \nabla \times \mathbf{A}$, it is often preferable to consider them as two independent fields. Indeed, \mathbf{B} acts on the spin of the electrons, while \mathbf{A} acts on the spatial component of the spin-orbitals. For instance, would we be interested only in studying orbital effects (*e.g.* paramagnetic current), we would neglect the spin effects. We would then take $\mathbf{B} = \mathbf{0}$ and $\mathbf{A} \neq \mathbf{0}$. Such an approximation leads to the so-called current-density functional theory [12]. In this article, we are interested in spin

effects. We therefore set $\mathbf{A} = \mathbf{0}$, which amounts to neglecting the paramagnetic currents, while keeping $\mathbf{B} \neq \mathbf{0}$. This approximation is commonly used to study phenomena such as spin dynamics [7] or frustrated solids [8]. With this approximation, our Hamiltonian for N electrons reads

$$H(V, \mathbf{B}) = \left(\sum_{i=1}^N -\frac{1}{2} \Delta_i + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \mathbb{I}_2 - \mu \sum_{i=1}^N \mathbf{B}(\mathbf{r}_i) \cdot \sigma_i.$$

This Hamiltonian acts on the fermionic Hilbert space

$$\bigwedge_{i=1}^N L^2(\mathbb{R}^3, \mathbb{C}^2) := \left\{ \Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N), \mathbf{r}_i \in \mathbb{R}^3, s_i \in \{\uparrow, \downarrow\}, \right. \\ \left. \sum_{s_1, \dots, s_N \in \{\uparrow, \downarrow\}^N} \int_{\mathbb{R}^{3N}} |\Psi(\mathbf{r}_1, s_1, \dots)|^2 d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N < \infty, \right. \\ \left. \forall p \in \mathfrak{S}_N, \quad \Psi(\mathbf{r}_{p(1)}, s_{p(1)}, \dots) = \epsilon(p) \Psi(\mathbf{r}_1, s_1, \dots) \right\},$$

where $\epsilon(p)$ is the parity of the permutation p , endowed with the scalar product

$$\langle \Psi_1 | \Psi_2 \rangle = \sum_{(s_1, \dots, s_N) \in \{\uparrow, \downarrow\}^N} \int_{\mathbb{R}^{3N}} \overline{\Psi_1(\mathbf{r}_1, s_1, \dots)} \Psi_2(\mathbf{r}_1, s_1, \dots) d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N.$$

Its form domain $\bigwedge_{i=1}^N H^1(\mathbb{R}^3, \mathbb{C}^2)$ is defined similarly.

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

$$E(V, \mathbf{B}) := \inf \left\{ \langle \Psi | H(V, \mathbf{B}) | \Psi \rangle, \quad \Psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3, \mathbb{C}^2), \quad \|\Psi\|_{L^2} = 1 \right\}.$$

In order to convexify the problem, we introduce, for a wave function $\Psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3, \mathbb{C}^2)$ satisfying $\|\Psi\| = 1$, the N -body density matrix

$$\Gamma_\Psi := |\Psi\rangle \langle \Psi|.$$

The minimization problem can be recast as

$$E(V, \mathbf{B}) = \inf \{ \text{Tr} (H(V, \mathbf{B}) \Gamma), \quad \Gamma \in \mathcal{W}_N \}$$

where \mathcal{W}_N is the set of pure state N -body density matrices defined by

$$\mathcal{W}_N := \left\{ \Gamma_\Psi, \quad \Psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3, \mathbb{C}^2), \quad \|\Psi\|_{L^2} = 1 \right\}.$$

In this article, we study the extended-Kohn-Sham model based on mixed-state N -body density matrices, for this problem has better properties mathematically speaking, and allows one to handle more general physical situations as, for instance, positive temperatures. The set \mathcal{M}_N of mixed state N -body density matrices is defined as the convex hull of \mathcal{W}_N . The minimization problem for mixed states reads

$$E(V, \mathbf{B}) := \inf \{ \text{Tr} (H(V, \mathbf{B}) \Gamma), \quad \Gamma \in \mathcal{M}_N \}.$$

Then, for $\Gamma \in \mathcal{M}_N$, direct calculations lead to

$$\text{Tr} (H(V, \mathbf{B}) \Gamma) = \text{Tr} (H(0, \mathbf{0}) \Gamma) + \int_{\mathbb{R}^3} \text{tr}_{\mathbb{C}^2} \left[\begin{pmatrix} V - \mu B_z & -\mu B_x + i\mu B_y \\ -\mu B_x - i\mu B_y & V + \mu B_z \end{pmatrix} \begin{pmatrix} \rho_\Gamma^{\uparrow\uparrow} & \rho_\Gamma^{\uparrow\downarrow} \\ \rho_\Gamma^{\downarrow\uparrow} & \rho_\Gamma^{\downarrow\downarrow} \end{pmatrix} \right], \quad (2)$$

where, for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$,

$$\rho_{\Gamma}^{\alpha\beta}(\mathbf{r}) := N \sum_{(s_2, \dots, s_N) \in \{\uparrow, \downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r}, \alpha, \mathbf{r}_2, s_2, \dots; \mathbf{r}, \beta, \mathbf{r}_2, s_2, \dots) d^3 \mathbf{r}_2 \cdots d^3 \mathbf{r}_N.$$

where $\Gamma(\mathbf{r}_1, s_1, \dots; \mathbf{r}'_1, s'_1, \dots)$ denotes the kernel of Γ . In the following, we write

$$U := \begin{pmatrix} V - \mu B_z & -\mu B_x + i\mu B_y \\ -\mu B_x - i\mu B_y & V + \mu B_z \end{pmatrix} \quad \text{and} \quad R_{\Gamma} := \begin{pmatrix} \rho_{\Gamma}^{\uparrow\uparrow} & \rho_{\Gamma}^{\uparrow\downarrow} \\ \rho_{\Gamma}^{\downarrow\uparrow} & \rho_{\Gamma}^{\downarrow\downarrow} \end{pmatrix}.$$

This last 2×2 matrix is called the spin density matrix. Note that when $\mathbf{B} = \mathbf{0}$, one recovers the usual potential energy density $V\rho_{\Gamma}$ appearing in spin-unpolarized DFT. Introducing the spin angular momentum density $\mathbf{m}_{\Gamma} = \text{tr}_{\mathbb{C}^2} [\sigma \cdot R_{\Gamma}]$, and the total electronic density $\rho_{\Gamma} = \rho_{\Gamma}^{\uparrow\uparrow} + \rho_{\Gamma}^{\downarrow\downarrow}$, it holds

$$\text{tr}_{\mathbb{C}^2} [UR_{\Gamma}] = V\rho_{\Gamma} - \mu\mathbf{B} \cdot \mathbf{m}_{\Gamma}. \quad (3)$$

We now apply the constrained search method introduced and studied by Levy [13], Valone [14] and Lieb [15], and write the minimization problem (2) in terms of R_{Γ} :

$$E(V, \mathbf{B}) = \inf \left\{ F(R) + \int_{\mathbb{R}^3} \text{tr}_{\mathbb{C}^2} [UR], \quad R \in \mathcal{J}_N \right\}, \quad (4)$$

with

$$F(R) := \inf \{ \text{Tr} [H(0, \mathbf{0})\Gamma], \quad \Gamma \in \mathcal{M}_N, \quad R_{\Gamma} = R \}.$$

The set \mathcal{J}_N is defined as

$$\mathcal{J}_N := \{ R \in \mathcal{M}_{2 \times 2}(L^1(\mathbb{R}^3)), \quad \exists \Gamma \in \mathcal{M}_N, \quad R_{\Gamma} = R \}, \quad (5)$$

where $\mathcal{M}_{2 \times 2}(L^1(\mathbb{R}^3))$ is the space of 2×2 matrices with entries in $L^1(\mathbb{R}^3)$. This is the set of mixed state N -representable spin density matrices. We recently proved [16] the following characterization for \mathcal{J}_N :

$$\mathcal{J}_N = \left\{ R \in \mathcal{M}_{2 \times 2}(L^1(\mathbb{R}^3)), \quad R^* = R, \quad R \geq 0, \quad \int_{\mathbb{R}^3} \text{tr}_{\mathbb{C}^2} [R] = N, \quad \sqrt{R} \in \mathcal{M}_{2 \times 2}(H^1(\mathbb{R}^3)) \right\}.$$

As mentioned before, the functional F cannot be straightforwardly evaluated. In order to make this problem practical, we approximate F . It is standard since the work of Kohn and Sham [3] to approximate this functional by studying a system of non-interacting electrons. For this purpose, we introduce, for a mixed state $\Gamma \in \mathcal{M}_N$, the 1-body density matrix

$$\gamma_{\Gamma} := \begin{pmatrix} \gamma_{\Gamma}^{\uparrow\uparrow} & \gamma_{\Gamma}^{\uparrow\downarrow} \\ \gamma_{\Gamma}^{\downarrow\uparrow} & \gamma_{\Gamma}^{\downarrow\downarrow} \end{pmatrix}$$

where

$$\gamma_{\Gamma}^{\alpha\beta}(\mathbf{r}, \mathbf{r}') := N \sum_{(s_2, s_3, \dots) \in \{\uparrow, \downarrow\}^{N-1}} \int_{\mathbb{R}^{3(N-1)}} \Gamma(\mathbf{r}, \alpha, \mathbf{r}_2, s_2, \dots; \mathbf{r}', \beta, \mathbf{r}_2, s_2, \dots) d^3 \mathbf{r}_2 \cdots d^3 \mathbf{r}_N.$$

The set of mixed-state 1-body density matrices is

$$\mathcal{P}_N := \{ \gamma_{\Gamma}, \quad \Gamma \in \mathcal{M}_N \},$$

and, identifying the kernel $\gamma(\mathbf{r}, \mathbf{r}')$ with the corresponding operator of $\mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2))$, the space of self-adjoint operators on $L^2(\mathbb{R}^3, \mathbb{C}^2)$, Coleman [17] proved that

$$\mathcal{P}_N = \{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2)), \quad 0 \leq \gamma \leq 1, \quad \text{Tr}(\gamma) = N, \quad \text{Tr}(-\Delta\gamma) < \infty \}.$$

Physically speaking, this is the set of one-body density matrices of systems with N -electrons ($\text{Tr}(\gamma) = N$), satisfying the Pauli principle ($0 \leq \gamma \leq 1$), and with finite kinetic energy ($\text{Tr}(-\Delta\gamma) < \infty$). In a similar way, we can define, for $\lambda > 0$,

$$\mathcal{P}_\lambda := \{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2)), \quad 0 \leq \gamma \leq 1, \quad \text{Tr}(\gamma) = \lambda, \quad \text{Tr}(-\Delta\gamma) < \infty\}. \quad (6)$$

