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Abstract

This article is concerned with the mathematical analysis of the Kohn-Sham and extended Kohn-Sham models, in the local density approximation (LDA) and generalized gradient approximation (GGA) frameworks. After recalling the mathematical derivation of the Kohn-Sham and extended Kohn-Sham LDA and GGA models from the Schrödinger equation, we prove that the extended Kohn-Sham LDA model has a solution for neutral and positively charged systems. We then prove a similar result for the spin-unpolarized Kohn-Sham GGA model for two-electron systems, by means of a concentration-compactness argument.

1 Introduction

Density Functional Theory (DFT) is a powerful, widely used method for computing approximations of ground state electronic energies and densities in chemistry, materials science, biology and nanosciences.

According to DFT [10, 15], the electronic ground state energy and density of a given molecular system can be obtained by solving a minimization problem of the form

$$\inf \left\{ F(\rho) + \int_{\mathbb{R}^3} \rho V, \ \rho \geq 0, \ \sqrt{\rho} \in H^1(\mathbb{R}^3), \ \int_{\mathbb{R}^3} \rho = N \right\}$$

where N is the number of electrons in the system, V the electrostatic potential generated by the nuclei, and F some functional of the electronic density ρ, the functional F being universal, in the sense that it does not depend on the molecular system under consideration. Unfortunately, no tractable expression for F is known, which could be used in numerical simulations.

The groundbreaking contribution which turned DFT into a useful tool to perform calculations, is due to Kohn and Sham [11], who introduced the local density approximation (LDA) to DFT. The resulting Kohn-Sham LDA model is still commonly used, in particular in solid state physics. Improvements of this model have then been proposed by many authors, giving rise to Kohn-Sham GGA models [12, 21, 2, 20], GGA being the abbreviation of Generalized Gradient Approximation. While there is basically a unique Kohn-Sham LDA model, there are several Kohn-Sham GGA models, corresponding to different approximations of the so-called exchange-correlation functional. A given GGA model will be known to perform well for some classes of molecular system, and poorly for some other classes. In some cases, the best result will be obtained with LDA. It is to be noticed that each Kohn-Sham model exists in two versions: the standard version, with integer occupation numbers, and the extended version with "fractional" occupation numbers. As explained below, the former one originates from Levy-Lieb's (pure state) contruction of the density functional, while the latter is derived from Lieb's (mixed state) construction.

To our knowledge, there are very few results on Kohn-Sham LDA and GGA models in the mathematical literature. In fact, we are only aware of a proof of existence of a minimizer for the standard Kohn-Sham LDA model by Le Bris [13]. In this contribution, we prove the existence of a minimizer for the extended Kohn-Sham LDA model, as well as for the two-electron standard and extended Kohn-Sham GGA models, under some conditions on the GGA exchange-correlation functional.

Our article is organized as follows. First, we provide a detailed presentation of the various Kohn-Sham models, which, despite their importance in physics and chemistry [24], are not very well known in the mathematical community. The mathematical foundations of DFT are recalled in section 2, and the derivation of the (standard and extended) Kohn-Sham LDA and GGA models is discussed in section 3. We state our main results in section 4, and postpone the proofs until section 5.

We restrict our mathematical analysis to closed-shell, spin-unpolarized models. All our results related to the LDA setting can be easily extended to open-shell, spin-polarized models (i.e. to the local spin-density approximation LSDA). Likewise, we only deal with all electron descriptions, but valence electron models with usual pseudo-potential approximations (norm conserving [29], ultrasoft [30], PAW [3]) can be dealt with in a similar way.

2 Mathematical foundations of DFT

As mentioned previously, DFT aims at calculating electronic ground state energies and densities. Recall that the ground state electronic energy of a molecular system composed of M nuclei of charges z_1, ..., z_M ($z_k \in \mathbb{N} \setminus \{0\}$ in atomic units) and N electrons is the bottom of the spectrum of the electronic hamiltonian

$$H_N = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1}$$

where $\mathbf{r}_i$ and $\mathbf{R}_k$ are the positions in $\mathbb{R}^3$ of the $i^{\rm th}$ electron and the $k^{\rm th}$ nucleus respectively. The hamiltonian H_N acts on electronic wavefunctions $\Psi(\mathbf{r}_1, \sigma_1; \cdots; \mathbf{r}_N, \sigma_N)$, $\sigma_i \in \Sigma := \{|\uparrow\rangle, |\downarrow\rangle\}$ denoting the spin variable of the $i^{\rm th}$ electron, the nuclear coordinates $\{\mathbf{R}_k\}_{1 \le k \le M}$ playing the role of parameters. It is convenient to denote by $\mathbb{R}^3_\Sigma := \mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}$ and $\mathbf{x}_i := (\mathbf{r}_i, \sigma_i)$. As electrons are fermions, electonic wavefunctions are antisymmetric with respect to the renumbering of electrons, i.e.

$$\Psi(\mathbf{x}_{p(1)}, \cdots, \mathbf{x}_{p(N)}) = \epsilon(p)\Psi(\mathbf{x}_1, \cdots, \mathbf{x}_N)$$

where $\epsilon(p)$ is the signature of the permutation p. Note that (in the absence of magnetic fields) $H_N\Psi$ is real-valued if Ψ is real-valued. Our purpose being the calculation of the bottom of the spectrum of H_N, there is therefore no restriction in considering real-valued wavefunctions only. In other words, H_N can be considered here as an operator on the real Hilbert space

$$\mathcal{H}_N = \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3_\Sigma),$$

endowed with the inner product

$$\langle \Psi | \Psi' \rangle_{\mathcal{H}_N} = \int_{(\mathbb{R}^3_\Sigma)^N} \Psi(\mathbf{x}_1, \cdots, \mathbf{x}_N)\, \Psi'(\mathbf{x}_1, \cdots, \mathbf{x}_N)\, d\mathbf{x}_1 \cdots d\mathbf{x}_N,$$

where

$$\int_{\mathbb{R}^3_\Sigma} f(\mathbf{x})\, d\mathbf{x} := \sum_{\sigma \in \Sigma} \int_{\mathbb{R}^3} f(\mathbf{r}, \sigma)\, d\mathbf{r},$$

and the corresponding norm $\| \cdot \|_{\mathcal{H}_N} = \langle \cdot | \cdot \rangle_{\mathcal{H}_N}^{\frac{1}{2}}$. It is well-known that H_N is a self-adjoint operator on $\mathcal{H}_N$ with form domain

$$\mathcal{Q}_N = \bigwedge_{i=1}^{N} H^1(\mathbb{R}^3_\Sigma).$$

Denoting by

$$Z = \sum_{k=1}^{M} z_k$$

the total nuclear charge of the system, it results from Zhislin's theorem that for neutral or positively charged systems ($Z \geq N$), H_N has an infinite number of negative eigenvalues below the bottom of its essential spectrum. In particular, the electronic ground state energy $\lambda_1(H_N)$ is an eigenvalue of H_N, and more precisely the lowest one.

In any case, i.e. whatever Z and N, we always have

$$\lambda_1(H_N) = \inf \left\{ \langle \Psi | H_N | \Psi \rangle,\ \Psi \in \mathcal{Q}_N,\ \|\Psi\|_{\mathcal{H}_N} = 1 \right\}. \tag{2}$$

Note that it also holds

$$\lambda_1(H_N) = \inf \left\{ \mathrm{Tr}\,(H_N \Gamma),\ \Gamma \in \mathcal{S}(\mathcal{H}_N),\ \mathrm{Ran}(\Gamma) \subset \mathcal{Q}_N,\ 0 \leq \Gamma \leq 1,\ \mathrm{Tr}\,(\Gamma) = 1 \right\}. \tag{3}$$

In the above expression, $\mathcal{S}(\mathcal{H}_N)$ is the vector space of bounded self-adjoint operators on $\mathcal{H}_N$, and the condition $0 \leq \Gamma \leq 1$ stands for $0 \leq \langle \Psi | \Gamma | \Psi \rangle \leq \|\Psi\|^2_{\mathcal{H}_N}$ for all $\Psi \in \mathcal{H}_N$. Note that if H is a bounded-from-below self-adjoint operator on some Hilbert space $\mathcal{H}$, with form domain $\mathcal{Q}$, and if D is a positive trace-class self-adjoint operator on $\mathcal{H}$, $\mathrm{Tr}\,(HD)$ can always be defined in $\mathbb{R}_+ \cup \{+\infty\}$ as $\mathrm{Tr}\,(HD) = \mathrm{Tr}\,((H-a)^{\frac{1}{2}} D (H-a)^{\frac{1}{2}}) + a\mathrm{Tr}\,(D)$ where a is any real number such that $H \geq a$.

From a physical viewpoint, (2) and (3) mean that the ground state energy can be computed either by minimizing over pure states (characterized by wavefunctions Ψ) or by minimizing over mixed states (characterized by density operators Γ).

With any N-electron wavefunction $\Psi \in \mathcal{H}_N$ such that $\|\Psi\|_{\mathcal{H}_N} = 1$ can be associated the electronic density

$$\rho_\Psi(\mathbf{r}) = N \sum_{\sigma \in \Sigma} \int_{(\mathbb{R}^3_\Sigma)^{N-1}} |\Psi(\mathbf{r}, \sigma; \mathbf{x}_2, \cdots; \mathbf{x}_N)|^2\, d\mathbf{x}_2 \cdots d\mathbf{x}_N.$$

Likewise, one can associate with any N-electron density operator $\Gamma \in \mathcal{S}(\mathcal{H}_N)$ such that $0 \le \Gamma \le 1$ and $\mathrm{Tr}\,(\Gamma) = 1$, the electronic density

$$\rho_\Gamma(\mathbf{r}) = N \sum_{\sigma \in \Sigma} \int_{(\mathbb{R}^3_\Sigma)^{N-1}} \Gamma(\mathbf{r}, \sigma; \mathbf{x}_2, \cdots, \mathbf{x}_N; \mathbf{r}, \sigma; \mathbf{x}_2, \cdots; \mathbf{x}_N)\, d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

(here and below, we use the same notation for an operator and its Green kernel).

Let us denote by

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

the electrostatic potential generated by the nuclei, and by

$$H_N^1 = -\frac{1}{2} \sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{4}$$

It is easy to see that

$$\langle \Psi | H_N | \Psi \rangle = \langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho_\Psi V \quad \text{and} \quad \mathrm{Tr}\,(H_N \Gamma) = \mathrm{Tr}\,(H_N^1 \Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma V.$$

Besides, it can be checked that

$$\begin{aligned} \mathcal{R}_N &= \{\rho \mid \exists \Psi \in \mathcal{Q}_N,\ \|\Psi\|_{\mathcal{H}_N} = 1,\ \rho_\Psi = \rho\} \\ &= \{\rho \mid \exists \Gamma \in \mathcal{S}(\mathcal{H}_N),\ \mathrm{Ran}(\Gamma) \subset \mathcal{Q}_N,\ 0 \le \Gamma \le 1,\ \mathrm{Tr}\,(\Gamma) = 1,\ \rho_\Gamma = \rho\} \\ &= \left\{\rho \ge 0 \mid \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \rho = N\right\}. \end{aligned}$$

It therefore follows that

$$I_N = \inf \left\{ F_{\mathrm{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V,\ \rho \in \mathcal{R}_N \right\} \tag{5}$$

$$= \inf \left\{ F_{\mathrm{L}}(\rho) + \int_{\mathbb{R}^3} \rho V,\ \rho \in \mathcal{R}_N \right\} \tag{6}$$

where Levy-Lieb's and Lieb's density functionals [14, 15] are respectively defined by

$$F_{\mathrm{LL}}(\rho) = \inf \left\{ \langle \Psi | H_N^1 | \Psi \rangle,\ \Psi \in \mathcal{Q}_N,\ \|\Psi\|_{\mathcal{H}_N} = 1,\ \rho_\Psi = \rho \right\} \tag{7}$$

$$\begin{aligned} F_{\mathrm{L}}(\rho) = \inf \big\{ &\mathrm{Tr}\,(H_N^1 \Gamma),\ \Gamma \in \mathcal{S}(\mathcal{H}_N),\ \mathrm{Ran}(\Gamma) \subset \mathcal{Q}_N, \\ &0 \le \Gamma \le 1,\ \mathrm{Tr}\,(\Gamma) = 1,\ \rho_\Gamma = \rho \big\}. \end{aligned} \tag{8}$$

Note that the functionals F_{LL} and F_{L} are independent of the nuclear potential V, i.e. they do not depend on the molecular system. They are therefore universal functionals of the density. It is also shown in [15] that F_{L} is the Legendre transform of the function $V \mapsto I_N$. More precisely, expliciting the dependency of I_N on V, it holds

$$F_{\mathrm{L}}(\rho) = \sup \left\{ I_N(V) - \int_{\mathbb{R}^3} \rho V,\ V \in L^{\frac{3}{2}}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \right\},$$

from which it follows in particular that F_L is convex on the convex set $\mathcal{R}_N$ (and can be extended to a convex functional on $L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$).

Formulae (5) and (6) show that, in principle, it is possible to compute the electronic ground state energy (and the corresponding groud state density if it exists) by solving a minimization problem on $\mathcal{R}_N$. At this stage no approximation has been made. But, as neither $F_{\rm LL}$ nor $F_{\rm L}$ can be easily evaluated for the real system of interest (N interacting electrons), approximations are needed to make of the density functional theory a practical tool for computing electronic ground states. Approximations rely on exact, or very accurate, evaluations of the density functional for reference systems "close" to the real system:

- in Thomas-Fermi and related models, the reference system is an homogeneous electron gas;
- in Kohn-Sham models (by far the most commonly used), it is a system of N *non-interacting* electrons.

3 Kohn-Sham models

For a system of N non-interacting electrons, universal density functionals are obtained as explained in the previous section; it suffices to replace the interacting hamiltonian H_N^1 of the physical system (formula (4)) with the hamiltonian of the reference system

$$H_N^0 = -\sum_{i=1}^N \frac{1}{2}\Delta_{\mathbf{r}_i}. \tag{9}$$

The analogue of the Levy-Lieb density functional (7) then is the Kohn-Sham type kinetic energy functional

$$\widetilde{T}_{\rm KS}(\rho) = \inf\left\{\langle\Psi|H_N^0|\Psi\rangle,\ \Psi\in\mathcal{Q}_N,\ \|\Psi\|_{\mathcal{H}_N}=1,\ \rho_\Psi=\rho\right\}, \tag{10}$$

while the analogue of the Lieb functional (8) is the Janak kinetic energy functional

$$T_{\rm J}(\rho) = \inf\left\{{\rm Tr}\ (H_N^0\Gamma),\ \Gamma\in\mathcal{S}(\mathcal{H}_N),\ {\rm Ran}(\Gamma)\subset\mathcal{Q}_N,\ 0\le\Gamma\le 1,\ {\rm Tr}\ (\Gamma)=1,\ \rho_\Gamma=\rho\right\}.$$

Let Γ be in the above minimization set. The energy ${\rm Tr}\ (H_N^0\Gamma)$ can be rewritten as a function of the one-electron reduced density operator Υ_Γ associated with Γ. Recall that Υ_Γ is the self-adjoint operator on $L^2(\mathbb{R}^3_\Sigma)$ with kernel

$$\Upsilon_\Gamma(\mathbf{x},\mathbf{x}') = N\int_{(\mathbb{R}^3_\Sigma)^{N-1}} \Gamma(\mathbf{x},\mathbf{x}_2,\cdots,\mathbf{x}_N;\mathbf{x}',\mathbf{x}_2,\cdots,\mathbf{x}_N)\,d\mathbf{x}_2\cdots d\mathbf{x}_N.$$

Indeed, a simple calculation yields ${\rm Tr}\ (H_N^0\Gamma) = {\rm Tr}\ (-\frac{1}{2}\Delta_{\mathbf{r}}\Upsilon_\Gamma)$, where $\Delta_{\mathbf{r}}$ is the Laplace operator on $L^2(\mathbb{R}^3_\Sigma)$ - acting on the space coordinate $\mathbf{r}$. Besides, it is known (see e.g. [5]) that

$$\begin{aligned}&\{\Upsilon\mid\exists\Gamma\in\mathcal{S}(\mathcal{H}_N),\ {\rm Ran}(\Gamma)\subset\mathcal{Q}_N,\ 0\le\Gamma\le1,\ {\rm Tr}\ (\Gamma)=1,\ \Upsilon_\Gamma=\Upsilon,\ \rho_\Gamma=\rho\}\\ &=\left\{\Upsilon\in\mathcal{S}(L^2(\mathbb{R}^3_\Sigma)),\ 0\le\Upsilon\le1,\ {\rm Ran}(\Upsilon)\subset H^1(\mathbb{R}^3_\Sigma),\ {\rm Tr}\ (\Upsilon)=N,\ \rho_\Upsilon=\rho\right\},\end{aligned} \tag{11}$$

where

$$\rho_\Upsilon(\mathbf{r}) := \sum_{\sigma\in\Sigma}\Upsilon(\mathbf{r},\sigma;\mathbf{r},\sigma).$$

Hence,

$$\begin{aligned}T_{\rm J}(\rho) \;=\; \inf\Bigg\{&{\rm Tr}\ \left(-\frac{1}{2}\Delta_{\mathbf{r}}\Upsilon\right),\ \Upsilon\in\mathcal{S}(L^2(\mathbb{R}^3_\Sigma)),\ 0\le\Upsilon\le1,\\ &{\rm Ran}(\Upsilon)\subset H^1(\mathbb{R}^3_\Sigma),\ {\rm Tr}\ (\Upsilon)=N,\ \rho_\Upsilon=\rho\Bigg\}.\end{aligned} \tag{12}$$

It is to be noticed that no such simple expression for $\widetilde{T}_{\rm KS}(\rho)$ is available because one lacks an N-representation result similar to (11) for pure state one-particle reduced density operators. In the standard Kohn-Sham model, $\widetilde{T}_{\rm KS}(\rho)$ is replaced with the Kohn-Sham kinetic energy functional

$$T_{\rm KS}(\rho) = \inf\left\{\langle\Psi|H_N^0|\Psi\rangle,\ \Psi\in\mathcal{Q}_N,\ \Psi \text{ is a Slater determinant},\ \rho_\Psi=\rho\right\}, \qquad (13)$$

where we recall that a Slater determinant is a wavefunction Ψ of the form

$$\Psi(\mathbf{x}_1,\cdots,\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\det(\phi_i(\mathbf{x}_j)) \quad \text{with} \quad \phi_i\in L^2(\mathbb{R}^3_\Sigma), \quad \int_{\mathbb{R}^3}\phi_i(\mathbf{x})\phi_j(\mathbf{x})\,d\mathbf{x}=\delta_{ij}.$$

It is then easy to check that

$$T_{\rm KS}(\rho) = \inf\left\{\frac{1}{2}\sum_{i=1}^N\int_{\mathbb{R}^3_\Sigma}|\nabla\phi_i(\mathbf{x})|^2\,d\mathbf{x}, \quad \Phi=(\phi_1,\cdots,\phi_N)\in\mathcal{W}_N, \quad \rho_\Phi=\rho\right\}, \qquad (14)$$

where we have set

$$\mathcal{W}_N = \left\{\Phi=(\phi_1,\cdots,\phi_N) \quad | \quad \phi_i\in H^1(\mathbb{R}^3_\Sigma),\ \int_{\mathbb{R}^3_\Sigma}\phi_i(\mathbf{x})\phi_j(\mathbf{x})\,d\mathbf{x}=\delta_{ij}\right\}$$

and

$$\rho_\Phi(\mathbf{r}) = \sum_{i=1}^N\sum_{\sigma\in\Sigma}|\phi_i(\mathbf{r},\sigma)|^2.$$

Note that for an arbitrary $\rho\in\mathcal{R}_N$, it holds

$$T_{\rm J}(\rho)\le\widetilde{T}_{\rm KS}(\rho)\le T_{\rm KS}(\rho).$$

It is not difficult to check that (12) always has a minimizer. If one of the minimizers Υ of (12) is of rank N, then $\Upsilon=\sum_{i=1}^N|\phi_i\rangle\langle\phi_i|$ with $\Phi=(\phi_1,\cdots,\phi_N)\in\mathcal{W}_N$, Φ being then a minimizer of (13) and $T_{\rm KS}(\rho)=T_{\rm J}(\rho)$. Otherwise, $T_{\rm KS}(\rho)>T_{\rm J}(\rho)$.

The density functionals $T_{\rm KS}$ and T_J associated with the non interacting hamiltonian H_0 are expected to provide acceptable approximations of the kinetic energy of the real (interacting) system. Likewise, the Coulomb energy

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

representing the electrostatic energy of a *classical* charge distribution of density ρ is a reasonable guess for the electronic interaction energy in a system of N electrons of density ρ. The errors on both the kinetic energy and the electrostatic interaction are put together in the *exchange-correlation energy* defined as the difference

$$E_{\rm xc}(\rho)=F_{\rm LL}(\rho)-T_{\rm KS}(\rho)-J(\rho), \qquad (15)$$

or

$$E_{\rm xc}(\rho)=F_{\rm L}(\rho)-T_{\rm J}(\rho)-J(\rho), \qquad (16)$$

depending on the choices for the interacting and non-interacting density functionals. We finally end up with the so-called Kohn-Sham and extended Kohn-Sham models

$$\begin{aligned} I_N^{\rm KS} \;=\; \inf\Bigg\{&\frac{1}{2}\sum_{i=1}^N\int_{\mathbb{R}^3_\Sigma}|\nabla\phi_i(\mathbf{x})|^2\,d\mathbf{x}+\int_{\mathbb{R}^3}\rho_\Phi V+J(\rho_\Phi)+E_{\rm xc}(\rho_\Phi),\\ &\Phi=(\phi_1,\cdots,\phi_N)\in\mathcal{W}_N\Bigg\}, \end{aligned} \qquad (17)$$

and

$$I_N^{\rm EKS} = \inf\left\{ \mathrm{Tr}\,\left(-\frac{1}{2}\Delta_{\mathbf{r}}\Upsilon\right) + \int_{\mathbb{R}^3} \rho_\Upsilon V + J(\rho_\Upsilon) + E_{\rm xc}(\rho_\Upsilon), \right.$$
$$\left. \Upsilon \in \mathcal{S}(L^2(\mathbb{R}^3_\Sigma)),\ 0 \le \Upsilon \le 1,\ \mathrm{Tr}\,(\Upsilon) = N,\ \mathrm{Tr}\,(-\Delta_{\mathbf{r}}\Upsilon) < \infty \right\}, \quad (18)$$

the condition on $\mathrm{Tr}\,(-\Delta_{\mathbf{r}}\Upsilon)$ ensuring that each term of the energy functional is well-defined.

