

MINIMIZERS FOR OPEN-SHELL, SPIN-POLARISED KOHN-SHAM EQUATIONS FOR NON-RELATIVISTIC AND QUASI-RELATIVISTIC MOLECULAR SYSTEMS*

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Abstract. We study the open-shell, spin-polarized Kohn-Sham models for non-relativistic and quasi-relativistic N -electron Coulomb systems, that is, systems where the kinetic energy of the electrons is given by either the non-relativistic operator $-\Delta_{x_n}$ or the quasi-relativistic operator $\sqrt{-\alpha^{-2}\Delta_{x_n} + \alpha^{-4}} - \alpha^{-2}$. For standard and extended Kohn-Sham models in the local density approximation, we prove existence of a ground state (or minimizer) provided that the total charge Z_{tot} of K nuclei is greater than $N - 1$. For the quasi-relativistic setting we also need that Z_{tot} is smaller than a critical charge $Z_c = 2\alpha^{-1}\pi^{-1}$.

Key words. open-shell, spin-polarised Kohn-Sham equations, ground state, variational methods, concentration-compactness.

AMS subject classifications. Primary 35J60; Secondary 47J10, 58Z05, 81V55.

1. Introduction. Nowadays the Density Functional Theory (DFT) of Kohn and Sham [20, 22, 31, 35] is the most widely-used method of electronic structure calculation in both quantum chemistry and condensed matter physics. For spin-polarised molecular systems with N^\uparrow electrons with spin up and N^\downarrow electrons with spin down, we establish existence of a ground state (or minimizer) for the non-relativistic Kohn-Sham problem given by

$$\begin{aligned}
 I_{N^\uparrow, N^\downarrow}^{\text{SPKS}}(V) = \inf \left\{ \sum_{n=1}^{N^\uparrow} \int_{\mathbb{R}^3} |\nabla \phi_n^\uparrow(\mathbf{r})|^2 d\mathbf{r} + \sum_{n=1}^{N^\downarrow} \int_{\mathbb{R}^3} |\nabla \phi_n^\downarrow(\mathbf{r})|^2 d\mathbf{r} \right. \\
 \left. + \int_{\mathbb{R}^3} V(\mathbf{r})(\rho_{\Phi^\uparrow} + \rho_{\Phi^\downarrow})(\mathbf{r}) d\mathbf{r} + \mathcal{J}(\rho_{\Phi^\uparrow} + \rho_{\Phi^\downarrow}, \rho_{\Phi^\uparrow} + \rho_{\Phi^\downarrow}) \right. \\
 \left. + E_{\text{xc}}[\rho_{\Phi^\uparrow}] + E_{\text{xc}}[\rho_{\Phi^\downarrow}] : \rho_{\Phi^\#} = \sum_{n=1}^{N^\#} |\phi_n^\#|^2, \quad \Phi^\# \in \mathcal{C}_{N^\#}, \quad \# = \uparrow, \downarrow \right\}
 \end{aligned} \tag{1.1}$$

and for the quasi-relativistic Kohn-Sham problem given by

$$\begin{aligned}
 I_{N^\uparrow, N^\downarrow}^{\text{QRSPKS}}(V) = \inf \left\{ \alpha^{-1} \sum_{n=1}^{N^\uparrow} \int_{\mathbb{R}^3} \left(|T_0^{1/2} \phi_n^\uparrow(\mathbf{r})|^2 - |\phi_n^\uparrow(\mathbf{r})|^2 \right) d\mathbf{r} \right. \\
 \left. + \alpha^{-1} \sum_{n=1}^{N^\downarrow} \int_{\mathbb{R}^3} \left(|T_0^{1/2} \phi_n^\downarrow(\mathbf{r})|^2 - |\phi_n^\downarrow(\mathbf{r})|^2 \right) d\mathbf{r} \right. \\
 \left. + \int_{\mathbb{R}^3} V(\mathbf{r})(\rho_{\Phi^\uparrow} + \rho_{\Phi^\downarrow})(\mathbf{r}) d\mathbf{r} + \mathcal{J}(\rho_{\Phi^\uparrow} + \rho_{\Phi^\downarrow}, \rho_{\Phi^\uparrow} + \rho_{\Phi^\downarrow}) \right. \\
 \left. + E_{\text{xc}}[\rho_{\Phi^\uparrow}] + E_{\text{xc}}[\rho_{\Phi^\downarrow}] : \rho_{\Phi^\#} = \sum_{n=1}^{N^\#} |\phi_n^\#|^2, \quad \Phi^\# \in \mathcal{C}_{N^\#}, \quad \# = \uparrow, \downarrow \right\}
 \end{aligned} \tag{1.2}$$

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with

$$\mathcal{C}_{N^\uparrow} = \left\{ \Phi^\uparrow = \left(\phi_1^\uparrow, \dots, \phi_{N^\uparrow}^\uparrow \right) : \phi_n^\uparrow \in \mathbf{H}^\ddagger(\mathbb{R}^3), \langle \phi_m^\uparrow, \phi_n^\uparrow \rangle_{L^2(\mathbb{R}^3)} = \delta_{mn} \right\}, \quad (1.3)$$

$$\mathcal{C}_{N^\downarrow} = \left\{ \Phi^\downarrow = \left(\phi_1^\downarrow, \dots, \phi_{N^\downarrow}^\downarrow \right) : \phi_n^\downarrow \in \mathbf{H}^\ddagger(\mathbb{R}^3), \langle \phi_m^\downarrow, \phi_n^\downarrow \rangle_{L^2(\mathbb{R}^3)} = \delta_{mn} \right\}. \quad (1.4)$$

where $\ddagger = 1$ for the non-relativistic case and $\ddagger = 1/2$ for the quasi relativistic case.

Here the first two terms within the brackets in (1.1) are the non-relativistic kinetic energies of the N^\uparrow spin-up electrons and the N^\downarrow spin-down electrons, each term being defined on $\mathbf{H}^1(\mathbb{R}^3)$, the Sobolev space of order one, whereas the first two terms in (1.2) are the corresponding quasi-relativistic kinetic energies of the spin-up and spin-down electrons. Therein $T_0 = \sqrt{-\Delta_{\mathbf{r}_n} + \alpha^{-2}}$ is (essentially) the quasi-relativistic kinetic energy of the n th electron located at $\mathbf{r}_n \in \mathbb{R}^3$ ($\Delta_{\mathbf{r}_n}$ being the Laplacian with respect to \mathbf{r}_n), α is Sommerfeld's fine structure constant and $\mathbf{H}^{1/2}(\mathbb{R}^3)$ is the Sobolev space in (2.1). The potential $V(\cdot)$ is the attractive interaction between an electron and the K nuclei (with charges $Z_k > 0$, $k = 1, 2, \dots, K$, and locations $\mathbf{R}_k \in \mathbb{R}^3$, $k = 1, 2, \dots, K$)

$$V(\mathbf{r}) = \sum_{k=1}^K V_k(\mathbf{r}); \quad V_k(\mathbf{r}) = -\frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|}, \quad (1.5)$$

and the Coulomb energy $\mathcal{J}(\cdot, \cdot)$ is given by

$$\mathcal{J}(\rho, \chi) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r})\chi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (1.6)$$

The spin-up electron density, respectively, spin-down electron density, is given by

$$\rho_{\Phi^\uparrow}(\mathbf{r}) = \sum_{n=1}^{N^\uparrow} |\phi_n^\uparrow|^2, \quad \text{respectively,} \quad \rho_{\Phi^\downarrow}(\mathbf{r}) = \sum_{n=1}^{N^\downarrow} |\phi_n^\downarrow|^2,$$

and the total electron density is $\rho = \rho_{\Phi^\uparrow} + \rho_{\Phi^\downarrow}$. The exchange-correlation functional is chosen as

$$E_{\text{xc}}(\rho) = \int_{\mathbb{R}^3} g(\rho(\mathbf{r})) d\mathbf{r}, \quad (1.7)$$

yielding the Local Density Approximation (abbreviated LDA), and the following assumptions imposed on the function g ensure that (1.7) incorporates all approximate LDA functionals used in practical implementations (see, e.g., [32]):

ASSUMPTION 1.1. Let g be a twice differentiable function which satisfies

$$g \in C^1(\mathbb{R}_+, \mathbb{R}) \quad (1.8)$$

$$g(0) = 0 \quad (1.9)$$

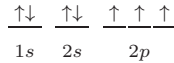
$$g' \leq 0 \quad (1.10)$$

$$\exists 0 < \beta_- \leq \beta_+ < \nu \text{ such that } \sup_{\rho \in \mathbb{R}_+} \frac{|g'(\rho)|}{\rho^{\beta_-} + \rho^{\beta_+}} < \infty \quad (1.11)$$

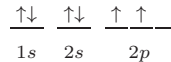
$$\exists 1 \leq \gamma < 3/2 \text{ such that } \limsup_{\rho \rightarrow 0^+} \frac{g(\rho)}{\rho^\gamma} < 0, \tag{1.12}$$

where $\nu = 2/3$ for the non-relativistic case and $\nu = 1/3$ for the quasi-relativistic case.

It is well-known that a spin-polarised version of DFT improves the description of the electronic structure of atoms, molecules and solids [34, 31]. The *unrestricted* Kohn-Sham model (1.1)-(1.4) is used for *open shell* atomic and molecular systems. In the context of atomic orbitals, an open shell is a valence shell which is not completely filled with electrons or that has not given all of its valence electrons through chemical bonds with other atoms or molecules during a chemical reaction. For molecules it signifies that there are unpaired electrons [18, 31]. In other words, it models molecular system with an odd number of electrons such as radials, e.g., nitrogen, and systems with an even number of electrons whose ground state is not a spin singlet state [17, p 185], e.g., carbon. Indeed, it is common to see the electron configuration for a nitrogen atom in its ground state depicted as



The 1s and 2s orbitals are filled with one spin-up electron and one spin-down electron, whereas the three 2p orbitals holds a single spin-up electron each. Similarly, it is not unusual to see the electron configuration for a carbon atom depicted as



In particular, the 2p orbital of carbon in its ground state is not a singlet state. Both of these are good examples of open-shell problems in electronic structure theory, showing that even in the absence of an additional, external potential, the systems have an excess of spin-up electrons. Of course, in intense magnetic fields and in other situations, it is known experimentally that the ground state of the system is spin-polarised. A spin-polarised theory, like the unrestricted Kohn-Sham model, is one which accounts for an excess of spin-up (or spin-down) electrons. Numerous physicists and chemists working in DFT have realised that spin-polarised theories can lead to improved approximations [34, 18, 31] of molecular bonding energies, kinetic energies, and other quantities of interest, e.g., the spin potential [12, 13].

We establish the following theorem for the minimization problem (1.1), (1.3) and (1.4) as well as its extended version formulated in Section 4.

THEOREM 1.2 (Non-relativistic case). *Suppose that $N = N^\uparrow + N^\downarrow$ is a positive integer satisfying $N \leq Z_{\text{tot}} = \sum_{k=1}^K Z_k$. Moreover, let Assumption 1.1 be satisfied. Then the spin-polarised Kohn-Sham LDA problem (1.1), (1.3) and (1.4) (and its extended version) has a minimizer $\mathcal{D} := \mathcal{D}^{(\text{NR})} := \text{diag}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ satisfying*

$$\mathcal{D} = \mathbf{1}_{(-\infty, \epsilon_F)}(\mathbf{T}_{\mathcal{D}^\uparrow, \mathcal{D}^\downarrow}) + \mathcal{D}^{(\delta)} \tag{1.13}$$

for some $\epsilon_F \leq 0$, where $\mathbf{T}_{\mathcal{D}^\uparrow, \mathcal{D}^\downarrow} = \text{diag}(T_\uparrow, T_\downarrow)$ with entries given by

$$\begin{aligned} T_\uparrow &= -\frac{1}{2}\Delta + V + g'(\rho_{\mathcal{D}^\uparrow}) + (\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|}, \\ T_\downarrow &= -\frac{1}{2}\Delta + V + g'(\rho_{\mathcal{D}^\downarrow}) + (\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|}, \end{aligned}$$

and where $\mathbf{1}_{(-\infty, \epsilon_F)}$ is the characteristic function of the range $(-\infty, \epsilon_F)$ and $\mathbf{D}^{(\delta)} = \text{diag}(\mathcal{D}_\uparrow^\delta, \mathcal{D}_\downarrow^\delta)$ has entries $\mathcal{D}_\#^\delta \in \mathcal{S}(L^2(\mathbb{R}^3))$, $\# = \uparrow, \downarrow$ satisfying $0 \leq \mathcal{D}_\#^\delta \leq 1$ and $\text{Ran}(\mathbf{D}^{(\delta)}) \subset \text{Ker}(\mathbf{T}_{\mathcal{D}_\uparrow, \mathcal{D}_\downarrow} - \epsilon_F)$. Here $\mathcal{S}(L^2(\mathbb{R}^3))$ is the space of all bounded, self-adjoint operators on $L^2(\mathbb{R}^3)$; see Section 4.

Analogously, we establish the following result for the quasi-relativistic, spin-polarised Kohn-Sham problem (1.2), (1.3) and (1.4) and its extended version (4.2)-(4.3).

THEOREM 1.3 (Quasi-relativistic case). *Suppose that $N = N^\uparrow + N^\downarrow$ is a positive integer satisfying $N \leq Z_{\text{tot}} = \sum_{k=1}^K Z_k < Z_c = 2\alpha^{-1}\pi^{-1}$ and let Assumption 1.1 be satisfied. Then the extended spin-polarised Kohn-Sham LDA problem (4.2)-(4.3) has a minimizer $\mathbf{D} := \mathbf{D}^{(\text{QR})} = \text{diag}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ satisfying*

$$\mathbf{D} = \mathbf{1}_{(-\infty, \epsilon_F)}(\mathbf{T}_{\mathcal{D}^\uparrow, \mathcal{D}^\downarrow}) + \mathbf{D}^{(\delta)} \quad (1.14)$$

for some $\epsilon_F \leq 0$, where $\mathbf{T}_{\mathcal{D}^\uparrow, \mathcal{D}^\downarrow} = \text{diag}(T_\uparrow, T_\downarrow)$ with entries given by

$$\begin{aligned} T_\uparrow &= \alpha^{-1}\tilde{T}_0 + V + g'(\rho_{\mathcal{D}^\uparrow}) + (\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|}, \\ T_\downarrow &= \alpha^{-1}\tilde{T}_0 + V + g'(\rho_{\mathcal{D}^\downarrow}) + (\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|}, \end{aligned}$$

and where $\mathbf{1}_{(-\infty, \epsilon_F)}$ is the characteristic function of the range $(-\infty, \epsilon_F)$ and $\mathbf{D}^{(\delta)} = \text{diag}(\mathcal{D}_\uparrow^\delta, \mathcal{D}_\downarrow^\delta)$ has entries $\mathcal{D}_\#^\delta \in \mathcal{S}(L^2(\mathbb{R}^3))$, $\# = \uparrow, \downarrow$ satisfying $0 \leq \mathcal{D}_\#^\delta \leq 1$ and $\text{Ran}(\mathbf{D}^{(\delta)}) \subset \text{Ker}(\mathbf{T}_{\mathcal{D}^\uparrow, \mathcal{D}^\downarrow} - \epsilon_F)$.

We give the proof of Theorem 1.3 in all details herein. For the proof of Theorem 1.2 we refer to the exposition in [3].

In the mathematical literature, there are few rigorous results on Kohn-Sham theory. In the non-relativistic setting, Le Bris [23, 24] treated the standard spin-unpolarized LDA Kohn-Sham model. Le Bris proved existence of a ground state using concentration-compactness type arguments as pioneered by Lions in his work on Thomas-Fermi type models [28, 29]. Using the same method of proof, Anantharaman and Cancès [2, Theorem 1] proved existence of a ground state for the closed-shell (or, restricted) spin-unpolarized Kohn-Sham models (standard and extended ones).