A more practical and equivalent formulation of the Coleman result is that, using the spectral theory for compact self-adjoint operators, we can write the components $\gamma^{\alpha\beta}$ of any $\gamma \in \mathcal{P}_\lambda$ in the form

$$\begin{aligned} \gamma^{\alpha\beta}(\mathbf{r}, \mathbf{r}') &= \sum_{k=1}^{\infty} n_k \phi_k^\alpha(\mathbf{r}) \overline{\phi_k^\beta(\mathbf{r}')}, \quad 0 \leq n_k \leq 1, \quad \sum_{k=1}^{\infty} n_k = \lambda, \quad \Phi_k = \begin{pmatrix} \phi_k^\uparrow \\ \phi_k^\downarrow \end{pmatrix} \in L^2(\mathbb{R}^3, \mathbb{C}^2), \quad \langle \Phi_k | \Phi_l \rangle = \delta_{kl}, \\ \text{Tr}(-\Delta\gamma) &:= \sum_{k=1}^{\infty} n_k \|\nabla \Phi_k\|_{L^2}^2 = \text{Tr}(-\Delta\gamma^{\uparrow\uparrow}) + \text{Tr}(-\Delta\gamma^{\downarrow\downarrow}) < \infty. \end{aligned} \quad (7)$$

Notice that $\gamma_\Gamma(\mathbf{r}, \mathbf{r}) = R_\Gamma(\mathbf{r})$, so that we will write $R_\gamma(\mathbf{r}) := \gamma(\mathbf{r}, \mathbf{r})$ for $\gamma \in \mathcal{P}_N$. We finally introduce, similarly as in (5),

$$\mathcal{J}_\lambda := \{R \in \mathcal{M}_{2 \times 2}(L^1(\mathbb{R}^3)), \quad \exists \gamma \in \mathcal{P}_\lambda, \quad R = R_\gamma\}.$$

The extended version of the Kohn-Sham approach consists then in splitting the unknown functional $F(R)$ into three parts:

$$F(R) = T_{\text{KS}}(R) + J(\rho_R) + E_{\text{xc}}(R).$$

The first term T_{KS} represents the kinetic energy of a non-interacting electronic system. It reads, in the one-body formalism,

$$\forall R \in \mathcal{J}_\lambda, \quad T_{\text{KS}}(R) := \inf \left\{ \frac{1}{2} \text{Tr}(-\Delta\gamma), \quad \gamma \in \mathcal{P}_\lambda, \quad R_\gamma = R \right\}.$$

The second term is the Hartree term, defined by

$$J(\rho) := \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'.$$

Finally, the last term is the exchange-correlation functional defined by

$$E_{\text{xc}}(R) := F(R) - T_{\text{KS}}(R) - J(R).$$

Notice that because F is a non-explicit functional, E_{xc} is also a non-explicit functional. It is however possible to construct explicit approximations of E_{xc} giving rise to accurate predictions of the ground state energies of most molecular systems [18]. Note that the case $E_{\text{xc}} = 0$ corresponds to the reduced Hartree-Fock model [19].

The local-spin density approximation introduced by von Barth and Hedin [6] consists in writing

$$E_{\text{xc}}(R) \approx E_{\text{xc}}^{\text{LSDA}}(\rho^+, \rho^-) := \frac{1}{2} [E_{\text{xc}}^{\text{LDA}}(2\rho^+) + E_{\text{xc}}^{\text{LDA}}(2\rho^-)] \quad (8)$$

where $\rho^{+/-}$ are the two eigenvalues of the 2×2 matrix R , and $E_{\text{xc}}^{\text{LDA}}$ is the standard exchange-correlation functional in the non-polarized case, that we can write under the form [3]

$$E_{\text{xc}}^{\text{LDA}}(\rho) = \int_{\mathbb{R}^3} g(\rho(\mathbf{r})) d^3\mathbf{r}. \quad (9)$$

We emphasize that the polarization rule (8) is exact for the exchange part of the exchange-correlation energy, and that von Barth and Hedin proposed to use the same formula for the

correlation part. The fact that $E_{\text{xc}}^{\text{LSDA}}$ only depends on R via its eigenvalues comes from the locality of the functional. Indeed, this energy functional must be invariant with respect to local spin rotations. Because R is hermitian at each point, we can always diagonalize R locally, so that a local energy can only depend on the two eigenvalues of R .

In this article, we will deal with exchange-correlation functionals of the form (8)-(9). The most common choices for g are the ones derived from the homogeneous electron gas. Several choices exist (VWS [20], PZ81 [21], CP [22], PW92 [23], ...), and they all satisfy the same asymptotic conditions for low and high densities. Their mathematical properties are similar to the ones of the $X\alpha$ -functional introduced by Slater [24]

$$E_{\text{xc}}^{\text{LDA},X\alpha}(\rho) = -C_X \int_{\mathbb{R}^3} \rho^{4/3}(\mathbf{r}) d^3\mathbf{r}.$$

Altogether, by recasting problem (4) in terms of the one-body density matrices, we end up with a variational problem of the form

$$I_\lambda := \inf \{ \mathcal{E}(\gamma), \quad \gamma \in \mathcal{P}_\lambda \} \quad (10)$$

where

$$\mathcal{E}(\gamma) = \frac{1}{2} \text{Tr} (-\Delta \gamma^{\uparrow\uparrow}) + \frac{1}{2} \text{Tr} (-\Delta \gamma^{\downarrow\downarrow}) + J(\rho_\gamma) + \int_{\mathbb{R}^3} \text{tr}_{\mathbb{C}^2} [UR\gamma] d^3\mathbf{r} + E_{\text{xc}}^{\text{LSDA}}(\rho_\gamma^+, \rho_\gamma^-)$$

and where \mathcal{P}_λ has been defined in (6). The physical situation corresponds to $\lambda = N \in \mathbb{N}$, but as usual in variational problems set on the whole space, it is useful to relax the constraint $\text{Tr}(\gamma) = N$ to allow the particles to escape to infinity.

We can recover some other common models by further constraining the minimization set. For instance, the collinear-SDFt consists in minimizing the functional \mathcal{E} onto the set

$$\mathcal{P}_\lambda^{\text{collinear}} := \{ \gamma \in \mathcal{P}_\lambda, \quad \gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0 \}.$$

In this case, the matrices γ and R are both diagonal. In particular, the two eigenvalues of R are $\{\rho^+, \rho^-\} = \{\rho^{\uparrow\uparrow}, \rho^{\downarrow\downarrow}\}$. In this model, it holds that

$$\int_{\mathbb{R}^3} \text{tr}_{\mathbb{C}^2} [UR] = \int_{\mathbb{R}^3} V(\rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}) - \mu \int_{\mathbb{R}^3} B_z(\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow}) = \int_{\mathbb{R}^3} V\rho - \mu \int_{\mathbb{R}^3} B_z \rho \zeta.$$

where

$$\zeta := \frac{\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow}}{\rho^{\uparrow\uparrow} + \rho^{\downarrow\downarrow}} \in [-1, 1]$$

is the relative spin-polarization. This model is therefore simpler than the non-collinear spin-polarized model, as we are not dealing with fields of matrices, but with two scalar fields. Physically, it corresponds to constraining the spin along a fixed direction on the whole space. This method provides results in good agreement with experiments whenever the energy accounting for the non-collinearity of the spins is negligible.

Then, the unpolarized case consists in minimizing the functional \mathcal{E} onto the set

$$\mathcal{P}_\lambda^{\text{unpolarized}} := \{ \gamma \in \mathcal{P}_\lambda, \quad \gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0, \quad \gamma^{\uparrow\uparrow} = \gamma^{\downarrow\downarrow} \}.$$

Equivalently, it corresponds to the collinear case with $\zeta \equiv 0$. It then holds that

$$\int_{\mathbb{R}^3} \text{tr}_{\mathbb{C}^2} [UR] = \int_{\mathbb{R}^3} V\rho,$$

so that the model is independent of the magnetic field \mathbf{B} , and can be used whenever spin effects are negligible. We refer to [1] for a mathematical introduction of this model.

3 An existence result for the Kohn-Sham LSDA model

The main result of this article is the following

Theorem 1. *Under the following assumptions*

1/ *the function g in (9) is of class $C^1(\mathbb{R}^+)$ and satisfies:*

$$\begin{cases} g(0) = 0 \\ g' \leq 0 \\ \exists 0 < \beta^- \leq \beta^+ < \frac{2}{3}, \quad \sup_{\rho \in \mathbb{R}^+} \frac{|g'(\rho)|}{\rho^{\beta^-} + \rho^{\beta^+}} < \infty \\ \exists 1 \leq \alpha < \frac{3}{2}, \quad \limsup_{\rho \rightarrow 0^+} \frac{g(\rho)}{\rho^\alpha} < 0, \end{cases} \quad (11)$$

2/ *all entries of U are in $L^{\frac{3}{2}+\epsilon}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and vanish at infinity, and $V := \text{tr}_{\mathbb{C}^2}(U)$ has the form (1),*

the problem I_λ defined in (10) has a minimizer whenever $\lambda \leq Z$.

Remark 1. The assumptions (11) are the same as in [1], and are satisfied for all common functionals. Theorem 1 extends [1, Theorem 1] to the case when the system is spin-polarized by an external magnetic field \mathbf{B} . While the strategy of proof, based on concentration-compactness arguments, is similar to that in [1], an additional technical tool is needed to handle the Zeeman term. This tool seems to be new to the best of the author's knowledge. We have called it the flip transformation (see Equation (12) below).

Remark 2. This result does not make any assumption on the strength of the magnetic field \mathbf{B} other than that it vanishes at infinity. If \mathbf{B} becomes infinite at infinity, it is easy to see that the energy is not bounded below: we can orientate the spins of all electrons along the magnetic field and push them to infinity, so that the energy can be arbitrarily negative.

Proof of Theorem 1:

We use the concentration-compactness method introduced in [4]. We therefore introduce the problem at infinity

$$I_\lambda^\infty = \inf \{ \mathcal{E}^\infty(\gamma), \quad \gamma \in \mathcal{P}_\lambda \},$$

where

$$\mathcal{E}^\infty(\gamma) := \frac{1}{2} \text{Tr}(-\Delta \gamma^{\uparrow\uparrow}) + \frac{1}{2} \text{Tr}(-\Delta \gamma^{\downarrow\downarrow}) + J(\rho) + E_{\text{xc}}^{\text{LSDA}}(\rho^+, \rho^-).$$

We will need several lemmas, the proofs of which are postponed until the following section for the sake of clarity. We begin with some functional inequalities:

Lemma 1. *There exists a constant C such that for all $\lambda > 0$ and all $\gamma \in \mathcal{P}_\lambda$, it holds*

$$\|\nabla R_\gamma\|_{L^{3/2}} \leq C \text{Tr}(-\Delta \gamma) \quad \text{and} \quad \|\nabla \rho_\gamma^{+/-}\|_{L^{3/2}} \leq C \text{Tr}(-\Delta \gamma).$$

In particular, for all $1 \leq p \leq 3$, there exists C_p such that, for all $\lambda > 0$ and all $\gamma \in \mathcal{P}_\lambda$,

$$\|R_\gamma\|_{L^p} \leq C_p \lambda^{\frac{3-p}{2p}} \text{Tr}(-\Delta \gamma)^{\frac{3(p-1)}{2p}},$$

and similarly for $\rho_\gamma^{+/-}$.