Up to now, no approximation has been made, in such a way that for the exact exchange-correlation functionals ((15) or (16)), $I_N^{\rm KS} = I_N^{\rm EKS} = \lambda_1(H_N)$ for all molecular system containing N electrons. Unfortunately, there is no tractable expression of $E_{\rm xc}(\rho)$ that can be used in numerical simulations. Before proceeding further, and for the sake of simplicity, we will restrict ourselves to closed-shell, spin-unpolarized, systems. This means that we will only consider molecular systems with an even number of electrons $N = 2N_p$, where N_p is the number of electron pairs in the system, and that we will assume that electrons "go by pairs". In the Kohn-Sham formalism, this means that the set of admissible states reduces to

$$\left\{ \Phi = (\varphi_1\alpha, \varphi_1\beta, \cdots, \varphi_{N_p}\alpha, \varphi_{N_p}\beta) \mid \varphi_i \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \varphi_i\varphi_j = \delta_{ij} \right\}$$

where $\alpha(|\uparrow\rangle) = 1$, $\alpha(|\downarrow\rangle) = 0$, $\beta(|\uparrow\rangle) = 0$ and $\beta(|\downarrow\rangle) = 1$, yielding the spin-unpolarized (or closed-shell, or restricted) Kohn-Sham model

$$I_N^{\rm RKS} = \inf\left\{ \sum_{i=1}^{N_p} \int_{\mathbb{R}^3} |\nabla\varphi_i|^2 + \int_{\mathbb{R}^3} \rho_\Phi V + J(\rho_\Phi) + E_{\rm xc}(\rho_\Phi), \right.$$
$$\left. \Phi = (\varphi_1, \cdots, \varphi_{N_p}) \in (H^1(\mathbb{R}^3))^{N_p}, \quad \int_{\mathbb{R}^3} \varphi_i\varphi_j = \delta_{ij}, \quad \rho_\Phi = 2\sum_{i=1}^{N_p} |\varphi_i|^2 \right\}, \quad (19)$$

where the factor 2 in the definition of ρ_Φ accounts for the spin. Likewise, the constraints on the one-electron reduced density operators originating from the closed-shell approximation read:

$$\Upsilon(\mathbf{r}, |\uparrow\rangle, \mathbf{r}', |\uparrow\rangle) = \Upsilon(\mathbf{r}, |\downarrow\rangle, \mathbf{r}', |\downarrow\rangle) \quad \text{and} \quad \Upsilon(\mathbf{r}, |\uparrow\rangle, \mathbf{r}', |\downarrow\rangle) = \Upsilon(\mathbf{r}, |\downarrow\rangle, \mathbf{r}', |\uparrow\rangle) = 0.$$

Introducing $\gamma(\mathbf{r}, \mathbf{r}') = \Upsilon(\mathbf{r}, |\uparrow\rangle, \mathbf{r}', |\uparrow\rangle)$ and denoting by $\rho_\gamma(\mathbf{r}) = 2\gamma(\mathbf{r}, \mathbf{r})$, we obtain the spin-unpolarized extended Kohn-Sham model

$$I_N^{\rm REKS} = \left\{ \mathcal{E}(\gamma), \quad \gamma \in \mathcal{K}_{N_p} \right\}$$

where

$$\mathcal{E}(\gamma) = \mathrm{Tr}\,(-\Delta\gamma) + \int_{\mathbb{R}^3} \rho_\gamma V + J(\rho_\gamma) + E_{\rm xc}(\rho_\gamma),$$

and

$$\mathcal{K}_{N_p} = \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \le \gamma \le 1,\ \mathrm{Tr}\,(\gamma) = N_p,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty \right\}.$$

Note that any $\gamma \in \mathcal{K}_{N_p}$ is of the form

$$\gamma = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle\langle\phi_i|$$

with

$$\phi_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad n_i \in [0,1], \quad \sum_{i=1}^{+\infty} n_i = N_p, \quad \sum_{i=1}^{+\infty} n_i \|\nabla \phi_i\|_{L^2}^2 < \infty.$$

In particular,

$$\rho_\gamma(\mathbf{r}) = 2 \sum_{i=1}^{+\infty} n_i |\phi_i(\mathbf{r})|^2.$$

Let us also remark that problem (19) can be recast in terms of density operators as follows

$$I_N^{\mathrm{RKS}} = \left\{ \mathcal{E}(\gamma), \quad \gamma \in \mathcal{K}_{N_p} \right\} \tag{20}$$

where

$$\mathcal{P}_{N_p} = \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid \gamma^2 = \gamma, \ \mathrm{Tr}\,(\gamma) = N_p, \ \mathrm{Tr}\,(-\Delta\gamma) < \infty \right\}$$

is a the set of finite energy rank-N_p orthogonal projectors (note that $\mathcal{K}_{N_p}$ is the convex hull of $\mathcal{P}_{N_p}$). The connection between (19) and (20) is given by the correspondence

$$\gamma = \sum_{i=1}^{N_p} |\phi_i\rangle\langle\phi_i|,$$

i.e. γ is the orthogonal projector on the vector space spanned by the ϕ_i. Indeed, as $|\nabla| = (-\Delta)^{\frac{1}{2}}$, it holds

$$\mathrm{Tr}\,(-\Delta\gamma) = \mathrm{Tr}\,(|\nabla|\gamma|\nabla|) = \sum_{i=1}^{N_p} \||\nabla|\phi_i\|_{L^2}^2 = \sum_{i=1}^{N_p} \|\nabla\phi_i\|_{L^2}^2 = \sum_{i=1}^{N_p} \int_{\mathbb{R}^3} |\nabla\phi_i|^2.$$

Let us now address the issue of constructing relevant approximations for $E_{\mathrm{xc}}(\rho)$. In their celebrated 1964 article, Kohn and Sham proposed to use an approximate exchange-correlation functional of the form

$$E_{\mathrm{xc}}(\rho) = \int_{\mathbb{R}^3} g(\rho(\mathbf{r}))\, d\mathbf{r} \qquad \text{(LDA exchange-correlation functional)} \tag{21}$$

where $\rho^{-1}g(\rho)$ is the exchange-correlation density for a uniform electron gas with density ρ, yielding the so-called local density approximation (LDA). In practical calculations, it is made use of approximations of the function $\rho \mapsto g(\rho)$ (from $\mathbb{R}_+$ to $\mathbb{R}$) obtained by interpolating asymptotic formulae for the low and high density regimes (see e.g. [6]) and accurate quantum Monte Carlo evaluations of $g(\rho)$ for a small number of values of ρ [4]. Several interpolation formulae are available [23, 22, 31], which provide similar results. In the 80's, refined approximations of E_{xc} have been constructed, which take into account the inhomogeneity of the electronic density in real molecular systems. Generalized gradient approximations (GGA) of the exchange-correlation functional are of the form

$$E_{\mathrm{xc}}(\rho) = \int_{\mathbb{R}^3} h(\rho(\mathbf{r}), \frac{1}{2}|\nabla\sqrt{\rho(\mathbf{r})}|^2)\, dx \qquad \text{(GGA exchange-correlation functional).} \tag{22}$$

Contrarily to the situation encountered for LDA, the function $(\rho,\kappa) \mapsto g(\rho,\kappa)$ (from $\mathbb{R}_+ \times \mathbb{R}_+$ to $\mathbb{R}$) does not have a univoque definition. Several GGA functionals have been proposed and new ones come up periodically.

Remark 1. *We have chosen the form (22) for the GGA exchange-correlation functional because it is well suited for the study of spin-unpolarized two electron systems (see Theorem 2 below). In the Physics literature, spin-unpolarized LDA and GGA exchange-correlation functionals are rather written as follows*

$$E_{\rm xc}(\rho) = E_{\rm x}(\rho) + E_{\rm c}(\rho)$$

with

$$E_{\rm x}(\rho) = \int_{\mathbb{R}^3} \rho(\mathbf{r})\, \epsilon_{\rm x}(\rho(\mathbf{r}))\, F_{\rm x}(s_\rho(\mathbf{r}))\, d\mathbf{r} \tag{23}$$

$$E_{\rm c}(\rho) = \int_{\mathbb{R}^3} \rho(\mathbf{r})\, \left[\epsilon_{\rm c}(r_\rho(\mathbf{r})) + H(r_\rho(\mathbf{r}), t_\rho(\mathbf{r}))\right]\, d\mathbf{r}. \tag{24}$$

In the above decomposition, $E_{\rm x}$ is the exchange energy, $E_{\rm c}$ is the correlation energy, $\epsilon_{\rm x}$ and $\epsilon_{\rm c}$ are respectively the exchange and correlation energy densities of the homogeneous electron gas, $r_\rho(\mathbf{r}) = \left(\frac{4}{3}\pi\rho(\mathbf{r})\right)^{-\frac{1}{3}}$ is the Wigner-Seitz radius, $s_\rho(\mathbf{r}) = \frac{1}{2(3\pi^2)^{\frac{1}{3}}}\frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{\frac{4}{3}}}$ is the (non-dimensional) reduced density gradient, $t_\rho(\mathbf{r}) = \frac{1}{4(3\pi^{-1})^{\frac{1}{6}}}\frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{\frac{7}{6}}}$ is the correlation gradient, $F_{\rm x}$ is the so-called exchange enhancement factor, and H is the gradient contribution to the correlation energy. While $\epsilon_{\rm x}$ has a simple analytical expression, namely

$$\epsilon_{\rm x}(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{1}{3}}$$

$\epsilon_{\rm c}$ has to be approximated (as explained above for the function g). For LDA, $F_{\rm x}$ is everywhere equal to one and $H = 0$. A popular GGA exchange-correlation energy is the PBE functional [20], for which

$$F_{\rm x}(s) = 1 + \frac{\mu s^2}{1+\mu\nu^{-1}s^2}$$

$$H(r,t) = \theta \ln\left(1 + \frac{\upsilon}{\theta}t^2 \frac{1+A(r)t^2}{1+A(r)t^2+A(r)^2t^4}\right) \quad \textit{with} \quad A(r) = \frac{\upsilon}{\theta}\left(e^{-\epsilon_{\rm c}(r)/\theta} - 1\right)^{-1},$$

the values of the parameters $\mu \simeq 0.21951$, $\nu \simeq 0.804$, $\theta = \pi^{-2}(1-\ln 2)$ and $\upsilon = 3\pi^{-2}\mu$ following from theoretical arguments.

4 Main results

Let us first set up and comment on the conditions on the LDA and GGA exchange-correlation functionals under which our results hold true:

- the function g in (21) is a C^1 function from $\mathbb{R}_+$ to $\mathbb{R}$, twice differentiable and such that

$$g(0) = 0 \tag{25}$$

$$g' \leq 0 \tag{26}$$

$$\exists 0 < \beta_- \leq \beta_+ < \frac{2}{3} \quad \text{s.t.} \quad \sup_{\rho\in\mathbb{R}_+} \frac{|g'(\rho)|}{\rho^{\beta_-}+\rho^{\beta_+}} < \infty \tag{27}$$

$$\exists 1 \leq \alpha < \frac{3}{2} \quad \text{s.t.} \quad \limsup_{\rho\to 0^+} \frac{g(\rho)}{\rho^\alpha} < 0; \tag{28}$$

- the function h in (21) is a C^1 function from $\mathbb{R}_+ \times \mathbb{R}_+$ to $\mathbb{R}$, twice differentiable with respect to the second variable, and such that

$$h(0,\kappa) = 0, \ \forall \kappa \in \mathbb{R}_+ \tag{29}$$

$$\frac{\partial h}{\partial \rho} \leq 0 \tag{30}$$

$$\exists 0 < \beta_- \leq \beta_+ < \frac{2}{3} \quad \text{s.t.} \quad \sup_{(\rho,\kappa)\in\mathbb{R}_+\times\mathbb{R}_+} \frac{\left|\frac{\partial h}{\partial \rho}(\rho,\kappa)\right|}{\rho^{\beta_-}+\rho^{\beta_+}} < \infty \tag{31}$$

$$\exists 1 \leq \alpha < \frac{3}{2} \quad \text{s.t.} \quad \limsup_{(\rho,\kappa)\to(0^+,0^+)} \frac{h(\rho,\kappa)}{\rho^\alpha} < 0 \tag{32}$$

$$\exists 0 < a \leq b < \infty \quad \text{s.t.} \quad \forall (\rho,\kappa) \in \mathbb{R}_+ \times \mathbb{R}_+, \quad a \leq 1 + \frac{\partial h}{\partial \kappa}(\rho,\kappa) \leq b \tag{33}$$

$$\forall (\rho,\kappa) \in \mathbb{R}_+ \times \mathbb{R}_+, \quad 1 + \frac{\partial h}{\partial \kappa}(\rho,\kappa) + 2\kappa \frac{\partial^2 h}{\partial \kappa^2}(\rho,\kappa) \geq 0. \tag{34}$$

Conditions (25)-(28) on the LDA exchange-correlation energy are not restrictive. They are obviously fulfilled by the LDA exchange functional ($g_{\rm x}^{\rm LDA}(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{4}{3}}$), and are also satisfied by all the approximate LDA correlation functionals currently used in practice (with $\alpha = \frac{4}{3}$ and $\beta_- = \beta^+ = \frac{1}{3}$). We have checked numerically that assumptions (29)-(34) are satisfied by the PZ81 functional defined in [23].

Remark 2. *Our results remain true if (26) and (30) are respectively replaced with the weaker conditions*

$$\exists \frac{1}{3} \leq \beta'_- \leq \beta_+ < \frac{2}{3} \quad s.t. \quad \sup_{\rho\in\mathbb{R}_+} \frac{\max(0, g'(\rho))}{\rho^{\beta'_-}+\rho^{\beta_+}} < \infty$$

and

$$\exists \frac{1}{3} \leq \beta'_- \leq \beta_+ < \frac{2}{3} \quad s.t. \quad \sup_{(\rho,\kappa)\in\mathbb{R}_+\times\mathbb{R}_+} \frac{\max\left(0, \frac{\partial h}{\partial \rho}(\rho,\kappa)\right)}{\rho^{\beta'_-}+\rho^{\beta_+}} < \infty.$$

As usual in the mathematical study of molecular electronic structure models, we embed (20) in the family of problems

$$I_\lambda = \inf\left\{\mathcal{E}(\gamma), \ \gamma \in \mathcal{K}_\lambda\right\} \tag{35}$$

parametrized by $\lambda \in \mathbb{R}_+$ where

$$\mathcal{K}_\lambda = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 1, \ \mathrm{Tr}\,(\gamma) = \lambda, \ \mathrm{Tr}\,(-\Delta\gamma) < \infty\right\},$$

and introduce the problem at infinity

$$I_\lambda^\infty = \inf\left\{\mathcal{E}^\infty(\gamma), \ \gamma \in \mathcal{K}_\lambda\right\} \tag{36}$$

where

$$\mathcal{E}^{\rm KS}(\gamma) = \mathrm{Tr}\,(-\Delta\gamma) + J(\rho_\gamma) + E_{\rm xc}(\rho_\gamma).$$

The following results hold true for both the LDA and GGA extended Kohn-Sham models.

Lemma 1. *Consider (35) and (36) with $E_{\rm xc}$ given either by (21) or by (22) together with the conditions (25)-(28) or (29)-(32). Then*

1. *$I_0 = I_0^\infty = 0$ and for all $\lambda > 0$, $-\infty < I_\lambda < I_\lambda^\infty < 0$;*

2. *the functions $\lambda \mapsto I_\lambda$ and $\lambda \mapsto I_\lambda^\infty$ are continuous and decreasing;*

3. *for all $0 < \mu < \lambda$,*
$$I_\lambda \leq I_\mu + I_{\lambda-\mu}^\infty. \tag{37}$$

Our main results are the following two theorems.

Theorem 1 (Extended KS-LDA model). *Assume that $Z \geq N = 2N_p$ (neutral or positively charged system) and that the function g satisfies (25)-(28). Then the extended Kohn-Sham LDA model (35) with $E_{\rm xc}$ given by (21) has a minimizer γ_0. Besides, γ_0 satisfies the self-consistent field equation*

$$\gamma_0 = \chi_{(-\infty,\epsilon_{\rm F})}(H_{\rho_{\gamma_0}}) + \delta \tag{38}$$

for some $\epsilon_{\rm F} \leq 0$, where

$$H_{\rho_{\gamma_0}} = -\frac{1}{2}\Delta + V + \rho_{\gamma_0} \star |\mathbf{r}|^{-1} + g'(\rho_{\gamma_0}),$$

where $\chi_{(-\infty,\epsilon_{\rm F})}$ is the characteristic function of the range $(-\infty, \epsilon_{\rm F})$ and where $\delta \in \mathcal{S}(L^2(\mathbb{R}^3))$ is such that $0 \leq \delta \leq 1$ and $Ran(\delta) = Ker(H_{\rho_{\gamma_0}} - \epsilon_{\rm F})$.

Theorem 2 (Extended KS-GGA model for two electron systems). *Assume that $Z \geq N = 2N_p = 2$ (neutral or positively charged system with two electrons) and that the function h satisfies (29)-(34). Then the extended Kohn-Sham GGA model (35) with $E_{\rm xc}$ given by (22) has a minimizer γ_0. Besides, $\gamma_0 = |\phi\rangle\langle\phi|$ where ϕ is a minimizer of the standard spin-unpolarized Kohn-Sham problem (19) for $N_p = 1$, hence satisfying the Euler equation*

$$-\frac{1}{2}\text{div}\,\left(\left(1 + \frac{\partial h}{\partial \kappa}(\rho_\phi, |\nabla\phi|^2)\right)\nabla\phi\right) + \left(V + \rho_\phi \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial \rho}(\rho_\phi, |\nabla\phi|^2)\right)\phi = \epsilon\phi \tag{39}$$

for some $\epsilon < 0$, where $\rho_\phi = 2\phi^2$. In addition, $\phi \in C^{0,\alpha}(\mathbb{R}^3)$ for some $0 < \alpha < 1$ and decays exponentially fast at infinity. Lastly, ϕ can be chosen non-negative and (ϵ, ϕ) is the lowest eigenpair of the self-adjoint operator

$$-\frac{1}{2}\text{div}\,\left(\left(1 + \frac{\partial h}{\partial \kappa}(\rho_\phi, |\nabla\phi|^2)\right)\nabla\cdot\right) + V + \rho_\phi \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial \rho}(\rho_\phi, |\nabla\phi|^2).$$

We have not been able to extend the results of Theorem 2 to the general case of N_p electron pairs. This is mainly due to the fact that the Euler equations for (35) with $E_{\rm xc}$ given by (22) do not have a simple structure for $N_p \geq 2$.

5 Proofs

For clarity, we will use the following notation

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

$$E_{\rm xc}^{\rm GGA}(\rho) = \int_{\mathbb{R}^3} h(\rho(\mathbf{r}), \frac{1}{2}|\nabla\sqrt{\rho}(\mathbf{r})|^2)\,d\mathbf{r}$$

$$\mathcal{E}^{\rm LDA}(\gamma) = \mathrm{Tr}\,(-\Delta\gamma) + \int_{\mathbb{R}^3}\rho_\gamma V + J(\rho_\gamma) + \int_{\mathbb{R}^3} g(\rho_\gamma(\mathbf{r}))\,d\mathbf{r}$$

$$\mathcal{E}^{\rm GGA}(\gamma) = \mathrm{Tr}\,(-\Delta\gamma) + \int_{\mathbb{R}^3}\rho_\gamma V + J(\rho_\gamma) + \int_{\mathbb{R}^3} h(\rho_\gamma(\mathbf{r}), \frac{1}{2}|\nabla\sqrt{\rho_\gamma}(\mathbf{r})|^2)\,d\mathbf{r}.$$

The notations $E_{\rm xc}(\rho)$ and $\mathcal{E}(\gamma)$ will refer indifferently to the LDA or the GGA setting.

5.1 Preliminary results

Most of the results of this section are elementary, but we provide them for the sake of completeness. Let us denote by $\mathfrak{S}_1$ the vector space of trace-class operators on $L^2(\mathbb{R}^3)$ (see e.g. [25]) and introduce the vector space

$$\mathcal{H} = \{\gamma \in \mathfrak{S}_1 \mid |\nabla|\gamma|\nabla| \in \mathfrak{S}_1\}$$

endowed with the norm $\|\cdot\|_{\mathcal{H}} = \mathrm{Tr}\,(|\cdot|) + \mathrm{Tr}\,(||\nabla|\cdot|\nabla||)$, and the convex set

$$\mathcal{K} = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \le \gamma \le 1,\ \mathrm{Tr}\,(\gamma) < \infty,\ \mathrm{Tr}\,(|\nabla|\gamma|\nabla|) < \infty\right\}.$$

Lemma 2. *For all $\gamma \in \mathcal{K}$, $\sqrt{\rho_\gamma} \in H^1(\mathbb{R}^3)$ and the following inequalities hold true*

$$\frac{1}{2}\|\nabla\sqrt{\rho_\gamma}\|_{L^2}^2 \le \mathrm{Tr}\,(-\Delta\gamma) \tag{40}$$

$$0 \le J(\rho_\gamma) \le C(\mathrm{Tr}\,\gamma)^{\frac{3}{2}}(\mathrm{Tr}\,(-\Delta\gamma))^{\frac{1}{2}} \tag{41}$$

$$-4Z(\mathrm{Tr}\,\gamma)^{\frac{1}{2}}(\mathrm{Tr}\,(-\Delta\gamma))^{\frac{1}{2}} \le \int_{\mathbb{R}^3}\rho_\gamma V \le 0 \tag{42}$$

$$-C\left((\mathrm{Tr}\,\gamma)^{1-\frac{\beta_-}{2}}(\mathrm{Tr}\,(-\Delta\gamma))^{\frac{3\beta_-}{2}} + (\mathrm{Tr}\,\gamma)^{1-\frac{\beta_+}{2}}(\mathrm{Tr}\,(-\Delta\gamma))^{\frac{3\beta_+}{2}}\right) \le E_{\rm xc}(\rho_\gamma) \le 0 \tag{43}$$

$$\mathcal{E}(\gamma) \ge \frac{1}{2}\left((\mathrm{Tr}\,(-\Delta\gamma))^{\frac{1}{2}} - 4Z(\mathrm{Tr}\,\gamma)^{\frac{1}{2}}\right)^2 - 8Z^2\mathrm{Tr}\,\gamma -C\left((\mathrm{Tr}\,\gamma)^{\frac{2-\beta_-}{2-3\beta_-}} + (\mathrm{Tr}\,\gamma)^{\frac{2-\beta_+}{2-3\beta_+}}\right) \tag{44}$$

$$\mathcal{E}^\infty(\gamma) \ge \frac{1}{2}\mathrm{Tr}\,(-\Delta\gamma) - C\left((\mathrm{Tr}\,\gamma)^{\frac{2-\beta_-}{2-3\beta_-}} + (\mathrm{Tr}\,\gamma)^{\frac{2-\beta_+}{2-3\beta_+}}\right), \tag{45}$$

for a positive constant C independent of γ. In particular, the minimizing sequences of (35) and those of (36) are bounded in $\mathcal{H}$.