Argaez and Melgaard [4] proved the existence of a minimizer within the quasi-relativistic setting and in the present paper ground states are shown to exist both for non-relativistic and quasi-relativistic systems when one considers an open-shell, spin-polarised (unrestricted) LDA models, using the concentration-compactness method. To the best of our knowledge, no proof has yet been given for the spin-polarised case, until now. We write out the proof for the quasi-relativistic case only because it is slightly more technical than the non-relativistic case and, in some sense, it is more timely. We emphasise that, for both cases, all steps in [2, 4] needs to be modified slightly and analysis requiring new arguments enters in many lemmas, propositions and theorems, e.g. Proposition 5.3, Lemma 6.1, Proposition 5.3 and Theorem 1.3. In particular, new ‘‘mixed’’ terms of the form $\mathcal{J}(\rho, \mu)$ require special attention throughout the analysis. The notation is cumbersome and the analysis is rather tedious. The first rigorous existence results on spin-polarised theories were established by Goldstein and Ruiz Rieder for the Thomas-Fermi model [15]. In a series of papers on this and closely related models [14, 15, 7, 8, 16], they use PDE techniques, entirely

different from the arguments in the present work, going back to original ideas by B enilan and Brezis [5, 6]. Although using different methods, however, the results on the Thomas-Fermi model with Fermi-Amaldi correction in Goldstein *et al* [8, 16] and Le Bris [25] coincide to some extent. For other papers, where the quasi-relativistic kinetic operator enters for different physical models, we refer to [9, 30]; the methods used therein are also different from the one in the present paper.

2. Preliminaries. Throughout the paper we denote by c and C (with or without indices) various positive constants whose precise value is of no importance. Moreover, we will denote the complex conjugate of $z \in \mathbb{C}$ by \bar{z} .

Function spaces. For $1 \leq p \leq \infty$, let $L^p(\mathbb{R}^3)$ be the space of (equivalence classes of) complex-valued functions ϕ which are measurable and satisfy $\int_{\mathbb{R}^3} |\phi(x)|^p dx < \infty$ if $p < \infty$ and $\|\phi\|_{L^\infty(\mathbb{R}^3)} = \text{ess sup } |\phi| < \infty$ if $p = \infty$. The measure dx is the Lebesgue measure. For any p the $L^p(\mathbb{R}^3)$ space is a Banach space with norm $\|\cdot\|_{L^p(\mathbb{R}^3)} = (\int_{\mathbb{R}^3} |\cdot|^p dx)^{1/p}$. In the case $p = 2$, $L^2(\mathbb{R}^3)$ is a complex and separable Hilbert space with scalar product $\langle \phi, \psi \rangle_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} \phi \bar{\psi} dx$ 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 $\langle \phi, \psi \rangle = \sum_{n=1}^N \langle \phi_n, \psi_n \rangle_{L^2(\mathbb{R}^3)}$. The space of infinitely differentiable complex-valued functions with compact support will be denoted $C_0^\infty(\mathbb{R}^3)$. The Fourier transform is given by

$$(\mathcal{F}\psi)(\xi) = \hat{\psi}(\xi) = (2\pi)^{-1/2} \int_{\mathbb{R}^3} e^{-ix\xi} \psi(x) dx.$$

Define

$$\mathbf{H}^{1/2}(\mathbb{R}^3) = \{ \phi \in L^2(\mathbb{R}^3) : (1 + |\xi|)^{1/2} \hat{\phi} \in L^2(\mathbb{R}^3) \}, \tag{2.1}$$

which, equipped with the scalar product

$$\langle \phi, \psi \rangle_{\mathbf{H}^{1/2}(\mathbb{R}^3)} = \int_{\mathbb{R}^3} (1 + |\xi|) \hat{\phi}(\xi) \overline{\hat{\psi}(\xi)} d\xi,$$

becomes a Hilbert space; evidently, $\mathbf{H}^1(\mathbb{R}^3) \subset \mathbf{H}^{1/2}(\mathbb{R}^3)$. We have that $C_0^\infty(\mathbb{R}^3)$ is dense in $\mathbf{H}^{1/2}(\mathbb{R}^3)$ and the continuous embedding $\mathbf{H}^{1/2}(\mathbb{R}^3) \hookrightarrow L^r(\mathbb{R}^3)$ holds whenever $2 \leq r \leq 3$ [1].

Moreover, we shall use that any weakly convergent sequence in $\mathbf{H}^{1/2}(\mathbb{R}^3)$ converges strongly in $L^p_{\text{loc}}(\mathbb{R}^3)$, $p < 3$, and it has a pointwise convergent subsequence. Standard arguments yield the following result; an analogue of Lions' result [28, Part II, Lemma I.1].

PROPOSITION 2.1. *Let $r > 0$ and $2 \leq q < 3$. If the sequence $\{u_j\}$ is bounded in $\mathbf{H}^{1/2}(\mathbb{R}^3)$ and if*

$$\sup_{y \in \mathbb{R}^3} \int_{B(y,r)} |u_j|^q \longrightarrow 0 \text{ as } j \rightarrow \infty$$

then $u_j \rightarrow 0$ in $L^r(\mathbb{R}^3)$ for any $2 < r < 3$.

Operators. Let T be a self-adjoint operator on a Hilbert space \mathcal{H} with domain $\mathfrak{D}(T)$. The spectrum and resolvent set are denoted by $\text{spec}(T)$ and $\rho(T)$, respectively. We use standard terminology for the various parts of the spectrum; see, e.g., [10, 21].

The resolvent is $R(\zeta) = (T - \zeta)^{-1}$. The spectral family associated to T is denoted by $E_T(\lambda)$, $\lambda \in \mathbb{R}$. For a lower semi-bounded self-adjoint operator T , the counting function is defined by

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

The space of trace operators, respectively, Hilbert-Schmidt operators, on $\mathfrak{h} = L^2(\mathbb{R}^3)$ is denoted by $\mathfrak{S}_1(\mathfrak{h})$, respectively $\mathfrak{S}_2(\mathfrak{h})$ or, in short, \mathfrak{S}_j , $j = 1, 2$. The space of bounded self-adjoint operators is designated by $\mathcal{S}(\mathfrak{h})$.

We need the following abstract operator result by Lions [29, Lemma II.2].

LEMMA 2.2. *Let T be a self-adjoint operator on a Hilbert space \mathcal{H} , and let $\mathcal{H}_1, \mathcal{H}_2$ be two subspaces of \mathcal{H} such that $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$, $\dim \mathcal{H}_1 = \mathfrak{h}_1 < \infty$ and $P_2 T P_2 \geq 0$, where P_2 is the orthogonal projection onto \mathcal{H}_2 . Then T has at most \mathfrak{h}_1 negative eigenvalues.*

3. Atomic and molecular Hamiltonians. By p we denote the momentum operator $-i\nabla$ on $L^3(\mathbb{R}^3)$. The operator $T_0 = \sqrt{p^2 + \alpha^{-2}}$ is generated by the closed, (strictly) positive form $\mathfrak{t}_0[\phi, \phi] = \langle T_0^{1/2}\phi, T_0^{1/2}\phi \rangle_{\mathcal{H}}$ on the form domain $\mathfrak{D}(\mathfrak{t}_0) = \mathbf{H}^{1/2}(\mathbb{R}^3)$. Set $S(x) = Z\alpha/|x|$, $Z > 0$, $Z_c = 2\alpha^{-1}\pi^{-1}$, and let $\tilde{T}_0 = T_0 - \alpha^{-1}$. The following facts are well-known for the perturbed one-particle operator $H_{1,1,\alpha} = \tilde{T}_0 - S(x)$ [19, 21]:

Small perturbations. If $Z < \frac{\pi}{2}Z_c$ then S is \tilde{T}_0 -bounded with relative bound equal to two. If, on the other hand, $(2\alpha)^{-1} < Z < Z_c$ then S is \tilde{T}_0 -form bounded with relative bound less than one.

We prove the above-mentioned form-boundedness. It follows from the following inequality (first observed, it seems, by Kato [21, Paragraph V-§5.4]):

$$\langle S\phi, \phi \rangle_{L^2(\mathbb{R}^3)} \leq (Z/Z_c) \|\phi\|_{\mathbf{H}^{1/2}(\mathbb{R}^3)}^2, \quad \forall \phi \in \mathbf{H}^{1/2}(\mathbb{R}^3). \tag{3.1}$$

Indeed, if, for any $\psi, \phi \in \mathbf{H}^{1/2}(\mathbb{R}^3)$, we define the sesquilinear forms

$$\begin{aligned} \mathfrak{s}[\psi, \phi] &:= \langle S^{1/2}\psi, S^{1/2}\phi \rangle_{L^2(\mathbb{R}^3)}, \\ \mathfrak{t}_0[\psi, \phi] &:= \langle T_0^{1/2}\psi, T_0^{1/2}\phi \rangle_{L^2(\mathbb{R}^3)}, \text{ and } \tilde{\mathfrak{t}}_0[\psi, \phi] := \mathfrak{t}_0[\psi, \phi] - \alpha^{-1}\langle \psi, \phi \rangle_{L^2(\mathbb{R}^3)}, \end{aligned}$$

then (3.1) shows that \mathfrak{s} is well-defined and also, by invoking the inequality $|-i\tilde{\nabla}| \leq T_0$, we infer that, for all $\phi \in \mathbf{H}^{1/2}(\mathbb{R}^3)$,

$$\mathfrak{s}[\phi, \phi] < \mathfrak{t}_0[\phi, \phi] \text{ provided } Z < Z_c. \tag{3.2}$$

This is the *Coulomb uncertainty principle* in the quasi-relativistic setting. The KLMN theorem (see, e.g., [21, Paragraph VI-1.7]) implies that there exists a unique self-adjoint operator, denoted $H_{1,1,\alpha}$, generated by the closed sesquilinear form

$$\mathfrak{h}_{1,1,\alpha}[\psi, \phi] := \tilde{\mathfrak{t}}_0[\psi, \phi] - \mathfrak{s}[\psi, \phi], \quad \psi, \phi \in \mathfrak{D}(\mathfrak{h}_{1,1,\alpha}) = \mathbf{H}^{1/2}(\mathbb{R}^3), \tag{3.3}$$

which is bounded below by $-\alpha^{-1}$. It is well-known [19] that

$$\begin{aligned} \text{spec}(H_{1,1,\alpha}) \cap [-\alpha^{-1}, 0) &\text{ is discrete} \\ \text{spec}(H_{1,1,\alpha}) \cap [0, \infty) &\text{ is absolutely continuous.} \end{aligned} \tag{3.4}$$

In particular, $\text{spec}_{\text{ess}}(H_{1,1,\alpha}) = [0, \infty)$. The form construction of the atomic Hamiltonian $H_{1,1,\alpha}$ can be generalized to the molecular case, describing a molecule with N electrons and K nuclei of charges $\mathbf{Z} = (Z_1, \dots, Z_K)$, $Z_k > 0$, located at R_1, \dots, R_K , $R_k \in \mathbb{R}^3$, if we substitute \mathfrak{s} by

$$\mathfrak{v}[\psi, \phi] = \sum_{k=1}^K \langle V_k^{1/2}, \psi, V_k^{1/2} \phi \rangle, \quad \psi, \phi \in \mathbf{H}^{1/2}(\mathbb{R}^3), \tag{3.5}$$

where V_k is defined in (1.5) and by assuming that $Z_{\text{tot}} < Z_c$. We shall use the following IMS-type localization estimate [26, Lemma A.1].

LEMMA 3.1. *Suppose $\{\xi_j\}_{j \in J}$ is a smooth partition of unity such that $\sum_{j \in J} \xi_j(x)^2 \equiv 1$ and $\nabla \xi_j \in L^s(\mathbb{R}^n)$ with $s \in (2n, \infty]$. Then the following IMS type estimate holds for T_0 :*

$$T_0 \geq \sum_{j \in J} \xi_j T_0 \xi_j - \frac{1}{\pi} \int_0^\infty \frac{1}{T_0^2 + \tau} \left(\sum_{j \in J} |\nabla \xi_j|^2 \right) \frac{1}{T_0^2 + \tau} \sqrt{\tau} d\tau.$$

Moreover, we need the following spectral result found in [11]. Its proof is based on Glazman’s lemma for the counting function (see, e.g, [33, Lemma A.3]).

LEMMA 3.2. *Assume $\vartheta < Z_{\text{tot}} < Z_c$, and let $\rho \in L^1(\mathbb{R}^3) \cap L^{4/3}(\mathbb{R}^3)$ such that $\int_{\mathbb{R}^3} \rho dx < \vartheta$. Define the quasi-relativistic Schrödinger operator $T = \alpha^{-1} \widetilde{T}_0 + V + \rho * (1/|x|)$.*

Then, for any $\kappa \geq 1$ and any $0 \leq \vartheta < Z_{\text{tot}}$, there exists $\epsilon_{\kappa, \vartheta} > 0$ such that

$$\text{Coun}(-\epsilon_{\kappa, \vartheta}; T) \geq \kappa.$$

4. Density operator framework. In order to turn the minimization problem (1.2)-(1.4) into a convex problem, we proceed to extend the definition of the unrestricted spin-polarised Kohn-Sham energy functional. We can re-express the energy functional and the Kohn-Sham ground state energy via the one-to-one correspondence between elements of $\mathcal{C}_{N^\#}$, $\# = \uparrow, \downarrow$, and projections onto finite-dimensional subspaces of $L^2(\mathbb{R}^3)$. Indeed, given an element $\{\phi_n^\#\}_{n=1}^{N^\#}$ in $\mathcal{C}_{N^\#}$ we can associate a canonical projection operator, $\mathcal{D}^\# = \sum_{n=1}^{N^\#} \langle \cdot, \phi_n^\# \rangle \phi_n^\#$ with trace equal to $N^\#$. We may therefore write the energy functional as

$$\begin{aligned} \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) &= \alpha^{-1} (\text{Tr} [\widetilde{T}_0 \mathcal{D}^\uparrow] + \alpha^{-1} (\text{Tr} [\widetilde{T}_0 \mathcal{D}^\downarrow] - \text{Tr} [V(\mathcal{D}^\uparrow + \mathcal{D}^\downarrow)] \\ &\quad + \mathcal{J}(\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}, \rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) + E_{\text{xc}}[\rho_{\mathcal{D}^\uparrow}] + E_{\text{xc}}[\rho_{\mathcal{D}^\downarrow}]). \end{aligned} \tag{4.1}$$

where

$$\begin{aligned} \text{Tr} [\widetilde{T}_0 \mathcal{D}] &= \sum_{n=1}^N \mathfrak{t}_0[\phi_n, \phi_n] - \alpha^{-1} [\phi_n, \phi_n], \\ \text{Tr} [V \mathcal{D}] &= \sum_{n=1}^N \mathfrak{v}[\phi_n, \phi_n]. \end{aligned}$$

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

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

and the exchange-correlation functional defined as in (1.7). Then we embed (1.2)-(1.4) in the collection of problems

$$I_{\lambda, \omega} = \inf \{ \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) : (\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \in \mathcal{K}_\lambda^\uparrow \oplus \mathcal{K}_\omega^\downarrow \} \tag{4.2}$$

parametrized by $(\lambda, \omega) \in \mathbb{R}_+ \times \mathbb{R}_+$, where

$$\mathcal{K}_\lambda^\uparrow = \{ \mathcal{D}^\uparrow \in \mathcal{S}(L^2(\mathbb{R}^3)) : 0 \leq \mathcal{D}^\uparrow \leq 1, \operatorname{Tr}(\mathcal{D}^\uparrow) = \lambda, \operatorname{Tr}(T_0^{1/2} \mathcal{D}^\uparrow T_0^{1/2}) < \infty \}, \tag{4.3}$$

with $\mathcal{S}(L^2(\mathbb{R}^3))$ being the space of all bounded, self-adjoint operators on $L^2(\mathbb{R}^3)$. The space $\mathcal{K}_\omega^\downarrow$ is defined in a similar way. In addition, we introduce the problem at infinity

$$I_{\lambda, \omega}^\infty = \inf \{ \mathcal{E}^\infty(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) : (\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \in \mathcal{K}_\lambda^\uparrow \oplus \mathcal{K}_\omega^\downarrow \}, \tag{4.4}$$

where

$$\begin{aligned} \mathcal{E}^\infty(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) &= \alpha^{-1} \operatorname{Tr}[\tilde{T}_0 \mathcal{D}^\uparrow] + \alpha^{-1} \operatorname{Tr}[\tilde{T}_0 \mathcal{D}^\downarrow] \\ &\quad + \mathcal{J}(\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}, \rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) + E_{\text{xc}}[\rho_{\mathcal{D}^\uparrow}] + E_{\text{xc}}[\rho_{\mathcal{D}^\downarrow}]. \end{aligned} \tag{4.5}$$