We easily deduce from the above lemma that the energies I_λ and I_λ^∞ are bounded below:

Lemma 2. *For all $\lambda > 0$, we have $I_\lambda > -\infty$ and $I_\lambda^\infty > -\infty$. Moreover, all minimizing sequences (γ_n) for I_λ or I_λ^∞ are bounded in the Banach space \mathcal{B} , where*

$$\mathcal{B} := \{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3, \mathbb{C}^2)), \quad \|\gamma\|_{\mathcal{B}} := \text{Tr}(|\gamma|) + \text{Tr}(\|\nabla|\gamma|\nabla\|) < \infty \}.$$

In the following, we consider sequences $(\gamma_n)_{n \in \mathbb{N}^*} \in \mathcal{B}$, and we will write $R_n := R_{\gamma_n}$ and $\rho_n := \rho_{\gamma_n}$.

Lemma 3. *Let $(\gamma_n)_{n \in \mathbb{N}^*}$ be a bounded sequence of \mathcal{B} . Then, there exists $\gamma_0 \in \mathcal{B}$, such that, up to a subsequence, γ_n converges to γ_0 for the weak-* topology of \mathcal{B} , all components of R_n converge to their respective components in R_0 strongly in $L^p_{\text{loc}}(\mathbb{R}^3)$ for $1 \leq p < 3$, weakly in $L^p(\mathbb{R}^3)$ for $1 \leq p \leq 3$, and almost everywhere. The eigenvalues of R_n converge to the eigenvalues of R_0 strongly in $L^p_{\text{loc}}(\mathbb{R}^3)$ for $1 \leq p < 3$, weakly in $L^p(\mathbb{R}^3)$ for $1 \leq p \leq 3$ and almost everywhere.*

Moreover, if $\gamma_n \in \mathcal{P}_\lambda$ for all n , and $\gamma_0 \in \mathcal{P}_\lambda$, the convergences hold strongly in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$, and $\mathcal{E}(\gamma_0) \leq \liminf \mathcal{E}(\gamma_n)$.

It follows from Lemma 2 and Lemma 3 that one can extract from any minimizing sequence $(\gamma_n)_{n \in \mathbb{N}^*}$ of (10) a minimizing sequence, still denoted by (γ_n) , converging to some γ_0 for the weak-* topology of \mathcal{B} . In particular, $0 \leq \gamma_0 \leq 1$ and $\text{Tr}(-\Delta\gamma_0) < \infty$. To prove that γ_0 is indeed a minimizer of (10), it remains to prove that $\text{Tr}(\gamma_0) = \lambda$. Let $\alpha = \text{Tr}(\gamma_0)$. It is easy to get $\alpha \leq \lambda$. If $\alpha < \lambda$, then we have loss of compactness (some electrons leak away). Therefore, to prove that $\alpha = \lambda$ (at least when $\lambda \leq Z$), we need to control the behavior at infinity of the minimizers, which is not as simple as in [1] because of the Zeeman term $-\mu \int \mathbf{B} \cdot \mathbf{m}$. In order to control this term, we introduce the following flip transformation:

$$\begin{aligned} \text{for } \Phi = \begin{pmatrix} \phi^\uparrow \\ \phi^\downarrow \end{pmatrix}, \text{ we define } \tilde{\Phi} := \begin{pmatrix} \overline{\phi^\downarrow} \\ -\phi^\uparrow \end{pmatrix}, \\ \text{for } \gamma = \sum n_k |\Phi_k\rangle \langle \Phi_k|, \text{ we define } \tilde{\gamma} := \sum n_k |\tilde{\Phi}_k\rangle \langle \tilde{\Phi}_k|. \end{aligned} \quad (12)$$

Note that if

$$\gamma = \begin{pmatrix} \gamma^{\uparrow\uparrow} & \gamma^{\uparrow\downarrow} \\ \gamma^{\downarrow\uparrow} & \gamma^{\downarrow\downarrow} \end{pmatrix} \quad \text{and} \quad R_\gamma = \begin{pmatrix} R^{\uparrow\uparrow} & R^{\uparrow\downarrow} \\ R^{\downarrow\uparrow} & R^{\downarrow\downarrow} \end{pmatrix},$$

then

$$\tilde{\gamma}(\mathbf{x}, \mathbf{y}) = \begin{pmatrix} \gamma^{\downarrow\downarrow} & -\gamma^{\uparrow\downarrow} \\ -\gamma^{\downarrow\uparrow} & \gamma^{\uparrow\uparrow} \end{pmatrix}(\mathbf{y}, \mathbf{x}) \quad \text{and} \quad R_{\tilde{\gamma}} = \begin{pmatrix} R^{\downarrow\downarrow} & -R^{\uparrow\downarrow} \\ -R^{\downarrow\uparrow} & R^{\uparrow\uparrow} \end{pmatrix},$$

from which we deduce the following lemma, whose proof is straightforward.

Lemma 4. *If $\gamma \in \mathcal{P}_\lambda$, then $\tilde{\gamma} \in \mathcal{P}_\lambda$. Moreover, it holds that $\text{Tr}(-\Delta\tilde{\gamma}_n) = \text{Tr}(-\Delta\gamma_n)$, $\tilde{\rho} = \rho$, and $\tilde{\mathbf{m}} = -\mathbf{m}$, where ρ and \mathbf{m} have been defined in (3). In particular, it holds that*

$$\text{tr}_{\mathbb{C}^2} [UR] + \text{tr}_{\mathbb{C}^2} [U\tilde{R}] = 2 \int_{\mathbb{R}^3} V\rho. \quad (13)$$

In other words, this transformation flips the spin-up and spin-down channels. This lemma allows to cancel the Zeeman term, and is an essential tool throughout the proof. We can first prove

Lemma 5.

- (i) For all $\lambda > 0$, $-\infty < I_\lambda < I_\lambda^\infty < 0$.
- (ii) For all $0 < \mu < \lambda$, $I_\lambda \leq I_\mu + I_{\lambda-\mu}^\infty$.
- (iii) The functions $\lambda \mapsto I_\lambda$ and $\lambda \mapsto I_\lambda^\infty$ are non increasing.

We then have the important result

Lemma 6. *Let $\lambda > 0$ and $(\gamma_n)_{n \in \mathbb{N}^*} \in \mathcal{P}_\lambda$ be any minimizing sequence of I_λ that converges to some γ_0 for the weak-* topology of \mathcal{B} . Let $\alpha := \text{Tr}(\gamma_0)$. Then*

- (i) $\alpha \leq \lambda$.

(ii) $\alpha \neq 0$.

(iii) If $0 < \alpha < \lambda$, then γ_0 is a minimizer for the problem I_α , there exists $\beta > 0$ with $\alpha + \beta \leq \lambda$ such that I_β^∞ has also a minimizer, and $I_\lambda = I_\alpha + I_\beta^\infty + I_{\lambda-\alpha-\beta}^\infty$.

According to this lemma, if $\alpha < \lambda$, γ_0 is a minimizer for I_α . In this case, it satisfies the Euler-Lagrange equation

$$\gamma_0 = \mathbf{1}_{(-\infty, \epsilon_F)}(H_{\gamma_0}) + \delta \quad \text{with} \quad \delta \subset \text{Ker}(H_{\gamma_0} - \epsilon_F)$$

for some $\epsilon_F < 0$ called the Fermi energy, and with H_{γ_0} as defined in (25). Here, $\mathbf{1}_{(-\infty, \epsilon_F)}$ is the characteristic function of the interval $(-\infty, \epsilon_F)$, and the spectral projection $\mathbf{1}_{(-\infty, \epsilon_F)}(H_{\gamma_0})$ is defined by the functional calculus. We then use the very general

Lemma 7. *It holds $\sigma_{\text{ess}}(H_{\gamma_0}) = [0, +\infty[$. Moreover, if $0 < \lambda < Z$, then H_{γ_0} has infinitely many negative eigenvalues, and every eigenvector corresponding to such an eigenvalue is exponentially decreasing.*

From this lemma, we deduce the concentration-compactness result:

Lemma 8. *Let $0 < \alpha, \beta$ be such that $\alpha + \beta \leq Z$. Suppose that I_α and I_β^∞ admit minimizers. Then*

$$I_{\alpha+\beta} < I_\alpha + I_\beta^\infty \quad (< I_\alpha).$$

The end of the proof goes as follows. Let us suppose that $\lambda \leq Z$, and $\alpha < \lambda$. Then, according to Lemma 6, γ_0 is a minimizer for I_α , and there exists $\beta > 0$ such that $\alpha + \beta \leq \lambda \leq Z$ so that I_β^∞ has also a minimizer, and it holds $I_\lambda = I_\alpha + I_\beta^\infty + I_{\lambda-\alpha-\beta}^\infty$. Moreover, Lemma 8 holds, and $I_{\alpha+\beta} < I_\alpha + I_\beta^\infty$. Finally, we get

$$I_\lambda = I_\alpha + I_\beta^\infty + I_{\lambda-\alpha-\beta}^\infty > I_{\alpha+\beta} + I_{\lambda-\alpha-\beta}^\infty,$$

which contradicts the second point of Lemma 5.

Therefore, it holds $\alpha = \lambda$, and, according to Lemma 3, γ_0 is a minimizer for I_λ , which concludes the proof.