Proof. Any $\gamma \in \mathcal{K}$ can be diagonalized in an orthonormal basis of $L^2(\mathbb{R}^3)$ as follows

$$\gamma = \sum_{i=1}^{+\infty} n_i|\phi\rangle\langle\phi_i|$$

with $n_i \in [0,1]$, $\phi_i \in H^1(\mathbb{R}^3)$, $\int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}$, $\mathrm{Tr}\,(\gamma) = \sum_{i=1}^{+\infty} n_i < \infty$ and $\mathrm{Tr}\,(-\Delta\gamma) = \sum_{i=1}^{+\infty} n_i \|\nabla\phi_i\|_{L^2}^2 < \infty$. As

$$|\nabla\sqrt{\rho_\gamma}|^2 = 2\frac{\left|\sum_{i=1}^{+\infty} n_i\phi_i\nabla\phi_i\right|^2}{\sum_{i=1}^{+\infty} n_i\phi_i^2},$$

(40) is a straightforward consequence of Cauchy-Schwarz inequality. Using Hardy-Littlewood-Sobolev [16], interpolation, and Gagliardo-Nirenberg-Sobolev inequalities, we obtain

$$J(\rho_\gamma) \le C_1\|\rho_\gamma\|_{L^{\frac{6}{5}}}^2 \le C_1\|\rho_\gamma\|_{L^1}^{\frac{3}{2}}\|\rho_\gamma\|_{L^3}^{\frac{1}{2}} \le C_2\|\rho_\gamma\|_{L^1}^{\frac{3}{2}}\|\nabla\sqrt{\rho_\gamma}\|_{L^2}.$$

Hence (41), using (40) and the relation $\|\rho_\gamma\|_{L^1} = 2\mathrm{Tr}\,(\gamma)$. It follows from Cauchy-Schwarz and Hardy inequalities and from the above estimates that

$$\int_{\mathbb{R}^3} \frac{\rho_\gamma}{|\cdot - \mathbf{R}_k|} \le 2\|\rho_\gamma\|_{L^1}^{\frac{1}{2}}\|\nabla\sqrt{\rho_\gamma}\|_{L^2} \le 4(\mathrm{Tr}\,\gamma)^{\frac{1}{2}}(\mathrm{Tr}\,(-\Delta\gamma))^{\frac{1}{2}}.$$

Hence (42). Conditions (25)-(28) for LDA and (29)-(32) for GGA imply that $E_{\mathrm{xc}}(\rho) \le 0$ and there exists $1 < p_- < p_+ < \frac{5}{3}$ ($p_\pm = 1 + \beta_\pm$) and some constant $C \in \mathbb{R}_+$ such that

$$\forall \rho \in \mathcal{K}, \quad |E_{\mathrm{xc}}(\rho)| \le C\left(\int_{\mathbb{R}^3} \rho^{p_-} + \int_{\mathbb{R}^3} \rho^{p_+}\right), \tag{46}$$

from which we deduce (43), using interpolation and Gagliardo-Nirenberg-Sobolev inequalities. Lastly, the estimates (44) and (45) are straightforward consequences of (41)-(43). $\square$

Lemma 3. *Let $\lambda > 0$ and $\gamma \in \mathcal{K}_\lambda$. There exists a sequence $(\gamma_n)_{n\in\mathbb{N}}$ such that*

1. *for all $n \in \mathbb{N}$, $\gamma_n \in \mathcal{K}_\lambda$, γ_n is finite-rank and Ran$(\gamma_n) \subset C_c^\infty(\mathbb{R}^3)$;*
2. *$(\gamma_n)_{n\in\mathbb{N}}$ converges to γ strongly in $\mathcal{H}$;*
3. *$(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ converges to $\sqrt{\rho_\gamma}$ strongly in $H^1(\mathbb{R}^3)$;*
4. *$(\rho_{\gamma_n})_{n\in\mathbb{N}}$ and $(\nabla\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ converge almost everywhere to ρ_γ and $\nabla\sqrt{\rho_\gamma}$ respectively.*

In particular

$$\lim_{n\to\infty} \mathcal{E}(\gamma_n) = \mathcal{E}(\gamma) \quad \text{and} \quad \lim_{n\to\infty} \mathcal{E}^\infty(\gamma_n) = \mathcal{E}^\infty(\gamma). \tag{47}$$

Proof. Let $\gamma \in \mathcal{K}_\lambda$. It holds

$$\gamma = \sum_{i=1}^{+\infty} n_i|\phi_i\rangle\langle\phi_i|$$

with $n_i \in [0,1]$, $\phi_i \in H^1(\mathbb{R}^3)$, $\int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}$, $\mathrm{Tr}\,(\gamma) = \sum_{i=1}^{+\infty} n_i = \lambda$ and $\mathrm{Tr}\,(-\Delta\gamma) = \sum_{i=1}^{+\infty} n_i\|\nabla\phi_i\|_{L^2}^2 < \infty$.

We first prove that γ can be approached by a sequence of finite-rank operators. Let $N_0 \in \mathbb{N}$ such that $0 < n_{N_0} < 1$ (if no such N_0 exists, then γ is finite-rank and one can directly proceed to the second part of the proof). For all $N \in \mathbb{N}$, we set

$$\widetilde{\gamma}_N = \sum_{i=1}^{N} n_i|\phi_i\rangle\langle\phi_i| + \left(\lambda - \sum_{i=1}^{N} n_i\right)|\phi_{N_0}\rangle\langle\phi_{N_0}|.$$

For N large enough, $\widetilde{\gamma}_N \in \mathcal{K}_\lambda$, and the sequence $(\widetilde{\gamma}_N)$ obviously converges to γ in $\mathcal{H}$. Besides, $(\rho_{\widetilde{\gamma}_N})$ converges a.e. to ρ_γ and

$$|\rho_{\widetilde{\gamma}_N} - \rho_\gamma| \le \left(n_{N_0} + \lambda - \sum_{i=1}^{N} n_i \right) \phi_{N_0}^2 + \sum_{i=N+1}^{+\infty} n_i |\phi_i|^2 \le \rho_\gamma + \lambda \phi_{N_0}^2.$$

Hence the convergence of $(\rho_{\widetilde{\gamma}_N})$ to ρ_γ in $L^p(\mathbb{R}^3)$ for all $1 \le p \le 3$. Besides, for all $N \ge N_0$,

$$|\nabla \sqrt{\rho_{\widetilde{\gamma}_N}}|^2 = 2 \, \frac{\left| \displaystyle\sum_{i=1,\, i \neq N_0}^{N} n_i \phi_i \nabla \phi_i + \left(n_{N_0} + \lambda - \sum_{i=1}^{N} n_i \right) \phi_{N_0} \nabla \phi_{N_0} \right|^2}{\displaystyle\sum_{i=1,\, i \neq N_0}^{N} n_i |\phi_i|^2 + \left(n_{N_0} + \lambda - \sum_{i=1}^{N} n_i \right) |\phi_{N_0}|^2} \le 2 \sum_{i=1}^{+\infty} n_i |\nabla \phi_i|^2 + 2\lambda |\nabla \phi_{N_0}|^2.$$

Using Lebesgue dominated convergence theorem, we obtain that the sequence $(\|\nabla \sqrt{\rho_{\widetilde{\gamma}_N}}\|_{L^2})$ converges to $\|\nabla \sqrt{\rho_\gamma}\|_{L^2}$, from which we deduce that $(\sqrt{\rho_{\widetilde{\gamma}_N}})$ converges to $\sqrt{\rho_\gamma}$ strongly in $H^1(\mathbb{R}^3)$.

The second part of the proof consists in approaching each ϕ_i by a sequence of regular compactly supported functions. For each i, we consider a sequence $(\phi_{i,k})_{k \in \mathbb{N}}$ of functions of $C_c^\infty(\mathbb{R}^3)$ such that

- $\mathrm{supp}(\phi_{i,k}) \subset \mathrm{supp}(\phi_i)$ and $\int_{\mathbb{R}^2} \phi_{i,k} \phi_{j,k} = \delta_{ij}$ for all k,
- $(\phi_{i,k})_{k \in \mathbb{N}}$ converges to ϕ_i strongly in $H^1(\mathbb{R}^3)$ and almost everywhere,
- there exists $h_i \in L^2(\mathbb{R}^3)$ such that $|\nabla \phi_{i,k}| \le h_i$ for all k.

It is then easy to check that the sequence $(\widetilde{\gamma}_{N,k})_{k \in \mathbb{N}}$ defined by

$$\widetilde{\gamma}_{N,k} = \sum_{i=1}^{N} n_i |\phi_{i,k}\rangle\langle\phi_{i,k}| + \left(\lambda - \sum_{i=1}^{N} n_i \right) |\phi_{N_0,k}\rangle\langle\phi_{N_0,k}|$$

converges to $\widetilde{\gamma}_N$ in $\mathcal{H}$ and is such that $(\sqrt{\rho_{\widetilde{\gamma}_{N,k}}})_{k \in \mathbb{N}}$ converges to $\sqrt{\rho_{\widetilde{\gamma}_N}}$ strongly in $H^1(\mathbb{R}^3)$.

One can then extract from $(\widetilde{\gamma}_{N,k})_{(N,k) \in \mathbb{N}^* \times \mathbb{N}}$ a subsequence $(\gamma_n)_{n \in \mathbb{N}}$ which converges to γ in $\mathcal{H}$ and is such that $(\sqrt{\rho_{\gamma_n}})_{n \in \mathbb{N}}$ converges to $\sqrt{\rho_\gamma}$ strongly in $H^1(\mathbb{R}^3)$, and there is no restriction in assuming that $(\rho_{\gamma_n})_{n \in \mathbb{N}}$ and $(\nabla \sqrt{\rho_{\gamma_n}})_{n \in \mathbb{N}}$ converge almost everywhere to ρ_γ and $\nabla \sqrt{\rho_\gamma}$ respectively.

The linear form $\gamma \mapsto \mathrm{Tr}\,(-\Delta \gamma)$ being continuous on $\mathcal{H}$ and the functionals $u \mapsto \int_{\mathbb{R}^3} u^2 V$ and $u \mapsto J(u^2) + E_{\mathrm{xc}}(u^2)$ being continuous on $H^1(\mathbb{R}^3)$, (47) holds true. $\square$

5.2 Proof of Lemma 1

Obviously, $I_0 = I_0^\infty = 0$ and $I_\lambda \le I_\lambda^\infty$ for all $\lambda \in \mathbb{R}_+$.

Let us first prove assertion 3. Let $0 < \mu < \lambda$, $\epsilon > 0$ and $\gamma \in \mathcal{K}_\mu$ such that $I_\mu \le \mathcal{E}(\gamma) \le I_\mu + \epsilon$. It follows from Lemma 3 that there is no restriction in choosing γ of the form

$$\gamma = \sum_{i=1}^{N} n_i |\phi_i\rangle\langle\phi_i|$$

with $0 \leq n_i \leq 1$, $\sum_{i=1}^N n_i = \mu$, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ and $\phi_i \in C_c^\infty(\mathbb{R}^3)$. Likewise, there exists

$$\gamma' = \sum_{i=1}^{N'} n_i' |\phi_i'\rangle\langle\phi_i'|$$

with $0 \leq n_i' \leq 1$, $\sum_{i=1}^{N'} n_i' = \lambda - \mu$, $\langle \phi_i' | \phi_j' \rangle = \delta_{ij}$ and $\phi_i' \in C_c^\infty(\mathbb{R}^3)$, such that $I_{\lambda-\mu}^\infty \leq \mathcal{E}^\infty(\gamma') \leq I_{\lambda-\mu}^\infty + \epsilon$. Let $\mathbf{e}$ be a unit vector of $\mathbb{R}^3$ and τ_a the translation operator on $L^2(\mathbb{R}^3)$ defined by $\tau_a f = f(\cdot - a)$ for all $f \in L^2(\mathbb{R}^3)$. For $n \in \mathbb{N}$, we define

$$\gamma_n = \gamma + \tau_{n\mathbf{e}} \gamma' \tau_{-n\mathbf{e}}.$$

It is easy to check that for n large enough, $\gamma_n \in \mathcal{K}_\lambda$ and

$$I_\lambda \leq \mathcal{E}(\gamma_n) \leq \mathcal{E}(\gamma) + \mathcal{E}^\infty(\gamma) + D(\rho_\gamma, \tau_{n\mathbf{e}} \rho_{\gamma'}) \leq I_\mu + I_{\lambda-\mu}^\infty + 3\epsilon,$$

where

$$D(\rho, \rho') := \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r})\, \rho'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}'.$$

Hence (37).

Making use of similar arguments, it can also be proved that

$$I_\lambda^\infty \leq I_\mu^\infty + I_{\lambda-\mu}^\infty. \tag{48}$$

Let us now consider a function $\phi \in C_c^\infty(\mathbb{R}^3)$ such that $\|\phi\|_{L^2} = 1$. For all $\sigma > 0$ and all $0 \leq \lambda \leq 1$, the density operator $\gamma_{\sigma,\lambda}$ with density matrix

$$\gamma_{\sigma,\lambda}(\mathbf{r}, \mathbf{r}') = \lambda \sigma^3 \, \phi(\sigma \mathbf{r}) \, \phi(\sigma \mathbf{r}')$$

is in $\mathcal{K}_\lambda$. Using (28) for LDA and (32) for GGA, we obtain that there exists $1 \leq \alpha < \frac{3}{2}$, $c > 0$ and $\sigma_0 > 0$ such that for all $0 \leq \lambda \leq 1$ and all $0 \leq \sigma \leq \sigma_0$,

$$I_\lambda^\infty \leq \mathcal{E}^\infty(\gamma_{\sigma,\lambda}) \leq \lambda \sigma^2 \int_{\mathbb{R}^3} |\nabla \phi|^2 + \lambda^2 \sigma J(2|\phi|^2) - c \lambda^\alpha \sigma^{3(\alpha-1)} \int_{\mathbb{R}^3} |\phi|^{2\alpha}.$$

Therefore $I_\lambda^\infty < 0$ for λ positive and small enough. It follows from (37) and (48) that the functions $\lambda \mapsto I_\lambda$ and $\lambda \mapsto I_\lambda^\infty$ are decreasing, and that for all $\lambda > 0$,

$$-\infty < I_\lambda \leq I_\lambda^\infty < 0.$$

To proceed further, we need the following lemma.

Lemma 4. *Let $\lambda > 0$ and $(\gamma_n)_{n \in \mathbb{N}}$ be a minimizing sequence for (35). Then the sequence $(\rho_{\gamma_n})_{n \in \mathbb{N}}$ cannot vanish, which means that*

$$\exists R > 0 \quad s.t. \quad \lim_{n \to \infty} \sup_{x \in \mathbb{R}^3} \int_{x + B_R} \rho_{\gamma_n} > 0.$$

The same holds true for the minimizing sequences of (36).

Proof. Let $(\gamma_n)_{n\in\mathbb{N}}$ be a minimizing sequence for (35). By contradiction, assume that

$$\forall R > 0, \quad \lim_{n\to\infty} \sup_{x\in\mathbb{R}^3} \int_{x+B_R} \rho_n = 0.$$

Let $1 < p < \frac{5}{3}$. For $\rho \geq 0$ such that $\sqrt{\rho} \in H^1(\mathbb{R}^3)$, it holds for all $k \in \mathbb{Z}^3$,

$$\int_{k+B_1} \rho^p \leq \left(\int_{k+B_1} \rho\right)^{p-1} \left(\int_{k+B_1} \rho^{\frac{1}{2-p}}\right)^{2-p} \leq C_p \left(\int_{k+B_1} \rho\right)^{p-1} \left(\int_{k+B_1} (\rho + |\nabla\sqrt{\rho}|^2)\right)$$

(where the constant C_p does not depend on k). We therefore obtain

$$\begin{aligned} \int_{\mathbb{R}^3} \rho^p &\leq \sum_{k\ \in\mathbb{Z}^3} \int_{k+B_1} \rho^p \\ &\leq C_p \sum_{k\ \in\mathbb{Z}^3} \left(\int_{k+B_1} \rho\right)^{p-1} \left(\int_{k+B_1} (\rho + |\nabla\sqrt{\rho}|^2)\right) \\ &\leq 8C_p \left(\sup_{x\in\mathbb{R}^3} \int_{x+B_1} \rho\right)^{p-1} \left(\int_{\mathbb{R}^3} (\rho + \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2)\right). \end{aligned}$$

Hence, for all $\gamma \in \mathcal{K}$,

$$\int_{\mathbb{R}^3} \rho_\gamma^p \leq 16C_p \left(\sup_{x\in\mathbb{R}^3} \int_{x+B_1} \rho_\gamma\right)^{p-1} \|\gamma\|_{\mathcal{H}}^2.$$

As we know that any minimizing sequence of (35) is bounded in $\mathcal{H}$, we deduce from the above inequality that for all $1 < p < \frac{5}{3}$,

$$\lim_{n\to\infty} \int_{\mathbb{R}^3} \rho_{\gamma_n}^p = 0.$$

In particular, it follows from (46) that

$$\lim_{n\to\infty} \int_{\mathbb{R}^3} E_{\rm xc}(\rho_{\gamma_n}) = 0.$$

Let us now fix $1 < p < \frac{3}{2}$, $\epsilon > 0$ and $R > 0$ such that $|V| \leq \epsilon\lambda^{-1}$ on B_R^c. For n large enough, we have

$$\left|\int_{\mathbb{R}^3} \rho_{\gamma_n} V\right| \leq \int_{B_R} \rho_{\gamma_n}|V| + \int_{B_R^c} \rho_{\gamma_n}|V| \leq \left(\int_{B_R} |V|^{p'}\right)^{\frac{1}{p'}} \left(\int_{B_R} \rho_{\gamma_n}^p\right)^{\frac{1}{p}} + \frac{\epsilon}{\lambda}\int_{B_R^c} \rho_{\gamma_n} \leq 2\epsilon.$$

Therefore

$$\lim_{n\to\infty} \int_{\mathbb{R}^3} \rho_{\gamma_n} V = 0.$$

As,

$$\mathcal{E}(\gamma_n) \geq \int_{\mathbb{R}^3} \rho_{\gamma_n} V + E_{\rm xc}(\rho_{\gamma_n}),$$

we obtain that $I_\lambda \geq 0$. This is in contradiction with the previously proved result stating that $I_\lambda < 0$. Hence $(\rho_{\gamma_n})_{n\in\mathbb{N}}$ cannot vanish. The case of problem (36) is easier since the only non-positive term in the energy functional is $E_{\rm xc}(\rho)$. $\square$

We can now prove that $I_\lambda < I_\lambda^\infty$. For this purpose let us consider a minimizing sequence $(\gamma_n)_{n\in\mathbb{N}}$ for (36). We deduce from Lemma 4 that there exists $\eta > 0$ and $R > 0$, such that for n large enough, there exists $x_n \in \mathbb{R}^3$ such that

$$\int_{x_n+B_R} \rho_{\gamma_n} \geq \eta.$$

Let us introduce $\widetilde{\gamma}_n = \tau_{\bar{x}_1 - x_n} \gamma_n \tau_{x_n - \bar{x}_1}$. Clearly $\widetilde{\gamma}_n \in \mathcal{K}_\lambda$ and

$$\mathcal{E}(\widetilde{\gamma}_n) \leq \mathcal{E}^\infty(\gamma_n) - \frac{z_1 \eta}{R}.$$

Thus,

$$I_\lambda \leq I_\lambda^\infty - \frac{z_1\eta}{R} < I_\lambda^\infty.$$

It remains to prove that the functions $\lambda \mapsto I_\lambda$ and $\lambda \mapsto I_\lambda^\infty$ are continuous. We will deal here with the former one, the same arguments applying to the latter one. The proof is based on the following lemma.

Lemma 5. *Let $(\alpha_k)_{k\in\mathbb{N}}$ be a sequence of positive real numbers converging to* 1*, and $(\rho_k)_{k\in\mathbb{N}}$ a sequence of non-negative densities such that $(\sqrt{\rho_k})_{k\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$. Then*

$$\lim_{k\to\infty} \left(E_{\rm xc}(\alpha_k \rho_k) - E_{\rm xc}(\rho_k)\right) = 0.$$

Proof. In the LDA setting, we deduce from (28) that there exists $1 < p_- \leq p_+ < \frac{5}{3}$ and $C \in \mathbb{R}_+$ such that for k large enough

$$\left|E_{\rm xc}^{\rm LDA}(\alpha_k\rho_k) - E_{\rm xc}^{\rm LDA}(\rho_k)\right| \leq C\,|\alpha_k - 1| \int_{\mathbb{R}^3} (\rho_k^{p_-} + \rho_k^{p_+}).$$

In the GGA setting, we obtain from (31) and (33) that there exists $1 < p_- \leq p_+ < \frac{5}{3}$ and $C \in \mathbb{R}_+$ such that for k large enough

$$\left|E_{\rm xc}^{\rm GGA}(\alpha_k\rho_k) - E_{\rm xc}^{\rm GGA}(\rho_k)\right| \leq C\,|\alpha_k - 1| \int_{\mathbb{R}^3} (\rho_k^{p_-} + \rho_k^{p_+} + |\nabla\sqrt{\rho_k}|^2).$$

As $(\sqrt{\rho_k})_{k\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$, $(\rho_k)_{k\in\mathbb{N}}$ is bounded in $L^p(\mathbb{R}^3)$ for all $1 \leq p \leq 3$ and $(\nabla\sqrt{\rho_k})_{k\in\mathbb{N}}$ is bounded in $(L^2(\mathbb{R}^3))^3$, hence the result. ☐

We can now complete the proof of Lemma 1.

Left-continuity of $\lambda \mapsto I_\lambda$. Let $\lambda > 0$, and $(\lambda_k)_{k\in\mathbb{N}}$ be an increasing sequence of positive real numbers converging to λ. Let $\epsilon > 0$ and $\gamma \in \mathcal{K}_\lambda$ such that

$$I_\lambda \leq \mathcal{E}(\gamma) \leq I_\lambda + \frac{\epsilon}{2}.$$

For all $k \in \mathbb{N}$, $\gamma_k = \lambda_k \lambda^{-1} \gamma$ is in $\mathcal{K}_{\lambda_k}$ so that

$$\forall k \in \mathbb{N}, \quad \forall n \in \mathbb{N}, \quad I_\lambda \leq I_{\lambda_k} \leq \mathcal{E}(\gamma_k).$$

Besides,

$$\mathcal{E}(\gamma_k) = \frac{\lambda_k}{\lambda}{\rm Tr}\,(-\Delta\gamma) + \frac{\lambda_k}{\lambda}\int_{\mathbb{R}^3} \rho_\gamma V + \frac{\lambda_k^2}{\lambda^2} J(\rho_\gamma) + E_{\rm xc}\left(\frac{\lambda_k}{\lambda}\rho_\gamma\right) \underset{k\to\infty}{\longrightarrow} \mathcal{E}(\gamma)$$

in virtue of Lemma 5. Thus

$$I_\lambda \le I_{\lambda_k} \le I_\lambda + \epsilon$$

for k large enough.

Right-continuity of $\lambda \mapsto I_\lambda$. Let $\lambda > 0$, and $(\lambda_k)_{k\in\mathbb{N}}$ be an decreasing sequence of positive real numbers converging to λ. For each $k \in \mathbb{N}$, we choose $\gamma_k \in \mathcal{K}_{\lambda_k}$ such that

$$I_{\lambda_k} \le \mathcal{E}(\gamma_k) \le I_{\lambda_k} + \frac{1}{k}.$$

For all $k \in \mathbb{N}$, we set $\widetilde{\gamma}_k = \lambda\lambda_k^{-1}\gamma_k$. As $\widetilde{\gamma}_k \in \mathcal{K}_\lambda$, it holds

$$I_\lambda \le \mathcal{E}(\widetilde{\gamma}_k) = \frac{\lambda}{\lambda_k}\mathrm{Tr}\,(-\Delta\gamma_k) + \frac{\lambda}{\lambda_k}\int_{\mathbb{R}^3}\rho_{\gamma_k}V + \frac{\lambda}{\lambda_k^2}J(\rho_{\gamma_k}) + E_{\mathrm{xc}}\left(\frac{\lambda}{\lambda_k}\rho_{\gamma_k}\right).$$

As $(\gamma_k)_{k\in\mathbb{N}}$ is bounded in $\mathcal{H}$ and $(\sqrt{\rho_{\gamma_k}})_{k\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$, we deduce from Lemma 5 that

$$\lim_{k\to\infty}\left(\mathcal{E}(\widetilde{\gamma}_k) - \mathcal{E}(\gamma_k)\right) = 0.$$

Let $\epsilon > 0$ and $k_\epsilon \ge 2\epsilon^{-1}$ such that for all $k \ge k_\epsilon$,

$$|\mathcal{E}(\widetilde{\gamma}_k) - \mathcal{E}(\gamma_k)| \le \frac{\epsilon}{2}.$$

Then,

$$\forall k \ge k_\epsilon, \quad I_\lambda - \epsilon \le I_{\lambda_k} \le I_\lambda.$$

This proves the right-continuity of $\lambda \mapsto I_\lambda$ on $\mathbb{R}_+\setminus\{0\}$. Lastly, it results from the estimates established in Lemma2 that

$$\lim_{\lambda\to 0^+} I_\lambda = 0.$$

5.3 Proof of Theorem 1

Let us first prove the following lemma.