The operator $\mathcal{D}^\#$ is the so-called (reduced) one-particle density operator. The general theory of trace class operators on $L^2(\mathbb{R}^3)$ asserts that any operator $\mathcal{D}^\#$ in $\mathcal{K}^\#$ admits a complete set of eigenfunctions $\{\phi_i\}$ in $\mathbf{H}^{1/2}(\mathbb{R}^3)$ associated to the eigenvalues $\nu_n \in [0, 1]$, counted with multiplicity. Hence we may decompose $\mathcal{D}^\#$ along such an eigenbasis of $L^2(\mathbb{R}^3)$, in such a way that its Hilbert-Schmidt kernel may be written as

$$\rho^\#(x, y) = \sum_{n \geq 1} \nu_n \phi_n^\#(x) \overline{\phi_n^\#(y)}.$$

Since $\mathcal{D}^\#$ is trace class, the corresponding density is well-defined as a nonnegative function in $L^1(\mathbb{R}^3)$ through $\rho^\#(x, x) = \sum_{n \geq 1} \nu_n |\phi_n^\#(x)|^2$, and $\operatorname{Tr} \mathcal{D}^\# = \int_{\mathbb{R}^3} \rho^\#(x, x) \, dx = \sum_{n \geq 1} \nu_n$. Furthermore, the spectral decomposition of $\mathcal{D}^\#$ enable us to give sense to

$$\operatorname{Tr}[T_0 \mathcal{D}^\#] = \sum_{n \geq 1} \nu_n \int_{\mathbb{R}^3} |T_0^{1/2} \phi_n^\#(x)|^2 \, dx. \tag{4.6}$$

By \mathfrak{S}_1 we designate the vector space of trace-class operators on $L^2(\mathbb{R}^3)$ and we define the vector spaces

$$\mathfrak{h}^\# = \{ \mathcal{D}^\# \in \mathfrak{S}_1 : T_0^{1/2} \mathcal{D}^\# T_0^{1/2} \in \mathfrak{S}_1 \}, \quad \# = \uparrow, \downarrow,$$

equipped with the norm $\|\cdot\|_{\mathfrak{h}^\#} = \operatorname{Tr}(\cdot) + \operatorname{Tr}(T_0^{1/2} \cdot T_0^{1/2})$. Moreover, we define the space $\mathcal{H} = \mathfrak{h}^\uparrow \oplus \mathfrak{h}^\downarrow$ having norm

$$\|\cdot\|_{\mathcal{H}}^2 = \|\cdot\|_{\mathfrak{h}^\uparrow}^2 + \|\cdot\|_{\mathfrak{h}^\downarrow}^2.$$

Finally, for $\# = \uparrow, \downarrow$, we introduce the following convex sets

$$\mathcal{K}^\# = \{ \mathcal{D}^\# \in \mathcal{S}(L^2(\mathbb{R}^3)) : 0 \leq \mathcal{D}^\# \leq 1, \operatorname{Tr}[\mathcal{D}^\#] < \infty, \operatorname{Tr}(T_0^{1/2} \mathcal{D}^\# T_0^{1/2}) < \infty \},$$

and we let $\mathcal{K} = \mathcal{K}^\uparrow \oplus \mathcal{K}^\downarrow$; $\mathcal{S}(L^2(\mathbb{R}^3))$ being the space of all bounded, self-adjoint operators on $L^2(\mathbb{R}^3)$.

5. Concentration-compactness type inequalities. The aim of this section is to establish concentration-compactness type inequalities, see Proposition 5.3. To achieve this we need to prove a series of auxiliary results.

LEMMA 5.1. *For any $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \in \mathcal{K}^\uparrow \oplus \mathcal{K}^\downarrow$ one has $\sqrt{\rho_{\mathcal{D}^\#}} \in \mathbf{H}^{1/2}(\mathbb{R}^3)$, $\# = \uparrow, \downarrow$, and, moreover, the following inequalities are valid for some positive constants:
Lower bound on the kinetic energy:*

$$\|\nabla\sqrt{\rho_{\mathcal{D}^\uparrow}}\|_{\mathbf{H}^{1/2}(\mathbb{R}^3)}^2 + \|\nabla\sqrt{\rho_{\mathcal{D}^\downarrow}}\|_{\mathbf{H}^{1/2}(\mathbb{R}^3)}^2 \leq C \operatorname{Tr} [T_0\mathcal{D}^\uparrow] + C \operatorname{Tr} [T_0\mathcal{D}^\downarrow]. \tag{5.1}$$

Upper bound on Coulomb energy:

$$0 \leq \mathcal{J}(\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}, \rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) \leq C \operatorname{Tr} [T_0\mathcal{D}^\uparrow] \operatorname{Tr} [\mathcal{D}^\uparrow] + C \operatorname{Tr} [T_0\mathcal{D}^\downarrow] \operatorname{Tr} [\mathcal{D}^\downarrow]. \tag{5.2}$$

Bounds on nuclei-electron interaction: for $Z_{\text{tot}} < Z_c = 2/(\alpha\pi)$,

$$-C_1 \operatorname{Tr} [T_0\mathcal{D}^\uparrow] - C_2 \operatorname{Tr} [T_0\mathcal{D}^\downarrow] \leq \int V(\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) dx \leq 0. \tag{5.3}$$

Bounds on exchange correlation energy: With $\# = \uparrow, \downarrow$,

$$\begin{aligned} & -C \left(\operatorname{Tr} [\mathcal{D}^\#]^{1-\frac{\beta_-}{2}} (\operatorname{Tr} [T_0\mathcal{D}^\#])^{3\beta_-} + \operatorname{Tr} [\mathcal{D}^\#]^{1-\frac{\beta_+}{2}} (\operatorname{Tr} [T_0\mathcal{D}^\#])^{3\beta_+} \right) \\ & \leq E_{\text{xc}}(\rho_{\mathcal{D}^\#}^\#) \leq 0. \end{aligned} \tag{5.4}$$

Lower bound on total energy: for $Z_{\text{tot}} < Z_c = 2/(\alpha\pi)$,

$$\begin{aligned} \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) & \geq \alpha^{-1} \operatorname{Tr} [T_0\mathcal{D}^\uparrow] - \alpha^{-2} \operatorname{Tr} [\mathcal{D}^\uparrow] + \alpha^{-1} \operatorname{Tr} [T_0\mathcal{D}^\downarrow] - \alpha^{-2} \operatorname{Tr} [\mathcal{D}^\downarrow] \\ & \quad - C_1 \operatorname{Tr} [T_0\mathcal{D}^\uparrow] - C_1 \operatorname{Tr} [\mathcal{D}^\uparrow] - C_2 \left\{ (\operatorname{Tr} [\mathcal{D}^\uparrow])^{\frac{1-\beta_-}{2-5\beta_-}} + (\operatorname{Tr} [\mathcal{D}^\uparrow])^{\frac{1-\beta_+}{2-5\beta_+}} \right. \\ & \quad \left. + (\operatorname{Tr} [\mathcal{D}^\downarrow])^{\frac{1-\beta_-}{2-5\beta_-}} + (\operatorname{Tr} [\mathcal{D}^\downarrow])^{\frac{1-\beta_+}{2-5\beta_+}} \right\}. \end{aligned} \tag{5.5}$$

Lower bound on the energy at infinity:

$$\begin{aligned} & \mathcal{E}^\infty(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \\ & \geq \alpha^{-1} \operatorname{Tr} [T_0\mathcal{D}^\uparrow] - \alpha^{-2} \operatorname{Tr} [\mathcal{D}^\uparrow] + \alpha^{-1} \operatorname{Tr} [T_0\mathcal{D}^\downarrow] - \alpha^{-2} \operatorname{Tr} [\mathcal{D}^\downarrow] \\ & \quad - 2C \operatorname{Tr} [T_0\mathcal{D}^\uparrow] - 2C \operatorname{Tr} [T_0\mathcal{D}^\downarrow] \\ & \quad - C \left\{ (\operatorname{Tr} [\mathcal{D}^\uparrow])^{\frac{1-\beta_-}{2-5\beta_-}} + (\operatorname{Tr} [\mathcal{D}^\uparrow])^{\frac{1-\beta_+}{2-5\beta_+}} + (\operatorname{Tr} [\mathcal{D}^\downarrow])^{\frac{1-\beta_-}{2-5\beta_-}} + (\operatorname{Tr} [\mathcal{D}^\downarrow])^{\frac{1-\beta_+}{2-5\beta_+}} \right\}. \end{aligned} \tag{5.6}$$

In particular, the minimizing sequences of (4.2) and those of (4.4) are bounded in \mathcal{H} .

Proof. The inequalities are straightforward implications of the ones in [4, Lemma 5.1]; we omit the details. \square

LEMMA 5.2. *The functionals \mathcal{E} and \mathcal{E}^∞ are continuous on $\mathcal{H} = \mathfrak{h}^\uparrow \oplus \mathfrak{h}^\downarrow$.*

Proof. By definition of the norm in \mathcal{H} , $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \mapsto \operatorname{Tr} [\tilde{T}_0\mathcal{D}^\uparrow] + \operatorname{Tr} [\tilde{T}_0\mathcal{D}^\downarrow]$ is continuous on \mathcal{H} . For the term $\int V_{\text{en}}u^2$, the continuity follows from the Cauchy-Schwarz inequality and the Hardy inequality :

$$\left| \int V u^2 - V \tilde{u}^2 \right| \leq \int V |u - \tilde{u}| |u + \tilde{u}| dx \leq C \int V |u - \tilde{u}|^2 \leq C \|u - \tilde{u}\|_{\mathbf{H}^{1/2}}^2.$$

Let $W := 1/|x| = W_1 + W_2$ where $W_1 \in L^4$ and $W_2 \in L^\infty$. For the term $\mathcal{J}(\cdot, \cdot)$ the estimate

$$\begin{aligned} & |\mathcal{J}(\rho_{\mathcal{D}}, \rho_{\mathcal{D}}) - \mathcal{J}(\rho_{\tilde{\mathcal{D}}}, \rho_{\tilde{\mathcal{D}}})| \\ &= \left| \frac{1}{2} \int [(\rho_{\mathcal{D}} - \rho_{\tilde{\mathcal{D}}}) * W](\rho_{\mathcal{D}} + \rho_{\tilde{\mathcal{D}}}) dx \right| \\ &\leq C \|\rho_{\mathcal{D}} - \rho_{\tilde{\mathcal{D}}}\|_{L^1} (\|W_1\|_{L^4} \|\rho_{\mathcal{D}} - \rho_{\tilde{\mathcal{D}}}\|_{L^{4/3}} + \|W_2\|_{L^\infty} \|\rho_{\mathcal{D}} + \rho_{\tilde{\mathcal{D}}}\|_{L^1}) \end{aligned}$$

establishes the continuity. Now,

$$\begin{aligned} |E_{xc}(\rho_{\mathcal{D}}) - E_{xc}(\rho_{\tilde{\mathcal{D}}})| &\leq C \int_{\mathbb{R}^3} |\rho_{\mathcal{D}}^{1+\beta_\pm} - \rho_{\tilde{\mathcal{D}}}^{1+\beta_\pm}| d\mathbf{r} \\ &\leq C \left(\int |\rho_{\mathcal{D}} - \rho_{\tilde{\mathcal{D}}}|^{1/(1-\beta_\pm)} \right)^{1-\beta_\pm} \left(\int (\rho_{\mathcal{D}}^{\beta_\pm} + \rho_{\tilde{\mathcal{D}}}^{\beta_\pm})^{1/\beta_\pm} \right)^{\beta_\pm}. \end{aligned}$$

Using the Sobolev embedding $\mathbf{H}^{1/2} \hookrightarrow L^r(\mathbb{R}^3)$, $2 \leq 2r \leq 3$, we have that

$$\|\rho_{\mathcal{D}} - \rho_{\tilde{\mathcal{D}}}\|_{L^r(\mathbb{R}^3)} \leq C \left(\int |\sqrt{\rho_{\mathcal{D}}} - \sqrt{\rho_{\tilde{\mathcal{D}}}}|^{2r} \right)^{1/r} \leq C \|\sqrt{\rho_{\mathcal{D}}} - \sqrt{\rho_{\tilde{\mathcal{D}}}}\|_{\mathbf{H}^{1/2}}^2.$$

Since $\|\mathcal{D} - \tilde{\mathcal{D}}\|_{\mathcal{H}} \rightarrow 0$, [4, Lemma 8.1] implies that $\sqrt{\rho_{\mathcal{D}}}$ converges strongly to $\sqrt{\rho_{\tilde{\mathcal{D}}}}$ in $\mathbf{H}^{1/2}(\mathbb{R}^3)$, we have established the continuity of E_{xc} . \square

With these preparations we are ready to establish concentration-compactness type inequalities.

PROPOSITION 5.3. *Let Assumption 1.1 be satisfied. Then the minimization problems in (4.2) and (4.4) have the following properties:*

1. $I_{0,0} = I_{0,0}^\infty = 0$ and for all $\lambda, \omega > 0$, one has $-\infty < I_{\lambda,\omega} < I_{\lambda,\omega}^\infty < 0$;
2. For all $0 < \mu < \lambda$ and all $0 < \kappa < \omega$ one has

$$I_{\lambda,\omega} \leq I_{\mu,\nu} + I_{\lambda-\mu,\omega-\nu}^\infty. \tag{5.7}$$

The functions $(\lambda, \omega) \mapsto I_{\lambda,\omega}$ and $(\lambda, \omega) \mapsto I_{\lambda,\omega}^\infty$ are continuous and decreasing.

First part of proof. Evidently, $I_{0,0} = I_{0,0}^\infty = 0$ and $I_{\lambda,\omega} \leq I_{\lambda,\omega}^\infty$ for any $(\lambda, \omega) \in \mathbb{R}_+ \times \mathbb{R}_+$. Next we establish assertion 2.

Let $\epsilon > 0$, $0 < \mu < \lambda$, $0 < \kappa < \omega$, and let $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \in \mathcal{K}_\mu \oplus \mathcal{K}_\kappa$ such that

$$I_{\mu,\kappa} \leq \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \leq I_{\mu,\kappa} + \epsilon.$$

As a consequence of [4, Lemma 8.1] we may choose, without loss of generality, $\mathcal{D}^\#$ on the form ¹

$$\mathcal{D}^\# = \sum_{n=1}^{N^\#} \nu_n^\# |\phi_n^\#\rangle \langle \phi_n^\#|$$

with $\nu_n^\# \in [0, 1]$, $\sum_{n=1}^{N^\uparrow} \nu_n^\uparrow = \mu$, $\sum_{n=1}^{N^\downarrow} \nu_n^\downarrow = \kappa$, and $\langle \phi_m^\#, \phi_n^\# \rangle = \delta_{mn}$, $\phi_n^\# \in C_0^\infty(\mathbb{R}^3)$. Similarly, there exists $\tilde{\mathcal{D}}^\# = \sum_{n=1}^{N^\#} \tilde{\nu}_n^\# |\tilde{\phi}_n^\#\rangle \langle \tilde{\phi}_n^\#|$ with $\tilde{\nu}_n^\# \in [0, 1]$, $\sum_{n=1}^{N^\uparrow} \tilde{\nu}_n^\uparrow = \lambda - \mu$, $\sum_{n=1}^{N^\downarrow} \tilde{\nu}_n^\downarrow = \omega - \kappa$, and $\langle \tilde{\phi}_m^\#, \tilde{\phi}_n^\# \rangle = \delta_{mn}$, $\tilde{\phi}_n^\# \in C_0^\infty(\mathbb{R}^3)$ and satisfying

$$I_{\lambda-\mu,\omega-\kappa}^\infty \leq \mathcal{E}^\infty(\tilde{\mathcal{D}}^\uparrow, \tilde{\mathcal{D}}^\downarrow) \leq I_{\lambda-\mu,\omega-\kappa}^\infty + \epsilon.$$

¹Indeed, the finite-rank operators in \mathcal{H} are dense and $C_0^\infty(\mathbb{R}^3)$ is dense in $L^2(\mathbb{R}^3)$.