4 Proofs of the lemmas

Proof of lemma 1. Let $\lambda > 0$ and $\gamma \in \mathcal{P}_\lambda$. We use the representation (7) of γ , and write

$$\begin{aligned} \gamma^{\alpha\beta}(\mathbf{r}, \mathbf{r}') &= \sum_{k=1}^{\infty} n_k \phi_k^\alpha(\mathbf{r}) \overline{\phi_k^\beta(\mathbf{r}')}, \quad 0 \leq n_k \leq 1, \quad \sum_{k=1}^{\infty} n_k = \lambda, \\ \Phi_k &= \begin{pmatrix} \phi_k^\uparrow \\ \phi_k^\downarrow \end{pmatrix} \in L^2(\mathbb{R}^3, \mathbb{C}^2), \quad \langle \Phi_k | \Phi_l \rangle = \delta_{kl}, \quad \text{Tr}(-\Delta\gamma) := \sum_{k=1}^{\infty} n_k \|\nabla \Phi_k\|_{L^2}^2 < \infty. \end{aligned}$$

In particular, $\rho^{\alpha\beta}(\mathbf{r}) = \sum n_k \phi_k^\alpha(\mathbf{r}) \overline{\phi_k^\beta(\mathbf{r})}$. Differentiating this expression, and using the Cauchy-Schwarz inequality, it holds

$$\begin{aligned} |\nabla \rho^{\alpha\beta}|^2 &= \left| \sum_{k=1}^{\infty} n_k \left(\nabla \phi_k^\alpha(\mathbf{r}) \overline{\phi_k^\beta(\mathbf{r})} + \phi_k^\alpha(\mathbf{r}) \nabla \overline{\phi_k^\beta(\mathbf{r})} \right) \right|^2 \\ &\leq \left| \sum_{k=1}^{\infty} n_k \left(|\nabla \phi_k^\alpha|^2 + |\nabla \phi_k^\beta|^2 \right)^{1/2} \left(|\phi_k^\alpha|^2 + |\phi_k^\beta|^2 \right)^{1/2} \right|^2 \\ &\leq \left[\sum_{k=1}^{\infty} n_k \left(|\nabla \phi_k^\alpha|^2 + |\nabla \phi_k^\beta|^2 \right) \right] \left[\sum_{k=1}^{\infty} n_k \left(|\phi_k^\alpha|^2 + |\phi_k^\beta|^2 \right) \right]. \end{aligned}$$

We let $\tau^\alpha := \sum_{k=1}^{\infty} n_k |\nabla \phi_k^\alpha|^2$, so that $\tau^\alpha \in L^1(\mathbb{R}^3)$ and $\int_{\mathbb{R}^3} \tau^\alpha = \text{Tr}(-\Delta \gamma^{\alpha\alpha})$. The previous inequality leads to the point-wise estimate

$$|\nabla \rho^{\alpha\beta}| \leq (\tau^\alpha + \tau^\beta)^{1/2} (\rho^{\alpha\alpha} + \rho^{\beta\beta})^{1/2}. \quad (14)$$

In particular, if $\alpha = \beta$, we recover the Hoffman-Ostenhof inequality [25]

$$\|\nabla \sqrt{\rho^{\alpha\alpha}}\|_{L^2}^2 \leq \text{Tr}(-\Delta \gamma^{\alpha\alpha}).$$

With the homogeneous Sobolev embedding $H^1(\mathbb{R}^3) \hookrightarrow L^6(\mathbb{R}^3)$, we deduce

$$\|\rho^{\alpha\alpha}\|_{L^3} \leq C \text{Tr}(-\Delta \gamma^{\alpha\alpha}).$$

Then, using the fact that $(\tau^\alpha + \tau^\beta)^{1/2} \in L^2(\mathbb{R}^3)$ and $(\rho^{\alpha\alpha} + \rho^{\beta\beta})^{1/2} \in L^6(\mathbb{R}^3)$ and the Hölder inequality, it follows from (14) that

$$\|\nabla \rho^{\alpha\beta}\|_{L^{3/2}} \leq \|(\tau^\alpha + \tau^\beta)^{1/2}\|_{L^2} \|(\rho^{\alpha\alpha} + \rho^{\beta\beta})^{1/2}\|_{L^6} \leq 4C \text{Tr}(-\Delta \gamma). \quad (15)$$

For $\rho^{+/-}$, we use the exact expression of the eigenvalues of a 2×2 hermitian matrix:

$$\rho^{+/-} = \frac{1}{2} \left(\rho \pm \sqrt{\rho^2 - 4 \det(R)} \right) = \frac{1}{2} \left(\rho \pm \sqrt{(\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow})^2 + 4|\rho^{\uparrow\downarrow}|^2} \right). \quad (16)$$

Noticing that, if f and g are non negative,

$$|\nabla \sqrt{f+g}| = \frac{|\nabla f + \nabla g|}{2\sqrt{f+g}} \leq \frac{|\nabla f|}{2\sqrt{f+g}} + \frac{|\nabla g|}{2\sqrt{f+g}} \leq \frac{|\nabla f|}{2\sqrt{f}} + \frac{|\nabla g|}{2\sqrt{g}} = |\nabla \sqrt{f}| + |\nabla \sqrt{g}|,$$

we differentiate (16) to get

$$\begin{aligned} |\nabla \rho^{+/-}| &\leq \frac{1}{2} |\nabla \rho| + \frac{1}{2} \left| \nabla \sqrt{(\rho^{\uparrow\uparrow} - \rho^{\downarrow\downarrow})^2 + 4|\rho^{\uparrow\downarrow}|^2} \right| \\ &\leq \frac{1}{2} |\nabla \rho^{\uparrow\uparrow}| + \frac{1}{2} |\nabla \rho^{\downarrow\downarrow}| + \frac{1}{2} (|\nabla \rho^{\uparrow\uparrow}| + |\nabla \rho^{\downarrow\downarrow}| + 2|\nabla |\rho^{\uparrow\downarrow}||). \end{aligned}$$

All the terms on the right-hand side are in $L^{3/2}(\mathbb{R}^3)$ and of norms bounded by $C \text{Tr}(-\Delta \gamma)$, hence the same holds for $\nabla \rho^{+/-}$.

Moreover, γ is in \mathcal{P}_λ , so that $\text{Tr}(\gamma) = \int_{\mathbb{R}^3} \rho = \lambda$. We get from the inequality $2|ab| \leq |a|^2 + |b|^2$ that

$$|\rho^{\alpha\beta}| = \left| \sum_{k=1}^{\infty} n_k \phi_k^\alpha(\mathbf{r}) \overline{\phi_k^\beta(\mathbf{r})} \right| \leq \sum_{k=1}^{\infty} \frac{n_k}{2} (|\phi_k^\alpha|^2 + |\phi_k^\beta|^2) \leq \sum_{k=1}^{\infty} n_k (|\phi_k^\uparrow|^2 + |\phi_k^\downarrow|^2) = \rho. \quad (17)$$

Integrating on \mathbb{R}^3 leads to $\|\rho^{\alpha\beta}\|_{L^1} \leq \lambda$. From the positiveness of R_γ , it also holds that $0 \leq \rho^{+/-} \leq \rho$ so that $\|\rho^{+/-}\|_{L^1} \leq \lambda$. We conclude from (15), the homogeneous Sobolev embedding $W^{1,3/2}(\mathbb{R}^3) \hookrightarrow L^3(\mathbb{R}^3)$, and the Hölder inequality with $1 \leq p \leq 3$, that

$$\|\rho^{\alpha\beta}\|_{L^p} \leq C_p \lambda^{\frac{3-p}{2p}} \text{Tr}(-\Delta \gamma)^{\frac{3(p-1)}{2p}}$$

and similarly for $\rho^{+/-}$. □

Proof of Lemma 2.

We prove that $I_\lambda > -\infty$. The proof is similar for I_λ^∞ . Let $\lambda > 0$, and $\gamma \in \mathcal{P}_\lambda$. Under conditions (11), a straightforward calculation shows that

$$\begin{aligned} |E_{\text{xc}}^{\text{LSDA}}(\rho^+, \rho^-)| &\leq C \left(\int_{\mathbb{R}^3} (\rho^+)^{p^-} + \int_{\mathbb{R}^3} (\rho^+)^{p^+} \right) + C \left(\int_{\mathbb{R}^3} (\rho^-)^{p^-} + \int_{\mathbb{R}^3} (\rho^-)^{p^+} \right) \\ &\leq 2C \left(\int_{\mathbb{R}^3} \rho^{p^+} + \int_{\mathbb{R}^3} \rho^{p^-} \right), \end{aligned}$$

where $p^{+/-} := 1 + \beta^{+/-} < 5/3$. We used the fact that R_γ is a positive hermitian matrix, so that $0 \leq \rho^{+/-} \leq \rho$. Therefore, because $J(\rho) \geq 0$, we have the estimate:

$$\mathcal{E}(\gamma) \geq \frac{1}{2} \text{Tr}(-\Delta\gamma) - C_1 \|U\|_{L^{\frac{3}{2}+\epsilon} + L^\infty} \|R\|_{L^1 \cap L^{3-\epsilon'}} - C_2 \left(\|\rho\|_{L^{p^+}}^{p^+} + \|\rho\|_{L^{p^-}}^{p^-} \right),$$

where $\epsilon' = 4\epsilon/(1+2\epsilon) > 0$ is chosen such that $L^{3-\epsilon'}$ is the dual space of $L^{\frac{3}{2}+\epsilon}$. With Lemma 1, it follows

$$\mathcal{E}(\gamma) \geq \frac{1}{2} \text{Tr}(-\Delta\gamma) - C'_1 \|U\|_{L^{\frac{3}{2}+\epsilon} + L^\infty} (1 + \text{Tr}(-\Delta\gamma)^{\alpha_1}) - C_2 (\text{Tr}(-\Delta\gamma)^{\alpha_2} + \text{Tr}(-\Delta\gamma)^{\alpha_3})$$

with $0 \leq \alpha_1, \alpha_2, \alpha_3 < 1$. The function $Y \mapsto \frac{1}{2}Y - C'_1(1 + Y^{\alpha_1}) - C_2Y^{\alpha_2} - C_2Y^{\alpha_3}$ goes to $+\infty$ when Y goes to $+\infty$ for $0 \leq \alpha_1, \alpha_2, \alpha_3 < 1$. Hence, $\mathcal{E}(\gamma) \geq -C$ for all $\gamma \in \mathcal{P}_\lambda$. It also follows from the above inequality that if (γ_n) is a minimizing sequence for I_λ , then $\text{Tr}(-\Delta\gamma_n)$ is uniformly bounded. In particular, (γ_n) is a bounded sequence of \mathcal{B} . \square

Proof of Lemma 3.

Let $(\gamma_n)_{n \in \mathbb{N}^*}$ be a bounded sequence in \mathcal{B} . According to Lemma 1, the sequences $(\rho_n^{\alpha\beta})$ for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$ and $(\rho_n^{+/-})$ are bounded in $W^{1,3/2}(\mathbb{R}^3)$. In virtue of the Banach-Alaoglu theorem, up to a subsequence, the sequence (γ_n) converges to some $\gamma_0 \in \mathcal{B}$ for the weak-* topology of \mathcal{B} , and $(\rho_n^{\alpha\beta})$ and $\rho_n^{+/-}$ converge for the weak topology of $W^{1,3/2}(\mathbb{R}^3)$. To identify the limits, we recall that, for any compact operator K on $L^2(\mathbb{R}^3, \mathbb{C}^2)$,

$$\text{Tr}(\gamma_n K) \xrightarrow{n \rightarrow \infty} \text{Tr}(\gamma_0 K) \quad \text{and} \quad \text{Tr}(|\nabla|\gamma_n|\nabla|K) \xrightarrow{n \rightarrow \infty} \text{Tr}(|\nabla|\gamma_0|\nabla|K). \quad (18)$$