Lemma 6. *Let $(\gamma_n)_{n\in\mathbb{N}}$ be a sequence of elements of $\mathcal{K}$, bounded in $\mathcal{H}$, which converges to γ for the weak-$*$ topology of $\mathcal{H}$. If $\lim_{n\to\infty}\mathrm{Tr}\,(\gamma_n) = \mathrm{Tr}\,(\gamma)$, then $(\rho_{\gamma_n})_{n\in\mathbb{N}}$ converges to ρ_γ strongly in $L^p(\mathbb{R}^3)$ for all $1 \le p < 3$ and*

$$\mathcal{E}^{\mathrm{LDA}}(\gamma) \le \liminf_{n\to\infty}\mathcal{E}^{\mathrm{LDA}}(\gamma_n) \quad \textit{and} \quad \mathcal{E}^{\mathrm{LDA},\infty}(\gamma) \le \liminf_{n\to\infty}\mathcal{E}^{\mathrm{LDA},\infty}(\gamma_n).$$

Proof. The fact that $(\gamma_n)_{n\in\mathbb{N}}$ converges to γ for the weak-$*$ topology of $\mathcal{H}$ means that for all compact operator K on $L^2(\mathbb{R}^3)$,

$$\lim_{n\to\infty}\mathrm{Tr}\,(\gamma_n K) = \mathrm{Tr}\,(\gamma K) \quad \text{and} \quad \lim_{n\to\infty}\mathrm{Tr}\,(|\nabla|\gamma_n|\nabla|K) = \mathrm{Tr}\,(|\nabla|\gamma|\nabla|K).$$

For all $W \in C_c^\infty(\mathbb{R}^3)$, the operator $(1+|\nabla|)^{-1}W(1+|\nabla|)^{-1}$ is compact (it is even in the Schatten class $\mathfrak{S}_p$ for all $p > \frac{3}{2}$ in virtue of the Kato-Seiler-Simon inequality [27]), yielding

$$\begin{aligned}\int_{\mathbb{R}^3}\rho_{\gamma_n}W &= 2\,\mathrm{Tr}\,(\gamma_n W) = 2\,\mathrm{Tr}\,((1+|\nabla|)\gamma_n(1+|\nabla|)(1+|\nabla|)^{-1}W(1+|\nabla|)^{-1}) \\ &\underset{n\to\infty}{\longrightarrow} 2\,\mathrm{Tr}\,((1+|\nabla|)\gamma(1+|\nabla|)(1+|\nabla|)^{-1}W(1+|\nabla|)^{-1}) = 2\,\mathrm{Tr}\,(\gamma W) = \int_{\mathbb{R}^3}\rho_\gamma W\end{aligned}$$

Hence, $(\rho_{\gamma_n})_{n\in\mathbb{N}}$ converges to ρ_γ in $\mathcal{D}'(\mathbb{R}^3)$. As by (40), $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$, it follows that $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ converges to $\sqrt{\rho_\gamma}$ weakly in $H^1(\mathbb{R}^3)$, and strongly in $L^p_{\rm loc}(\mathbb{R}^3)$ for all $2 \le p < 6$. In particular, $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ converges to $\sqrt{\rho_\gamma}$ weakly in $L^2(\mathbb{R}^3)$. But we also know that

$$\lim_{n\to\infty} \|\sqrt{\rho_{\gamma_n}}\|_{L^2}^2 = \lim_{n\to\infty} \int_{\mathbb{R}^3} \rho_{\gamma_n} = 2 \lim_{n\to\infty} \mathrm{Tr}\,(\gamma_n) = 2\mathrm{Tr}\,(\gamma) = \int_{\mathbb{R}^3} \rho_\gamma = \|\sqrt{\rho_\gamma}\|_{L^2}^2.$$

Therefore, the convergence of $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ to $\sqrt{\rho_\gamma}$ holds strongly in $L^2(\mathbb{R}^3)$. By an elementary bootstrap argument exploiting the boundedness of $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ in $H^1(\mathbb{R}^3)$, we obtain that $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ converges strongly to $\sqrt{\rho_\gamma}$ in $L^p(\mathbb{R}^3)$ for all $2 \le p < 6$, hence that $(\rho_{\gamma_n})_{n\in\mathbb{N}}$ converges to ρ_γ strongly in $L^p(\mathbb{R}^3)$ for all $1 \le p < 3$. This readily implies

$$\begin{aligned}
&\lim_{n\to\infty} \int_{\mathbb{R}^3} \rho_{\gamma_n} V = \int_{\mathbb{R}^3} \rho_\gamma V \\
&\lim_{n\to\infty} J(\rho_{\gamma_n}) = J(\rho_\gamma) \\
&\lim_{n\to\infty} E_{\rm xc}^{\rm LDA}(\rho_{\gamma_n}) = E_{\rm xc}^{\rm LDA}(\rho_\gamma).
\end{aligned}$$

Lastly, for any orthonormal basis $(\psi_k)_{k\in\mathbb{N}^*}$ of $L^2(\mathbb{R}^3)$ such that $\psi_k \in H^1(\mathbb{R}^3)$ for all k, we have

$$\begin{aligned}
\mathrm{Tr}\,(|\nabla|\gamma|\nabla|) &= \sum_{k=1}^{+\infty} \langle \psi_k||\nabla|\gamma|\nabla||\psi_k\rangle \\
&= \sum_{k=1}^{+\infty} \mathrm{Tr}\,(\gamma(||\nabla|\psi_k\rangle\langle|\nabla|\psi_k|)) \\
&= \sum_{k=1}^{+\infty} \lim_{n\to\infty} \mathrm{Tr}\,(\gamma_n(||\nabla|\psi_k\rangle\langle|\nabla|\psi_k|)) \\
&\le \liminf_{n\to\infty} \sum_{k=1}^{+\infty} \mathrm{Tr}\,(\gamma_n(||\nabla|\psi_k\rangle\langle|\nabla|\psi_k|)) \\
&= \liminf_{n\to\infty} \mathrm{Tr}\,(|\nabla|\gamma_n|\nabla|).
\end{aligned}$$

We thus obtain the desired result. □

We are now in position to prove Theorem 1. Let $(\gamma_n)_{n\in\mathbb{N}}$ be a minimizing sequence for I_λ. We know from Lemma 2 that $(\gamma_n)_{n\in\mathbb{N}}$ is bounded in $\mathcal{H}$ and that $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$. Replacing $(\gamma_n)_{n\in\mathbb{N}}$ by a suitable subsequence, we can assume that (γ_n) converges to some $\gamma \in \mathcal{K}$ for the weak-$*$ topology of $\mathcal{H}$ and that $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ converges to $\sqrt{\rho_\gamma}$ weakly in $H^1(\mathbb{R}^3)$, strongly in $L^p_{\rm loc}(\mathbb{R}^3)$ for all $2 \le p < 6$ and almost everywhere.

If $\mathrm{Tr}\,(\gamma) = \lambda$, then $\gamma \in \mathcal{K}_\lambda$ and according to Lemma 6,

$$\mathcal{E}^{\rm LDA}(\gamma) \le \liminf_{n\to+\infty} \mathcal{E}^{\rm LDA}(\gamma_n) = I_\lambda$$

yielding that γ is a minimizer of (35).

The rest of the proof consists in rulling out the eventuality when $\mathrm{Tr}\,(\gamma) < \lambda$. Let us therefore set $\alpha = \mathrm{Tr}\,(\gamma)$ and assume that $0 \le \alpha < \lambda$. Following e.g. [8], we consider a quadratic partition of the unity $\xi^2 + \chi^2 = 1$, where ξ is a smooth, radial function, nonincreasing in the radial direction, such that $\xi(0) = 1$, $0 \le \xi(x) < 1$ if $|x| > 0$, $\xi(x) = 0$

if $|x| \geq 1$, $\|\nabla \xi\|_{L^\infty} \leq 2$ and $\|\nabla(1-\xi^2)^{\frac{1}{2}}\|_{L^\infty} \leq 2$. We then set $\xi_R(\cdot) = \xi\left(\frac{\cdot}{R}\right)$. For all $n \in \mathbb{N}$, $R \mapsto \mathrm{Tr}\,(\xi_R \gamma_n \xi_R)$ is a continuous nondecreasing function which vanishes at $R=0$ and converges to $\mathrm{Tr}\,(\gamma_n) = \lambda$ when R goes to infinity. Let $R_n > 0$ be such that $\mathrm{Tr}\,(\xi_{R_n} \gamma_n \xi_{R_n}) = \alpha$. The sequence $(R_n)_{n\in\mathbb{N}}$ goes to infinity; otherwise, it would contain a subsequence $(R_{n_k})_{k\in\mathbb{N}}$ converging to a finite value R^*, and we would then get

$$\int_{\mathbb{R}^3} \rho_\gamma(x) \xi_{R^*}^2(x)\, dx = \lim_{n\to\infty} \int_{\mathbb{R}^3} \rho_{\gamma_n}(x) \xi_{R_n}^2(x)\, dx = 2 \lim_{n\to\infty} \mathrm{Tr}\,(\xi_{R_n} \gamma_n \xi_{R_n}) = 2\alpha = \int_{\mathbb{R}^3} \rho_\gamma(x)\, dx.$$

As $\xi_{R^*}^2 < 1$ on $\mathbb{R}^3 \setminus \{0\}$, we reach a contradiction. Consequently, $(R_n)_{n\in\mathbb{N}}$ indeed goes to infinity. Let us now introduce

$$\gamma_{1,n} = \xi_{R_n} \gamma_n \xi_{R_n} \quad \text{and} \quad \gamma_{2,n} = \chi_{R_n} \gamma_n \chi_{R_n}.$$

Note that $\gamma_{1,n}$ and $\gamma_{2,n}$ are trace-class self-adjoint operators on $L^2(\mathbb{R}^3)$ such that $0 \leq \gamma_{j,n} \leq 1$, that $\rho_{\gamma_n} = \rho_{\gamma_{1,n}} + \rho_{\gamma_{2,n}}$ and that $\mathrm{Tr}\,(\gamma_{1,n}) = \alpha$ while $\mathrm{Tr}\,(\gamma_{2,n}) = \lambda - \alpha$. Besides, using the IMS formula

$$-\Delta = \chi_{R_n}(-\Delta)\chi_{R_n} + \xi_{R_n}(-\Delta)\xi_{R_n} - |\nabla \chi_{R_n}|^2 - |\nabla \xi_{R_n}|^2,$$

it holds

$$\begin{aligned} \mathrm{Tr}\,(-\Delta\gamma_n) &= \mathrm{Tr}\,(-\Delta\gamma_{1,n}) + \mathrm{Tr}\,(-\Delta\gamma_{2,n}) - \mathrm{Tr}\,((|\nabla \chi_{R_n}|^2 + |\nabla \xi_{R_n}|^2)\gamma_n) \\ &\geq \mathrm{Tr}\,(-\Delta\gamma_{1,n}) + \mathrm{Tr}\,(-\Delta\gamma_{2,n}) - \frac{4\lambda}{R_n^2}, \end{aligned} \tag{49}$$

from which we infer that both $(\gamma_{1,n})_{n\in\mathbb{N}}$ and $(\gamma_{2,n})_{n\in\mathbb{N}}$ are bounded sequences of $\mathcal{H}$. As for all $\phi \in C_c^\infty(\mathbb{R}^3)$,

$$\begin{aligned} \mathrm{Tr}\,(\gamma_{1,n}(|\phi\rangle\langle\phi|)) &= \mathrm{Tr}\,(\gamma_n(|\xi_{R_n}\phi\rangle\langle\xi_{R_n}\phi|)) \\ &= \mathrm{Tr}\,(\gamma_n(|(\xi_{R_n}-1)\phi\rangle\langle\xi_{R_n}\phi|)) + \mathrm{Tr}\,(\gamma_n(|\phi\rangle\langle(\xi_{R_n}-1)\phi|)) + \mathrm{Tr}\,(\gamma_n(|\phi\rangle\langle\phi|)) \\ &\underset{n\to\infty}{\longrightarrow} \mathrm{Tr}\,(\gamma(|\phi\rangle\langle\phi|)), \end{aligned}$$

we obtain that $(\gamma_{1,n})_{n\in\mathbb{N}}$ converges to γ for the weak-$*$ topology of $\mathcal{H}$. Since $\mathrm{Tr}\,(\gamma_{1,n}) = \alpha = \mathrm{Tr}\,(\gamma)$ for all n, we deduce from Lemma 6 that $(\rho_{\gamma_{1,n}})_{n\in\mathbb{N}}$ converges to ρ_γ strongly in $L^p(\mathbb{R}^3)$ for all $1 \leq p < 3$, and that

$$\mathcal{E}^{\mathrm{LDA}}(\gamma) \leq \lim_{n\to\infty} \mathcal{E}^{\mathrm{LDA}}(\gamma_{1,n}). \tag{50}$$

As a by-product, we also obtain that $(\rho_{\gamma_{2,n}})_{n\in\mathbb{N}}$ converges strongly to zero in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for all $1 \leq p < 3$ (since $\rho_{\gamma_{2,n}} = \rho_{\gamma_n} - \rho_{\gamma_{1,n}}$ with $(\rho_{\gamma_n})_{n\in\mathbb{N}}$ and $(\rho_{\gamma_{1,n}})_{n\in\mathbb{N}}$ both converging to ρ_γ in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for all $1 \leq p < 3$). Besides, using again (49), it holds

$$\begin{aligned} \mathcal{E}^{\mathrm{LDA}}(\gamma_n) &= \mathrm{Tr}\,(-\Delta\gamma_n) + \int_{\mathbb{R}^3} \rho_{\gamma_n} V + J(\rho_{\gamma_n}) + \int_{\mathbb{R}^3} g(\rho_{\gamma_n}) \\ &\geq \mathrm{Tr}\,(-\Delta\gamma_{1,n}) + \mathrm{Tr}\,(-\Delta\gamma_{2,n}) + \int_{\mathbb{R}^3} \rho_{\gamma_{1,n}} V + \int_{\mathbb{R}^3} \rho_{\gamma_{2,n}} V \\ &\quad + J(\rho_{\gamma_{1,n}}) + J(\rho_{\gamma_{2,n}}) + \int_{\mathbb{R}^3} g(\rho_{\gamma_{1,n}} + \rho_{\gamma_{2,n}}) - \frac{4\lambda}{R_n^2} \\ &= \mathcal{E}^{\mathrm{LDA}}(\gamma_{1,n}) + \mathcal{E}^{\mathrm{LDA},\infty}(\gamma_{2,n}) + \int_{\mathbb{R}^3} \rho_{\gamma_{2,n}} V \\ &\quad + \int_{\mathbb{R}^3} (g(\rho_{\gamma_{1,n}} + \rho_{\gamma_{2,n}}) - g(\rho_{\gamma_{1,n}}) - g(\rho_{\gamma_{2,n}})) - \frac{4\lambda}{R_n^2}. \end{aligned}$$

For R large enough, one has on the one hand

$$\left|\int_{\mathbb{R}^3} \rho_{\gamma_{2,n}} V\right| \le 2Z \left(\int_{B_R} \rho_{\gamma_{2,n}}\right)^{\frac{1}{2}} \|\nabla\sqrt{\rho_{\gamma_{2,n}}}\|_{L^2} + \frac{2Z(\lambda-\alpha)}{R},$$

and on the other hand

$$\begin{aligned}
\left|\int_{\mathbb{R}^3} (g(\rho_{\gamma_{1,n}}+\rho_{\gamma_{2,n}}) - g(\rho_{\gamma_{1,n}}) - g(\rho_{\gamma_{2,n}}))\right| \ &\le \ \int_{B_R} |g(\rho_{\gamma_{1,n}}+\rho_{\gamma_{2,n}}) - g(\rho_{\gamma_{1,n}})| + \int_{B_R} |g(\rho_{\gamma_{2,n}})| \\
&+ \ \int_{B_R^c} |g(\rho_{\gamma_{1,n}}+\rho_{\gamma_{2,n}}) - g(\rho_{\gamma_{2,n}})| + \int_{B_R^c} |g(\rho_{\gamma_{1,n}})| \\
&\le \ C\left(\int_{B_R} (\rho_{\gamma_{2,n}} + \rho_{\gamma_{2,n}}^2) + \|\rho_{\gamma_{1,n}}\|_{L^2}\left(\int_{B_R} \rho_{\gamma_{2,n}}^2\right)^{\frac{1}{2}}\right) \\
&+ \ C\left(\int_{B_R} \rho_{\gamma_{2,n}}^{p_-} + \rho_{\gamma_{2,n}}^{p_+}\right) \\
&+ \ C\left(\int_{B_R^c} (\rho_{\gamma_{1,n}} + \rho_{\gamma_{1,n}}^2) + \|\rho_{\gamma_{2,n}}\|_{L^2}\left(\int_{B_R^c} \rho_{\gamma_{1,n}}^2\right)^{\frac{1}{2}}\right) \\
&+ \ C\left(\int_{B_R^c} \rho_{\gamma_{1,n}}^{p_-} + \rho_{\gamma_{1,n}}^{p_+}\right)
\end{aligned}$$

for some constant C independent of R and n. Yet, we know that $(\sqrt{\rho_{\gamma_{1,n}}})_{n\in\mathbb{N}}$ and $(\sqrt{\rho_{\gamma_{1,n}}})_{n\in\mathbb{N}}$ are bounded in $H^1(\mathbb{R}^3)$, that $(\rho_{\gamma_{1,n}})_{n\in\mathbb{N}}$ converges to ρ_γ in $L^p(\mathbb{R}^3)$ for all $1 \le p < 3$ and that $(\rho_{\gamma_{2,n}})_{n\in\mathbb{N}}$ converges to 0 in $L^p_{\rm loc}(\mathbb{R}^3)$ for all $1 \le p < 3$. Consequently, there exists for all $\epsilon > 0$, some $N \in \mathbb{N}$ such that for all $n \ge N$,

$$\mathcal{E}^{\rm LDA}(\gamma_n) \ge \mathcal{E}^{\rm LDA}(\gamma_{1,n}) + \mathcal{E}^{\rm LDA,\infty}(\gamma_{2,n}) - \epsilon \ge I_\alpha + I^\infty_{\lambda-\alpha} - \epsilon.$$

Letting n go to infinity, ϵ go to zero, and using (37), we obtain that $I_\lambda = I_\alpha + I^\infty_{\lambda-\alpha}$ and that $(\gamma_{1,n})_{n\in\mathbb{N}}$ and $(\gamma_{2,n})_{n\in\mathbb{N}}$ are minimizing sequences for I_α and $I^\infty_{\lambda-\alpha}$ respectively. It also follows from (50) that γ is a minimizer for I_α. In particular γ satisfies the Euler equation

$$\gamma = 1_{(-\infty,\epsilon_{\rm F})}(H_{\rho_\gamma}) + \delta$$

for some Fermi level $\epsilon_{\rm F} \in \mathbb{R}$, where

$$H_{\rho_\gamma} = -\frac{1}{2}\Delta + V + \rho_\gamma \star |\mathbf{r}|^{-1} + g'(\rho_\gamma),$$

and where $0 \le \delta \le 1$, $\mathrm{Ran}(\delta) \subset \mathrm{Ker}(H_{\rho_\gamma} - \epsilon_{\rm F})$. As $V + \rho_\gamma \star |\mathbf{r}|^{-1} + g'(\rho_\gamma)$ is Δ-compact, the essential spectrum of H_{ρ_γ} is $[0,+\infty)$. Besides, H_{ρ_γ} is bounded from below,

$$H_{\rho_\gamma} \le -\frac{1}{2}\Delta + V + \rho_\gamma \star |\mathbf{r}|^{-1},$$

and we know from [17, Lemma II.1] that as $-\sum_{k=1}^M z_k + \int_{\mathbb{R}^3} \rho_\gamma = -Z + 2\alpha < -Z + 2\lambda \le 0$, the right hand side operator has infinitely many negative eigenvalues of finite multiplicities. Therefore, so has H_{ρ_γ}. Eventually, $\epsilon_{\rm F} < 0$ and

$$\gamma = \sum_{i=1}^n |\phi_i\rangle\langle\phi_i| + \sum_{i=n+1}^m n_i |\phi_i\rangle\langle\phi_i|$$

where $0 \leq n_i \leq 1$ and where

$$-\frac{1}{2}\Delta\phi_i + V\phi_i + \left(\rho_\gamma \star |\mathbf{r}|^{-1}\right)\phi_i + g'(\rho_\gamma)\,\phi_i = \epsilon_i\ \phi_i$$

$\epsilon_1 < \epsilon_2 \leq \epsilon_3 \leq \cdots < 0$ denoting the negative eigenvalues of H_{ρ_γ} including multiplicities (by standard arguments the ground state eigenvalue of H_{ρ_γ} is non-degenerate). It then follows from elementary elliptic regularity results that all the ϕ_i, hence ρ_γ, are in $H^2(\mathbb{R}^3)$ and therefore vanish at infinity. Using Lemma 12, all the ϕ_i decay exponentially fast to zero at infinity.

Let us now analyze more in details the sequence $(\gamma_{2,n})_{n\in\mathbb{N}}$. As it is a minimizing sequence for $I^\infty_{\lambda-\alpha}$, $(\rho_{\gamma_{2,n}})_{n\in\mathbb{N}}$ cannot vanish, so that there exists $\eta > 0$, $R > 0$ and such for all $n \in \mathbb{N}$, $\int_{y_n+B_R}\rho_{\gamma_{2,n}} \geq \eta$ for some $y_n \in \mathbb{R}^3$. Thus, the sequence $(\tau_{y_n}\gamma_{2,n}\tau_{-y_n})_{n\in\mathbb{N}}$ converges for the weak-$*$ topology of $\mathcal{H}$ to some $\gamma' \in \mathcal{K}$ satisfying $\mathrm{Tr}\,(\gamma') \geq \eta > 0$. Let $\beta = \mathrm{Tr}\,(\gamma')$. Reasoning as above, one can easily check that γ' is a minimizer for I^∞_β, and that $I_\lambda = I_\alpha + I^\infty_\beta + I^\infty_{\lambda-\alpha-\beta}$. Besides,

$$\gamma' = 1_{(-\infty,\epsilon'_{\mathrm{F}})}(H^\infty_{\rho_{\gamma'}}) + \delta'$$

where

$$H^\infty_{\rho_{\gamma'}} = -\frac{1}{2}\Delta + \rho_{\gamma'} \star |\mathbf{r}|^{-1} + g'(\rho_{\gamma'}),$$

and where $0 \leq \delta' \leq 1$, $\mathrm{Ran}(\delta') \subset \mathrm{Ker}(H^\infty_{\rho_{\gamma'}} - \epsilon'_{\mathrm{F}})$, and $\epsilon_{\mathrm{F}'} \leq 0$.