Let \mathbf{e} be a unit vector of \mathbb{R}^3 and let $\mathcal{T}_{\mathbf{a}}$ be the translation operator on $L^2(\mathbb{R}^3)$ defined by $\mathcal{T}_{\mathbf{a}}f = f(\cdot - \mathbf{a})$ for any $f \in L^2(\mathbb{R}^3)$. Define, for $j \in \mathbb{N}$,

$$\mathcal{D}_j^\uparrow = \mathcal{D}^\uparrow + \mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\uparrow\mathcal{T}_{-j\mathbf{e}}, \text{ and } \mathcal{D}_j^\downarrow = \mathcal{D}^\downarrow + \mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\downarrow\mathcal{T}_{-j\mathbf{e}}.$$

For j large enough, we see that $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) \in \mathcal{K}_\lambda \oplus \mathcal{K}_\omega$ and, using the Pauli principle,

$$\begin{aligned} I_{\lambda,\omega} &\leq \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) \leq \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) + \mathcal{E}^\infty(\tilde{\mathcal{D}}^\uparrow, \tilde{\mathcal{D}}^\downarrow) + \sum_{\#=\uparrow,\downarrow} \int_{\mathbb{R}^3} V\rho_{\mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\#\mathcal{T}_{-j\mathbf{e}}} dr \\ &\quad + \mathcal{J}(\rho_{\mathcal{D}^\uparrow}, \mathcal{T}_{j\mathbf{e}}\rho_{\tilde{\mathcal{D}}^\uparrow}) + \mathcal{J}(\rho_{\mathcal{D}^\downarrow}, \mathcal{T}_{j\mathbf{e}}\rho_{\tilde{\mathcal{D}}^\downarrow}) + \mathcal{J}(\rho_{\mathcal{D}^\uparrow}, \rho_{\mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\downarrow\mathcal{T}_{-j\mathbf{e}}}) + \mathcal{J}(\rho_{\mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\uparrow\mathcal{T}_{-j\mathbf{e}}}, \rho_{\mathcal{D}^\downarrow}) \\ &\quad + \sum_{\#=\uparrow,\downarrow} \left(\int_{\mathbb{R}^3} \left\{ g(\rho_{\mathcal{D}^\#} + \rho_{\mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\#\mathcal{T}_{-j\mathbf{e}}}) - g(\rho_{\mathcal{D}^\#}) - g(\rho_{\tilde{\mathcal{D}}^\#}) \right\} \right) \\ &\leq I_{\mu,\kappa} + I_{\lambda-\mu,\omega-\kappa} + 8\epsilon. \end{aligned} \tag{5.8}$$

Similarly, we prove that

$$I_{\lambda,\omega}^\infty \leq I_{\mu,\kappa}^\infty + I_{\lambda-\mu,\omega-\kappa}^\infty. \tag{5.9}$$

Next, let $\phi \in C_0^\infty(\mathbb{R}^3)$ be a L^2 -normalized function. Following Le Bris [23, p 122] we introduce for all $\sigma > 0$ and all $\lambda, \omega \in [0, 1]$, the density operators $\mathcal{D}_{\sigma,\lambda}^\uparrow$ and $\mathcal{D}_{\sigma,\omega}^\downarrow$ with density matrices given by

$$\mathcal{D}_{\sigma,\lambda}^\uparrow(\mathbf{r}, \mathbf{r}') = \lambda\sigma^3\phi(\sigma\mathbf{r})\phi(\sigma\mathbf{r}'), \text{ and } \mathcal{D}_{\sigma,\omega}^\downarrow(\mathbf{r}, \mathbf{r}') = \omega\sigma^3\phi(\sigma\mathbf{r})\phi(\sigma\mathbf{r}').$$

Evidently, $\mathcal{D}_{\sigma,\lambda}^\uparrow \in \mathcal{K}_\lambda^\uparrow$ and $\mathcal{D}_{\sigma,\omega}^\downarrow \in \mathcal{K}_\omega^\downarrow$. In view of (1.12), we infer that there exists $1 \leq \gamma < 3/2$, $c > 0$ and $\sigma_0 > 0$ such that for all $\lambda, \omega \in [0, 1]$ and all $\sigma \in [0, \sigma_0]$, the estimate

$$\begin{aligned} I_{\lambda,\omega}^\infty &\leq \mathcal{E}(\mathcal{D}_{\sigma,\lambda}^\uparrow, \mathcal{D}_{\sigma,\omega}^\downarrow) \leq \lambda\sigma^2\tilde{\mathfrak{t}}_0[\phi, \phi] + \omega\sigma^2\tilde{\mathfrak{t}}_0[\phi, \phi] \\ &\quad + \lambda^2\sigma\mathcal{J}(2|\phi|^2) + \omega^2\sigma\mathcal{J}(2|\phi|^2) + \lambda\omega\sigma\mathcal{J}(2|\phi|^2) - c(\lambda^\gamma + \omega^\gamma)\sigma^{3(\gamma-1)} \int_{\mathbb{R}^3} |\phi|^{2\gamma} \\ &\leq \lambda\sigma^2\tilde{\mathfrak{t}}_0[\phi, \phi] + \omega\sigma^2\tilde{\mathfrak{t}}_0[\phi, \phi] + \frac{3}{2}\lambda^2\sigma\mathcal{J}(2|\phi|^2) + \frac{3}{2}\omega^2\sigma\mathcal{J}(2|\phi|^2) \\ &\quad - c(\lambda^\gamma + \omega^\gamma)\sigma^{3(\gamma-1)} \int_{\mathbb{R}^3} |\phi|^{2\gamma}. \end{aligned}$$

Hence $I_{\lambda,\omega}^\infty < 0$ provided $\lambda, \omega > 0$ are sufficiently small. As a consequence of (5.8) and (5.9) the functions $(\lambda, \omega) \mapsto I_{\lambda,\omega}$ and $(\lambda, \omega) \mapsto I_{\lambda,\omega}^\infty$ are decreasing and, for any positive λ, ω , we conclude that $-\infty < I_{\lambda,\omega} \leq I_{\lambda,\omega}^\infty < 0$. This ends the first part of the proof.

Before proceeding to the second part of the proof of Proposition 5.3, we need to show that minimizing sequences cannot tend to zero. Up to a few modifications, the following proof is identical to the one in [4, Lemma 5.3].

LEMMA 5.4. *Suppose $\lambda, \omega > 0$ and let $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_{j \in \mathbb{N}}$ be a minimizing sequence for (4.2). Then, for $\# = \uparrow, \downarrow$,*

$$\exists R > 0 \text{ such that } \lim_{j \rightarrow \infty} \sup_{x \in \mathbb{R}^3} \int_{x+B_R} \rho_{\mathcal{D}_j^\#} > 0.$$

A similar statement is valid for the minimizing sequence for (4.4).

Proof. We argue by contradiction. So, suppose $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_j$ is a minimizing sequence for (4.2) such that, for all $R > 0$ and $\# = \uparrow, \downarrow$,

$$\lim_{j \rightarrow \infty} \sup_{x \in \mathbb{R}^3} \int_{x+B_R} \rho_{\mathcal{D}_j^\#} = 0.$$

In view of Lemma 5.1 $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)$ is bounded in $\mathcal{H} = \mathfrak{h}^\uparrow \oplus \mathfrak{h}^\downarrow$. As a consequence, $(\rho_{\mathcal{D}_j^\uparrow}, \rho_{\mathcal{D}_j^\downarrow})$ is bounded in $\mathbf{H}^{1/2}(\mathbb{R}^3) \oplus \mathbf{H}^{1/2}(\mathbb{R}^3)$. Next we claim that the latter implies that $(\rho_{\mathcal{D}_j^\#})_j$ converges strongly to zero in $L^p(\mathbb{R}^3)$ provided $1 < p < 3/2$. In particular, it follows that $\lim_{j \rightarrow \infty} E_{\text{xc}}[\rho_{\mathcal{D}_j^\#}] = 0$. Indeed, for $r \in (1, 3/2)$ and $r^{-1} + q^{-1} = 1$, Hölder's inequality yields

$$|E_{\text{xc}}(\rho_{\mathcal{D}_j^\#})| \leq C \int_{\mathbb{R}^3} \rho_{\mathcal{D}_j^\#}^{1+\beta_\pm} \, d\mathbf{x} \leq C \left(\int_{\mathbb{R}^3} \rho_{\mathcal{D}_j^\#}^r \right)^{1/r} \left(\int_{\mathbb{R}^3} \rho_{\mathcal{D}_j^\#}^{q\beta_\pm} \right)^{1/q} \leq C \|\rho_{\mathcal{D}_j^\#}\|_{L^r} \rightarrow 0,$$

where we used that $\rho_{\mathcal{D}_j}$ converges (strongly) to zero in $L^p(\mathbb{R}^3)$ provided $1 < p < 3/2$.

For any $\epsilon > 0$ and $R > 0$ chosen such that $|V| \leq \epsilon \lambda^{-1}$ on B_R^c , we have that, provided j is sufficiently large,

$$\begin{aligned} \left| \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_j^\#} \right| &\leq \int_{B_R} V \rho_{\mathcal{D}_j^\#} + \int_{B_R^c} V \rho_{\mathcal{D}_j^\#} \\ &\leq \left(\int_{B_R} |V|^{p'} \right)^{\frac{1}{p'}} \left(\int_{B_R} \rho_{\mathcal{D}_j^\#}^p \right)^{\frac{1}{p}} + \frac{\epsilon}{\lambda} \int_{B_R^c} \rho_{\mathcal{D}_j^\#} \leq 2\epsilon, \end{aligned}$$

where, once again, we used that $\rho_{\mathcal{D}_j^\#}$ converges (strongly) to zero in $L^p(\mathbb{R}^3)$ provided $1 < p < 3/2$ and $V \in L^q + L^{q'}$ is clearly fulfilled for $3 < q, q' < \infty$. Hence $\lim_{j \rightarrow \infty} \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_j^\#} = 0$. Since

$$\begin{aligned} \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) &= \alpha^{-1} (\text{Tr} [\tilde{T}_0 \mathcal{D}_j^\uparrow] + \text{Tr} [\tilde{T}_0 \mathcal{D}_j^\downarrow]) + \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_j^\uparrow} + \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_j^\downarrow} \\ &\quad + \mathcal{J}(\rho_{\mathcal{D}_j^\uparrow} + \rho_{\mathcal{D}_j^\downarrow}, \rho_{\mathcal{D}_j^\uparrow} + \rho_{\mathcal{D}_j^\downarrow}) + E_{\text{xc}}[\rho_{\mathcal{D}_j^\uparrow}] + E_{\text{xc}}[\rho_{\mathcal{D}_j^\downarrow}] \\ &\geq \sum_{\# = \uparrow, \downarrow} \left\{ \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_j^\#} + E_{\text{xc}}[\rho_{\mathcal{D}_j^\#}] \right\}, \end{aligned}$$

we conclude that $I_{\lambda, \omega} \geq 0$, which contradicts the result in the first part of the proof of Proposition 5.3 (stating that $I_{\lambda, \omega} < 0$). Consequently, $(\rho_{\mathcal{D}_j^\#})_j$ cannot vanish. \square

Next we proceed to the second part of the proof of Proposition 5.3, where we begin by proving that $I_{\lambda, \omega} < I_{\lambda, \omega}^\infty$.

For this purpose, we consider a minimizing sequence $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_{j \in \mathbb{N}}$ for $I_{\lambda, \omega}^\infty$. An application of Lemma 5.4 ensures that there exist $\eta > 0$ and $R > 0$ such that, for j large enough, there exists $\mathbf{r}_j \in \mathbb{R}^3$ so that $\int_{\mathbf{r}_j+B_R} \rho_{\mathcal{D}_j^\#} \geq \eta$, $\# = \uparrow, \downarrow$. We define $\tilde{\mathcal{D}}_j^\# = \mathcal{T}_{\mathbf{R}_1 - \mathbf{r}_j} \mathcal{D}_j^\# \mathcal{T}_{\mathbf{r}_j - \mathbf{R}_1}$. Then $\tilde{\mathcal{D}}_j^\uparrow \in \mathcal{K}_\lambda^\uparrow$ and $\tilde{\mathcal{D}}_j^\downarrow \in \mathcal{K}_\omega^\downarrow$ and

$$\mathcal{E}(\tilde{\mathcal{D}}_j^\uparrow, \tilde{\mathcal{D}}_j^\downarrow) \leq \mathcal{E}^\infty(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) - \frac{Z_1 \eta}{R} - \frac{Z_1 \eta}{R},$$

whence,

$$I_{\lambda,\omega} \leq I_{\lambda,\omega}^\infty - \frac{Z_1\eta}{R} - \frac{Z_1\eta}{R} < I_{\lambda,\omega}^\infty.$$

To prove that the functions $(\lambda, \omega) \mapsto I_{\lambda,\omega}$ and $(\lambda, \omega) \mapsto I_{\lambda,\omega}^\infty$ are continuous we will apply Lemma 5.5; see below. We establish left-continuity of $(\lambda, \omega) \mapsto I_{\lambda,\omega}$. Let $\lambda, \omega > 0$, and let $(\lambda_k)_{k \in \mathbb{N}}, (\omega_k)_{k \in \mathbb{N}}$ be increasing sequences of positive real numbers converging to λ , respectively, ω . Let $\epsilon > 0$, $\mathcal{D}^\uparrow \in \mathcal{K}_\lambda$, and $\mathcal{D}^\downarrow \in \mathcal{K}_\omega$ such that $I_{\lambda,\omega} \leq \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \leq I_{\lambda,\omega} + (\epsilon/2)$. For all $k \in \mathbb{N}$, $\mathcal{D}_k^\uparrow = \lambda_k \lambda^{-1} \mathcal{D}^\uparrow \in \mathcal{K}_{\lambda_k}$ and $\mathcal{D}_k^\downarrow = \omega_k \omega^{-1} \mathcal{D}^\downarrow \in \mathcal{K}_{\omega_k}$ so that, for all $k \in \mathbb{N}$, $I_{\lambda,\omega} \leq I_{\lambda_k, \omega_k} \leq \mathcal{E}(\mathcal{D}_k^\uparrow, \mathcal{D}_k^\downarrow)$. Furthermore, by virtue of Lemma 5.5 we have that

$$\begin{aligned} \mathcal{E}(\mathcal{D}_k^\uparrow, \mathcal{D}_k^\downarrow) &= \frac{\lambda_k}{\lambda} \alpha^{-1} \text{Tr}(\tilde{T}_0 \mathcal{D}^\uparrow) + \frac{\omega_k}{\omega} \alpha^{-1} \text{Tr}(\tilde{T}_0 \mathcal{D}^\downarrow) + \frac{\lambda_k}{\lambda} \int_{\mathbb{R}^3} V \rho_{\mathcal{D}^\uparrow} + \frac{\omega_k}{\omega} \int_{\mathbb{R}^3} V \rho_{\mathcal{D}^\downarrow} \\ &\quad + \mathcal{J}((\lambda_k/\lambda)\rho_{\mathcal{D}^\uparrow}, (\lambda_k/\lambda)\rho_{\mathcal{D}^\uparrow}) + \mathcal{J}((\omega_k/\omega)\rho_{\mathcal{D}^\downarrow}, (\omega_k/\omega)\rho_{\mathcal{D}^\downarrow}) \\ &\quad + 2\mathcal{J}((\lambda_k/\lambda)\rho_{\mathcal{D}^\uparrow}, (\omega_k/\omega)\rho_{\mathcal{D}^\downarrow}) + E_{\text{xc}}\left[\frac{\lambda_k}{\lambda} \mathcal{D}_k^\uparrow\right] + E_{\text{xc}}\left[\frac{\omega_k}{\omega} \mathcal{D}_k^\downarrow\right] \xrightarrow[k \rightarrow \infty]{} \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow). \end{aligned}$$