Choose $W \in \mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{R})$. The operator $(1 + |\nabla|)^{-1}W(1 + |\nabla|)^{-1}$ is compact and in the Schatten class \mathfrak{S}_p for $p > \frac{3}{2}$ according to the Kato-Simon-Seiler inequality [26]. Taking successively in (18)

$$K = \begin{pmatrix} W & 0 \\ 0 & 0 \end{pmatrix}, \quad K = \begin{pmatrix} 0 & 0 \\ 0 & W \end{pmatrix}, \quad K = \begin{pmatrix} 0 & W \\ W & 0 \end{pmatrix} \quad \text{and} \quad K = \begin{pmatrix} 0 & iW \\ -iW & 0 \end{pmatrix},$$

we obtain that, for the first choice of K ,

$$\begin{aligned} \int_{\mathbb{R}^3} \rho_n^{\uparrow\uparrow} W &= \text{Tr}(\gamma_n W) = \text{Tr}((1 + |\nabla|)\gamma_n(1 + |\nabla|) \cdot (1 + |\nabla|)^{-1}W(1 + |\nabla|)^{-1}) \\ &\xrightarrow{n \rightarrow \infty} \text{Tr}((1 + |\nabla|)\gamma_0(1 + |\nabla|) \cdot (1 + |\nabla|)^{-1}W(1 + |\nabla|)^{-1}) = \int_{\mathbb{R}^3} \rho_0^{\uparrow\uparrow} W \end{aligned} \quad (19)$$

and similarly for $\rho_0^{\downarrow\downarrow}$, $\text{Re}(\rho_0^{\uparrow\downarrow})$ and $\text{Im}(\rho_0^{\uparrow\downarrow})$. We deduce that $(\rho_n^{\alpha\beta})$ converges to $\rho_0^{\alpha\beta}$ in $\mathcal{D}'(\mathbb{R}^3, \mathbb{C})$ for all $\alpha, \beta \in \{\uparrow, \downarrow\}^2$. Identifying the limits, the convergences hold also weakly in $W^{1,3/2}(\mathbb{R}^3)$, strongly in $L_{\text{loc}}^p(\mathbb{R}^3)$ for $1 \leq p < 3$, and almost everywhere, in virtue of the Sobolev embedding theorem. From formula (16) and the pointwise convergence of $(\rho_n^{\alpha\beta})$ to $\rho_0^{\alpha\beta}$, we also deduce that $(\rho_n^{+/-})$ pointwise converges to $\rho_0^{+/-}$. Again, by identifying the limits, the convergence also holds weakly in $W^{1,3/2}(\mathbb{R}^3)$ and strongly in $L_{\text{loc}}^p(\mathbb{R}^3)$ for $1 \leq p < 3$.

Then, let $\chi \in \mathcal{C}_0^\infty(\mathbb{R})$ be a cut-off function such that $\chi(x) = 1$ if $|x| < 1$ and $\chi(x) = 0$ if $x \geq 2$. We take $W_A = \chi(x/A)$ in (19), and let A go to infinity to obtain that

$$\rho_0^{\uparrow\uparrow} \in L^1(\mathbb{R}^3) \quad \text{and} \quad \int_{\mathbb{R}^3} \rho_0^{\uparrow\uparrow} \leq \liminf_{n \rightarrow \infty} \int_{\mathbb{R}^3} \rho_n^{\uparrow\uparrow}, \quad (20)$$

and similarly for $\rho_0^{\downarrow\downarrow}$. Now, if $\gamma_n \in \mathcal{P}_\lambda$ and $\gamma_0 \in \mathcal{P}_\lambda$, we get

$$\lambda = \int_{\mathbb{R}^3} \rho_0 = \int_{\mathbb{R}^3} \rho_0^{\uparrow\uparrow} + \rho_0^{\downarrow\downarrow} \leq \int_{\mathbb{R}^3} \rho_n^{\uparrow\uparrow} + \rho_n^{\downarrow\downarrow} = \lambda,$$

and the inequality (20) is an equality. Therefore, (ρ_n) converges to ρ_0 strongly in $L^1(\mathbb{R}^3)$. We deduce from (17) and $0 \leq \rho_n^{+/-} \leq \rho_n$ that $\rho_n^{\uparrow\downarrow}$ and $\rho_n^{+/-}$ are bounded in $L^1(\mathbb{R}^3)$. A classical application of the dominated convergence theorem then leads to the fact that $\rho_n^{\alpha\beta}$ converges to $\rho_0^{\alpha\beta}$ strongly in $L^1(\mathbb{R}^3)$ for $\alpha, \beta \in \{\uparrow, \downarrow\}^2$, and that $\rho_n^{+/-}$ converges strongly to $\rho_0^{+/-}$ in $L^1(\mathbb{R}^3)$. Finally, the strong convergence still holds in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$ according to the Hölder inequality.

The proof for the energy is similar to the one in [1, Lemma 3]. We do not repeat it here, but notice that the strong convergence of $(\rho_n^{+/-})$ to $\rho_0^{+/-}$ in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$ is needed for the convergence of the exchange-correlation functional. \square

Proof of Lemma 5.

(ii) Let us first prove that for $0 < \mu < \lambda$, it holds that $I_\lambda \leq I_\mu + I_{\lambda-\mu}^\infty$. Let $\varepsilon > 0$, $\gamma \in \mathcal{P}_\mu$ and $\gamma' \in \mathcal{P}_{\lambda-\mu}$ be such that $I_\mu \leq \mathcal{E}(\gamma) \leq I_\mu + \varepsilon$ and $I_{\lambda-\mu}^\infty \leq \mathcal{E}^\infty(\gamma') \leq I_{\lambda-\mu}^\infty + \varepsilon$. By density of finite-rank one-body density matrices in \mathcal{B} , and density of $\mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{C}^2)$ in $H^1(\mathbb{R}^3, \mathbb{C}^2)$, we can assume that γ and γ' are both of the form

$$\gamma^{(\prime)} = \sum_{i=1}^M n_k^{(\prime)} |\Phi_k^{(\prime)}\rangle \langle \Phi_k^{(\prime)}| \quad \text{with} \quad \Phi_k^{(\prime)} \in \mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{C}^2).$$

We consider $\gamma_n := \gamma + \tau_{n\mathbf{e}}\gamma'\tau_{-n\mathbf{e}}$ and $\gamma_n^\# := \gamma + \tau_{n\mathbf{e}}\tilde{\gamma}'\tau_{-n\mathbf{e}}$ where $\tau_{\mathbf{x}}f(\mathbf{r}) = f(\mathbf{r} - \mathbf{x})$, and \mathbf{e} is a non-null vector. We recall that $\tilde{\gamma}'$ is the flipped transformation of γ' , as introduced in (12). For n_0 large enough, and for $n \geq n_0$, the supports of the Φ_k 's and of the $\tau_{n\mathbf{e}}\Phi_k'$'s are disjoint, so that γ_n and $\gamma_n^\#$ are in \mathcal{P}_λ for all $n \geq n_0$. Also, for n large enough, $J(\rho_n) \leq J(\rho) + J(\rho') + \varepsilon$. Altogether, we get, for n large enough,

$$\begin{aligned} \mathcal{E}(\gamma_n) + \mathcal{E}(\gamma_n^\#) &= 2\mathcal{E}(\gamma) + 2\mathcal{E}^\infty(\gamma') + 2 \int V\rho'(\cdot - n\mathbf{e}) + 2\varepsilon \leq 2\mathcal{E}(\gamma) + 2\mathcal{E}^\infty(\gamma') + 2\varepsilon \\ &\leq 2I_\mu + 2I_{\lambda-\mu}^\infty + 6\varepsilon. \end{aligned}$$

Hence, either $\mathcal{E}(\gamma_n)$ or $\mathcal{E}(\gamma_n^\#)$ is smaller than $I_\mu + I_{\lambda-\mu}^\infty + 3\varepsilon$, and $I_\lambda \leq I_\mu + I_{\lambda-\mu}^\infty$. Similar arguments show that $I_\lambda^\infty \leq I_\mu^\infty + I_{\lambda-\mu}^\infty$.

(i) We first prove that there exists λ_0 small enough such that for all $0 < \lambda \leq \lambda_0$, $I_\lambda^\infty < 0$. We use a scaling argument. Let $\phi \in \mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{C})$ be such that $\|\phi\|_{L^2} = 1$, and let $\phi_\sigma = \sigma^{3/2}\phi(\sigma\cdot)$ for $\sigma > 0$. Note that $\|\phi_\sigma\|_{L^2} = 1$. For $\lambda \leq 1$, we introduce

$$\gamma_{\lambda\sigma}(\mathbf{r}, \mathbf{r}') = \lambda \begin{pmatrix} \phi_\sigma(\mathbf{r})\overline{\phi_\sigma(\mathbf{r}')} & 0 \\ 0 & 0 \end{pmatrix}$$

so that $\gamma_{\lambda\sigma} \in \mathcal{P}_\lambda$ for all $0 < \lambda \leq 1$ and $\sigma > 0$. Using (11), there exists $1 \leq \alpha < 3/2$ such that $E_{\text{xc}}^{\text{LSDA}}(\lambda|\phi_\sigma|^2, 0) \leq -C\lambda^\alpha\sigma^{3(\alpha-1)}\|\phi\|_{L^{2\alpha}}^{2\alpha}$. Direct calculations lead to

$$\begin{aligned} \mathcal{E}^\infty(\gamma_{\lambda\sigma}) &= \frac{\lambda\sigma^2}{2} \int_{\mathbb{R}^3} |\nabla\phi|^2 + \lambda^2\sigma J(|\phi|^2) + \int_{\mathbb{R}^3} E_{\text{xc}}^{\text{LSDA}}(|\phi_{\lambda\sigma}|^2, 0) \\ &\leq \frac{\lambda\sigma^2}{2} \int_{\mathbb{R}^3} |\nabla\phi|^2 + \lambda^2\sigma J(|\phi|^2) - C\lambda^\alpha\sigma^{3(\alpha-1)}\|\phi\|_{L^{2\alpha}}^{2\alpha}. \end{aligned}$$

It is easy to check that under the condition $\alpha < 3/2$, there exists $\lambda_0 > 0$ such that for all $0 < \lambda \leq \lambda_0$, there exists σ such that $\mathcal{E}(\gamma_{\lambda\sigma}) < 0$. In particular, $I_\lambda^\infty \leq \mathcal{E}^\infty(\gamma_{\lambda\sigma}) < 0$. Together with (ii), we deduce that, for all $\lambda > 0$, $I_\lambda^\infty < 0$ and $I_\lambda < 0$.

We now prove that $I_\lambda < I_\lambda^\infty$, for all $\lambda > 0$. Let (γ_n) be a minimizing sequence for I_λ^∞ . We first suppose that

$$\forall A > 0, \quad \lim_{n \rightarrow \infty} \sup_{x \in \mathbb{R}^3} \int_{x+B_A} \rho_n = 0,$$

where B_A is the ball of radius A centered at the origin. Because (ρ_n) is bounded in $W^{1,3/2}$ according to Lemma 2 and 3, we deduce from [4, Lemma I.1] that (ρ_n) converges to 0 strongly in $L^p(\mathbb{R}^3)$ for $1 < p < 3$. Also, because of (17), the components of R_n and its eigenvalues converge to 0 strongly in $L^p(\mathbb{R}^3)$ for $1 < p < 3$. Similarly to [1], we deduce that

$$I_\lambda^\infty = \liminf_{n \rightarrow \infty} \mathcal{E}^\infty(\gamma_n) = \liminf_{n \rightarrow \infty} \left\{ \frac{1}{2} \text{Tr}(-\Delta \gamma_n) + J(\rho_n) + E_{\text{xc}}^{\text{LSDA}}(\rho_n^+, \rho_n^-) \right\} = \liminf_{n \rightarrow \infty} \frac{1}{2} \text{Tr}(-\Delta \gamma_n) \geq 0$$

which contradicts the first point. Therefore

$$\exists A, \eta > 0, \quad \forall n \in \mathbb{N}, \quad \exists x_n \in \mathbb{R}^3, \quad \int_{x_n + B_A} \rho_n \geq \eta. \quad (21)$$

Up to translations of the γ_n 's, we can assume without loss of generality that $x_n = 0$.