Assume for a while that one can choose $\epsilon_{\mathrm{F}'} < 0$. Then

$$\gamma' = \sum_{i=1}^{n'} |\phi'_i\rangle\langle\phi'_i| + \sum_{i=n'+1}^{m'} n'_i|\phi'_i\rangle\langle\phi'_i|,$$

all the ϕ_i's being in $C^\infty(\mathbb{R}^3)$ and decaying exponentially fast at infinity. For $n \in \mathbb{N}$ large enough, the operator

$$\gamma_n = \min\left(1, \|\gamma + \tau_{n\mathbf{e}}\gamma'\tau_{-n\mathbf{e}}\|^{-1}\right)(\gamma + \tau_{n\mathbf{e}}\gamma'\tau_{-n\mathbf{e}})$$

then is in $\mathcal{K}$ and $\mathrm{Tr}\,(\gamma_n) \leq (\alpha + \beta)$. As both the ϕ_i's and the ϕ'_i's decay exponentially fast to zero, a simple calculation shows that there exists some $\delta > 0$ such that for n large enough

$$\mathcal{E}^{\mathrm{LDA}}(\gamma_n) = \mathcal{E}^{\mathrm{LDA}}(\gamma) + \mathcal{E}^{\mathrm{LDA},\infty}(\gamma') - \frac{2\alpha(Z-2\beta)}{n} + O(e^{-\delta n}) = I^\alpha + I^\infty_\beta - \frac{2\alpha(Z-2\beta)}{n} + O(e^{-\delta n}).$$

Hence, for n large enough

$$I_{\alpha+\beta} \leq I_{\mathrm{Tr}\,(\gamma_n)} \leq \mathcal{E}^{\mathrm{LDA}}(\gamma_n) < I^\alpha + I^\infty_\beta.$$

Adding $I^\infty_{\lambda-\alpha-\beta}$ to both sides, we obtain that

$$I_\lambda \leq I_{\alpha+\beta} + I^\infty_{\lambda-\alpha-\beta} < I^\alpha + I^\infty_\beta + I^\infty_{\lambda-\alpha-\beta},$$

which obviously contradicts the previously established equality $I_\lambda = I_\alpha + I^\infty_\beta + I^\infty_{\lambda-\alpha-\beta}$.

It remains to exclude the case when $\epsilon_{\mathrm{F}'}$ has to be chosen equal to zero. In this case, 0 is an eigenvalue of $H^\infty_{\rho_{\gamma'}}$ and there exists $\psi \in \mathrm{Ker}(H^\infty_{\rho_{\gamma'}}) \subset H^2(\mathbb{R}^3)$ such that $\|\psi\|_{L^2} = 1$ and $\gamma'\psi = \mu\psi$ with $\mu > 0$. We then define for $0 < \eta < \mu$ and $n \in \mathbb{N}$,

$$\begin{aligned}\gamma_{n,\eta} \quad = \quad & \min\left(1, \|\gamma + \eta|\phi_{m+1}\rangle\langle\phi_{m+1}| + \tau_{n\mathbf{e}}(\gamma' - \eta|\psi\rangle\langle\psi|)\tau_{-n\mathbf{e}}\|^{-1}\right) \\ & (\gamma + \eta|\phi_{m+1}\rangle\langle\phi_{m+1}| + \tau_{n\mathbf{e}}(\gamma' - \eta|\psi\rangle\langle\psi|)\tau_{-n\mathbf{e}}).\end{aligned}$$

As $\gamma_{n,\eta}$ is in $\mathcal{K}$ and such that $\mathrm{Tr}\,(\gamma_{n,\eta}) \leq \lambda$, it holds

$$I_\lambda \leq I_{\mathrm{Tr}\,(\gamma_{n,\eta})} \leq \mathcal{E}^{\mathrm{LDA}}(\gamma_{n,\eta}).$$

It is then easy to show that

$$\lim_{n\to\infty} \mathcal{E}^{\mathrm{LDA}}(\gamma_{n,\eta}) = \mathcal{E}^{\mathrm{LDA}}(\gamma + \eta|\phi_{m+1}\rangle\langle\phi_{m+1}|) + \mathcal{E}^{\mathrm{LDA},\infty}(\gamma' - \eta|\psi\rangle\langle\psi|).$$

Besides, for $\eta > 0$ small enough

$$\mathcal{E}^{\mathrm{LDA}}(\gamma+\eta|\phi_{m+1}\rangle\langle\phi_{m+1}|)+\mathcal{E}^{\mathrm{LDA},\infty}(\gamma'-\eta|\psi\rangle\langle\psi|) = \mathcal{E}^{\mathrm{LDA}}(\gamma)+\mathcal{E}^{\mathrm{LDA},\infty}(\gamma')+2\eta\epsilon_{m+1}+o(\eta).$$

Reasoning as above, we obtain that for $\eta > 0$ small enough

$$I_\lambda \leq I_\lambda + 2\eta\epsilon_{m+1} + o(\eta),$$

which is in contradiction with the fact that ϵ_{m+1} is negative. The proof is complete.

5.4 Proof of Theorem 2

For $\phi \in H^1(\mathbb{R}^3)$, we set $\rho_\phi(x) = 2|\phi(x)|^2$ and

$$E(\phi) = \int_{\mathbb{R}^3} |\nabla\phi|^2 + \int_{\mathbb{R}^3} \rho_\phi V + J(\rho_\phi) + E_{\mathrm{xc}}^{\mathrm{GGA}}(\rho_\phi).$$

For all $\phi \in H^1(\mathbb{R}^3)$ such that $\|\phi\|_{L^2} = 1$, $\gamma_\phi = |\phi\rangle\langle\phi| \in \mathcal{K}_1$ and $\mathcal{E}(\gamma_\phi) = E(\phi)$. Therefore,

$$I_1 \leq \inf\left\{E(\phi),\ \phi \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} |\phi|^2 = 1\right\}.$$

Conversely, for all $\gamma \in \mathcal{K}_1$, $\phi_\gamma = \sqrt{\frac{\rho_\gamma}{2}}$ satisfies $\phi_\gamma \in H^1(\mathbb{R}^3)$, $\|\phi\|_{L^2} = 1$ and

$$\mathcal{E}^{\mathrm{GGA}}(\gamma) = \mathcal{E}^{\mathrm{GGA}}(|\phi_\gamma\rangle\langle\phi_\gamma|) + \mathrm{Tr}\,(-\Delta\gamma) - \frac{1}{2}\int_{\mathbb{R}^3} |\nabla\sqrt{\rho_\gamma}|^2 \geq \mathcal{E}^{\mathrm{GGA}}(|\phi_\gamma\rangle\langle\phi_\gamma|) = E(\phi_\gamma).$$

Consequently,

$$I_1 = \inf\left\{E(\phi),\ \phi \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} |\phi|^2 = 1\right\} \tag{51}$$

and (20) has a minimizer for $N_p = 1$, if and only if (51) has a minimizer ϕ (γ_ϕ then is a minimizer of (20) for $N_p = 1$). We are therefore led to study the minimization problem (51). In the GGA setting we are interested in, $E(\phi)$ can be rewritten as

$$E(\phi) = \int_{\mathbb{R}^3} |\nabla\phi|^2 + \int_{\mathbb{R}^3} \rho_\phi V + J(\rho_\phi) + \int_{\mathbb{R}^3} h(\rho_\phi, |\nabla\phi|^2).$$

Conditions (29)-(33) guarantee that E is Fréchet differentiable on $H^1(\mathbb{R}^3)$ (see [1] for details) and that for all $(\phi, w) \in H^1(\mathbb{R}^3) \times H^1(\mathbb{R}^3)$,

$$E'(\phi)\cdot w = 2\left(\frac{1}{2}\int_{\mathbb{R}^3}\left(1 + \frac{\partial h}{\partial\kappa}\left(\rho_\phi, |\nabla\phi|^2\right)\right)\nabla\phi\cdot\nabla w + \int_{\mathbb{R}^3}\left(V + \rho_\phi \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial\rho}\left(\rho_\phi, |\nabla\phi|^2\right)\right)\phi w\right).$$

We now embed (51) in the family of problems

$$J_\lambda = \inf\left\{E(\phi),\ \phi \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} |\phi|^2 = \lambda\right\} \tag{52}$$

and introduce the problem at infinity

$$J_\lambda^\infty = \inf\left\{E^\infty(\phi),\ \phi\in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3}|\phi|^2=\lambda\right\} \tag{53}$$

where

$$E^\infty(\phi)=\int_{\mathbb{R}^3}|\nabla\phi|^2+J(\rho_\phi)+\int_{\mathbb{R}^3}h(\rho_\phi,|\nabla\phi|^2).$$

Note that reasoning as above, one can see that $J_\lambda=I_\lambda$ and $J_\lambda^\infty=I_\lambda^\infty$ for all $0\le\lambda\le 1$ (while these equalities do not *a priori* hold true for $\lambda>1$).

The rest of this section consists in proving that (52) has a minimizer for all $0\le\lambda\le 1$. Let us start with a simple lemma.

Lemma 7. *Let $0\le\mu\le 1$ and let $(\phi_n)_{n\in\mathbb{N}}$ be a minimizing sequence for J_μ (resp. for J_μ^∞) which converges to some $\phi\in H^1(\mathbb{R}^3)$ weakly in $H^1(\mathbb{R}^3)$. Assume that $\|\phi\|_{L^2}^2=\mu$. Then ϕ is a minimizer for J_μ (resp. for J_μ^∞).*

Proof. Let $(\phi_n)_{n\in\mathbb{N}}$ be a minimizing sequence for J_μ which converges to ϕ weakly in $H^1(\mathbb{R}^3)$. For almost all $x\in\mathbb{R}^3$, the function $z\mapsto|z|^2+h(\rho_\phi(x),|z|^2)$ is convex on $\mathbb{R}^3$. Besides the function $t\mapsto t+h(\rho_\phi(x),t)$ is Lipschitz on $\mathbb{R}_+$, uniformly in x. It follows that the functional

$$\psi\mapsto\int_{\mathbb{R}^3}\left(|\nabla\psi|^2+h(\rho_\phi,|\nabla\psi|^2)\right)$$

is convex and continuous on $H^1(\mathbb{R}^3)$. As $(\phi_n)_{n\in\mathbb{N}}$ converges to ϕ weakly in $H^1(\mathbb{R}^3)$, we get

$$\int_{\mathbb{R}^3}\left(|\nabla\phi|^2+h(\rho_\phi,|\nabla\phi|^2)\right)\le\lim_{n\to\infty}\int_{\mathbb{R}^3}\left(|\nabla\phi_n|^2+h(\rho_\phi,|\nabla\phi_n|^2)\right).$$

Besides, we deduce from (31) that

$$\left|\int_{\mathbb{R}^3}\left(h(\rho_{\phi_n},|\nabla\phi_n|^2)-h(\rho_\phi,|\nabla\phi_n|^2)\right)\right|\le C\|\phi_n-\phi\|_{L^2},$$

where the constant C only depends on h and on the H^1 bound of $(\phi_n)_{n\in\mathbb{N}}$. As $(\phi_n)_{n\in\mathbb{N}}$ converges to ϕ weakly in $L^2(\mathbb{R}^3)$ and as $\|\phi\|_{L^2}=\|\phi_n\|_{L^2}$ for all $n\in\mathbb{N}$, the convergence of $(\phi_n)_{n\in\mathbb{N}}$ to ϕ holds strongly in $L^2(\mathbb{R}^3)$. Therefore,

$$\begin{aligned}\int_{\mathbb{R}^3}|\nabla\phi|^2+E_{\rm xc}^{\rm GGA}(\rho_\phi) &= \int_{\mathbb{R}^3}\left(|\nabla\phi|^2+h(\rho_\phi,|\nabla\phi|^2)\right)\\ &\le \liminf_{n\to\infty}\int_{\mathbb{R}^3}\left(|\nabla\phi_n|^2+h(\rho_\phi,|\nabla\phi_n|^2)\right)\\ &\quad+\lim_{n\to\infty}\int_{\mathbb{R}^3}\left(h(\rho_{\phi_n},|\nabla\phi_n|^2)-h(\rho_\phi,|\nabla\phi_n|^2)\right)\\ &= \liminf_{n\to\infty}\int_{\mathbb{R}^3}|\nabla\phi_n|^2+E_{\rm xc}^{\rm GGA}(\rho_{\phi_n}).\end{aligned}$$

Finally, as $(\phi_n)_{n\in\mathbb{N}}$ is bounded in H^1 and converges strongly to ϕ in $L^2(\mathbb{R}^3)$, we infer that the convergence holds strongly in $L^p(\mathbb{R}^3)$ for all $2\le p<6$, yielding

$$\lim_{n\to\infty}\int_{\mathbb{R}^3}\rho_{\phi_n}V+J(\rho_{\phi_n})=\int_{\mathbb{R}^3}\rho_\phi V+J(\rho_\phi).$$

Therefore,

$$E(\phi) \leq \liminf_{n\to\infty} E(\phi_n) = I_\mu.$$

As $\|\phi\|_{L^2}^2 = \mu$, ϕ is a minimizer for J_μ. Obviously, the same arguments can be applied to a minimizing sequence for J_μ^∞. $\square$

In order to prove that the minimizing sequences for J_λ (or at least some of them) are indeed precompact in $L^2(\mathbb{R}^3)$, we will use the concentration-compactness method due to P.-L. Lions [18]. Consider an Ekeland sequence $(\phi_n)_{n\in\mathbb{N}}$ for (52), that is [7] a sequence $(\phi_n)_{n\in\mathbb{N}}$ such that

$$\forall n \in \mathbb{N}, \quad \phi_n \in H^1(\mathbb{R}^3) \quad \text{and} \quad \int_{\mathbb{R}^3} \phi_n^2 = \lambda \tag{54}$$

$$\lim_{n\to+\infty} E(\phi_n) = J_\lambda \tag{55}$$

$$\lim_{n\to+\infty} E'(\phi_n) + \theta_n\phi_n = 0 \quad \text{in } H^{-1}(\mathbb{R}^3) \tag{56}$$

for some sequence $(\theta_n)_{n\in\mathbb{N}}$ of real numbers. As on the one hand, $|\phi| \in H^1(\mathbb{R}^3)$ and $E(|\phi|) = E(\phi)$ for all $\phi \in H^1(\mathbb{R}^3)$, and as on the other hand, the function $\lambda \mapsto J_\lambda$ is decreasing on $[0, 1]$, we can assume that

$$\forall n \in \mathbb{N}, \quad \phi_n \geq 0 \text{ a.e. on } \mathbb{R}^3 \quad \text{and} \quad \theta_n \geq 0. \tag{57}$$

Lastly, up to extracting subsequences, there is no restriction in assuming the following convergences:

$$\phi_n \rightharpoonup \phi \text{ weakly in } H^1(\mathbb{R}^3), \tag{58}$$

$$\phi_n \to \phi \text{ strongly in } L^p_{\text{loc}}(\mathbb{R}^3) \text{ for all } 2 \leq p < 6 \tag{59}$$

$$\phi_n \to \phi \text{ a.e. in } \mathbb{R}^3 \tag{60}$$

$$\theta_n \to \theta \text{ in } \mathbb{R}, \tag{61}$$

and it follows from (57) that $\phi \geq 0$ a.e. on $\mathbb{R}^3$ and $\theta \geq 0$. Note that the Ekeland condition (56) also reads

$$-\frac{1}{2}\text{div}\left(\left(1 + \frac{\partial h}{\partial \kappa}\left(\rho_{\phi_n}, |\nabla\phi_n|^2\right)\right)\nabla\phi_n\right) + \left(V + \rho_{\phi_n} \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial \rho}\left(\rho_{\phi_n}, |\nabla\phi_n|^2\right)\right)\phi_n + \theta_n\phi_n$$
$$= \eta_n \qquad \text{with} \qquad \eta_n \underset{n\to 0}{\longrightarrow} 0 \text{ in } H^{-1}(\mathbb{R}^3). \tag{62}$$

We can apply to the sequence $(\phi_n)_{n\in\mathbb{N}}$ the following version of the concentration-compactness lemma.

Lemma 8 (Concentration-compactness lemma [18]). *Let $\lambda > 0$ and $(\phi_n)_{n\in\mathbb{N}}$ be a bounded sequence in $H^1(\mathbb{R}^3)$ such that*

$$\forall n \in \mathbb{N}, \quad \int_{\mathbb{R}^N} \phi_n^2 = \lambda.$$

Then one can extract from $(\phi_n)_{n\in\mathbb{N}}$ a subsequence $(\phi_{n_k})_{k\in\mathbb{N}}$ such that one of the following three conditions holds true:

1. *(Compactness) There exists a sequence $(y_k)_{k\in\mathbb{N}}$ in $\mathbb{R}^3$, such that for all $\epsilon > 0$, there exists $R > 0$ such that*

$$\forall k \in \mathbb{N}, \qquad \int_{y_k+B_R} \phi_{n_k}^2 \geq \lambda - \epsilon.$$

2. *(Vanishing) For all $R > 0$,*

$$\lim_{k\to\infty} \sup_{y\in\mathbb{R}^3} \int_{y+B_R} \phi_{n_k}^2 = 0.$$

3. *(Dichotomy) There exists $0 < \delta < \lambda$, such that for all $\epsilon > 0$ there exists*

   - *a sequence $(y_k)_{k\in\mathbb{N}}$ of points of $\mathbb{R}^3$,*
   - *a positive real number R_1 and a sequence of positive real numbers $(R_{2,k})_{k\in\mathbb{N}}$ converging to $+\infty$,*
   - *two sequences $(\phi_{1,k})_{k\in\mathbb{N}}$ and $(\phi_{2,k})_{n\in\mathbb{N}}$ bounded in $H^1(\mathbb{R}^3)$ (uniformly in ϵ)*

   such that for all k:

$$\begin{cases} \phi_{n_k} = \phi_{1,k} \quad \text{on } y_k + B_{R_1} \\ \phi_{n_k} = \phi_{2,k} \quad \text{on } \mathbb{R}^3 \setminus (y_k + B_{R_{2,k}}) \\ \left| \int_{\mathbb{R}^3} \phi_{1,k}^2 - \delta \right| \leq \epsilon, \quad \left| \int_{\mathbb{R}^3} \phi_{2,k}^2 - (\lambda - \delta) \right| \leq \epsilon \\ \lim_{k\to\infty} \mathrm{dist}(\mathrm{Supp}\, \phi_{1,k}, \mathrm{Supp}\, \phi_{2,k}) = \infty \\ \|\phi_{n_k} - (\phi_{1,k} + \phi_{2,k})\|_{L^p(\mathbb{R}^3)} \leq C_p\, \epsilon^{\frac{6-p}{2p}} \qquad \text{for all } 2 \leq p < 6 \\ \|\phi_{n_k}\|_{L^p(y_k + (B_{R_{2,k}} \setminus \overline{B}_{R_1}))} \leq C_p\, \epsilon^{\frac{6-p}{2p}} \qquad \text{for all } 2 \leq p < 6 \\ \liminf_{k\to\infty} \int_{\mathbb{R}^3} \left(|\nabla \phi_{n_k}|^2 - |\nabla \phi_{1,k}|^2 - |\nabla \phi_{2,k}|^2 \right) \geq -C\epsilon, \end{cases}$$

where the constants C and C_p only depend on the H^1 bound of $(\phi_n)_{n\in\mathbb{N}}$.

We then conclude using the following result.

Lemma 9. *Let $(\phi_n)_{n\in\mathbb{N}}$ satisfying (54)-(61). Then using the terminology introduced in the concentration-compactness Lemma 8,*

1. *if some subsequence $(\phi_{n_k})_{k\in\mathbb{N}}$ of $(\phi_n)_{n\in\mathbb{N}}$ satisfies the compactness condition, then $(\phi_{n_k})_{k\in\mathbb{N}}$ converges to ϕ strongly in $L^p(\mathbb{R}^3)$ for all $2 \leq p < 6$;*

2. *a subsequence of $(\phi_n)_{n\in\mathbb{N}}$ cannot vanish ;*

3. *a subsequence of $(\phi_n)_{n\in\mathbb{N}}$ cannot satisfy the dichotomy condition.*

Consequently, $(\phi_n)_{n\in\mathbb{N}}$ converges to ϕ strongly in $L^p(\mathbb{R}^3)$ for all $2 \leq p < 6$. It follows that ϕ is a minimizer to (52).

As the explicit form of the functions $\phi_{1,k}$ and $\phi_{2,k}$ arising in Lemma 8 will be useful for proving the third assertion of Lemma 9, we briefly recall the proof of the former lemma.