Hence, for k large enough, $I_{\lambda,\omega} \leq I_{\lambda_k, \omega_k} \leq I_{\lambda,\omega} + \epsilon$. The right-continuity of $(\lambda, \omega) \mapsto I_{\lambda,\omega}$ can be shown by similar reasoning. \square

LEMMA 5.5. *Suppose $(a_k)_{k \in \mathbb{N}}$ is a sequence of positive real numbers which converges to 1, and let $(\rho_{\mathcal{D}_k^\#})_{k \in \mathbb{N}}$ be a sequence of nonnegative densities such that $(\sqrt{\rho_{\mathcal{D}_k^\#}})_{k \in \mathbb{N}}$ is bounded in $\mathbf{H}^{1/2}(\mathbb{R}^3)$. Then*

$$\lim_{k \rightarrow \infty} \left[E_{\text{xc}}(a_k \rho_{\mathcal{D}_k^\#}) - E_{\text{xc}}(\rho_{\mathcal{D}_k^\#}) \right] = 0, \quad \# = \uparrow, \downarrow.$$

Proof. Assumption 1.1 implies that there exists $1 < p_- \leq p_+ < 5/3$ and $C \in \mathbb{R}_+$ such that, provided k is sufficiently large,

$$|E_{\text{xc}}(\alpha_k \rho_k) - E_{\text{xc}}(\rho_k)| \leq C |\alpha_k - 1| \int_{\mathbb{R}^3} (\rho_k^{p_-} + \rho_k^{p_+}).$$

Since $(\sqrt{\rho_k})_{k \in \mathbb{N}}$ is bounded in $\mathbf{H}^{1/2}(\mathbb{R}^3)$, $(\rho_k)_{k \in \mathbb{N}}$ is bounded in $L^p(\mathbb{R}^3)$ for all $1 \leq p \leq 3/2$, and $(T_0^{1/2} \sqrt{\rho_k^\#})_{k \in \mathbb{N}}$ is bounded in $(L^2(\mathbb{R}^3))^3$, the result follows. \square

6. Decreasing property. We proceed to establish the following decreasing property.

LEMMA 6.1. *Let $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_{j \in \mathbb{N}}$ be a sequence in $\mathcal{K} = \mathcal{K}^\uparrow \oplus \mathcal{K}^\downarrow$, bounded in $\mathcal{H} = \mathfrak{h}^\uparrow \oplus \mathfrak{h}^\downarrow$, such that $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) \rightarrow (\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ in the weak-* topology of \mathcal{H} . If $\lim_{j \rightarrow \infty} \text{Tr}(\mathcal{D}_j^\uparrow) = \text{Tr}(\mathcal{D}^\uparrow)$, respectively, $\lim_{j \rightarrow \infty} \text{Tr}(\mathcal{D}_j^\downarrow) = \text{Tr}(\mathcal{D}^\downarrow)$ then $\rho_{\mathcal{D}_j^\uparrow}$, respectively, $\rho_{\mathcal{D}_j^\downarrow}$, converges to $\rho_{\mathcal{D}^\uparrow}$, respectively, $\rho_{\mathcal{D}^\downarrow}$, strongly in $L^p(\mathbb{R}^3)$ for all $p \in [1, 3/2)$. Furthermore,*

$$\mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \leq \liminf_{j \rightarrow \infty} \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) \text{ and } \mathcal{E}^\infty(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \leq \liminf_{j \rightarrow \infty} \mathcal{E}^\infty(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow).$$

Proof. We recall that the convergence of $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_{j \in \mathbb{N}}$ to $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ in the weak-* topology of $\mathcal{H} = \mathfrak{h}^\uparrow \oplus \mathfrak{h}^\downarrow$ means that, for any compact K on $L^2(\mathbb{R}^3)$, $\# = \uparrow, \downarrow$,

$$\lim_{j \rightarrow \infty} \text{Tr}(\mathcal{D}_j^\# K) = \text{Tr}(\mathcal{D}^\# K), \text{ and } \lim_{j \rightarrow \infty} \text{Tr}(T_0^{1/2} \mathcal{D}_j^\# T_0^{1/2} K) = \text{Tr}(T_0^{1/2} \mathcal{D}^\# T_0^{1/2} K).$$

In view of (3.4) we introduce $P_+(\alpha)$ as the projection onto the pure point spectral subspace of $H_{1,1,\alpha}$ in $\mathfrak{H} := L^2(\mathbb{R}^3)$ and we let $P_-(\alpha) = 1 - P_+(\alpha)$. Then, as in [4], we decompose the functional $\mathcal{E}(\cdot, \cdot)$ into three terms $\alpha \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) = P_1(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) + P_2(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) + \mathcal{L}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)$, where

$$P_1(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) := P_1(\mathcal{D}_j^\uparrow) + P_1(\mathcal{D}_j^\downarrow) \tag{6.1}$$

$$:= \text{Tr} \left[P_+(\alpha) H_{1,1,\alpha} P_+(\alpha) \mathcal{D}_j^\uparrow \right] + \text{Tr} \left[P_+(\alpha) H_{1,1,\alpha} P_+(\alpha) \mathcal{D}_j^\downarrow \right],$$

$$P_2(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) := P_2(\mathcal{D}_j^\uparrow) + P_2(\mathcal{D}_j^\downarrow) \tag{6.2}$$

$$:= \text{Tr} \left[P_-(\alpha) H_{1,1,\alpha} P_-(\alpha) \mathcal{D}_j^\uparrow \right] + \text{Tr} \left[P_-(\alpha) H_{1,1,\alpha} P_-(\alpha) \mathcal{D}_j^\downarrow \right],$$

$$\mathcal{L}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) := \frac{1}{2} \left(\mathcal{J}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) - E_{\text{xc}}(\mathcal{D}_j^\uparrow) - E_{\text{xc}}(\mathcal{D}_j^\downarrow) \right). \tag{6.3}$$

Step 1. We begin by proving that $P_1(\mathcal{D}^\#) \leq \liminf_j P_1(\mathcal{D}_j^\#)$. We select an orthonormal basis $\{e_k\}$ in $\mathfrak{H} = L^2(\mathbb{R}^3)$ such that $e_k \in \mathbf{H}^{1/2}(\mathbb{R}^3)$. Moreover, we introduce the functions $\psi_k = [P_+(\alpha) H_{1,1,\alpha} P_+(\alpha)]^{1/2} e_k$. If $\langle \cdot, \cdot \rangle$ denotes the scalar product in \mathfrak{H} , then the weak convergence in $\mathfrak{S}_2(\mathfrak{H})$ implies

$$\begin{aligned} P_1(\mathcal{D}_j^\#) &= \text{Tr} \left([P_+(\alpha) H_{1,1,\alpha} P_+(\alpha)]^{1/2} \mathcal{D}_j^\# [P_+(\alpha) H_{1,1,\alpha} P_+(\alpha)]^{1/2} \right) \\ &= \sum_k \langle \psi_k \mathcal{D}_j^\# \psi_k \rangle = \sum_k \langle T_0^{-1/2} \psi_k, \widetilde{\mathcal{D}}^\#{}^{(j)} T_0^{-1/2} \psi_k \rangle \end{aligned}$$

where $\widetilde{\mathcal{D}}^\#{}^{(j)} = T_0^{1/2} \mathcal{D}_j^\# T_0^{1/2}$. An application of Fatou's lemma, together with the nonnegativity of the Hilbert-Schmidt operator $T_k = \langle \cdot, T_0^{-1/2} \psi_k \rangle T_0^{-1/2} \psi_k$ and the hypothesis yield

$$\liminf_{j \rightarrow \infty} P_1(\mathcal{D}_j^\#) = \liminf_{j \rightarrow \infty} \sum_k \text{Tr}[T_k \widetilde{\mathcal{D}}^\#{}^{(j)}] \geq \sum_k \text{Tr}[T_k \widetilde{\mathcal{D}}^\#] = P_1(\mathcal{D}^\#).$$

A similar argument is found in [4].

Step 2. Since $P_-(\alpha) H_{1,1,\alpha} P_-(\alpha)$ is a Hilbert-Schmidt operator and thus compact, we immediately obtain

$$\lim_{j \rightarrow \infty} P_2(\mathcal{D}_j^\#) = \lim_j \text{Tr}[P_-(\alpha) H_{1,1,\alpha} P_-(\alpha) \mathcal{D}_j^\#] = \text{Tr}[P_-(\alpha) H_{1,1,\alpha} P_-(\alpha) \mathcal{D}^\#] = P_2(\mathcal{D}^\#).$$

Step 3. We have seen that $(\sqrt{\rho_{\mathcal{D}_j^\#}})_{j \in \mathbb{N}}$ is a bounded sequence in $\mathbf{H}^{1/2}(\mathbb{R}^3)$, so $\sqrt{\rho_{\mathcal{D}_j^\#}} \rightarrow \sqrt{\rho_{\mathcal{D}^\#}}$ weakly in $\mathbf{H}^{1/2}(\mathbb{R}^3)$ and strongly in $L^p(\mathbb{R}^3)$ for all $p \in [2, 3)$. In particular, $\sqrt{\rho_{\mathcal{D}_j^\#}}$ converges weakly to $\sqrt{\rho_{\mathcal{D}^\#}}$ in $L^2(\mathbb{R}^3)$. On the other hand, we know that

$$\lim_{j \rightarrow \infty} \left\| \sqrt{\rho_{\mathcal{D}_j^\#}} \right\|_{L^2}^2 = \lim_{j \rightarrow \infty} \int_{\mathbb{R}^3} \rho_{\mathcal{D}_j^\#} = \lim_{j \rightarrow \infty} \text{Tr}[\mathcal{D}_j^\#] = \text{Tr}[\mathcal{D}^\#] = \int_{\mathbb{R}^3} \rho_{\mathcal{D}^\#} = \|\sqrt{\rho_{\mathcal{D}^\#}}\|_{L^2}^2.$$

We conclude that $\sqrt{\rho_{\mathcal{D}_j^\#}} \rightarrow \sqrt{\rho_{\mathcal{D}^\#}}$ strongly in $L^2(\mathbb{R}^3)$. A standard bootstrap argument, using that $\|\sqrt{\rho_{\mathcal{D}_j^\#}}\|_{L^p} < C$ for any $2 \leq p \leq 3$ and interpolation, implies that $\{\sqrt{\rho_{\mathcal{D}_j^\#}}\}_{j \in \mathbb{N}}$ converges strongly to $\sqrt{\rho_{\mathcal{D}^\#}}$ in $L^p(\mathbb{R}^3)$ for all $p \in [2, 3)$ and, consequently, $\{\rho_{\mathcal{D}_j}\}_{j \in \mathbb{N}}$ converges to $\rho_{\mathcal{D}}$ strongly in $L^p(\mathbb{R}^3)$ for all $p \in [1, 3/2)$. As we show below, this allows us to conclude that

$$\begin{aligned} \lim_{j \rightarrow \infty} \mathcal{J}(\rho_{\mathcal{D}_j^\#}, \rho_{\mathcal{D}_j^\#}) &= \mathcal{J}(\rho_{\mathcal{D}^\#}, \rho_{\mathcal{D}^\#}), & \lim_{j \rightarrow \infty} \mathcal{J}(\rho_{\mathcal{D}_j^\uparrow}, \rho_{\mathcal{D}_j^\downarrow}) &= \mathcal{J}(\rho_{\mathcal{D}^\uparrow}, \rho_{\mathcal{D}^\downarrow}) \\ \text{and } \lim_{j \rightarrow \infty} E_{\text{xc}}[\rho_{\mathcal{D}_j^\#}] &= E_{\text{xc}}[\rho_{\mathcal{D}^\#}]. \end{aligned}$$

Indeed, as before let $W := 1/|x| = W_1 + W_2$ where $W_1 \in L^4$ and $W \in L^\infty$,

$$\begin{aligned} \left| \mathcal{J}(\rho_{\mathcal{D}_j^\#}, \rho_{\mathcal{D}_j^\#}) - \mathcal{J}(\rho_{\mathcal{D}^\#}, \rho_{\mathcal{D}^\#}) \right| &\leq c \|\rho_{\mathcal{D}_j^\#} - \rho_{\mathcal{D}^\#}\| \left\{ \|W_1\|_{L^4} \|\rho_{\mathcal{D}_j^\#} + \rho_{\mathcal{D}^\#}\|_{L^{4/3}} \right. \\ &\quad \left. + \|W_2\|_{L^\infty} \|\rho_{\mathcal{D}_j^\#} + \rho_{\mathcal{D}^\#}\|_{L^1} \right\}. \end{aligned}$$

Then we use that $\rho_{\mathcal{D}_j^\#} \rightarrow \rho_{\mathcal{D}^\#}$ in $L^p(\mathbb{R}^3)$, $p \in [1, 3/2)$. Similarly, Hölder’s inequality and the strong convergence yield

$$\begin{aligned} &|E_{\text{xc}}(\rho_{\mathcal{D}_j^\#}) - E_{\text{xc}}(\rho_{\mathcal{D}^\#})| \\ &\leq C \int |\rho_{\mathcal{D}_j^\#} - \rho_{\mathcal{D}^\#}| (\rho_{\mathcal{D}_j^\#}^{\beta_\pm} + \rho_{\mathcal{D}^\#}^{\beta_\pm}) \, d\mathbf{r} \\ &\leq C \left(\int |\rho_{\mathcal{D}_j^\#} - \rho_{\mathcal{D}^\#}|^{1/(1-\beta_\pm)} \right)^{1-\beta_\pm} \left(\int (\rho_{\mathcal{D}_j^\#}^{\beta_\pm} + \rho_{\mathcal{D}^\#}^{\beta_\pm})^{1/\beta_\pm} \right)^{\beta_\pm} \xrightarrow{j \rightarrow \infty} 0. \end{aligned}$$

To prove that

$$\lim_{j \rightarrow \infty} \mathcal{J}(\rho_{\mathcal{D}_j^\uparrow}, \rho_{\mathcal{D}_j^\downarrow}) = \mathcal{J}(\rho_{\mathcal{D}^\uparrow}, \rho_{\mathcal{D}^\downarrow}) \tag{6.4}$$

we use two facts. First, we know that $(\rho_{\mathcal{D}_j^\#})_j$ converges strongly to $\rho_{\mathcal{D}^\#}$ in $L^p(\mathbb{R}^3)$ for all $1 \leq p < 3/2$. Second, since $(\rho_{\mathcal{D}_j^\#})_j$ is bounded in $L^p(\mathbb{R}^3)$ (follows from the first fact) and $(1/|x|) \in L^3_w(\mathbb{R}^3)$, the generalized Young inequality yields that $((1/|x|) * \rho_{\mathcal{D}_j^\#})_j$ is bounded in $L^q(\mathbb{R}^3)$ provided $3/2 < q < \infty$ [27]. Let $\psi_j = \rho_{\mathcal{D}_j^\uparrow} * (1/|x|)$, $\psi = \rho_{\mathcal{D}^\uparrow} * (1/|x|)$, and choose $w \in \mathbf{H}^{1/2}(\mathbb{R}^3)$. Then

$$\begin{aligned} &\left\langle \psi_j \sqrt{\rho_{\mathcal{D}_j^\uparrow}} - \psi \sqrt{\rho_{\mathcal{D}^\uparrow}}, w \right\rangle_{\mathbf{H}^{-1/2}, \mathbf{H}^{1/2}} \\ &= \left\langle \psi_j \sqrt{\rho_{\mathcal{D}_j^\uparrow}} - \psi_j \sqrt{\rho_{\mathcal{D}^\uparrow}} + \psi_j \sqrt{\rho_{\mathcal{D}^\uparrow}} - \psi \sqrt{\rho_{\mathcal{D}^\uparrow}}, w \right\rangle_{\mathbf{H}^{-1/2}, \mathbf{H}^{1/2}} \\ &= \left\langle \psi_j (\sqrt{\rho_{\mathcal{D}_j^\uparrow}} - \sqrt{\rho_{\mathcal{D}^\uparrow}}), w \right\rangle + \langle (\psi_j - \psi) \sqrt{\rho_{\mathcal{D}^\uparrow}}, w \rangle. \end{aligned} \tag{6.5}$$