We now introduce $\tilde{\gamma}_n$, the flipped version of γ_n introduced in (12). Using (13) and the fact that $V(\mathbf{r}) \leq -\frac{z_1}{r}$, we get

$$\begin{aligned} \mathcal{E}(\gamma_n) + \mathcal{E}(\tilde{\gamma}_n) &= \text{Tr}(-\Delta \gamma_n) + 2J(\rho_n) + 2E_{\text{xc}}^{\text{LSDA}}(\rho_n^+, \rho_n^-) + 2 \int_{\mathbb{R}^3} V \rho_n \\ &= 2\mathcal{E}^\infty(\gamma_n) + 2 \int_{\mathbb{R}^3} V \rho_n \leq 2\mathcal{E}^\infty(\gamma_n) - 2 \int_{B_R} \frac{z_1}{|\mathbf{r}|} \rho_n \leq 2\mathcal{E}^\infty(\gamma_n) - 2 \frac{z_1}{R} \eta. \end{aligned}$$

Hence, either $\mathcal{E}(\gamma_n)$ or $\mathcal{E}(\tilde{\gamma}_n)$ is smaller than $\mathcal{E}^\infty(\gamma_n) - z_1 R^{-1} \eta$. Therefore, $I_\lambda \leq I_\lambda^\infty - z_1 R^{-1} \eta < I_\lambda^\infty$.

(iii) The fact that $\lambda \mapsto I_\lambda$ and $\lambda \mapsto I_\lambda^\infty$ are non increasing can be read from the other statements. □

Proof of Lemma 6.

Let $\lambda > 0$, and let $(\gamma_n)_{n \in \mathbb{N}^*} \in \mathcal{P}_\lambda$ be a minimizing sequence for I_λ . According to Lemma 2, up to a subsequence, we can assume that (γ_n) converges to some $\gamma_0 \in \mathcal{B}$ for the weak-* topology of \mathcal{B} .

(i) The fact that $\alpha \leq \lambda$ can be directly deduced from (20).

(ii) Suppose that $\alpha = 0$, so that $\gamma = 0$. Then, we have $I_\lambda = \liminf \mathcal{E}(\gamma_n) = \mathcal{E}(\gamma_0) = 0$ (we used the continuity of \mathcal{E} , which can be proved similarly to [1]). This contradicts the first point of Lemma 5. Hence, $\alpha \neq 0$.

(iii) Suppose that $0 < \alpha < \lambda$. Following [1, 27], we let $\chi, \xi \in \mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{R}^+)$ be radial functions such that $\chi^2 + \xi^2 = 1$, with $\chi(0) = 1$, $\chi < 1$ on $\mathbb{R}^3 \setminus \{0\}$, $\chi(x) = 0$ for $|x| > 1$, $\|\nabla \chi\|_{L^\infty} \leq 2$ and $\|\nabla \xi\|_{L^\infty} \leq 2$. We introduce $\chi_A(x) := \chi(x/A)$ and $\xi_A(x) := \xi(x/A)$ and finally $\gamma_{n,A} := \chi_A \gamma_n \chi_A$. With those notations, $A \mapsto \text{Tr}(\gamma_{n,A})$ is a continuous and increasing function from 0 to λ . Therefore, there exists A_n such that γ_{n,A_n} is in \mathcal{P}_α .

The sequence (A_n) goes to infinity. Otherwise, we would have for A large enough and according to (20),

$$\int_{\mathbb{R}^3} \rho_0 \chi_A^2 = \lim_{n \rightarrow \infty} \int_{\mathbb{R}^3} \rho_n \chi_A^2 \geq \lim_{n \rightarrow \infty} \int_{\mathbb{R}^3} \rho_n \chi_{A_n}^2 = \alpha = \int_{\mathbb{R}^3} \rho_0$$

which is impossible, for $|\chi_A^2| < 1$ on \mathbb{R}^3 .

We introduce $\gamma_{1,n} := \chi_{A_n} \gamma_n \chi_{A_n}$ and $\gamma_{2,n} := \xi_{A_n} \gamma_n \xi_{A_n}$. Note that $\gamma_{1,n} \in \mathcal{P}_\alpha$ and $\gamma_{2,n} \in \mathcal{P}_{\lambda-\alpha}$, and that $\rho_n = \rho_{1,n} + \rho_{2,n}$. From the decomposition (7) of γ_n : $\gamma_n = \sum_{k=1}^\infty n_{k,n} |\Phi_{k,n}\rangle \langle \Phi_{k,n}|$, $0 \leq n_{k,n} \leq 1$, we deduce that

$$\text{Tr}(|\nabla| \gamma_{1,n} |\nabla|) + \text{Tr}(|\nabla| \gamma_{2,n} |\nabla|) \leq \text{Tr}(|\nabla| \gamma_n |\nabla|) + 8 \frac{\lambda}{A_n^2}.$$

Hence, $(\gamma_{1,n})$ and $(\gamma_{2,n})$ are bounded in \mathcal{B} . Also, direct calculations lead to

$$\mathrm{Tr}(-\Delta\gamma_{1,n}) + \mathrm{Tr}(-\Delta\gamma_{2,n}) \leq \mathrm{Tr}(-\Delta\gamma_n) + 8\frac{\lambda}{A_n^2}. \quad (22)$$

According to Lemma 2, up to a subsequence, $(\gamma_{1,n})$ converges for the weak-* topology of \mathcal{B} . In this case, for $\Phi = (\phi^\uparrow, \phi^\downarrow) \in \mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{C}^2)$, it holds that

$$\mathrm{Tr}(\gamma_{1,n}|\Phi\rangle\langle\Phi|) = \int_{\mathbb{R}^3} \rho_{1,n}^{\uparrow\uparrow} |\phi^\uparrow|^2 + \int_{\mathbb{R}^3} \rho_{1,n}^{\downarrow\downarrow} |\phi^\downarrow|^2 = \int_{\mathbb{R}^3} \chi_{A_n}^2 \rho_n^{\uparrow\uparrow} |\phi^\uparrow|^2 + \int_{\mathbb{R}^3} \chi_{A_n}^2 \rho_n^{\downarrow\downarrow} |\phi^\downarrow|^2.$$

For n large enough, the support of Φ is inside the support of χ_{A_n} , and

$$\mathrm{Tr}(\gamma_{1,n}|\Phi\rangle\langle\Phi|) = \mathrm{Tr}(\gamma_n|\chi_{A_n}\Phi\rangle\langle\chi_{A_n}\Phi|) \xrightarrow{n \rightarrow \infty} \mathrm{Tr}(\gamma|\Phi\rangle\langle\Phi|).$$

We deduce that $(\gamma_{1,n})$ converges to γ_0 for the weak-* topology of \mathcal{B} . Finally, because $\gamma_{1,n} \in \mathcal{P}_\alpha$ and $\gamma_0 \in \mathcal{P}_\alpha$, $\rho_{1,n}$ converges strongly to ρ_0 in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$, and $\mathcal{E}(\gamma_0) \leq \liminf \mathcal{E}(\gamma_{1,n})$ according to Lemma 3.

Let us look more closely to $\gamma_{2,n}$. Because $(\rho_{1,n})$ converges to ρ_0 strongly in $L^p(\mathbb{R}^3)$ and (ρ_n) converges to ρ_0 strongly in $L_{\mathrm{loc}}^p(\mathbb{R}^3)$ for $1 \leq p < 3$, we obtain that $\rho_{2,n} = \rho_n - \rho_{1,n}$ (and thus all the components of $R_{2,n}$ and its eigenvalues) converges strongly to 0 in $L_{\mathrm{loc}}^p(\mathbb{R}^3)$ for $1 \leq p < 3$. Also, it holds that $\rho_{1,n}^{+/-} + \rho_{2,n}^{+/-} = \rho_n^{+/-}$. Using (22) and the fact that $\iint \rho_{1,n}(\mathbf{r})\rho_{2,n}(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-1} d^3\mathbf{r} d^3\mathbf{r}' \geq 0$, we obtain

$$\begin{aligned} \mathcal{E}(\gamma_n) &= \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_n) + J(\rho_n) + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} [UR_n] + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_n^+, \rho_n^-) \\ &\geq \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_{1,n}) + \frac{1}{2}\mathrm{Tr}(-\Delta\gamma_{2,n}) - 4\frac{\lambda}{A_n^2} + J(\rho_{1,n}) + J(\rho_{2,n}) + \\ &+ \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} [UR_{1,n}] + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} [UR_{2,n}] + E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+ + \rho_{2,n}^+, \rho_{1,n}^- + \rho_{2,n}^-) \\ &\geq \mathcal{E}(\gamma_{1,n}) + \mathcal{E}^\infty(\gamma_{2,n}) - 4\frac{\lambda}{A_n^2} + \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} [UR_{2,n}] + \\ &+ E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+ + \rho_{2,n}^+, \rho_{1,n}^- + \rho_{2,n}^-) - E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{1,n}^+, \rho_{1,n}^-) - E_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{2,n}^+, \rho_{2,n}^-). \end{aligned}$$