Sketch of the proof of Lemma 8. The argument is based on the analysis of Levy's concentration function

$$Q_n(R) = \sup_{y \in \mathbb{R}^3} \int_{y+B_R} \phi_n^2.$$

The sequence $(Q_n)_{n\in\mathbb{N}}$ is a sequence of nondecreasing, nonnegative, uniformly bounded functions such that $\lim_{R\to\infty} Q_n(R) = \lambda$.
There exists consequently a subsequence $(Q_{n_k})_{k\in\mathbb{N}}$ and a nondecreasing nonnegative function Q such that $(Q_{n_k})_{k\in\mathbb{N}}$ converges pointwise to Q. We obviously have

$$\lim_{R\to\infty} Q(R) = \delta \in [0, \lambda].$$

The case $\delta = 0$ corresponds to vanishing, while $\delta = \lambda$ corresponds to compactness. We now consider more in details the case when $0 < \delta < \lambda$ (dichotomy). Let ξ, χ be in $C^\infty(\mathbb{R}^3)$ and such that $0 \le \xi, \chi \le 1$, $\xi(x) = 1$ if $|x| \le 1$, $\xi(x) = 0$ if $|x| \ge 2$, $\chi(x) = 0$ if $|x| \le 1$, $\chi(x) = 1$ if $|x| \ge 2$, $\|\nabla\chi\|_{L^\infty} \le 2$ and $\|\nabla\xi\|_{L^\infty} \le 2$. For $R > 0$, we denote by $\xi_R(\cdot) = \xi\left(\frac{\cdot}{R}\right)$ and $\chi_R(\cdot) = \chi\left(\frac{\cdot}{R}\right)$. Let $\epsilon > 0$ and $R_1 \ge \epsilon^{-1}$ large enough for $Q(R_1) \ge \delta - \frac{\epsilon}{2}$ to hold. Then, up to getting rid of the first terms of the sequence, we can assume that for all k, we have $Q_{n_k}(R_1) \ge \delta - \epsilon$ and $Q_{n_k}(2R_1) \le \delta + \frac{\epsilon}{2}$. Furthermore, there exists $y_k \in \mathbb{R}^3$ such that

$$Q_{n_k}(R_1) = \int_{y_k + B_{R_1}} \phi_{n_k}^2$$

and we can choose a sequence $(R'_k)_{k\in\mathbb{N}}$ of positive real numbers greater than R_1, converging to infinity, such that $Q_{n_k}(2R'_k) \le \delta + \epsilon$ for all $k \in \mathbb{N}$. Consider now

$$\phi_{1,k} = \xi_{R_1}(\cdot - y_k)\phi_{n_k} \quad \text{and} \quad \phi_{2,k} = \chi_{R'_k}(\cdot - y_k)\phi_{n_k}.$$

Denoting by $R_{2,k} = 2R'_k$, we clearly have

$$\left| \int_{\mathbb{R}^3} \phi_{1,k}^2 - \delta \right| \le \epsilon, \quad \left| \int_{\mathbb{R}^3} \phi_{2,k}^2 - (\lambda - \delta) \right| \le \epsilon,$$

$$\int_{y_k + (B_{R_{2,k}} \setminus \overline{B}_{R_1})} \phi_{n_k}^2 = \int_{R_1 < |\cdot - y_k| < R_{2,k}} \phi_{n_k}^2 \le Q_{n_k}(R_{2,k}) - Q_{n_k}(R_1) \le 2\epsilon,$$

and

$$\begin{aligned} \int_{\mathbb{R}^3} |\phi_{n_k} - (\phi_{1,k} + \phi_{2,k})|^2 &\le \int_{\mathbb{R}^3} |1 - \xi_{R_1}(\cdot - y_k) - \chi_{R'_k}(\cdot - y_k)|^2 \phi_{n_k}^2 \\ &\le \int_{R_1 \le |\cdot - y_k| \le R_{2,k}} \phi_{n_k}^2 \le 2\epsilon. \end{aligned}$$

Similarly, by Hölder and Gagliardo-Nirenberg-Sobolev inequalities, we have for all k and $2 \le p < 6$

$$\|\phi_{n_k} - (\phi_{1,k} + \phi_{2,k})\|_{L^p} \le \|\phi_{n_k}\|_{L^p(y_k + (B_{R_{2,k}} \setminus \overline{B}_{R_1}))} \le C_p \epsilon^{\frac{(6-p)}{2p}}$$

where the constant C_p only depends on p and on the H^1 bound on $(\phi_n)_{n\in\mathbb{N}}$. Finally, we have $\|\nabla\xi_{R_1}\|_{L^\infty} \le 2R_1^{-1} \le 2\epsilon$ and $\|\nabla\chi_{R'_k}\|_{L^\infty} \le 2(R'_k)^{-1} \le 2\epsilon$, so that

$$\left| \int_{\mathbb{R}^3} |\nabla\phi_{1,k}|^2 - \xi_{R_1}^2(\cdot - y_k)|\nabla\phi_{n_k}|^2 \right| \le C\frac{\epsilon}{2}$$

and

$$\left| \int_{\mathbb{R}^3} |\nabla \phi_{2,k}|^2 - \chi^2_{R'_k}(\cdot - y_k) |\nabla \phi_{n_k}|^2 \right| \leq C\frac{\epsilon}{2}$$

where the constant C only depend on the H^1 bound on $(\phi_n)_{n\in\mathbb{N}}$. Thus

$$\begin{aligned} \int_{\mathbb{R}^3} |\nabla \phi_{n_k}|^2 - |\nabla \phi_{1,k}|^2 - |\nabla \phi_{2,k}|^2 &\geq \int_{\mathbb{R}^3} (1 - \xi^2_{R_1}(\cdot - y_k) - \chi^2_{R'_k}(\cdot - y_k)) |\nabla \phi_{n_k}|^2 - C\epsilon \\ &\geq -C\epsilon. \end{aligned}$$

□

Proof of the first two assertions of Lemma 9. Assume that there exists a sequence $(y_k)_{k\in\mathbb{N}}$ in $\mathbb{R}^3$, such that for all $\epsilon > 0$, there exists $R > 0$ such that

$$\forall k \in \mathbb{N}, \quad \int_{y_k + B_R} \phi^2_{n_k} \geq \lambda - \epsilon.$$

Two situations may be encountered: either $(y_k)_{k\in\mathbb{N}}$ has a converging subsequence, or $\lim_{k\to\infty} |y_k| = \infty$. In the latter case, we would have $\phi = 0$, and therefore

$$\lim_{k\to\infty} \int_{\mathbb{R}^3} \phi^2_{n_k} V = 0.$$

Hence

$$I^\infty_\lambda \leq \lim_{k\to\infty} E^\infty(\phi_{n_k}) = \lim_{k\to\infty} E(\phi_{n_k}) = I_\lambda,$$

which is in contradiction with the first assertion of Lemma (1). Therefore, $(y_k)_{k\in\mathbb{N}}$ has a converging subsequence. It is then easy to see, using the strong convergence of $(\phi_n)_{n\in\mathbb{N}}$ to ϕ in $L^2_{\rm loc}(\mathbb{R}^3)$, that

$$\int_{\mathbb{R}^3} \phi^2 \geq \int_{y+B_R} \phi^2 \geq \lambda - \epsilon,$$

where y is the limit of some converging subsequence of $(y_k)_{k\in\mathbb{N}}$. This implies that $\|\phi\|^2_{L^2} = \lambda$, hence that $(\phi_n)_{n\in\mathbb{N}}$ converges to ϕ strongly in $L^2(\mathbb{R}^3)$. As $(\phi_n)_{n\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$, this convergence holds strongly in $L^p(\mathbb{R}^3)$ for all $2 \leq p < 6$.

Assume now that $(\phi_{n_k})_{k\in\mathbb{N}}$ is vanishing. Then we would have $\phi = 0$, an eventuality that has already been excluded. □

Proof of the third assertion of Lemma 9. Replacing $(\phi_n)_{n\in\mathbb{N}}$ with a subsequence and using a diagonal extraction argument, we can assume that in addition to (54)-(61), there exists

- a sequence $(y_n)_{n\in\mathbb{N}}$ of points in $\mathbb{R}^3$,
- two increasing sequences of positive real numbers $(R_{1,n})_{n\in\mathbb{N}}$ and $(R_{2,n})_{n\in\mathbb{N}}$ such that

$$\lim_{n\to\infty} R_{1,n} = \infty \quad \text{and} \quad \lim_{n\to\infty} R_{2,n} - R_{1,n} = \infty$$

- two sequences $(\phi_{1,n})_{n\in\mathbb{N}}$ and $(\phi_{2,n})_{n\in\mathbb{N}}$ bounded in $H^1(\mathbb{R}^3)$

such that

$$\begin{cases} \phi_n = \phi_{1,n} \quad \text{on } y_n + B_{R_{1,n}} \\ \phi_n = \phi_{2,n} \quad \text{on } \mathbb{R}^3 \setminus (y_n + B_{R_{2,n}}) \\ \lim\limits_{n\to\infty} \int_{\mathbb{R}^3} \phi_{1,n}^2 = \delta, \quad \lim\limits_{n\to\infty} \int_{\mathbb{R}^3} \phi_{2,n}^2 = \lambda - \delta \\ \lim\limits_{n\to\infty} \|\phi_n - (\phi_{1,n} + \phi_{2,n})\|_{L^p(\mathbb{R}^3)} = 0 \quad \text{for all } 2 \le p < 6 \\ \lim\limits_{n\to\infty} \|\phi_n\|_{L^p(y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}}))} = 0 \quad \text{for all } \; 2 \le p < 6 \\ \lim\limits_{n\to\infty} \mathrm{dist}(\mathrm{Supp}\, \phi_{1,\mathrm{n}}, \mathrm{Supp}\, \phi_{2,\mathrm{n}}) = \infty \\ \liminf\limits_{n\to\infty} \int_{\mathbb{R}^3} \left(|\nabla \phi_n|^2 - |\nabla \phi_{1,n}|^2 - |\nabla \phi_{2,n}|^2 \right) \ge 0. \end{cases}$$

Besides, it follows from the construction of the functions $\phi_{1,n}$ and $\phi_{2,n}$ that

$$\forall n \in \mathbb{N}, \quad \phi_{1,n} \ge 0 \quad \text{and} \quad \phi_{2,n} \ge 0 \quad \text{a.e. on } \mathbb{R}^3. \tag{63}$$

A straightforward calculation leads to

$$\begin{aligned} E(\phi_n) \quad &= \quad E^\infty(\phi_{1,n}) + \int_{\mathbb{R}^3} \rho_{\phi_{1,n}} V + E^\infty(\phi_{2,n}) + \int_{\mathbb{R}^3} \rho_{\phi_{2,n}} V \\ &\quad + \int_{\mathbb{R}^3} \left(|\nabla \phi_n|^2 - |\nabla \phi_{1,n}|^2 - |\nabla \phi_{2,n}|^2 \right) + \int_{\mathbb{R}^3} \widetilde{\rho}_n V \\ &\quad + D(\rho_{\phi_{1,n}}, \rho_{\phi_{2,n}}) + D(\widetilde{\rho}_n, \rho_{\phi_{1,n}} + \rho_{\phi_{2,n}}) + \frac{1}{2} D(\widetilde{\rho}_n, \widetilde{\rho}_n) \\ &\quad + \int_{\mathbb{R}^3} (h(\rho_{\phi_n}, |\nabla \phi_n|^2) - h(\rho_{\phi_{1,n}}, |\nabla \phi_{1,n}|^2) - h(\rho_{\phi_{2,n}}, |\nabla \phi_{2,n}|^2)), \end{aligned} \tag{64}$$

where we have denoted by $\widetilde{\rho}_n = \rho_n - \rho_{\phi_{1,n}} - \rho_{\phi_{2,n}}$. As

$$|\widetilde{\rho}_n| \le 2 \chi_{y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}})} |\phi_n|^2,$$

the sequence $(\widetilde{\rho}_n)_{n\in\mathbb{N}}$ goes to zero in $L^p(\mathbb{R}^3)$ for all $1 \le p < 3$, yielding

$$\int_{\mathbb{R}^3} \widetilde{\rho}_n V + D(\widetilde{\rho}_n, \rho_{\phi_{1,n}} + \rho_{\phi_{2,n}}) + \frac{1}{2} D(\widetilde{\rho}_n, \widetilde{\rho}_n) \underset{n\to\infty}{\longrightarrow} 0.$$

Besides,

$$D(\rho_{\phi_{1,n}}, \rho_{\phi_{2,n}}) \le 4\, \mathrm{dist}(\mathrm{Supp}\, \phi_{1,\mathrm{n}}, \mathrm{Supp}\, \phi_{2,\mathrm{n}})^{-1} \, \|\phi_{1,n}\|_{L^2}^2 \, \|\phi_{2,n}\|_{L^2}^2 \underset{n\to\infty}{\longrightarrow} 0$$

and

$$\begin{aligned} &\left| \int_{\mathbb{R}^3} (h(\rho_{\phi_n}, |\nabla \phi_n|^2) - h(\rho_{\phi_{1,n}}, |\nabla \phi_{1,n}|^2) - h(\rho_{\phi_{2,n}}, |\nabla \phi_{2,n}|^2)) \right| \\ &\le \int_{y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}})} \left| h(\rho_{\phi_n}, |\nabla \phi_n|^2) \right| + \left| h(\rho_{\phi_{1,n}}, |\nabla \phi_{1,n}|^2) \right| + \left| h(\rho_{\phi_{2,n}}, |\nabla \phi_{2,n}|^2) \right| \\ &\le C \left(\|\rho_{\phi_n}\|_{L^{p_-}(y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}}))}^{p_-} + \|\rho_{\phi_n}\|_{L^{p_+}(y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}}))}^{p_+} \right) \underset{n\to\infty}{\longrightarrow} 0 \end{aligned}$$

(recall that $1 < p_\pm = 1 + \beta_\pm < \frac{5}{3}$). Lastly, as $\lim_{n\to\infty} \mathrm{dist}(\mathrm{Supp}\, \phi_{1,\mathrm{n}}, \mathrm{Supp}\, \phi_{2,\mathrm{n}}) = \infty$,

$$\min \left(\left| \int_{\mathbb{R}^3} \rho_{\phi_{1,n}} V \right|, \left| \int_{\mathbb{R}^3} \rho_{\phi_{2,n}} V \right| \right) \underset{n\to\infty}{\longrightarrow} 0.$$

It therefore follows from (64) and from the continuity of the functions $\lambda \mapsto J_\lambda$ and $\lambda \mapsto J_\lambda^\infty$ that at least one of the inequalities below holds true

$$J_\lambda \geq J_\delta + J_{\lambda-\delta}^\infty \quad \text{(case 1)} \quad \text{or} \quad J_\lambda \geq J_\delta^\infty + J_{\lambda-\delta} \quad \text{(case 2).} \tag{65}$$

As the opposite inequalities are always satisfied, we obtain

$$J_\lambda = J_\delta + J_{\lambda-\delta}^\infty \quad \text{(case 1)} \quad \text{or} \quad J_\lambda = J_\delta^\infty + J_{\lambda-\delta} \quad \text{(case 2)} \tag{66}$$

and that (still up to extraction)

$$\left\{ \begin{array}{l} \lim\limits_{n\to\infty} E(\phi_{1,n}) = J_\delta \\ \lim\limits_{n\to\infty} E^\infty(\phi_{2,n}) = J_{\lambda-\delta}^\infty \end{array} \right. \quad \text{(case 1)} \quad \text{or} \quad \left\{ \begin{array}{l} \lim\limits_{n\to\infty} E^\infty(\phi_{1,n}) = J_\delta^\infty \\ \lim\limits_{n\to\infty} E(\phi_{2,n}) = J_{\lambda-\delta} \end{array} \right. \quad \text{(case 2).} \tag{67}$$

Let us now prove that the sequence $(\psi_n)_{n\in\mathbb{N}}$, where $\psi_n = \phi_n - (\phi_{1,n} + \phi_{2,n})$, goes to zero in $H^1(\mathbb{R}^3)$. For convenience, we rewrite ψ_n as $\psi_n = e_n\phi_n$ where $e_n = 1 - \xi_{R_{1,n}}(\cdot - y_n) - \chi_{R_{2,n}/2}(\cdot - y_n)$ and Ekeland's condition (62) as

$$-\text{div } (a_n \nabla\phi_n) + V\phi_n + (\rho_{\phi_n} \star |\mathbf{r}|^{-1})\phi_n + V_n^- \phi_n^{1+2\beta_-} + V_n^+ \phi_n^{1+2\beta_+} + \theta_n\phi_n = \eta_n \tag{68}$$

where

$$\left\{ \begin{array}{l} a_n = \dfrac{1}{2}\left(1 + \dfrac{\partial h}{\partial \kappa}(\rho_{\phi_n}, |\nabla\phi_n|^2)\right) \\ V_n^- = 2^{\beta_-}\rho_{\phi_n}^{-\beta_-}\dfrac{\partial h}{\partial \rho}(\rho_{\phi_n}, |\nabla\phi_n|^2)\chi_{\rho_{\phi_n}\leq 1} \\ V_n^+ = 2^{\beta_+}\rho_{\phi_n}^{-\beta_+}\dfrac{\partial h}{\partial \rho}(\rho_{\phi_n}, |\nabla\phi_n|^2)\chi_{\rho_{\phi_n}> 1}. \end{array} \right.$$

The sequence $(V\phi_n + (\rho_{\phi_n} \star |\mathbf{r}|^{-1})\phi_n + V_n^-\phi_n^{1+2\beta_-} + V_n^+\phi_n^{1+2\beta_+} + \theta_n\phi_n)_{n\in\mathbb{N}}$ is bounded in $L^2(\mathbb{R}^3)$, $(\eta_n)_{n\in\mathbb{N}}$ goes to zero in $H^{-1}(\mathbb{R}^3)$, and the sequence $(\psi_n)_{n\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$ and goes to zero in $L^2(\mathbb{R}^3)$. We therefore infer from (68) that

$$\int_{\mathbb{R}^3} a_n\nabla\phi_n \cdot \nabla\psi_n \underset{n\to\infty}{\longrightarrow} 0.$$

Besides $\nabla\psi_n = e_n\nabla\phi_n + \phi_n\nabla e_n$ with $0 \leq e_n \leq 1$ and $\|\nabla e_n\|_{L^\infty} \to 0$. Thus

$$\int_{\mathbb{R}^3} a_n e_n |\nabla\phi_n|^2 \underset{n\to\infty}{\longrightarrow} 0.$$

As

$$0 < \frac{a}{2} \leq a_n = \frac{1}{2}\left(1 + \frac{\partial h}{\partial \kappa}(\rho_{\phi_n}, |\nabla\phi_n|^2)\right) \leq \frac{b}{2} < \infty \quad \text{a.e. on } \mathbb{R}^3 \tag{69}$$

and $0 \leq e_n^2 \leq e_n \leq 1$, we finally obtain

$$\int_{\mathbb{R}^3} e_n^2 |\nabla\phi_n|^2 \underset{n\to\infty}{\longrightarrow} 0,$$

from which we conclude that $(\nabla\psi_n)_{n\in\mathbb{N}}$ goes to zero in $H^1(\mathbb{R}^3)$. Plugging this information in (68) and using the fact that the supports of $\phi_{1,n}$ and $\phi_{2,n}$ are disjoint and go far apart when n goes to infinity, we obtain

$$-\text{div } (a_n \nabla\phi_{1,n}) + V\phi_{1,n} + (\rho_{\phi_{1,n}} \star |\mathbf{r}|^{-1})\phi_{1,n} + V_n^- \phi_{1,n}^{1+2\beta_-} + V_n^+ \phi_{1,n}^{1+2\beta_+} + \theta_n\phi_{1,n} \xrightarrow[n\to\infty]{H^{-1}} 0$$

$$-\text{div } (a_n \nabla\phi_{2,n}) + V\phi_{2,n} + (\rho_{\phi_{2,n}} \star |\mathbf{r}|^{-1})\phi_{2,n} + V_n^- \phi_{2,n}^{1+2\beta_-} + V_n^+ \phi_{2,n}^{1+2\beta_+} + \theta_n\phi_{2,n} \xrightarrow[n\to\infty]{H^{-1}} 0.$$

We can now assume that the sequences $(\phi_{1,n})_{n\in\mathbb{N}}$ and $(\phi_{2,n})_{n\in\mathbb{N}}$, which are bounded in $H^1(\mathbb{R}^3)$, respectively converge to u_1 and u_2 weakly in $H^1(\mathbb{R}^3)$, strongly in $L^p_{\rm loc}(\mathbb{R}^3)$ for all $2 \le p < 6$ and a.e. in $\mathbb{R}^3$. In virtue of (63), we also have $u_1 \ge 0$ and $u_2 \ge 0$ a.e. on $\mathbb{R}^3$. To pass to the limit in the above equations, we use a H-convergence result proved in Appendix (Lemma 10). The sequence $(a_n)_{n\in\mathbb{N}}$ satisfying (69), there exists $a_\infty \in L^\infty(\mathbb{R}^3)$ such that $\frac{a}{2} \le a_\infty \le \frac{b^2}{2a}$ and (up to extraction) $a_n I_3 \rightharpoonup_H a_\infty I_3$ (where I_3 is the rank-3 identity matrix). Besides, the sequence $(V_n^\pm)_{n\in\mathbb{N}}$ is bounded in $L^\infty(\mathbb{R}^3)$, so that there exists $V^\pm \in L^\infty(\mathbb{R}^3)$, such that (up to extraction) $(V_n^\pm)_{n\in\mathbb{N}}$ converges to $V^\pm$ for the weak-$*$ topology of $L^\infty(\mathbb{R}^3)$. Hence for $j = 1, 2$ (and up to extraction)

$$\left\{\begin{array}{l} V\phi_{j,n} \underset{n\to\infty}{\longrightarrow} Vu_j \quad \text{strongly in } H^{-1}(\mathbb{R}^3) \\ V_n^\pm \phi_{j,n}^{1+2\beta_\pm} \underset{n\to\infty}{\rightharpoonup} V^\pm u_j^{1+2\beta_\pm} \quad \text{weakly in } L^2_{\rm loc}(\mathbb{R}^3) \\ (\rho_{\phi_{j,n}} \star |\mathbf{r}|^{-1})\phi_{j,n} + \theta_n \phi_{j,n} \underset{n\to\infty}{\rightharpoonup} (\rho_{u_j} \star |\mathbf{r}|^{-1})u_j + \theta u_j \quad \text{stronly in } L^2_{\rm loc}(\mathbb{R}^3). \end{array}\right.$$

We end up with

$$-\mathrm{div}\,(a_\infty \nabla u_1) + Vu_1 + (\rho_{u_1} \star |\mathbf{r}|^{-1})u_1 + V^- u_1^{1+2\beta_-} + V^+ u_1^{1+2\beta_+} + \theta u_1 = 0 \quad (70)$$
$$-\mathrm{div}\,(a_\infty \nabla u_2) + Vu_2 + (\rho_{u_2} \star |\mathbf{r}|^{-1})u_2 + V^- u_2^{1+2\beta_-} + V^+ u_2^{1+2\beta_+} + \theta u_2 = 0. \quad (71)$$

By classical elliptic regularity arguments [9] (see also the proof of Lemma 12 below), both u_1 and u_2 are in $C^{0,\alpha}(\mathbb{R}^3)$ for some $0 < \alpha < 1$ and vanish at infinity. Besides, exactly one of the two functions u_1 and u_2 is different from zero. Indeed, if both u_1 and u_2 were equal to zero, then we would have $\phi = 0$, hence

$$J_\lambda = \lim_{n\to\infty} E(\phi_n) = \lim_{n\to\infty} E^\infty(\phi_n) = J_\lambda^\infty,$$

which is in contradiction with the first assertion of Lemma 1 (recall that $J_\lambda = I_\lambda$ and $J_\lambda^\infty = I_\lambda^\infty$ for all $0 \le \lambda \le 1$). On the other hand, as $\mathrm{dist}(\mathrm{Supp}\,\phi_{1,\rm n}, \mathrm{Supp}\,\phi_{2,\rm n}) \to \infty$, at least one of the functions u_1 and u_2 is equal to zero.