By the boundedness of ψ_j in $L^q(\mathbb{R}^3)$ and the strong convergence of $\rho_{\mathcal{D}_j^\#}$ to $\rho_{\mathcal{D}^\#}$ in $L^r(\mathbb{R}^3)$ in combination with the Hölder inequality it follows that $\left\langle \psi_j (\sqrt{\rho_{\mathcal{D}_j^\uparrow}} - \sqrt{\rho_{\mathcal{D}^\uparrow}}), w \right\rangle \xrightarrow{j \rightarrow \infty} 0$. For the second term on the right-hand side of (6.5)

we use the strong convergence of ψ_j to ψ in $L^q(\mathbb{R}^3)$ and the Hölder inequality to deduce that $\langle (\psi_j - \psi)\sqrt{\rho_{\mathcal{D}^\uparrow}}, w \rangle \xrightarrow{j \rightarrow \infty} 0$. Hence

$$\psi_j \sqrt{\rho_{\mathcal{D}_j^\uparrow}} = \left(\rho_{\mathcal{D}_j^\downarrow} * \frac{1}{|x|} \right) \rho_{\mathcal{D}_j^\uparrow} \xrightarrow{\mathbf{H}^{-1/2}} \left(\rho_{\mathcal{D}^\downarrow} * \frac{1}{|x|} \right) \rho_{\mathcal{D}^\uparrow}.$$

On the other hand, by the boundedness of $(\sqrt{\rho_{\mathcal{D}_j^\uparrow}})_j$ in $\mathbf{H}^{1/2}(\mathbb{R}^3)$ and the boundedness of $(\rho_{\mathcal{D}_j^\downarrow} * (1/|x|))_j$ in $L^q(\mathbb{R}^3)$ we have that $((\rho_{\mathcal{D}_j^\downarrow} * (1/|x|))\rho_{\mathcal{D}_j^\uparrow})_j$ is bounded in $L^1(\mathbb{R}^3)$. These facts, together with the pointwise convergence of $((1/|x|) * \rho_{\mathcal{D}_j^\downarrow})\rho_{\mathcal{D}_j^\uparrow}$ to $((1/|x|) * \rho_{\mathcal{D}^\downarrow})\rho_{\mathcal{D}^\uparrow}$ in \mathbb{R}^3 and Lebesgue’s dominated convergence theorem yields (6.4). Finally, Fatou’s theorem for nonnegative trace-class operators implies that

$$\text{Tr} [|\nabla|\mathcal{D}^\#|\nabla|] \leq \liminf_{j \rightarrow \infty} \text{Tr} [|\nabla|\mathcal{D}_j^\#|\nabla|]$$

which completes the proof. \square

By means of Lemma 3.2 we can prove the following result.

PROPOSITION 6.2. *Suppose $a, b, l, m > 0$ and $a + l < N^\uparrow + N^\downarrow \leq Z_{\text{tot}}$. If the problems associated to $I_{a,l}$ and $I_{b,m}^\infty$ have minimizers, then the following strict inequality holds:*

$$I_{a+b,l+m} < I_{a,l} + I_{b,m}^\infty. \tag{6.6}$$

Proof. If $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ is a minimizer for the problem $I_{a,l}$, then $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ is a minimizer to the Euler-Lagrange equations (or *spin-polarised Kohn-Sham equations*). Introduce

$$\begin{aligned} T_\uparrow &:= T_{\rho_{\mathcal{D}^\uparrow}} := \alpha^{-1}\tilde{T}_0 + V + g'(\rho_{\mathcal{D}^\uparrow}) + (\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|} \\ T_\downarrow &:= T_{\rho_{\mathcal{D}^\downarrow}} := \alpha^{-1}\tilde{T}_0 + V + g'(\rho_{\mathcal{D}^\downarrow}) + (\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|} \end{aligned}$$

together with

$$\mathbf{T}_{\uparrow,\downarrow} := \text{diag}(T_\uparrow, T_\downarrow) \text{ and } \mathcal{D} := \text{diag}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow).$$

Then we can write the Euler equations as

$$\mathcal{D} = 1_{(-\infty, \epsilon_F)}(\mathbf{T}_{\uparrow,\downarrow}) + \mathcal{D}^{(\delta)}$$

for some Fermi level $\epsilon_F \in \mathbb{R}$ and some matrix valued operator

$$\mathcal{D}^{(\delta)} = \text{diag}(\mathcal{D}_\uparrow^\delta, \mathcal{D}_\downarrow^\delta) \text{ with } 0 \leq \mathcal{D}_\#^\delta \leq 1, \text{ and } \text{Ran}(\mathcal{D}^{(\delta)}) \subset \text{Ker}(\mathbf{T}_{\uparrow,\downarrow} - \epsilon_F).$$

The essential spectrum of $\mathbf{T}_{\uparrow,\downarrow}$ equals the union of the essential spectra of $T_\#, \# = \uparrow, \downarrow$, i.e., $\text{spec}_{\text{ess}}(\mathbf{T}_{\uparrow,\downarrow}) = [0, +\infty)$. The operator $T_\#$ is bounded from below; indeed,

$$T_\# \leq \alpha^{-1}\tilde{T}_0 + V + (\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * |\mathbf{r}|^{-1}. \tag{6.7}$$

Since

$$-\sum_{k=1}^M Z_k + \int_{\mathbb{R}^3} \rho_{\mathcal{D}^\uparrow} + \int_{\mathbb{R}^3} \rho_{\mathcal{D}^\downarrow} = -Z_{\text{tot}} + a + l < Z_{\text{tot}} + N^\uparrow + N^\downarrow \leq 0$$

we may apply Lemma 3.2 which tells us that the operator on the right-hand side of (6.7) has infinitely many negative eigenvalues of finite multiplicity and $T_\#$ inherits this property. We infer that the same property holds for $\mathbf{T}_{\uparrow,\downarrow}$. Hence, we will have $\epsilon_F < 0$ and

$$\begin{aligned} \mathcal{D}^\uparrow &= \sum_{n=1}^{N^\uparrow} |\phi_n^\uparrow\rangle\langle\phi_n^\uparrow| + \sum_{n=N^\uparrow+1}^{M^\uparrow} \nu_n^\uparrow |\phi_n^\uparrow\rangle\langle\phi_n^\uparrow|, \\ \mathcal{D}^\downarrow &= \sum_{n=1}^{N^\downarrow} |\phi_n^\downarrow\rangle\langle\phi_n^\downarrow| + \sum_{n=N^\downarrow+1}^{M^\downarrow} \nu_n^\downarrow |\phi_n^\downarrow\rangle\langle\phi_n^\downarrow| \end{aligned}$$

where $0 \leq \nu_n^\# \leq 1$ and

$$\begin{aligned} \alpha^{-1}\tilde{T}_0\phi_n^\uparrow + V\phi_n^\uparrow + \left\{(\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|}\right\} \phi_n^\uparrow + g'(\rho_{\mathcal{D}^\uparrow})\phi_n^\uparrow &= \epsilon_n\phi_n^\uparrow \\ \alpha^{-1}\tilde{T}_0\phi_n^\downarrow + V\phi_n^\downarrow + \left\{(\rho_{\mathcal{D}^\uparrow} + \rho_{\mathcal{D}^\downarrow}) * \frac{1}{|\mathbf{r}|}\right\} \phi_n^\downarrow + g'(\rho_{\mathcal{D}^\downarrow})\phi_n^\downarrow &= \epsilon_n\phi_n^\downarrow \end{aligned}$$

with $\epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \dots < 0$ denoting the negative eigenvalues of $\mathbf{T}_{\uparrow,\downarrow}$ including multiplicities. The following facts follow immediately from the ones summarised in [4]:

1. ϵ_1 is a nondegenerated eigenvalue of $\mathbf{T}_{\uparrow,\downarrow}$;
2. For every n and $\# = \uparrow, \downarrow$, the function $\phi_n^\#$ (and hence $\rho_{\mathcal{D}^\uparrow}$ and $\rho_{\mathcal{D}^\downarrow}$) belongs to $\mathbf{H}^1(\mathbb{R}^3)$;
3. For every n and $\# = \uparrow, \downarrow$, the function $\phi_n^\#$ decays exponentially fast to zero at infinity.

Next suppose $(\tilde{\mathcal{D}}^\uparrow, \tilde{\mathcal{D}}^\downarrow)$ is a minimizer for the problem associated to $I_{b,m}^\infty$. Then $\tilde{\mathcal{D}} = 1_{(-\infty, \tilde{\epsilon}_F)}(\tilde{T}_{\uparrow,\downarrow}^\infty) + \tilde{\mathcal{D}}^{(\delta)}$, where $\tilde{\mathcal{D}} = \text{diag}(\tilde{\mathcal{D}}^\uparrow, \tilde{\mathcal{D}}^\downarrow)$ and

$$\begin{aligned} T_\uparrow^\infty &= \alpha^{-1}\tilde{T}_0 + g'(\rho_{\tilde{\mathcal{D}}^\uparrow}) + (\rho_{\tilde{\mathcal{D}}^\uparrow} + \rho_{\tilde{\mathcal{D}}^\downarrow}) * \frac{1}{|\mathbf{r}|} \\ T_\downarrow^\infty &= \alpha^{-1}\tilde{T}_0 + g'(\rho_{\tilde{\mathcal{D}}^\downarrow}) + (\rho_{\tilde{\mathcal{D}}^\uparrow} + \rho_{\tilde{\mathcal{D}}^\downarrow}) * \frac{1}{|\mathbf{r}|} \end{aligned}$$

are the entries of $\mathbf{T}_{\uparrow,\downarrow}^\infty = \text{diag}(T_\uparrow^\infty, T_\downarrow^\infty)$. Furthermore, $\epsilon_F \in \mathbb{R}$ is the Fermi level and $\tilde{\mathcal{D}}^{(\delta)}$ is a matrix valued operator satisfying

$$\tilde{\mathcal{D}}^{(\delta)} = \text{diag}(\tilde{\mathcal{D}}_\uparrow^\delta, \tilde{\mathcal{D}}_\downarrow^\delta) \text{ with } 0 \leq \tilde{\mathcal{D}}_\#^\delta \leq 1, \text{ and } \text{Ran}(\tilde{\mathcal{D}}^{(\delta)}) \subset \text{Ker}(T_{\uparrow,\downarrow}^\infty - \tilde{\epsilon}_F).$$

Case $\tilde{\epsilon}_F < 0$: for $\# = \uparrow, \downarrow$ we have that $\tilde{\mathcal{D}}^\# = \sum_{n=1}^{\tilde{N}^\#} |\tilde{\phi}_n^\#\rangle\langle\tilde{\phi}_n^\#| + \sum_{n=\tilde{N}^\#+1}^{\tilde{M}^\#} \tilde{\nu}_n^\# |\tilde{\phi}_n^\#\rangle\langle\tilde{\phi}_n^\#|$, where every $\tilde{\phi}_n^\#$ decays exponentially to zero at infinity. By choosing $j \in \mathbb{N}$ large enough, we infer that the operators

$$\mathcal{D}_j^\# := \min\{1, \|\mathcal{D}^\# + \mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\#\mathcal{T}_{-j\mathbf{e}}\|^{-1}\} \left(\mathcal{D}^\# + \mathcal{T}_{j\mathbf{e}}\tilde{\mathcal{D}}^\#\mathcal{T}_{-j\mathbf{e}}\right), \quad \# = \uparrow, \downarrow,$$

belongs to \mathcal{K} (recall $\mathcal{K} = \mathcal{K} \oplus \mathcal{K}$), $\text{Tr}[\mathcal{D}_j^\uparrow] \leq a + b$ and $\text{Tr}[\mathcal{D}_j^\downarrow] \leq l + m$ which, in view of Proposition 5.3, implies that $I_{a+b, l+m} \leq I_{\text{Tr}[\mathcal{D}_j^\uparrow], \text{Tr}[\mathcal{D}_j^\downarrow]}$. Since both $\phi_n^\#$ and $\tilde{\phi}_n^\#$ decay exponentially to zero at infinity, a straightforward computation implies that there exists some $\delta > 0$ such that for j sufficiently large,

$$\begin{aligned} \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) &= \mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) + \mathcal{E}^\infty(\tilde{\mathcal{D}}^\uparrow, \tilde{\mathcal{D}}^\downarrow) \\ &\quad - \frac{2b(Z_{\text{tot}} - a - l)}{j} - \frac{2m(Z_{\text{tot}} - a - l)}{j} + \mathcal{O}(e^{-\delta j}) \\ &= I_{a,l} + I_{b,m}^\infty - \frac{2b(Z_{\text{tot}} - a - l)}{j} - \frac{2m(Z_{\text{tot}} - a - l)}{j} + \mathcal{O}(e^{-\delta j}) \end{aligned}$$

whence, for j large enough, (we have, by hypothesis, that $(a+l) < (N^\uparrow + N^\downarrow) \leq Z_{\text{tot}}$)

$$I_{a+b, l+m} \leq I_{\text{Tr}[\mathcal{D}_j^\uparrow], \text{Tr}[\mathcal{D}_j^\downarrow]} \leq \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) < I_{a,l} + I_{b,m}^\infty.$$

Case $\tilde{\epsilon}_F = 0$: if $\tilde{\epsilon}_F = 0$, then zero is an eigenvalue of $\mathbf{T}_{\uparrow, \downarrow}^\infty$ and there exists $(\psi^\uparrow, \psi^\downarrow)^\text{T} \in \text{Ker}(\mathbf{T}_{\uparrow, \downarrow}^\infty) \subset \mathbf{H}^{1/2}(\mathbb{R}^3) \oplus \mathbf{H}^{1/2}(\mathbb{R}^3)$ such that $\|(\psi^\uparrow, \psi^\downarrow)^\text{T}\|_{L^2 \oplus L^2}^2 = \|\psi^\uparrow\|_{L^2}^2 + \|\psi^\downarrow\|_{L^2}^2 = 1$. Due to the diagonal structure of $\mathbf{T}_{\uparrow, \downarrow}^\infty$, we infer that $T_{\uparrow}^\infty \psi^\uparrow = 0$ and $T_{\downarrow}^\infty \psi^\downarrow = 0$ and there exist $\mu^\uparrow, \mu^\downarrow > 0$ such that $\tilde{\mathcal{D}}^\uparrow \psi^\uparrow = \mu^\uparrow \psi^\uparrow$, and $\tilde{\mathcal{D}}^\downarrow \psi^\downarrow = \mu^\downarrow \psi^\downarrow$. For $0 < \eta^\uparrow < \mu^\uparrow$, both $\mathcal{D}^\uparrow + \eta^\uparrow |\phi_{m+1}^\uparrow\rangle\langle\phi_{m+1}^\uparrow|$ and $\tilde{\mathcal{D}}^\uparrow - \eta^\uparrow |\psi^\uparrow\rangle\langle\psi^\uparrow|$ are in \mathcal{K}^\uparrow . Similarly, for $0 < \eta^\downarrow < \mu^\downarrow$, both

$$\mathcal{D}^\downarrow + \eta^\downarrow |\phi_{m+1}^\downarrow\rangle\langle\phi_{m+1}^\downarrow| \quad \text{and} \quad \tilde{\mathcal{D}}^\downarrow - \eta^\downarrow |\psi^\downarrow\rangle\langle\psi^\downarrow|$$

are in \mathcal{K}^\downarrow . A straightforward computation shows that

$$\begin{aligned} &\mathcal{E}(\mathcal{D}^\uparrow + \eta^\uparrow |\phi_{m+1}^\uparrow\rangle\langle\phi_{m+1}^\uparrow|, \mathcal{D}^\downarrow + \eta^\downarrow |\phi_{m+1}^\downarrow\rangle\langle\phi_{m+1}^\downarrow|) \\ &= I_{a,l} + 2(\eta^\uparrow + \eta^\downarrow)\epsilon_{m+1} + o(\eta^\uparrow + \eta^\downarrow) \end{aligned}$$

and

$$\mathcal{E}^\infty(\tilde{\mathcal{D}}^\uparrow - \eta^\uparrow |\psi^\uparrow\rangle\langle\psi^\uparrow|, \tilde{\mathcal{D}}^\downarrow - \eta^\downarrow |\psi^\downarrow\rangle\langle\psi^\downarrow|) = I_{b,m}^\infty + o(\eta^\uparrow + \eta^\downarrow).$$