We first consider the term $\int \mathrm{tr}_{\mathbb{C}^2} [UR_{2,n}]$. We have for $A \geq 0$, (we use, for a matrix M , the notation $|M|$ for the sum of the absolute values of the entries of M)

$$\begin{aligned} \left| \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} [UR_{2,n}] \right| &= \left| \int_{B_A} \mathrm{tr}_{\mathbb{C}^2} [UR_{2,n}] \right| + \left| \int_{(B_A)^c} \mathrm{tr}_{\mathbb{C}^2} [UR_{2,n}] \right| \\ &\leq \|U\|_{L^{\frac{3}{2}+\epsilon} + L^\infty(B_A)} \|R_{2,n}\|_{L^1 \cap L^{3-\epsilon'}(B_A)} + \sup_{x \in (B_A)^c} |U(x)| \int_{(B_A)^c} |R_{2,n}| \\ &\leq \|U\|_{L^{\frac{3}{2}+\epsilon} + L^\infty(\mathbb{R}^3)} \|R_{2,n}\|_{L^1 \cap L^{3-\epsilon'}(B_A)} + \sup_{x \in (B_A)^c} |U(x)| \int_{\mathbb{R}^3} |R_{2,n}|, \end{aligned}$$

where $\epsilon' = 4\epsilon/(1+2\epsilon) > 0$ is chosen such that $L^{3-\epsilon'}$ is the dual space of $L^{\frac{3}{2}+\epsilon}$. Using inequality (17), and the fact that $\int \rho_{2,n}^{\alpha\beta} \leq \lambda$, we get an inequality of the form

$$\left| \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} [UR_{2,n}] \right| \leq C_1 \|R_{2,n}\|_{L^1 \cap L^{3-\epsilon'}(B_A)} + C_2 \sup_{x \in (B_A)^c} |U(x)|$$

with C_1 and C_2 independent of A and n . Because all entries of U are vanishing at infinity, we can first choose A large enough to control the second term, and then use the convergence of $R_{2,n}$ to 0

strongly in $L^p(B_A)$ for $1 \leq p < 3$, to establish the convergence of the right-hand-side to 0. For the last term, using (11), it holds (we write $g_2(\rho) = g(2\rho)$)

$$\begin{aligned} & E_{\text{xc}}^{\text{LSDA}}(\rho_{1,n}^+ + \rho_{2,n}^+, \rho_{1,n}^- + \rho_{2,n}^-) - E_{\text{xc}}^{\text{LSDA}}(\rho_{1,n}^+, \rho_{1,n}^-) - E_{\text{xc}}^{\text{LSDA}}(\rho_{2,n}^+, \rho_{2,n}^-) = \\ & \frac{1}{2} \left[\int_{\mathbb{R}^3} (g_2(\rho_{1,n}^+ + \rho_{2,n}^+) - g_2(\rho_{1,n}^+) - g_2(\rho_{2,n}^+)) + \int_{\mathbb{R}^3} (g_2(\rho_{1,n}^- + \rho_{2,n}^-) - g_2(\rho_{1,n}^-) - g_2(\rho_{2,n}^-)) \right]. \end{aligned} \quad (23)$$

Then, we get (dropping the super-script $+/-$ for the sake of clarity)

$$\begin{aligned} & \left| \int_{\mathbb{R}^3} g_2(\rho_{1,n} + \rho_{2,n}) - g_2(\rho_{1,n}) - g_2(\rho_{2,n}) \right| \\ & \leq \int_{B_A} |g_2(\rho_{1,n} + \rho_{2,n}) - g_2(\rho_{1,n})| + \int_{B_A} |g_2(\rho_{2,n})| + \\ & \quad + \int_{(B_A)^c} |g_2(\rho_{1,n} + \rho_{2,n}) - g_2(\rho_{2,n})| + \int_{(B_A)^c} |g_2(\rho_{2,n})| \\ & \leq C \left(\int_{B_A} \rho_{2,n} (\rho_n^{p^+} + \rho_n^{p^-}) + \int_{B_A} ((\rho_{2,n})^{p^-} + (\rho_{2,n})^{p^+}) \right) \\ & \quad + C \left(\int_{(B_A)^c} \rho_{1,n} (\rho_n^{p^+} + \rho_n^{p^-}) + \int_{(B_A)^c} ((\rho_{1,n})^{p^-} + (\rho_{1,n})^{p^+}) \right). \end{aligned}$$

We recall that $p^{+/-} = 1 + \beta^{+/-} < 5/3$. Because $(\rho_{1,n})$ and (ρ_n) are bounded in $L^p(\mathbb{R}^3)$ for $1 \leq p < 3$, and because $(\rho_{2,n})$ converges to 0 in $L_{\text{loc}}^p(\mathbb{R}^3)$ for $1 \leq p < 3$, we deduce that (23) goes to 0 when n goes to infinity (first take A large enough, then n large enough, as before). Altogether, for $\epsilon > 0$, for n large enough,

$$\mathcal{E}(\gamma_n) \geq \mathcal{E}(\gamma_{1,n}) + \mathcal{E}^\infty(\gamma_{2,n}) - 3\epsilon \geq I_\alpha + I_{\lambda-\alpha}^\infty - 3\epsilon.$$

Therefore, $\mathcal{E}(\gamma_n) \geq I_\alpha + I_{\lambda-\alpha}^\infty$, and $I_\lambda \geq I_\alpha + I_{\lambda-\alpha}^\infty$. The second point of Lemma 5 states that $I_\lambda \leq I_\alpha + I_{\lambda-\alpha}^\infty$. Hence $I_\lambda = I_\alpha + I_{\lambda-\alpha}^\infty$, and $(\gamma_{2,n})$ is a minimizing sequence for $I_{\lambda-\alpha}^\infty$.

As in the proof of Lemma 5, it holds (21):

$$\exists A, \eta > 0, \quad \forall n \in \mathbb{N}, \quad \exists x_n \in \mathbb{R}^3, \quad \int_{x_n + B_A} \rho_{2,n} \geq \eta.$$

We let $\gamma'_{2,n} = \tau_{x_n} \gamma_{2,n} \tau_{-x_n}$. Then, $(\gamma_{2,n})$ is bounded for the weak-* topology of \mathcal{B} , and converges, up to a subsequence, to some γ'_0 satisfying $\text{Tr}(\gamma'_0) \geq \eta$. Let $\beta := \text{Tr}(\gamma'_0)$. We can repeat the same arguments as before and truncate $\gamma'_{2,n}$ to ensure that $\text{Tr}(\chi_{A_n} \gamma_{2,n} \chi_{A_n}) = \beta$. We deduce as before that γ'_0 is a minimizer for I_β^∞ , and that $I_\lambda = I_\alpha + I_\beta^\infty + I_{\lambda-\alpha-\beta}^\infty$. \square

Proof of Lemma 7.

Let us first derive the expression of H_{γ_0} . Suppose that $\gamma_0 \in \mathcal{P}_\lambda$ is a minimizer for I_λ . Then for $\gamma \in \mathcal{P}_\lambda$ and $0 \leq t \leq 1$, it holds $\mathcal{E}(t\gamma + (1-t)\gamma_0) \geq \mathcal{E}(\gamma_0)$. In particular, one must have

$$\left. \frac{\partial \mathcal{E}(t\gamma + (1-t)\gamma_0)}{\partial t} \right|_{t=0} \geq 0. \quad (24)$$

To perform the calculations, we use the explicit formula (16) for $\rho^{+/-}$, and get

$$\begin{aligned} & \left. \frac{\partial (t\rho + (1-t)\rho_0)^{+/-}}{\partial t} \right|_{t=0} = \\ & \frac{1}{2} \text{tr}_{\mathbb{C}^2} \left(\left(\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \pm \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}} \begin{pmatrix} \rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow} \\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow} \end{pmatrix} \right) (R - R_0) \right). \end{aligned}$$

Similarly to [1, 28], we conclude that

$$\frac{\partial \mathcal{E}(t\gamma + (1-t)\gamma_0)}{\partial t} \Big|_{t=0} = \text{Tr} (H_{\gamma_0}(\gamma - \gamma_0))$$

with

$$\begin{aligned} H_{\gamma_0} &= \left(-\frac{1}{2}\Delta + \rho_0 \star |\cdot|^{-1} \right) \mathbb{I}_2 + U \\ &+ \frac{g'(\rho_0^+)}{2} \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}} \begin{pmatrix} \rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow} \\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow} \end{pmatrix} \right] \\ &+ \frac{g'(\rho_0^-)}{2} \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}} \begin{pmatrix} \rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow} \\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow} \end{pmatrix} \right]. \end{aligned} \quad (25)$$

Using (24), we deduce that $\gamma_0 \in \text{arginf}\{\text{Tr} (H_{\gamma_0}\gamma), \gamma \in \mathcal{P}_\lambda\}$. Finally,

$$\gamma_0 = \mathbb{1}_{(-\infty, \epsilon_F)}(H_{\gamma_0}) + \delta \quad \text{with} \quad \delta \subset \text{Ker}(H_{\gamma_0} - \epsilon_F),$$

where ϵ_F is the Fermi energy, determined by the condition $\text{Tr}(\gamma_0) = \lambda$.

Let us first calculate the essential spectrum of H_{γ_0} . We recall that $H_0 = -\frac{1}{2}\Delta\mathbb{I}_2$ has domain $H^2(\mathbb{R}^3, \mathbb{C}^2)$ and that if $u \in H^2(\mathbb{R}^3, \mathbb{C})$, then u vanishes at infinity. We also recall that for all $V \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2) + L^\infty_\epsilon(\mathbb{R}^3, \mathbb{C}^2)$, the set of functions V that can be written $V = V_{3/2} + V_\infty$ with $V_{3/2} \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2)$, $V_\infty \in L^\infty(\mathbb{R}^3)$ and $\|V_\infty\|_{L^\infty}$ arbitrary small, V is a compact perturbation of H_0 . In our case, we can easily check that $\rho_0 \star \widehat{|\cdot|^{-1}} = \widehat{\rho_0} |\cdot|^{-2} \in L^1(\mathbb{R}^3)$, so that $\rho_0 \star |\cdot|^{-1}$ vanishes at infinity. Altogether,

- $\rho_0 \star |\cdot|^{-1} \in L^{3/2}(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$
- $U \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2) + L^\infty(\mathbb{R}^3, \mathbb{C}^2)$ and all entries of U vanishes at infinity
- $|g'(\rho_0^{+/-})| \leq C(\rho_0^{\beta^-} + \rho_0^{\beta^+})$ hence $g'(\rho_0^{+/-}) \in L^{3/2}(\mathbb{R}^3, \mathbb{C}^2)$.

Therefore, according to the Weyl's theorem, the domain of H_{γ_0} is $H^2(\mathbb{R}^3, \mathbb{C}^2)$, and $\sigma_{\text{ess}}(H_{\gamma_0}) = \sigma_{\text{ess}}(H_0) = [0, +\infty[$.