We only consider here the case when $u_2 = 0$, corresponding to case 1 in (65)-(67), since the other case can be dealt with the same arguments. A key point of the proof consists in noticing that apply Lemma 11 (proved in Appendix) to (70) (note that $W = V^- u_1^{\beta_-} + V^+ u_1^{\beta_+}$ is nonpositive and goes to zero at infinity) yields

$$\theta > 0. \quad (72)$$

Consider now the sequence $(\widetilde{\phi}_{1,n})_{n\in\mathbb{N}}$ defined by $\widetilde{\phi}_{1,n} = \delta^{\frac{1}{2}} \phi_{1,n} \|\phi_{1,n}\|_{L^2}^{-1}$. It is easy to check that

$$\left\{\begin{array}{l} \forall n \in \mathbb{N}, \quad \widetilde{\phi}_{1,n} \in H^1(\mathbb{R}^3), \quad \displaystyle\int_{\mathbb{R}^3} \widetilde{\phi}_{1,n}^2 = \delta \quad \text{and} \quad \widetilde{\phi}_{1,n} \ge 0 \text{ a.e. on } \mathbb{R}^3 \\ \displaystyle\lim_{n\to+\infty} E(\widetilde{\phi}_{1,n}) = J_\delta \\ -\mathrm{div}\,(a_{1,n} \nabla \widetilde{\phi}_{1,n}) + V\widetilde{\phi}_{1,n} + (\rho_{\widetilde{\phi}_{1,n}} \star |\mathbf{r}|^{-1})\widetilde{\phi}_{1,n} + V_{1,n}^- \widetilde{\phi}_{1,n}^{1+2\beta_-} + V_{1,n}^+ \widetilde{\phi}_{1,n}^{1+2\beta_+} + \theta_n \widetilde{\phi}_{1,n} \underset{n\to\infty}{\overset{H^{-1}}{\longrightarrow}} 0 \\ (\widetilde{\phi}_{1,n})_{n\in\mathbb{N}} \text{ converges to } \widetilde{v}_1 \ne 0 \text{ weakly in } H^1, \text{ strongly in } L^p_{\rm loc} \text{ for } 2 \le p < 6 \text{ and a.e. on } \mathbb{R}^3 \end{array}\right.$$

(with in fact $v_1 = \phi$). Likewise, the sequence $((\lambda-\delta)^{\frac{1}{2}} \|\phi_{2,n}\|_{L^2}^{-1} \phi_{2,n})_{n\in\mathbb{N}}$ being a minimizing sequence for $J_{\lambda-\delta}^\infty$, it cannot vanish. Therefore, there exists $\gamma > 0$, $R > 0$ and a sequence $(x_n)_{n\in\mathbb{N}}$ of points of $\mathbb{R}^3$ such that $\int_{x_n+B_R} |\phi_{2,n}|^2 \ge \gamma$. Then, denoting by $\widetilde{\phi}_{2,n} = (\lambda -$

$\delta)^{\frac{1}{2}} \|\phi_{2,n}\|_{L^2}^{-1} \phi_{2,n}(\cdot - x_n)$,

$$\left\{ \begin{array}{l} \forall n \in \mathbb{N}, \quad \widetilde{\phi}_{2,n} \in H^1(\mathbb{R}^3), \quad \displaystyle\int_{\mathbb{R}^3} \widetilde{\phi}_{2,n}^2 = \lambda - \delta \quad \text{and} \quad \widetilde{\phi}_{2,n} \geq 0 \text{ a.e. on } \mathbb{R}^3 \\ \displaystyle\lim_{n \to +\infty} E^\infty(\widetilde{\phi}_{2,n}) = J^\infty_{\lambda-\delta} \\ -\text{div}\,(a_{2,n} \nabla \widetilde{\phi}_{2,n}) + (\rho_{\widetilde{\phi}_{2,n}} \star |\mathbf{r}|^{-1})\widetilde{\phi}_{2,n} + V_{2,n}^- \widetilde{\phi}_{2,n}^{1+2\beta_-} + V_{2,n}^+ \widetilde{\phi}_{2,n}^{1+2\beta_+} + \theta_n \widetilde{\phi}_{2,n} \underset{n \to \infty}{\overset{H^{-1}}{\longrightarrow}} 0 \\ (\widetilde{\phi}_{2,n})_{n \in \mathbb{N}} \text{ converges to } v_2 \neq 0 \text{ weakly in } H^1, \text{ strongly in } L^p_{\text{loc}} \text{ for } 2 \leq p < 6 \text{ and a.e. on } \mathbb{R}^3. \end{array} \right.$$

It is important to note that the sequence $(a_{j,n})_{n \in \mathbb{N}}$ and $(V_{j,n}^\pm)_{n \in \mathbb{N}}$ are such that

$$\frac{a}{2} \leq a_{j,n} \leq \frac{b}{2} \quad \text{and} \quad \|V_{j,n}^\pm\|_{L^\infty} \leq 2^{\beta_+} C,$$

where the constants a, b and C are those arising in (31) and (33).

We can now apply the concentration-compactness lemma to $(\widetilde{\phi}_{1,n})_{n \in \mathbb{N}}$ and to $(\widetilde{\phi}_{2,n})_{n \in \mathbb{N}}$. As $(\widetilde{\phi}_{j,n})_{n \in \mathbb{N}}$ does not vanish, either it is compact or it splits into subsequences that are either compact or split, and so on. The next step consists in showing that this process necessarily terminates after a finite number of iterations. By contradiction, assume that it is not the case. We could then construct by repeated applications of the concentration-compactness lemma (see [1] for details) an infinity of sequences $(\widetilde{\psi}_{k,n})_{n \in \mathbb{N}}$, such that for all $k \in \mathbb{N}$

$$\left\{ \begin{array}{l} \forall n \in \mathbb{N}, \quad \widetilde{\psi}_{k,n} \in H^1(\mathbb{R}^3), \quad \displaystyle\int_{\mathbb{R}^3} \widetilde{\psi}_{k,n}^2 = \delta_k \quad \text{and} \quad \widetilde{\psi}_{k,n} \geq 0 \text{ a.e. on } \mathbb{R}^3 \\ -\text{div}\,(\widetilde{a}_{k,n} \nabla \widetilde{\psi}_{k,n}) + (\rho_{\widetilde{\psi}_{k,n}} \star |\mathbf{r}|^{-1})\widetilde{\psi}_{k,n} + \widetilde{V}_{k,n}^- \widetilde{\psi}_{k,n}^{1+2\beta_-} + \widetilde{V}_{k,n}^+ \widetilde{\psi}_{k,n}^{1+2\beta_+} + \theta_n \widetilde{\psi}_{k,n} \underset{n \to \infty}{\overset{H^{-1}}{\longrightarrow}} 0 \\ (\widetilde{\psi}_{k,n})_{n \in \mathbb{N}} \text{ converges to } w_k \neq 0 \text{ weakly in } H^1, \text{ strongly in } L^p_{\text{loc}} \text{ for } 2 \leq p < 6 \text{ and a.e. on } \mathbb{R}^3, \end{array} \right.$$

with

$$\sum_{k \in \mathbb{N}} \delta_k \leq \lambda, \tag{73}$$

and with for all $k \in \mathbb{N}$,

$$\frac{a}{2} \leq \widetilde{a}_{k,n} \leq \frac{b}{2} \quad \text{and} \quad \|\widetilde{V}_{k,n}^\pm\|_{L^\infty} \leq 2^{\beta_+} C.$$

Using Lemma 10 to pass to the limit with respect to n in the equation satisfied by $\widetilde{\psi}_{k,n}$, we obtain

$$-\text{div}\,(\widetilde{a}_k \nabla w_k) + (\rho_{w_k} \star |\mathbf{r}|^{-1}) w_k + \widetilde{V}_k^- w_k^{1+2\beta_-} + \widetilde{V}_k^+ w_k^{1+2\beta_+} + \theta w_k = 0, \tag{74}$$

with

$$\frac{a}{2} \leq \widetilde{a}_k \leq \frac{b^2}{2a} \quad \text{and} \quad \|\widetilde{V}_k^\pm\|_{L^\infty} \leq 2^{\beta_+} C.$$

Besides, we infer from (73) that $\displaystyle\sum_{k \in \mathbb{N}} \|w_k\|_{L^2}^2 \leq \lambda$, hence that

$$\lim_{k \to \infty} \|w_k\|_{L^2} = 0.$$

It then easily follows from (74) that

$$\lim_{k \to \infty} \|\text{div}\,(a_k \nabla w_k)\|_{L^2} = 0.$$

We can now make use of the elliptic regularity result [9] (see also the proof of Lemma 12) stating that there exists a constant C, depending only on the positive constants a and b, such that for all $u \in H^1(\mathbb{R}^3)$ such that $\mathrm{div}\,(\widetilde{a}_k \nabla u) \in L^2(\mathbb{R}^3)$, $u \in L^\infty(\mathbb{R}^3)$ and

$$\|u\|_{L^\infty} \leq C\left(\|u\|_{L^2} + \|\mathrm{div}\,(\widetilde{a}_k \nabla u)\|_{L^2}\right)$$

and obtain

$$\lim_{k\to\infty} \|w_k\|_{L^\infty} = 0.$$

Lastly, we deduce from (74) that

$$\theta \|w_k\|_{L^2}^2 \leq C\left(\|w_k\|_{L^\infty}^{2\beta_-} + \|w_k\|_{L^\infty}^{2\beta_+}\right)\|w_k\|_{L^2}^2.$$

As $\|w_k\|_{L^2} > 0$ for all $k \in \mathbb{N}$, we obtain that

$$\theta \leq C\left(\|w_k\|_{L^\infty}^{2\beta_-} + \|w_k\|_{L^\infty}^{2\beta_+}\right) \underset{k\to\infty}{\longrightarrow} 0,$$

which obviously contradicts (72). We therefore conclude from this analysis that, if dichotomy occurs, $(\phi_n)_{n\in\mathbb{N}}$ splits in a finite number of compact bits. We are now going to prove that this cannot be.

If this was the case, there would exist $\delta_1 > 0$ and $\delta_2 > 0$ such that $0 < \delta_1 + \delta_2 \leq \lambda$ and two sequences $(u_{1,n})_{n\in\mathbb{N}}$ and $(u_{2,n})_{n\in\mathbb{N}}$ such that

$$\begin{cases} \forall n \in \mathbb{N}, \quad u_{1,n} \in H^1(\mathbb{R}^3), \quad \displaystyle\int_{\mathbb{R}^3} |u_{1,n}|^2 = \delta_1, \quad u_1 \geq 0 \text{ a.e. on } \mathbb{R}^3 \\ \displaystyle\lim_{n\to\infty} E(u_{1,n}) = I_{\delta_1} \\ -\mathrm{div}\,(\alpha_{1,n}\nabla u_{1,n}) + V u_{1,n} + (\rho_{u_{1,n}} \star |\mathbf{r}|^{-1})u_{1,n} + v_{1,n}^- u_{1,n}^{1+2\beta_-} + v_{1,n}^+ u_{1,n}^{1+2\beta_+} + \theta_n u_{1,n} \underset{n\to\infty}{\overset{H^{-1}}{\longrightarrow}} 0 \end{cases}$$

and

$$\begin{cases} \forall n \in \mathbb{N}, \quad u_{2,n} \in H^1(\mathbb{R}^3), \quad \displaystyle\int_{\mathbb{R}^3} |u_{2,n}|^2 = \delta_2, \quad u_2 \geq 0 \text{ a.e. on } \mathbb{R}^3 \\ \displaystyle\lim_{n\to\infty} E^\infty(u_{2,n}) = I_{\delta_2} \\ -\mathrm{div}\,(\alpha_{2,n}\nabla u_{2,n}) + (\rho_{u_{2,n}} \star |\mathbf{r}|^{-1})u_{2,n} + v_{2,n}^- u_{2,n}^{1+2\beta_-} + v_{2,n}^+ u_{2,n}^{1+2\beta_+} + \theta_n u_{2,n} \underset{n\to\infty}{\overset{H^{-1}}{\longrightarrow}} 0 \end{cases}$$

and converging weakly in $H^1(\mathbb{R}^3)$ to u_1 and u_2 respectively, with $\|u_1\|_{L^2} = \delta_1$ and $\|u_2\|_{L^2} = \delta_2$ (as the weak limit of $(\phi_n)_{n\in\mathbb{N}}$ in $L^2(\mathbb{R}^3)$ is nonzero, one bit stays at finite distance from the nuclei). It then follows from Lemma 7 that u_1 and u_2 are minimizers for J_{δ_1} and $J_{\delta_2}^\infty$ respectively:

$$E(u_1) = J_{\delta_1}, \quad \|u_1\|_{L^2}^2 = \delta_1, \quad E(u_2) = J_{\delta_2}^\infty, \quad \|u_2\|_{L^2}^2 = \delta_2.$$

Letting n go to infinity in the equations satisfied by $u_{1,n}$ and $u_{2,n}$ we also have

$$-\mathrm{div}\,(\alpha_1 \nabla u_1) + V u_1 + (\rho_{u_1} \star |\mathbf{r}|^{-1})u_1 + v_1^- u_1^{1+2\beta_-} + v_1^+ u_1^{1+2\beta_+} + \theta u_1 = 0 \qquad (75)$$

and

$$-\mathrm{div}\,(\alpha_2 \nabla u_2) + (\rho_{u_2} \star |\mathbf{r}|^{-1})u_2 + v_2^- u_2^{1+2\beta_-} + v_2^+ u_2^{1+2\beta_+} + \theta u_2 = 0, \qquad (76)$$

with $\frac{a}{2} \leq \alpha_j \leq \frac{b^2}{2a}$ and $\|v_j^\pm\|_{L^\infty} \leq 2^{\beta_+} C$. This shows in particular that u_1 and u_2 are in $L^\infty(\mathbb{R}^3)$. Applying Lemma 12, we then obtain that there exists $\gamma > 0$, $f_1 \in H^1(\mathbb{R}^3)$, $f_2 \in H^1(\mathbb{R}^3)$, $g_1 \in (L^2(\mathbb{R}^3))^3$ and $g_2 \in (L^2(\mathbb{R}^3))^3$ such that

$$u_1 = e^{-\gamma|\cdot|} f_1, \quad u_2 = e^{-\gamma|\cdot|} f_2, \quad \nabla u_1 = e^{-\gamma|\cdot|} g_1, \quad \nabla u_2 = e^{-\gamma|\cdot|} g_2. \qquad (77)$$

In addition, as $u_1 \geq 0$ and $u_2 \geq 0$, we also have $f_1 \geq 0$ and $f_2 \geq 0$. Let $\mathbf{e}$ be a given unit vector of $\mathbb{R}^3$. For $t > 0$, we set

$$w_t(\mathbf{r}) = \alpha_t \left(u_1(\mathbf{r}) + u_2(\mathbf{r} - t\mathbf{e})\right) \quad \text{where} \quad \alpha_t = (\delta_1 + \delta_2)^{\frac{1}{2}} \, \|u_1 + u_2(\cdot - t\mathbf{e})\|_{L^2}^{-1}.$$

Obviously, $w_t \in H^1(\mathbb{R}^3)$ and $\|w_t\|_{L^2} = \delta_1 + \delta_2$, so that

$$E(w_t) \geq J_{\delta_1+\delta_2}. \tag{78}$$

Besides,

$$\begin{aligned} \|u_1 + u_2(\cdot - t\mathbf{e})\|_{L^2}^2 &= \int_{\mathbb{R}^3} u_1^2 + \int_{\mathbb{R}^3} u_2^2 + 2\int_{\mathbb{R}^3} f_1(\mathbf{r})\, f_2(\mathbf{r} - t\mathbf{e})\, e^{-\gamma(|\mathbf{r}|+|\mathbf{r}-t\mathbf{e}|)}\, d\mathbf{r} \\ &= \delta_1 + \delta_2 + 2\int_{\mathbb{R}^3} f_1(\mathbf{r})\, f_2(\mathbf{r} - t\mathbf{e})\, e^{-\gamma(|\mathbf{r}|+|\mathbf{r}-t\mathbf{e}|)}\, d\mathbf{r} \\ &= \delta_1 + \delta_2 + O(e^{-\gamma t}), \end{aligned}$$

yielding

$$\alpha_t = 1 + O(e^{-\gamma t}).$$

Likewise, we have

$$\int_{\mathbb{R}^3} |\nabla w_t|^2 = \int_{\mathbb{R}^3} |\nabla u_1|^2 + \int_{\mathbb{R}^3} |\nabla u_2|^2 + O(e^{-\gamma t}) \tag{79}$$

$$\int_{\mathbb{R}^3} V|w_t|^2 = \int_{\mathbb{R}^3} V|u_1|^2 + \int_{\mathbb{R}^3} V|u_2(\cdot - t\mathbf{e})|^2 + O(e^{-\gamma t}) \tag{80}$$

$$D(\rho_{w_t}, \rho_{w_t}) = D(\rho_{u_1}, \rho_{u_1}) + D(\rho_{u_2}, \rho_{u_2}) + 2D(\rho_{u_1}, \rho_{u_2(\cdot - t\mathbf{e})}) + O(e^{-\gamma t}). \tag{81}$$

The exchange-correlation term can then be dealt with as follows. Denoting by

$$r_t = \rho_{w_t} - \rho_{u_1} - \rho_{u_2(\cdot - t\mathbf{e})} = 2(\alpha_t^2 - 1)(|u_1|^2 + |u_2(\cdot - t\mathbf{e})|^2) + 4\alpha_t^2 u_1 u_2(\cdot - t\mathbf{e})$$

and

$$s_t = |\nabla w_t|^2 - |\nabla u_1|^2 - |\nabla u_2(\cdot - t\mathbf{e})|^2 = (\alpha_t^2 - 1)(|\nabla u_1|^2 + |\nabla u_2(\cdot - t\mathbf{e})|^2) + 2\alpha_t^2 \nabla u_1 \cdot \nabla u_2(\cdot - t\mathbf{e}),$$

and using (31), (33), (77) and the fact that u_1 and u_2 are bounded in $L^\infty(\mathbb{R}^3)$, we obtain

$$\begin{aligned} &\left| \int_{\mathbb{R}^3} h(\rho_{w_t}, |\nabla w_t|^2) - h(\rho_{u_1}, |\nabla u_1|^2) - h(\rho_{u_2(\cdot - t\mathbf{e})}, |\nabla u_2(\cdot - t\mathbf{e})|^2) \right| \\ \leq\ & \int_{B_{\frac{t}{2}}} \left| h(\rho_{u_1} + \rho_{u_2(\cdot - t\mathbf{e})} + r_t, |\nabla u_1|^2 + |\nabla u_2(\cdot - t\mathbf{e})|^2 + s_t) - h(\rho_{u_1}, |\nabla u_1|^2) \right| \\ +\ & \int_{t\mathbf{e} + B_{\frac{t}{2}}} \left| h(\rho_{u_2(\cdot - t\mathbf{e})} + \rho_{u_1} + r_t, |\nabla u_2(\cdot - t\mathbf{e})|^2 + |\nabla u_1|^2 + s_t) - h(\rho_{u_2(\cdot - t\mathbf{e})}, |\nabla u_2(\cdot - t\mathbf{e})|^2) \right| \\ +\ & \int_{B_{\frac{t}{2}}} \left| h(\rho_{u_2(\cdot - t\mathbf{e})}, |\nabla u_2(\cdot - t\mathbf{e})|^2) \right| + \int_{t\mathbf{e} + B_{\frac{t}{2}}} \left| h(\rho_{u_1}, |\nabla u_1|^2) \right| \\ +\ & \int_{\mathbb{R}^3 \setminus \left(B_{\frac{t}{2}} \cup (t\mathbf{e} + B_{\frac{t}{2}}) \right)} |h(\rho_{w_t}, |\nabla w_t|^2)| + h(\rho_{u_1}, |\nabla u_1|^2)| + |h(\rho_{u_2(\cdot - t\mathbf{e})}, |\nabla u_2(\cdot - t\mathbf{e})|^2)| = O(e^{-\gamma t}). \end{aligned}$$

Combining (79)-(81) together with the above inequality, we obtain

$$E(w_t) \leq J_{\delta_1} + J_{\delta_2}^{\infty} + \int_{\mathbb{R}^3} V|u_2(\cdot - t\mathbf{e})|^2 + D(\rho_{u_1}, \rho_{u_2(\cdot - t\mathbf{e})}) + O(e^{-\gamma t}).$$

Next, using (77), we get

$$\begin{aligned}\int_{\mathbb{R}^3} V\rho_{u_2(\cdot-t\mathbf{e})} + D(\rho_{u_1}, \rho_{u_2(\cdot-t\mathbf{e})}) &= -Zt^{-1}\int_{\mathbb{R}^3}\rho_{u_2} + t^{-1}\int_{\mathbb{R}^3}\rho_{u_1}\int_{\mathbb{R}^3}\rho_{u_2} + o(t^{-1}) \\ &= -2\delta_2(Z-2\delta_1)t^{-1} + o(t^{-1}).\end{aligned}$$

Finally,

$$E(w_t) \le J_{\delta_1} + J^{\infty}_{\delta_2} - 2\delta_2(Z-2\delta_1)t^{-1} + o(t^{-1}) \le J_{\delta_1+\delta_2} - 2\delta_2(Z-2\delta_1)t^{-1} + o(t^{-1}) < J_{\delta_1+\delta_2}$$

for t large enough, which contradicts (78). □

End of the proof of Lemma 9. As a consequence of the concentration-compactness lemma and of the first three assertions of Lemma 9, the sequence $(\phi_n)_{n\in\mathbb{N}}$ converges to ϕ weakly in $H^1(\mathbb{R}^3)$ and strongly in $L^p(\mathbb{R}^3)$ for all $2 \le p < 6$. In particular,

$$\int_{\mathbb{R}^3}\phi^2 = \lim_{n\to\infty}\int_{\mathbb{R}^3}\phi_n^2 = \lambda.$$

It follows from Lemma 7 that ϕ is a minimizer to (52). □

Appendix

In this appendix, we prove three technical lemmas, which we make use of in the proof of Theorem 2. These lemmas are concerned with second-order elliptic operators of the form $-\mathrm{div}\,(A\nabla\cdot)$. For the sake of generality, we deal with the case when A is a matrix-valued function, although A is a real-valued function in the two-electron GGA model.

For Ω an open subset of $\mathbb{R}^3$ and $0 < \lambda \le \Lambda < \infty$, we denote by $M(\lambda,\Lambda,\Omega)$ the closed convex subset of $L^\infty(\Omega,\mathbb{R}^{3\times 3})$ consisting of the matrix fields $A \in L^\infty(\Omega,\mathbb{R}^{3\times 3})$ such that for all $\xi \in \mathbb{R}^3$ and almost all $x \in \Omega$,

$$\lambda|\xi|^2 \le A(x)\xi\cdot\xi \quad \text{and} \quad |A(x)\xi| \le \Lambda|\xi|.$$

We also introduce the set $M^s(\lambda,\Lambda,\Omega)$ of the matrix fields $A \in M(\lambda,\Lambda,\Omega)$ such that $A(x)$ is symmetric for almost all $x \in \Omega$. Obviously, $M^s(\lambda,\Lambda,\Omega)$ also is a closed convex subset of $L^\infty(\Omega,\mathbb{R}^{3\times 3})$.

The first lemma is a H-convergence result, in the same line as those proved in the original article by Murat and Tartar [19], which allows to pass to the limit in the Ekeland condition (62). Recall that a sequence $(A_n)_{n\in\mathbb{N}}$ of elements of $M(\lambda,\Lambda,\Omega)$ is said to H-converge to some $A \in M(\lambda',\Lambda',\Omega)$, which is denoted by $A_n \rightharpoonup_{\mathrm{H}} A$, if for every $\omega \subset\subset \Omega$ the following property holds : $\forall f \in H^{-1}(\omega)$, the sequence $(u_n)_{n\in\mathbb{N}}$ of the elements of $H^1_0(\omega)$ such that

$$-\mathrm{div}(A_n\nabla u_n) = f|_\omega \quad \text{in } H^{-1}(\omega)$$

satisfies

$$\begin{cases} u_n \rightharpoonup u \ \text{ weakly in } H^1_0(\omega) \\ A_n\nabla u_n \rightharpoonup A\nabla u \ \text{ weakly in } L^2(\omega)\end{cases}$$

where u is the solution in $H^1_0(\omega)$ to $-\mathrm{div}(A\nabla u) = f|_\omega$. It is known [19] that from any bounded sequence $(A_n)_{n\in\mathbb{N}}$ in $M(\lambda,\Lambda,\Omega)$ (resp. in $M(\lambda,\Lambda,\Omega)$) one can extract a subsequence which H-converges to some $A \in M(\lambda,\lambda^{-1}\Lambda^2,\Omega)$ (resp. to some $A \in M^s(\lambda,\lambda^{-1}\Lambda^2,\Omega)$).