Since

$$\text{Tr}[\mathcal{D}^\uparrow + \eta^\uparrow |\phi_{m+1}^\uparrow\rangle\langle\phi_{m+1}^\uparrow|] = a + \eta^\uparrow \quad \text{and} \quad \text{Tr}[\mathcal{D}^\downarrow + \eta^\downarrow |\phi_{m+1}^\downarrow\rangle\langle\phi_{m+1}^\downarrow|] = l + \eta^\downarrow,$$

and

$$\text{Tr}[\tilde{\mathcal{D}}^\uparrow - \eta^\uparrow |\psi^\uparrow\rangle\langle\psi^\uparrow|] = b - \eta^\uparrow \quad \text{and} \quad \text{Tr}[\tilde{\mathcal{D}}^\downarrow - \eta^\downarrow |\psi^\downarrow\rangle\langle\psi^\downarrow|] = m - \eta^\downarrow,$$

we infer that

$$I_{a+\eta^\uparrow, l+\eta^\downarrow} \leq I_{a,l} + (\eta^\uparrow + \eta^\downarrow)\epsilon_{m+1} + o(\eta^\uparrow + \eta^\downarrow)$$

and

$$I_{b-\eta^\uparrow, m-\eta^\downarrow}^\infty \leq I_{b,m}^\infty + o(\eta^\uparrow + \eta^\downarrow).$$

Then, by virtue of Proposition 5.3 and for η^\uparrow and η^\downarrow small enough, we conclude that

$$\begin{aligned} I_{a+b, l+m} &\leq I_{a+\eta^\uparrow, l+\eta^\downarrow} + I_{b-\eta^\uparrow, m-\eta^\downarrow}^\infty \\ &\leq I_{a,l} + I_{b,m}^\infty + (\eta^\uparrow + \eta^\downarrow)\epsilon_{m+1} + o(\eta^\uparrow + \eta^\downarrow) < I_{a,l} + I_{b,m}^\infty. \end{aligned}$$

□

7. Proof of main result. We are ready to give the proof of Theorem 1.3.

Proof. Let $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_{j \in \mathbb{N}}$ be a minimizing sequence for $I_{\lambda, \omega}$ with $\lambda \leq N^\uparrow$ and $\omega \leq N^\downarrow$.

From Lemma 5.1 it is known that $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_{j \in \mathbb{N}}$ is bounded in $\mathcal{H} = \mathfrak{h}^\uparrow \oplus \mathfrak{h}^\downarrow$ and that $(\sqrt{\rho_{\mathcal{D}_j^\#}})_{j \in \mathbb{N}}$, $\# = \uparrow, \downarrow$, is bounded in $\mathbf{H}^{1/2}(\mathbb{R}^3)$. We can assume (if necessary, by extracting a subsequence) that $(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow)_{j \in \mathbb{N}}$ converges to some $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \in \mathcal{K} = \mathcal{K}^\uparrow \oplus \mathcal{K}^\downarrow$ for the weak-* topology of $\mathcal{H} = \mathfrak{h}^\uparrow \oplus \mathfrak{h}^\downarrow$ and that $(\sqrt{\rho_{\mathcal{D}_j^\#}})_{j \in \mathbb{N}}$, $\# = \uparrow, \downarrow$, converges to $\sqrt{\rho_{\mathcal{D}_j^\#}}$ weakly in $\mathbf{H}^{1/2}(\mathbb{R}^3)$, strongly in $L^p_{\text{loc}}(\mathbb{R}^3)$, $2 \leq p < 3$, and almost everywhere.

Case $\text{Tr}[\mathcal{D}^\uparrow] = \lambda$ and $\text{Tr}[\mathcal{D}^\downarrow] = \omega$: evidently, $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \in \mathcal{K}_{\lambda, \omega} = \mathcal{K}_\lambda \oplus \mathcal{K}_\omega$ and, as a consequence of Lemma 6.1,

$$\mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \leq \liminf_{j \rightarrow \infty} \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) = I_{\lambda, \omega},$$

showing that $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ is a minimizer of (4.2).

Case $\text{Tr}[\mathcal{D}^\uparrow] = 0$ and $\text{Tr}[\mathcal{D}^\downarrow] = 0$: we can rule out this case in the following way. Arguing by contradiction, we assume that $\text{Tr}[\mathcal{D}^\uparrow] = 0$ and $\text{Tr}[\mathcal{D}^\downarrow] = 0$, which imply that $\rho_{\mathcal{D}^\uparrow} = 0$ and $\rho_{\mathcal{D}^\downarrow} = 0$. Then, for $\# = \uparrow, \downarrow$, $(\rho_{\mathcal{D}_j^\#})_{j \in \mathbb{N}}$ converges to 0 strongly in $L^p_{\text{loc}}(\mathbb{R}^3)$ for $2 \leq p < 3$ which implies that

$$\lim_{j \rightarrow \infty} \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_j^\#} = 0.$$

From which we deduce that

$$I_{\lambda, \omega}^\infty \leq \lim_{j \rightarrow \infty} \mathcal{E}^\infty(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) = \lim_{j \rightarrow \infty} \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) = I_{\lambda, \omega},$$

and the latter is a contradiction to assertion 1 of Proposition 5.3.

Case $\text{Tr}[\mathcal{D}^\uparrow] < \lambda$ and $\text{Tr}[\mathcal{D}^\downarrow] < \omega$. Define $a := \text{Tr}[\mathcal{D}^\uparrow]$, $l := \text{Tr}[\mathcal{D}^\downarrow]$ and suppose that $0 < a < \lambda$ and $0 < l < \omega$. Let χ be a smooth, radial function, nonincreasing in the radial direction, which satisfies $\chi(0) = 1$, $0 \leq \chi(x) < 1$ if $|x| > 0$, $\chi(x) = 0$ if $|x| \geq 1$, $\|\nabla \chi\|_{L^\infty} \leq 2$ and $\|\nabla(1 - \chi^2)^{1/2}\|_{L^\infty} \leq 2$. Introduce the quadratic partition of unity $\chi^2 + \zeta^2 = 1$ and put $\chi_R(\cdot) = \chi(\cdot/R)$. For any $j \in \mathbb{N}$, $R^\# \mapsto \text{Tr}(\chi_{R^\#} \mathcal{D}_j^\# \chi_{R^\#})$ is a continuous nondecreasing function which equals zero at $R^\# = 0$ and $\lim_{R^\uparrow \rightarrow \infty} \text{Tr}(\chi_{R^\uparrow}^\uparrow \mathcal{D}_j^\uparrow \chi_{R^\uparrow}^\uparrow) = \text{Tr}(\mathcal{D}_j^\uparrow) = \lambda$. Similarly, $\lim_{R^\downarrow \rightarrow \infty} \text{Tr}(\chi_{R^\downarrow}^\downarrow \mathcal{D}_j^\downarrow \chi_{R^\downarrow}^\downarrow) = \text{Tr}(\mathcal{D}_j^\downarrow) = \omega$.

Choose $R_j^\uparrow > 0$ such that $\text{Tr}(\chi_{R_j^\uparrow}^\uparrow \mathcal{D}^\uparrow \chi_{R_j^\uparrow}^\uparrow) = a$. Similarly, we choose R_k^\downarrow such that $\text{Tr}(\chi_{R_k^\downarrow}^\downarrow \mathcal{D}^\downarrow \chi_{R_k^\downarrow}^\downarrow) = l$. Then $R_j^\# \rightarrow \infty$, otherwise $(R_j^\#)_{j \in \mathbb{N}}$ contains a subsequence which converges to some (finite value) $\tilde{R}^\#$ and, consequently,

$$\begin{aligned} \int_{\mathbb{R}^3} \rho_{\mathcal{D}^\#}(x) \chi_{\tilde{R}^\#}^2(x) dx &= \lim_{k \rightarrow \infty} \int_{\mathbb{R}^3} \rho_{\mathcal{D}_{j_k}^\#}(x) \chi_{R_{j_k}^\#}^2 dx = \lim_{k \rightarrow \infty} \text{Tr}(\chi_{R_{j_k}^\#} \mathcal{D}_{j_k}^\# \chi_{R_{j_k}^\#}) \\ &= \begin{cases} a, & \# = \uparrow \\ l, & \# = \downarrow \end{cases} = \begin{cases} \int_{\mathbb{R}^3} \rho_{\mathcal{D}^\uparrow}(x), dx & \# = \uparrow \\ \int_{\mathbb{R}^3} \rho_{\mathcal{D}^\downarrow}(x), dx & \# = \downarrow. \end{cases} \end{aligned}$$

Since $\chi_{R^\#}^2 < 1$ on $\mathbb{R}^3 \setminus \{0\}$ we obtain a contradiction for both cases $\# = \uparrow, \downarrow$. As a consequence, $(R_j^\#)_{j \in \mathbb{N}}$ goes to infinity. Next we introduce $\mathcal{D}_{1,j}^\# = \chi_{R_j^\#} \mathcal{D}_j^\# \chi_{R_j^\#}$ and $\mathcal{D}_{2,j}^\# = \zeta_{R_j^\#} \mathcal{D}_j^\# \zeta_{R_j^\#}$. Then:

1. $0 \leq \mathcal{D}_{i,j}^\# \leq 1$;
2. $\mathcal{D}_{i,j}^\#$ are trace class self-adjoint operators on $L^2(\mathbb{R}^3)$;
3. $\rho_{\mathcal{D}_j^\#} = \rho_{\mathcal{D}_{1,j}^\#} + \rho_{\mathcal{D}_{2,j}^\#}$; and
4. $\text{Tr}(\mathcal{D}_{1,j}^\uparrow) = a$, $\text{Tr}(\mathcal{D}_{2,j}^\uparrow) = \lambda - a$; and
5. $\text{Tr}(\mathcal{D}_{1,j}^\downarrow) = l$, $\text{Tr}(\mathcal{D}_{2,j}^\downarrow) = \omega - l$.

The IMS formula, stated in Lemma 3.1,

$$T_0 \geq \chi_{R_j^\#} T_0 \chi_{R_j^\#} + \zeta_{R_j^\#} T_0 \zeta_{R_j^\#} - \frac{1}{\pi} \int_0^\infty \frac{1}{T_0^2 + \tau} \left(|\nabla \chi_{R_j^\#}|^2 + |\nabla \zeta_{R_j^\#}|^2 \right) \frac{1}{T_0^2 + \tau} \sqrt{\tau} d\tau$$

is useful at this stage. Indeed, using $\|\nabla \chi_{R_j^\#}\|_{L^\infty}^2 + \|\nabla \zeta_{R_j^\#}\|_{L^\infty}^2 \leq C/R^{\#2}$ and the uniform boundedness of $\text{Tr}(\mathcal{D}_j^\#)$, we obtain,

$$\text{Tr}(T_0 \mathcal{D}_j^\#) = \text{Tr}(T_0 \mathcal{D}_{1,j}^\#) + \text{Tr}(T_0 \mathcal{D}_{2,j}^\#) - \begin{cases} -\frac{4\lambda}{(R_j^\uparrow)^2}, & \# = \uparrow, \\ -\frac{4\omega}{(R_j^\downarrow)^2}, & \# = \downarrow. \end{cases} \tag{7.1}$$

We deduce that the sequences $(\mathcal{D}_{1,j}^\#)$, $(\mathcal{D}_{2,j}^\#)$, $\# = \uparrow, \downarrow$, are bounded sequences in $\mathfrak{h}^\#$. Taking $\phi \in C_0^\infty(\mathbb{R}^3)$, we find that

$$\begin{aligned} \text{Tr}(\mathcal{D}_{1,j}^\# |\phi\rangle\langle\phi|) &= \text{Tr}(\mathcal{D}_{1,j}^\# (|\chi_{R_j^\#} \phi\rangle\langle\chi_{R_j^\#} \phi|)) \\ &= \text{Tr}(\mathcal{D}_{1,j}^\# (|(\chi_{R_j^\#} - 1)\phi\rangle\langle(\chi_{R_j^\#} - 1)\phi|)) \\ &\quad + \text{Tr}(\mathcal{D}_j^\# (|\phi\rangle\langle(\chi_{R_j^\#} - 1)\phi|)) + \text{Tr}(\mathcal{D}_j^\# (|\phi\rangle\langle\phi|)) \\ &\xrightarrow{j \rightarrow \infty} \text{Tr}(\mathcal{D}^\# (|\phi\rangle\langle\phi|)), \end{aligned}$$

which shows that $(\mathcal{D}_{1,j}^\#)_{j \in \mathbb{N}}$ converges to $\mathcal{D}^\#$ for the weak-* topology of $\mathfrak{h}^\#$. Since $\text{Tr}(\mathcal{D}_{1,j}^\uparrow) = a = \text{Tr}(\mathcal{D}^\uparrow)$ and $\text{Tr}(\mathcal{D}_{1,j}^\downarrow) = l = \text{Tr}(\mathcal{D}^\downarrow)$ for all j , we infer from Lemma 6.1 that $(\rho_{\mathcal{D}_{1,j}^\#})$ converges to $\rho_{\mathcal{D}^\#}$ strongly in $L^p(\mathbb{R}^3)$, $p \in [1, 3/2)$, and

$$\mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \leq \lim_{j \rightarrow \infty} \mathcal{E}(\mathcal{D}_{1,j}^\uparrow, \mathcal{D}_{1,j}^\downarrow) \tag{7.2}$$

because $\rho_{\mathcal{D}_{2,j}^\#} = \rho_{\mathcal{D}_j^\#} - \rho_{\mathcal{D}_{1,j}^\#}$. In particular, $(\rho_{\mathcal{D}_{2,j}^\#})$ converges strongly to zero in $L_{\text{loc}}^p(\mathbb{R}^3)$, $p \in [1, 3/2)$, and $(\rho_{\mathcal{D}_j^\#})$ and $(\rho_{\mathcal{D}_{1,j}^\#})$ converge to $\rho_{\mathcal{D}^\#}$ in L_{loc}^p . Another

application of (7.1) yields

$$\begin{aligned}
 \mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) &= \alpha^{-1} \operatorname{Tr}(\tilde{T}_0 \mathcal{D}_j^\uparrow) + \alpha^{-1} \operatorname{Tr}(\tilde{T}_0 \mathcal{D}_j^\downarrow) + \int_{\mathbb{R}^3} V(\rho_{\mathcal{D}_j^\uparrow} + \rho_{\mathcal{D}_j^\downarrow}) \\
 &\quad + \mathcal{J}(\rho_{\mathcal{D}_j^\uparrow} + \rho_{\mathcal{D}_j^\downarrow}, \rho_{\mathcal{D}_j^\uparrow} + \rho_{\mathcal{D}_j^\downarrow}) + \sum_{\#=\uparrow, \downarrow} \int_{\mathbb{R}^3} g(\rho_{\mathcal{D}_j^\#}) \\
 &\geq \alpha^{-1} \operatorname{Tr}(\tilde{T}_0 \mathcal{D}_{1,j}^\uparrow) + \alpha^{-1} \operatorname{Tr}(\tilde{T}_0 \mathcal{D}_{2,j}^\uparrow) + \alpha^{-1} \operatorname{Tr}(\tilde{T}_0 \mathcal{D}_{1,j}^\downarrow) + \alpha^{-1} \operatorname{Tr}(\tilde{T}_0 \mathcal{D}_{2,j}^\downarrow) \\
 &\quad - \frac{4\lambda}{(R_j^\uparrow)^2} - \frac{4\omega}{(R_j^\downarrow)^2} + \int_{\mathbb{R}^3} V(\rho_{\mathcal{D}_{1,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\uparrow}) + \int_{\mathbb{R}^3} V(\rho_{\mathcal{D}_{1,j}^\downarrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}) \\
 &\quad + \mathcal{J}(\rho_{\mathcal{D}_{1,j}^\uparrow} + \rho_{\mathcal{D}_{1,j}^\downarrow}, \rho_{\mathcal{D}_{1,j}^\uparrow} + \rho_{\mathcal{D}_{1,j}^\downarrow}) + \mathcal{J}(\rho_{\mathcal{D}_{2,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}, \rho_{\mathcal{D}_{2,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}) \\
 &\quad + \mathcal{J}(\rho_{\mathcal{D}_{1,j}^\uparrow} + \rho_{\mathcal{D}_{1,j}^\downarrow}, \rho_{\mathcal{D}_{2,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}) + \mathcal{J}(\rho_{\mathcal{D}_{2,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}, \rho_{\mathcal{D}_{1,j}^\uparrow} + \rho_{\mathcal{D}_{1,j}^\downarrow}) \\
 &\quad + E_{\text{xc}}[\rho_{\mathcal{D}_{1,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\uparrow}] + E_{\text{xc}}[\rho_{\mathcal{D}_{1,j}^\downarrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}] \\
 &= \mathcal{E}(\mathcal{D}_{1,j}^\uparrow, \mathcal{D}_{1,j}^\downarrow) + \mathcal{E}^\infty(\mathcal{D}_{2,j}^\uparrow, \mathcal{D}_{2,j}^\downarrow) + \int_{\mathbb{R}^3} V(\rho_{\mathcal{D}_{2,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}) \\
 &\quad + \int_{\mathbb{R}^3} g(\rho_{\mathcal{D}_{1,j}^\uparrow} + \rho_{\mathcal{D}_{2,j}^\uparrow}) - g(\rho_{\mathcal{D}_{1,j}^\uparrow}) - g(\rho_{\mathcal{D}_{2,j}^\uparrow}) \\
 &\quad + \int_{\mathbb{R}^3} g(\rho_{\mathcal{D}_{1,j}^\downarrow} + \rho_{\mathcal{D}_{2,j}^\downarrow}) - g(\rho_{\mathcal{D}_{1,j}^\downarrow}) - g(\rho_{\mathcal{D}_{2,j}^\downarrow}) - \frac{4\lambda}{(R_j^\uparrow)^2} - \frac{4\omega}{(R_j^\downarrow)^2}.
 \end{aligned}$$