Let us now prove that H_{γ_0} has infinitely many negative eigenvalues whenever $\lambda < Z$. First notice that the matrix

$$\frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}} \begin{pmatrix} \rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow} \\ 2\rho_0^{\downarrow\uparrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow} \end{pmatrix}$$

has two eigenvalues, respectively -1 and 1 , so that the matrices appearing into the two pairs of brackets in (25) have 0 and 2 as eigenvalues, and therefore are hermitian positive. Also, recall that under the conditions (11) on g , it holds $g' \leq 0$. Altogether, for $\psi \in \mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{C})$, $\Psi = (\psi, \psi)^T \in \mathcal{C}_0^\infty(\mathbb{R}^3, \mathbb{C}^2)$, and $\tilde{\Psi}$ defined as in (12), it holds that

$$\begin{aligned} \langle \Psi | H_{\gamma_0} | \Psi \rangle + \langle \tilde{\Psi} | H_{\gamma_0} | \tilde{\Psi} \rangle &\leq \left\langle \Psi \left| \left(\left(-\frac{1}{2}\Delta + \rho_0 \star |\cdot|^{-1} \right) \mathbb{I}_2 + U \right) \right| \Psi \right\rangle \\ &\quad + \left\langle \tilde{\Psi} \left| \left(\left(-\frac{1}{2}\Delta + \rho_0 \star |\cdot|^{-1} \right) \mathbb{I}_2 + U \right) \right| \tilde{\Psi} \right\rangle \\ &\leq 4 \left\langle \psi \left| -\frac{1}{2}\Delta + \rho_0 \star |\cdot|^{-1} + V \right| \psi \right\rangle = \langle \psi | H_1 | \psi \rangle_1 \end{aligned}$$

where $H_1 := -\frac{1}{2}\Delta + \rho_0 \star |\cdot|^{-1} + V$ acts on $L^2(\mathbb{R}^3, \mathbb{C})$, and V is defined in (1). We used the subscript 1 to emphasize that $\langle \cdot | \cdot \rangle_1$ is the scalar product on $L^2(\mathbb{R}^3, \mathbb{C})$, whereas $\langle \cdot | \cdot \rangle$ is the one on $L^2(\mathbb{R}^3, \mathbb{C}^2)$. In virtue of [29, Lemma 2.1], the operator H_1 has infinitely many negative eigenvalues of finite multiplicity whenever $\lambda < Z$. So has H_{γ_0} by the min-max principle. Eventually, $\epsilon_F < 0$, and

$$\gamma_0 = \sum_{i=1}^{N_1} |\Phi_i\rangle \langle \Phi_i| + \sum_{i=N_1+1}^{N_2} n_i |\Phi_i\rangle \langle \Phi_i| \quad \text{with} \quad \langle \Phi_i | \Phi_j \rangle = \delta_{ij} \quad \text{and} \quad H_{\gamma_0} \Phi_i = \epsilon_i \Phi_i.$$

It holds $\epsilon_i < \epsilon_F$ if $i \leq N_1$, and $\epsilon_i = \epsilon_F$ if $N_1 + 1 \leq i \leq N_2$. In the following, we set $n_i := 1$ for $i \leq N_1$.

Finally, we prove that all eigenvectors associated with negative eigenvalues are exponentially decreasing. Any function u satisfying $H_{\gamma_0} u = \lambda u$ is in $H^2(\mathbb{R}^3, \mathbb{C}^2)$, and each component of u vanishes at infinity. As a byproduct, we obtain that $\rho_0 = \sum_{i=1}^{N_2} n_i |\Phi_i|^2$ also vanishes at infinity. Finally, all the components of

$$U_{\gamma_0} := \rho_0 \star |\cdot|^{-1} \mathbb{I}_2 + U + \sum_{\delta=\pm/\mp} \frac{g'(\rho_0^\delta)}{2} \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + (-1)^\delta \frac{1}{\sqrt{(\rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow})^2 + 4|\rho_0^{\uparrow\downarrow}|^2}} \begin{pmatrix} \rho_0^{\uparrow\uparrow} - \rho_0^{\downarrow\downarrow} & 2\rho_0^{\uparrow\downarrow} \\ 2\rho_0^{\uparrow\downarrow} & \rho_0^{\downarrow\downarrow} - \rho_0^{\uparrow\uparrow} \end{pmatrix} \right]$$

vanish at infinity. Recall that $H_{\gamma_0} \Phi_i = -\frac{1}{2}\Delta \Phi_i + U_\gamma \Phi_i = \epsilon_i \Phi_i$. Multiplying this equation by Φ_i and adding all the terms with prefactors n_i , it holds that

$$\sum_{i=1}^{N_2} n_i \Phi_i^T \left(-\frac{1}{2}\Delta \right) \Phi_i + \sum_{i=1}^{N_2} n_i \Phi_i^T U_\gamma \Phi_i = \sum_{i=1}^{N_2} \epsilon_i n_i |\Phi_i|^2. \quad (26)$$

From the relation $\rho_0 = \sum_{i=1}^{N_2} n_i |\Phi_i|^2$, we get

$$\Delta \rho_0 = \sum_{i=1}^{N_2} 2n_i (\Phi_i^T (\Delta \Phi_i) + |\nabla \Phi_i|^2)$$

and (26) becomes

$$-\frac{\Delta}{4} \rho_0 + \underbrace{\sum_{i=1}^{N_2} \frac{n_i}{2} |\nabla \Phi_i|^2}_{\geq 0} + \sum_{i=1}^{N_2} n_i \Phi_i^T U_\gamma \Phi_i + \underbrace{\sum_{i=1}^{N_2} (\epsilon_F - \epsilon_i) n_i |\Phi_i|^2}_{\geq 0} - \epsilon_F \rho_0 = 0.$$

Let A be large enough such that, for all $\mathbf{r} \in \mathbb{R}^3$ with $|\mathbf{r}| \geq A$, the eigenvalues of the matrix $U_\gamma(\mathbf{r})$ are between $\frac{\epsilon_F}{2\lambda}$ and $-\frac{\epsilon_F}{2\lambda}$ (recall that $\epsilon_F < 0$). In particular, for $|\mathbf{r}| \geq A$, $|\Phi_i^T(\mathbf{r}) U_\gamma(\mathbf{r}) \Phi_i(\mathbf{r})| \leq -\frac{\epsilon_F}{2\lambda} |\Phi_i|^2$, and, on $(B_A)^c$,

$$-\frac{\Delta}{4} \rho_0 + \frac{\epsilon_F \lambda}{2\lambda} \rho_0 - \epsilon_F \rho_0 \leq 0 \quad \text{or} \quad -\frac{\Delta}{2} \rho_0 - \epsilon_F \rho_0 \leq 0.$$

We easily deduce that ρ_0 decreases exponentially. Hence, the same holds true for all the Φ_i 's with $1 \leq i \leq N_2$. A similar proof can be used for the remaining negative eigenvalues. \square

Proof of Lemma 8.

Let $\gamma_0 \in \mathcal{P}_\alpha$ be a minimizer for I_α , and $\gamma'_0 \in \mathcal{P}_\beta$ be a minimizer for I_β^∞ . According to the proof of Lemma 7, because $\alpha < \lambda$, γ_0 has the form

$$\gamma_0 = \sum_{i=1}^{N_2} n_i |\Phi_i\rangle \langle \Phi_i| \quad \text{with} \quad H_{\gamma_0} \Phi_i = \epsilon_i \Phi_i \quad \text{and} \quad \epsilon_i \leq \epsilon_F < 0.$$

We can derive a similar expression for γ'_0 :

$$\gamma'_0 = \sum_{i=1}^{\infty} n'_i |\Phi'_i\rangle \langle \Phi'_i| \quad \text{with} \quad H_{\gamma'_0}^{\infty} \Phi'_i = \epsilon_i \Phi'_i \quad \text{and} \quad \epsilon'_i \leq \epsilon'_F \leq 0, \quad (27)$$

where $H_{\gamma'_0}^{\infty}$ has a similar expression as $H_{\gamma'_0}$ in (25), without the U term. Note that in (27), we do not know whether $\epsilon'_F < 0$ or $\epsilon'_F = 0$.

First assume that $\epsilon'_F < 0$, so that Φ_i and Φ'_i are exponentially decreasing, and the sum in (27) is finite. We introduce $\gamma_n := \min\{1, \|\gamma_0 + \tau_n \gamma'_0 \tau_{-n}\|^{-1}\} (\gamma_0 + \tau_n \gamma'_0 \tau_{-n})$ and $\gamma_n^{\#} := \min\{1, \|\gamma_0 + \tau_n \tilde{\gamma}'_0 \tau_{-n}\|^{-1}\} (\gamma_0 + \tau_n \tilde{\gamma}'_0 \tau_{-n})$, where $\tilde{\gamma}'_0$ is the flipped transformation of γ'_0 , as defined in (12). Note that $\text{Tr}(\gamma_n) \leq \alpha + \beta$ and $\text{Tr}(\gamma_n^{\#}) \leq \alpha + \beta$, so that $I_{\alpha+\beta} \leq \mathcal{E}(\gamma_n)$ and $I_{\alpha+\beta} \leq \mathcal{E}(\gamma_n^{\#})$ according to the third assertion of Lemma 5. A straightforward calculation leads to

$$\begin{aligned} \mathcal{E}(\gamma_n) + \mathcal{E}(\gamma_n^{\#}) &= 2\mathcal{E}(\gamma_0) + 2\mathcal{E}^{\infty}(\tilde{\gamma}_0) - \frac{\beta(Z - \alpha)}{n} + O(e^{-\delta n}) \\ &= 2I_{\alpha} + 2I_{\beta}^{\infty} - \frac{\beta(Z - \alpha)}{n} + O(e^{-\delta n}). \end{aligned}$$

For n large enough, $-\beta(Z - \alpha)n^{-1} + O(e^{-\delta n})$ becomes negative. Hence, either $\mathcal{E}(\gamma_n)$ or $\mathcal{E}(\gamma_n^{\#})$ is strictly less than $I_{\alpha} + I_{\beta}^{\infty}$. Therefore, $I_{\alpha+\beta} < I_{\alpha} + I_{\beta}^{\infty}$.

Let us now assume that $\epsilon'_F = 0$. Then, there exists $\Psi \in H^2(\mathbb{R}^3, \mathbb{C}^2)$ such that $\|\Psi\|_{L^2} = 1$, $H_{\gamma'_0}^{\infty} \Psi = 0$ and $\gamma'_0 \Psi = \mu \Psi$ with $\mu > 0$. Then, for $0 < \eta < \mu$, we introduce $\gamma_{\eta} = \gamma_0 + \eta |\Phi_{N_2+1}\rangle \langle \Phi_{N_2+1}|$ and $\gamma'_{\eta} = \gamma'_0 - \eta |\Psi\rangle \langle \Psi|$, so that $\gamma_{\eta} \in \mathcal{P}_{\alpha+\eta}$ and $\gamma'_{\eta} \in \mathcal{P}_{\beta-\eta}$. Moreover,

$$\mathcal{E}(\gamma_{\eta}) = \mathcal{E}(\gamma_0) + 2\eta \epsilon_{N_2+1} + o(\eta) = I_{\alpha} + 2\eta \epsilon_{N_2+1} + o(\eta)$$

and

$$\mathcal{E}^{\infty}(\gamma'_{\eta}) = \mathcal{E}^{\infty}(\gamma'_0) + o(\eta) = I_{\beta}^{\infty} + o(\eta).$$

Using the facts that $\gamma_0 + \eta |\Phi_{N_2+1}\rangle \langle \Phi_{N_2+1}| \in \mathcal{P}_{\alpha+\eta}$ and $\gamma'_0 - \eta |\Psi\rangle \langle \Psi| \in \mathcal{P}_{\beta-\eta}$, it holds that

$$I_{\alpha+\beta} \leq I_{\alpha+\eta} + I_{\beta-\eta}^{\infty} \leq \mathcal{E}(\gamma_{\eta}) + \mathcal{E}^{\infty}(\gamma'_{\eta}) \leq I_{\alpha} + I_{\beta}^{\infty} + 2\eta \epsilon_{N_2+1} + o(\eta).$$

Because $\epsilon_{N_2+1} < 0$, for η small enough, the left hand side is strictly less than $I_{\alpha} + I_{\beta}^{\infty}$, which concludes the proof. \square

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