Now, on the one hand, by choosing R large enough, we have that

$$\left| \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_{2,j}^\uparrow} \right| \leq Z_{\text{tot}} \left(\int_{B(0,R)} \rho_{\mathcal{D}_{2,j}^\uparrow} \right)^{\frac{1}{2}} \|\sqrt{\rho_{\mathcal{D}_{2,j}^\uparrow}}\|_{\mathbf{H}^{1/2}} + \frac{Z_{\text{tot}}(\lambda - a)}{R}.$$

and, similarly,

$$\left| \int_{\mathbb{R}^3} V \rho_{\mathcal{D}_{2,j}^\downarrow} \right| \leq Z_{\text{tot}} \left(\int_{B(0,R)} \rho_{\mathcal{D}_{2,j}^\downarrow} \right)^{\frac{1}{2}} \|\sqrt{\rho_{\mathcal{D}_{2,j}^\downarrow}}\|_{\mathbf{H}^{1/2}} + \frac{Z_{\text{tot}}(\omega - l)}{R}.$$

Furthermore, for some constant C independent of R and j , we have that, for $\# = \uparrow, \downarrow$,

$$\begin{aligned}
 &\left| \int_{\mathbb{R}^3} \left(g(\rho_{\mathcal{D}_{1,j}^\#} + \rho_{\mathcal{D}_{2,j}^\#}) - g(\rho_{\mathcal{D}_{1,j}^\#}) - g(\rho_{\mathcal{D}_{2,j}^\#}) \right) \right| \\
 &\leq C \left\{ \int_{B_R} \left(\rho_{\mathcal{D}_{2,j}^\#} + \rho_{\mathcal{D}_{2,j}^\#}^2 \right) + \|\rho_{\mathcal{D}_{1,j}^\#}\|_{L^2} \left(\int_{B_R^c} \rho_{\mathcal{D}_{2,j}^\#}^2 \right)^{\frac{1}{2}} \right\} \\
 &\quad + C \left(\int_{B_R} \rho_{\mathcal{D}_{2,j}^\#}^{p_-} + \rho_{\mathcal{D}_{2,j}^\#}^{p_+} \right) \\
 &\quad + C \left\{ \int_{B_R^c} \left(\rho_{\mathcal{D}_{1,j}^\#} + \rho_{\mathcal{D}_{1,j}^\#}^2 \right) + \|\rho_{\mathcal{D}_{2,j}^\#}\|_{L^2} \left(\int_{B_R^c} \rho_{\mathcal{D}_{1,j}^\#}^2 \right)^{\frac{1}{2}} \right\} \\
 &\quad + C \left(\int_{B_R^c} \rho_{\mathcal{D}_{1,j}^\#}^{p_-} + \rho_{\mathcal{D}_{1,j}^\#}^{p_+} \right).
 \end{aligned}$$

We already know that the sequences $(\sqrt{\rho_{\mathcal{D}_{1,j}^\#}})_{n \in \mathbb{N}}$ and $(\sqrt{\rho_{\mathcal{D}_{2,j}^\#}})_{j \in \mathbb{N}}$ are bounded in $\mathbf{H}^{1/2}(\mathbb{R}^3)$, that $\rho_{\mathcal{D}_{1,j}^\#} \rightarrow \rho_{\mathcal{D}^\#}$ in $L^p(\mathbb{R}^3)$ for any $p \in [1, 3/2)$ and that $\rho_{\mathcal{D}_{2,j}^\#} \rightarrow 0$ in $L^p_{\text{loc}}(\mathbb{R}^3)$ for the same limits of p respectively of the case. Therefore, for all $\epsilon > 0$, there exists $J \in \mathbb{N}$ such that $\forall j \geq J$,

$$\mathcal{E}(\mathcal{D}_j^\uparrow, \mathcal{D}_j^\downarrow) \geq \mathcal{E}(\mathcal{D}_{1,j}^\uparrow, \mathcal{D}_{1,j}^\downarrow) + \mathcal{E}^\infty(\mathcal{D}_{2,j}^\uparrow, \mathcal{D}_{2,j}^\downarrow) - \epsilon \geq I_{a,l} + I_{\lambda-a,\omega-l}^\infty - \epsilon.$$

By letting j tend to infinity, ϵ tend to zero, and applying (5.7), we get that $I_{\lambda,\omega} = I_{a,l} + I_{\lambda-a,\omega-l}^\infty$ and that $(\mathcal{D}_{1,j}^\uparrow, \mathcal{D}_{1,j}^\downarrow)_{j \in \mathbb{N}}$, respectively $(\mathcal{D}_{2,j}^\uparrow, \mathcal{D}_{2,j}^\downarrow)_{j \in \mathbb{N}}$ is a minimizing sequence for $I_{a,l}$, respectively for $I_{\lambda-a,\omega-l}^\infty$. From (7.2), i.e. $\mathcal{E}(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow) \leq \lim_{j \rightarrow \infty} \mathcal{E}(\mathcal{D}_{1,j}^\uparrow, \mathcal{D}_{1,j}^\downarrow)$, it is seen that $(\mathcal{D}^\uparrow, \mathcal{D}^\downarrow)$ is a minimizer for $I_{a,l}$.

We take a closer look at the sequence $(\mathcal{D}_{2,j}^\uparrow, \mathcal{D}_{2,j}^\downarrow)_{j \in \mathbb{N}}$. Since it is a minimizing sequence for $I_{\lambda-a,\omega-l}^\infty$, the sequences $(\rho_{\mathcal{D}_{2,j}^\#})_{j \in \mathbb{N}}$, $\# = \uparrow, \downarrow$, cannot vanish. Therefore, there exist $\eta > 0$, $R > 0$ such that, for all $j \in \mathbb{N}$,

$$\int_{y_j^\# + B_R} \rho_{\mathcal{D}_{2,j}^\#} \geq \eta$$

for some $y_j^\# \in \mathbb{R}^3$ and, as a consequence, the sequence $(\mathcal{T}_{y_j^\#} \mathcal{D}_{2,j}^\#, \mathcal{T}_{-y_j^\#})_{j \in \mathbb{N}}$ converges in the weak-* topology of $\mathfrak{h}^\#$ to some $\tilde{\mathcal{D}}^\# \in \mathcal{K}^\#$ satisfying $\text{Tr}[\tilde{\mathcal{D}}^\#] \geq \eta > 0$, $\# = \uparrow, \downarrow$. By setting $b = \text{Tr}[\tilde{\mathcal{D}}^\uparrow]$ and $m = \text{Tr}[\tilde{\mathcal{D}}^\downarrow]$ we may argue as above to verify that $(\tilde{\mathcal{D}}^\uparrow, \tilde{\mathcal{D}}^\downarrow)$ is a minimizer for $I_{b,m}^\infty$ and, in addition,

$$I_{\lambda,\omega} = I_{a,l} + I_{b,m}^\infty + I_{\lambda-a-b,\omega-l-m}^\infty.$$

However, Proposition 6.2 informs us that $I_{a+b,l+m} < I_{a,l} + I_{b,m}^\infty$. Hence we conclude that $I_{a+b,l+m} + I_{\lambda-a-b,\omega-l-m}^\infty < I_{\lambda,\omega}$ which contradicts Proposition 5.3. This completes the proof. \square

REFERENCES

- [1] R. A. ADAMS, *Sobolev spaces*, Academic Press, 1975.
- [2] A. ANANTHARAMAN AND E. CANCÈS, *Existence of minimizers for Kohn-Sham models in quantum chemistry*, Ann. I. H. Poincaré - AN, 26 (2009), pp. 2425–2455.
- [3] C. ARGAEZ, *Rigorous results on nonlinear equations arising in quantum chemistry*, Ph.D. dissertation, DIT, Republic of Ireland, 2013.
- [4] C. ARGAEZ AND M. MELGAARD, *Existence of a minimizer for the quasi-relativistic Kohn-Sham model*, Elec. J. Diff. Eqs, 18 (2012), pp. 1–20.
- [5] P. BENILAN, H. BREZIS, AND M. G. CRANDALL, *A semilinear equation in $L^1(\mathbb{R}^N)$* , Ann. del. Scuola Norm. Sup. di Pisa, 2:4 (1975), pp. 523–555.
- [6] P. BENILAN AND H. BREZIS, *Nonlinear problems related to the Thomas-Fermi equation*, J. Evol. Equ., 3 (2004), pp. 673–770.
- [7] P. BENILAN, J. A. GOLDSTEIN, AND G. RUIZ RIEDER, *A nonlinear elliptic system arising in electron density theory*, Commun. P.D.E., 17 (1992), pp. 2079–2092.
- [8] P. BENILAN, J. A. GOLDSTEIN, AND G. RUIZ RIEDER, *The Fermi-Amaldi correction in spin polarized Thomas-Fermi theory*, Differential equations and mathematical physics (Birmingham, AL, 1990), Math. Sci. Engrg., vol. 186, Academic Press, Boston, MA, 1992, pp. 25–37.
- [9] A. DALL’ACQUA, T. Ø. SØRENSEN, AND E. STOCKMEYER, *Hartree-Fock theory for pseudorelativistic atoms*, Ann. Henri Poincaré, 9:4 (2008), pp. 711–742.
- [10] D. E. EDMUNDS AND W. D. EVANS, *Spectral Theory and Differential Operators*, Clarendon Press, Oxford University Press, New York, 1987.
- [11] M. ENSTEDT AND M. MELGAARD, *Existence of infinitely many solutions to the quasi-relativistic Hartree-Fock equations*, Int. J. Math. Math. Sci., Volume 2009, Article ID 651871, 20 pages.

- [12] M. GALVAN, A. VELA, AND J. L. GAZQUEZ, *Chemical reactivity in spin-polarized density functional theory*, J. Phys. Chem., 92 (1988), pp. 6470–6474.
- [13] M. GALVAN AND R. VARGAS, *Spin potential in Kohn-Sham theory*, J. Phys. Chem., 96 (1992), pp. 1625–1630.
- [14] J. A. GOLDSTEIN AND G. R. RIEDER, *A rigorous modified Thomas-Fermi theory for atomic systems*, J. Math. Phys., 28:5 (1987), pp. 1198–1202.
- [15] J. A. GOLDSTEIN AND G. R. RIEDER, *Spin-polarized Thomas-Fermi theory*, J. Math. Phys., 29 (1988), pp. 709–716.
- [16] J. A. GOLDSTEIN, G. R. RIEDER, AND W. JIA, *Thomas-Fermi theory with magnetic fields and the Fermi-Amaldi correction*, Differential Integral Equations, 8:6 (1995), pp. 1305–1316.
- [17] D. J. GRIFFITHS, *Introduction to Quantum Mechanics*, Pearson Prentice Hall, U.S.A., 2004.
- [18] W. J. HEHRE, L. RADOM, P.V.R. SCHLEYER, AND J. A. POPLE, *Ab initio molecular orbital theory*, Wiley, 1986.
- [19] I. W. HERBST, *Spectral theory of the operator $(p^2 + m^2)^{1/2} - Ze^2/r$* , Comm. Math. Phys., 53:3 (1977), pp. 285–294.
- [20] P. HOHENBERG AND W. KOHN, *Inhomogeneous electron gas*, Phys. Rev. B, 136 (1964), pp. 864–871.
- [21] T. KATO, *Perturbation Theory for Linear Operators*, Reprint of the 1980 edition. Classics in Mathematics. Springer-Verlag, Berlin, 1995.
- [22] W. KOHN AND L. J. SHAM, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. A, 140 (1965), 1133.
- [23] C. LE BRIS, *Quelques problèmes mathématiques en chimie quantique moléculaire*, These de l’Ecole Polytechnique, 1993.
- [24] C. LE BRIS, *Some results on the Thomas-Fermi-Dirac-von Weizsäcker model*, Diff. Int. Equ., 6:2 (1993), pp. 337–353.
- [25] C. LE BRIS, *On the spin polarized Thomas-Fermi model with the Fermi-Amaldi correction*, Nonlinear Anal., 25:7 (1995), pp. 669–679.
- [26] E. LENZMANN AND M. LEWIN, *Minimizers for the Hartree-Fock-Bogoliubov theory of neutron stars and white dwarfs*, Duke Math. J., 152:2 (2010), pp. 257–315.
- [27] P.-L. LIONS, *The Choquard equation and related equations*, Nonlinear Anal., 4 (1980), pp. 1063–1073.
- [28] P.-L. LIONS, *The concentration-compactness principle in the calculus of variations. The locally compact case. I and II*, Ann. Inst. Henri Poincaré, Anal. Non Linéaire, 1, pp. 109–145 and pp. 223–283.
- [29] P.-L. LIONS, *Solutions of Hartree-Fock equations for Coulomb systems*, Comm. Math. Phys., 109:1 (1987), pp. 33–97.
- [30] M. MELGAARD AND F. D. Y. ZONGO, *Multiple solutions of the quasi relativistic Choquard equation*, J. Math. Phys., 53, 033709 (12 pp).
- [31] R. G. PARR AND W. YANG, *Density-functional theory of atoms and molecules*, Oxford University Press, 1989.
- [32] J. P. PERDEW AND S. KURTH, *Density Functionals for Non-Relativistic Coulomb Systems in the New 16 Century*, in “A Primer in Density Functional Theory”, edited by C. Fiolhais, F. Nogueira, and M. Marques (Springer Lecture Notes in Physics, Vol. 620, 2003), pp. 1–55.
- [33] G. ROZENBLUM AND M. MELGAARD, *Schrödinger operators with singular potentials*, in: Stationary partial differential equations. Vol. II, pp. 407–517, Handb. Differ. Equ., Elsevier/North-Holland, Amsterdam, 2005.
- [34] J. C. SLATER, *Quantum theory of molecules and solids*, McGraw-Hill, New York, 1974.
- [35] A. SZABO AND N. S. OSTLUND, *Modern quantum chemistry: an introduction to advanced electronic structure theory*, MacMillan, 1982.