Lemma 10. *Let Ω be an open subset of $\mathbb{R}^3$, $0 < \lambda \le \Lambda < \infty$, $0 < \lambda' \le \Lambda' < \infty$, and $(A_n)_{n\in\mathbb{N}}$ a sequence of elements of $M(\lambda,\Lambda,\Omega)$ which H-converges to some $A \in M(\lambda',\Lambda',\Omega)$. Let $(u_n)_{n\in\mathbb{N}}$, $(f_n)_{n\in\mathbb{N}}$ and $(g_n)_{n\in\mathbb{N}}$ be sequences of elements of $H^1(\Omega)$, $H^{-1}(\Omega)$ and $L^2(\Omega)$ respectively, and $u \in H^1(\Omega)$, $f \in H^{-1}(\Omega)$ and $g \in L^2(\Omega)$ such that*

$$\begin{cases} -\operatorname{div}(A_n\nabla u_n) = f_n + g_n \quad \text{in } H^{-1}(\Omega) \text{ for all } n \in \mathbb{N} \\ u_n \rightharpoonup u \text{ weakly in } H^1(\Omega) \\ f_n \to f \text{ strongly in } H^{-1}(\Omega) \\ g_n \rightharpoonup g \text{ weakly in } L^2(\Omega). \end{cases}$$

Then $-\mathrm{div}\,(A\nabla u) = f + g$ and $A_n\nabla u_n \rightharpoonup A\nabla u$ weakly in $L^2(\Omega)$.

The second lemma is an extension of [17, Lemma II.1] and of a classical result on the ground state of Schrödinger operators [26]. Recall that

$$L^2(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3) \;=\; \Big\{\mathcal{W}\,|\,\forall\epsilon>0,\ \exists(\mathcal{W}_2,\mathcal{W}_\infty) \in L^2(\mathbb{R}^3)\times L^\infty(\mathbb{R}^3) \text{ s.t.} \\ \|\mathcal{W}_\infty\|_{L^\infty} \le \epsilon,\ \mathcal{W} = \mathcal{W}_2 + \mathcal{W}_\infty\Big\}.$$

Lemma 11. *Let $0 < \lambda \le \Lambda < \infty$, $A \in M^s(\lambda,\Lambda,\mathbb{R}^3)$, $W \in L^2(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$ such that $W_+ = \max(0,W) \in L^2(\mathbb{R}^3) + L^3(\mathbb{R}^3)$ and μ a positive Radon measure on $\mathbb{R}^3$ such that $\mu(\mathbb{R}^3) < Z = \sum_{k=1}^M z_k$. Then,*

$$H = -\mathrm{div}\,(A\nabla\cdot) + V + \mu \star |\mathbf{r}|^{-1} + W$$

defines a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain

$$D(H) = \left\{u \in H^1(\mathbb{R}^3)\,|\,\mathrm{div}\,(A\nabla u) \in L^2(\mathbb{R}^3)\right\}.$$

Besides, $D(H)$ is dense in $H^1(\mathbb{R}^3)$ and included in $L^\infty(\mathbb{R}^3) \cap C^{0,\alpha}(\mathbb{R}^3)$ for some $\alpha > 0$, and any function of $D(H)$ vanishes at infinity. In addition,

1. *H is bounded from below, $\sigma_{\rm ess}(H) \subset [0,\infty)$ and H has an infinite number of negative eigenvalues;*
2. *the lowest eigenvalue μ_1 of H is simple and there exists an eigenvector $u_1 \in D(H)$ of H associated with μ_1 such that $u_1 > 0$ on $\mathbb{R}^3$;*
3. *if $w \in D(H)$ is an eigenvector of H such that $w \ge 0$ on $\mathbb{R}^3$, then there exists $\alpha > 0$ such that $w = \alpha u_1$.*

The third lemma is used to prove that the ground state density of the GGA Kohn-Sham model exhibits exponential decay at infinity (at least for the two electron model considered in this article).

Lemma 12. *Let $0 < \lambda \le \Lambda < \infty$, $A \in M(\lambda,\Lambda,\mathbb{R}^3)$, $\mathcal{V}$ a function of $L^{\frac{6}{5}}_{\rm loc}(\mathbb{R}^3)$ which vanishes at infinity, $\theta > 0$ and $u \in H^1(\mathbb{R}^3)$ such that*

$$-\mathrm{div}(A\nabla u) + \mathcal{V}u + \theta u = 0 \quad \text{in } \mathcal{D}'(\mathbb{R}^3).$$

Then there exists $\gamma > 0$ depending on (λ,Λ,θ) such that $e^{\gamma|\mathbf{r}|}u \in H^1(\mathbb{R}^3)$.

Proof of Lemma 10. Let us denote by $\xi_n = A_n \nabla u_n$. One can extract from the sequence $(\xi_n)_{n\in\mathbb{N}}$, which is bounded in L^2, a subsequence $(\xi_{n_k})_{k\in\mathbb{N}}$ which converges weakly in $L^2(\Omega)$ to some ξ solution to $-\mathrm{div}\,(\xi) = f + g$ in $H^{-1}(\Omega)$. The proof will be completed if we can show that we necessarily have $\xi = A\nabla u$. Consider $\omega \subset\subset \Omega$, $q \in H^{-1}(\omega)$ and $v_n \in H_0^1(\omega)$ satisfying

$$-\mathrm{div}(A_n^* \nabla v_n) = q \quad \text{in } H^{-1}(\omega).$$

As the sequence $(A_n^*)_{n\in\mathbb{N}}$ H-converges to A^* [19], it holds

$$\begin{cases} v_n \rightharpoonup v \text{ in } H_0^1(\omega) \\ A_n^* \nabla v_n \rightharpoonup A^* \nabla v \text{ in } L^2(\omega) \end{cases}$$

where v is the solution to $-\mathrm{div}\,(A^* \nabla v) = q$ in $H_0^1(\omega)$. Let $\phi \in C_c^\infty(\omega)$. As

$$\begin{cases} \phi v_n \rightharpoonup \phi v \text{ in } H_0^1(\omega) \\ \phi v_n \to \phi v \text{ in } L^2(\omega) \\ \nabla\phi\, v_n \to \nabla\phi\, v \text{ in } (L^2(\omega))^3 \\ \nabla\phi\, u_n \to \nabla\phi\, u \text{ in } (L^2(\omega))^3, \end{cases}$$

we have on the one hand

$$\begin{aligned} \int_\omega \xi_{n_k} \cdot \nabla v_{n_k} \phi &= -(\mathrm{div}\xi_{\mathrm{n_k}}, \phi v_{n_k})_{H^{-1}(\omega), H_0^1(\omega)} - \int_\omega \xi_{n_k} \cdot \nabla\phi\, v_{n_k} \\ &= -(f_{n_k}, \phi v_{n_k})_{H^{-1}(\omega), H_0^1(\omega)} - \int_\omega g_{n_k} \phi v_{n_k} - \int_\omega \xi_{n_k} \cdot \nabla\phi\, v_{n_k} \\ &\to -(f, \phi v)_{H^{-1}(\omega), H_0^1(\omega)} - \int_\omega g\phi v - \int_\omega \xi \cdot \nabla\phi\, v \\ &= -(\mathrm{div}\xi, \phi v)_{H^{-1}(\omega), H_0^1(\omega)} - \int_\Omega \xi \cdot \nabla\phi\, v = \int_\Omega \xi \cdot \nabla v\, \phi, \end{aligned}$$

and on the other hand

$$\begin{aligned} \int_\omega \xi_{n_k} \cdot \nabla v_{n_k} \phi &= \int_\omega \nabla u_{n_k} \cdot (A^* \nabla v_{n_k}) \phi \\ &= -\int_\omega u_{n_k} (A^* \nabla v_{n_k}) \cdot \nabla\phi + \int_\omega u_{n_k} q \phi \\ &\to -\int_\omega u (A^* \nabla v) \cdot \nabla\phi + \int_\omega u q \phi = \int_\omega \nabla u \cdot (A^* \nabla v) \phi = \int_\omega (A\nabla u) \cdot \nabla v\, \phi. \end{aligned}$$

Therefore,

$$\int_\omega \xi \cdot \nabla v \phi = \int_\omega (A\nabla u) \cdot \nabla v \phi.$$

As the above equality holds true for all ω, all $v \in H_0^1(\omega)$ and all $\phi \in C_c^\infty(\omega)$, we finally obtain $\xi = A\nabla u$. $\square$

Proof of Lemma 11. The quadratic form q_0 on $L^2(\mathbb{R}^3)$ with domain $D(q_0) = H^1(\mathbb{R}^3)$, defined by

$$\forall (u,v) \in D(q_0) \times D(q_0), \quad q_0(u,v) = \int_{\mathbb{R}^3} A\nabla u \cdot \nabla v,$$

is symmetric and positive. It is also closed since the norm $\sqrt{\|\cdot\|_{L^2}^2 + q_0(\cdot)}$ is equivalent to the usual H^1 norm. This implies that q_0 is the quadratic form of a unique self-adjoint operator H_0 on $L^2(\mathbb{R}^3)$, whose domain $D(H_0)$ is dense in $H^1(\mathbb{R}^3)$. It is easy to check that $D(H_0) = \left\{u \in H^1(\mathbb{R}^3) \mid \text{div } (A\nabla u) \in L^2(\mathbb{R}^3)\right\}$ and that

$$\forall u \in D(H_0), \quad H_0 u = -\text{div } (A\nabla u).$$

Using classical elliptic regularity results [9], we obtain that there exists two constants $0 < \alpha < 1$ and $C \in \mathbb{R}_+$ (depending on λ and Λ) such that for all regular bounded domain $\Omega \subset\subset \mathbb{R}^3$, and all $v \in H^1(\Omega)$ such that div $(A\nabla v) \in L^2(\Omega)$,

$$\|v\|_{C^{0,\alpha}(\bar{\Omega})} := \sup_{\Omega} |v| + \sup_{(\mathbf{r},\mathbf{r}')\in\Omega\times\Omega} \frac{|v(\mathbf{r}) - v(\mathbf{r}')|}{|\mathbf{r}-\mathbf{r}'|^\alpha} \leq C\left(\|v\|_{L^2(\Omega)} + \|\text{div } (A\nabla v)\|_{L^2(\Omega)}\right).$$

It follows that on the one hand, $D(H_0) \hookrightarrow L^\infty(\mathbb{R}^3) \cap C^{0,\alpha}(\mathbb{R}^3)$, with

$$\forall u \in D(H_0), \quad \|u\|_{L^\infty(\mathbb{R}^3)} + \sup_{(\mathbf{r},\mathbf{r}')\in\mathbb{R}^3\times\mathbb{R}^3} \frac{|v(\mathbf{r}) - v(\mathbf{r}')|}{|\mathbf{r}-\mathbf{r}'|^\alpha} \leq C\left(\|u\|_{L^2} + \|H_0 u\|_{L^2}\right), \qquad (82)$$

and that on the other hand, any $u \in D(H_0)$ vanishes at infinity.

Let us now prove that the multiplication by $\mathcal{W} = V + \mu \star |\mathbf{r}|^{-1} + W$ defines a compact perturbation of H_0. For this purpose, we consider a sequence $(u_n)_{n\in\mathbb{N}}$ of elements of $D(H_0)$ bounded for the norm $\|\cdot\|_{H_0} = (\|\cdot\|_{L^2}^2 + \|H_0\cdot\|_{L^2}^2)^{\frac{1}{2}}$. Up to extracting a subsequence, we can assume without loss of generality that there exists $u \in D(H_0)$ such that:

$$\begin{cases} u_n \rightharpoonup u \text{ in } H^1(\mathbb{R}^3) \text{ and } L^p(\mathbb{R}^3) \text{ for } 2 \leq p \leq 6 \\ u_n \to u \text{ in } L^p_{loc}(\mathbb{R}^3) \text{ with } 2 \leq p < 6 \\ u_n \to u \ a.e. \end{cases}$$

Besides, it is then easy to check that the potential $\mathcal{W} = V + \mu \star |\mathbf{r}|^{-1} + W$ belongs to $L^2 + L^\infty_\epsilon(\mathbb{R}^3)$. Let $\epsilon > 0$ and $(\mathcal{W}_2, \mathcal{W}_\infty) \in L^2(\mathbb{R}^3) \times L^\infty(\mathbb{R}^3)$ such that $\|\mathcal{W}_\infty\|_{L^\infty} \leq \epsilon$ and $\mathcal{W} = \mathcal{W}_2 + \mathcal{W}_\infty$. On the one hand,

$$\|\mathcal{W}_\infty(u_n - u)\|_{L^2} \leq 2\,\epsilon \sup_{n\in\mathbb{N}} \|u_n\|_{H_0},$$

and on the other hand

$$\lim_{n\to\infty} \|\mathcal{W}_2(u_n - u)\|_{L^2} = 0.$$

The latter result is obtained from Lebesgue's dominated convergence theorem, using the fact that it follows from (82) that $(u_n)_{n\in\mathbb{N}}$ is bounded in $L^\infty(\mathbb{R}^3)$. Consequently,

$$\lim_{n\to\infty} \|\mathcal{W}u_n - \mathcal{W}u\|_{L^2} = 0,$$

which proves that $\mathcal{W}$ is a H_0-compact operator. We can therefore deduce from Weyl's theorem that $H = H_0 + \mathcal{W}$ defines a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $D(H) = D(H_0)$, and that $\sigma_{\text{ess}}(H) = \sigma_{\text{ess}}(H_0)$. As q_0 is positive, $\sigma(H_0) \subset \mathbb{R}_+$ and therefore $\sigma_{\text{ess}}(H) \subset \mathbb{R}_+$.

Let us now prove that H has an infinite number of negative eigenvalues which forms an increasing sequence converging to zero. First, H is bounded below since for all $v \in D(H)$ such that $\|v\|_{L^2} = 1$,

$$\begin{aligned} \langle v|H|v\rangle &= \int_{\mathbb{R}^3} A\nabla v \cdot \nabla v + \int_{\mathbb{R}^3} \mathcal{W} v^2 \\ &\geq \lambda\|\nabla v\|_{L^2}^2 - \|\mathcal{W}_2\|_{L^2}\|\nabla v\|_{L^2}^{\frac{3}{2}} - \epsilon \\ &\geq -\frac{27}{256}\lambda^{-3}\|\mathcal{W}_2\|^4 - \epsilon. \end{aligned}$$

In order to prove that H has at least N negative eigenvalues, including multiplicities, we can proceed as in the proof of [17, Lemma II.1]. Let us indeed consider N radial functions ϕ_1, ..., ϕ_N in $\mathcal{D}(\mathbb{R}^3)$ such that for all $1 \leq i \leq N$, $\mathrm{supp}(\phi_i) \in B_{i+1} \setminus \overline{B}_i$ and $\int_{\mathbb{R}^3} |\phi_i|^2 = 1$. Denoting by $\phi_{i,\sigma}(\cdot) = \sigma^{\frac{3}{2}} \phi_i(\sigma \cdot)$, we have

$$\int_{\mathbb{R}^3} A\nabla\phi_{i,\sigma} \cdot \nabla\phi_{i,\sigma} \leq \sigma^2 \Lambda \|\nabla\phi_i\|_{L^2}^2,$$

and

$$\begin{aligned}
\int_{\mathbb{R}^3} W|\phi_{i,\sigma}|^2 &\leq \left(\int_{B_{(i+1)\sigma^{-1}} \setminus \overline{B}_{i\sigma^{-1}}} W_2^2\right)^{\frac{1}{2}} \|\phi_{i,\sigma}\|_{L^4}^2 + \left(\int_{B_{(i+1)\sigma^{-1}} \setminus \overline{B}_{i\sigma^{-1}}} W_3^3\right)^{\frac{1}{2}} \|\phi_{i,\sigma}\|_{L^3}^2 \\
&= \sigma^{\frac{3}{2}} \left(\int_{B_{(i+1)\sigma^{-1}} \setminus \overline{B}_{i\sigma^{-1}}} W_2^2\right)^{\frac{1}{2}} \|\phi_i\|_{L^4}^2 + \sigma \left(\int_{B_{(i+1)\sigma^{-1}} \setminus \overline{B}_{i\sigma^{-1}}} W_3^3\right)^{\frac{1}{2}} \|\phi_i\|_{L^3}^2 \\
&= o(\sigma)
\end{aligned}$$

where we have split $W_+ = \max(0, W)$ as $W_+ = W_2 + W_3$ with $W_2 \in L^2(\mathbb{R}^3)$ and $W_3 \in L^3(\mathbb{R}^3)$. Besides, we deduce from Gauss theorem that

$$\int_{\mathbb{R}^3} (\mu \star |\mathbf{r}|^{-1}) \phi_{i,\sigma}^2 = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\phi_{i,\sigma}(\mathbf{r})|^2}{\max(|\mathbf{r}|, |\mathbf{r}'|)} \, d\mathbf{r} \, d\mu(\mathbf{r}') \leq \sigma \, \mu(\mathbb{R}^3) \int_{\mathbb{R}^3} \frac{|\phi(\mathbf{r})|^2}{|\mathbf{r}|} \, d\mathbf{r},$$

and that, for σ small enough,

$$\int_{\mathbb{R}^3} V|\phi_{i,\sigma}|^2 = \sigma \, Z \int_{\mathbb{R}^3} \frac{|\phi(\mathbf{r})|^2}{|\mathbf{r}|} \, d\mathbf{r}.$$

Thus,

$$\langle \phi_{i,\sigma} | H | \phi_{i,\sigma} \rangle \leq \sigma \left(\mu(\mathbb{R}^3) - Z \right) \int_{\mathbb{R}^3} \frac{|\phi(\mathbf{r})|^2}{|\mathbf{r}|} \, d\mathbf{r} + \underset{\sigma \to 0}{o}(\sigma),$$

yielding $\langle \phi_{i,\sigma} | H | \phi_{i,\sigma} \rangle < 0$ for $\sigma > 0$ small enough. As $\phi_{i,\sigma}$ and $\phi_{j,\sigma}$ have disjoint supports when $i \neq j$, we also have

$$\max_{\phi \in \mathrm{span}(\phi_{1,\sigma}, \cdots, \phi_{N,\sigma}), \, \|\phi\|_{L^2} = 1} \langle \phi | H | \phi \rangle < 0$$

for $\sigma > 0$ small enough. It follows from Courant-Fischer formula [26] and from the fact that $\sigma_{\mathrm{ess}}(H) \subset \mathbb{R}_+$ that H has at least N negative eigenvalues, including multiplicites.

The lowest eigenvalue of H, which we denote by μ_1, is characterized by

$$\mu_1 = \inf \left\{ \int_{\mathbb{R}^3} A\nabla u \cdot \nabla u + \int_{\mathbb{R}^3} \mathcal{W}|u|^2, \quad u \in H^1(\mathbb{R}^3), \quad \|u\|_{L^2} = 1 \right\}, \tag{83}$$

and the minimizers of (83) are exactly the set of the normalized eigenvectors of H associated with μ_1. Let u_1 be a minimizer (83). As for all $u \in H^1(\mathbb{R}^3)$, $|u| \in H^1(\mathbb{R}^3)$ and $\nabla|u| = \mathrm{sgn}(u)\nabla u$ a.e. on $\mathbb{R}^3$, $|u_1|$ also is a minimizer to (83). Up to replacing u_1 with $|u_1|$, there is therefore no restriction in assuming that $u_1 \geq 0$ on $\mathbb{R}^3$. We thus have

$$u_1 \in H^1(\mathbb{R}^3) \cap C^0(\mathbb{R}^3), \quad u_1 \geq 0 \quad \text{and} \quad -\operatorname{div}(A\nabla u_1) + g u_1 = 0$$

with $g = \mathcal{W} - \mu_1 \in L^p_{\rm loc}(\mathbb{R}^3)$ for some $p > \frac{3}{2}$ (take $p = 2$). A Harnack-type inequality due to Stampacchia [28] then implies that if u_1 has a zero in $\mathbb{R}^3$, then u_1 is identically zero. As $\|u_1\|_{L^2} = 1$, we therefore have $u_1 > 0$ on $\mathbb{R}^3$.

Consider now $w \in D(H) \setminus \{0\}$ such that $Hw = \mu w$ and $w \geq 0$ on $\mathbb{R}^3$. It holds

$$\mu \int_{\mathbb{R}^3} w_1 w = \langle w|H|w_1\rangle = \mu_1 \int_{\mathbb{R}^3} w_1 w.$$

As w is not identically equal to zero and as $w_1 > 0$ on $\mathbb{R}^3$, $\int_{\mathbb{R}^3} w_1 w > 0$, from which we deduce that $\mu = \mu_1$. It remains to prove that μ_1 is a non-degenerate eigenvalue. By contradiction, let us assume that there exists $v \in D(H)$ such that $Hv = \mu_1 v$, $\|v\|_{L^2} = 1$ and $(v, u_1)_{L^2} = 0$. Reasoning as above, $|v|$ also is an eigenvector of H associated with μ_1 and $|v| > 0$ on $\mathbb{R}^3$. Since $D(H) \subset C^0(\mathbb{R}^3)$, v is continuous on $\mathbb{R}^3$, so that either $v = |v|$ on $\mathbb{R}^3$ or $v = -|v|$ on $\mathbb{R}^3$. In any case, $\left|\int_{\mathbb{R}^3} u_1 v\right| = \int_{\mathbb{R}^3} u_1 |v| > 0$, which is in contradiction with the fact that $(u_1, v)_{L^2} = 0$. The proof is complete. ☐

Proof of Lemma 12. Consider $R > 0$ large enough to ensure

$$\frac{\theta}{2} \leq \mathcal{V}(\mathbf{r}) + \theta \leq \frac{3\theta}{2} \quad \text{a.e. on } B_R^c := \mathbb{R}^3 \setminus \overline{B}_R.$$

It is straightforward to see that u is the unique solution in $H^1(B_R^c)$ to the elliptic boundary problem

$$\begin{cases} -\mathrm{div}(A\nabla v) + \mathcal{V}v + \theta v = 0 & \text{in } B_R^c \\ \qquad\qquad\qquad\qquad v = u & \text{on } \partial B_R. \end{cases}$$

Let $\gamma > 0$, $\tilde{u} = u \exp^{-\gamma(|\cdot|-R)}$ and $w = u - \tilde{u}$. The function w is in $H^1(\mathbb{R}^3)$ and is the unique solution in $H^1(B_R^c)$ to

$$\begin{cases} -\mathrm{div}(A\nabla w) + \mathcal{V}w + \theta w = \mathrm{div}(A\nabla\tilde{u}) - \mathcal{V}\tilde{u} - \theta\tilde{u} & \text{in } B_R^c \\ \qquad\qquad\qquad\qquad w = 0 \quad \text{on } \partial B_R. \end{cases} \tag{84}$$

Let us now introduce the weighted Sobolev space $W_0^\gamma(B_R^c)$ defined by

$$W_0^\gamma(B_R^c) = \left\{ v \in H_0^1(B_R^c) \mid e^{\gamma|\cdot|} v \in H^1(B_R^c) \right\}$$

endowed with the inner product

$$(v, w)_{W_0^\gamma(B_R^c)} = \int_{B_R^c} e^{\gamma|\mathbf{r}|} (v(\mathbf{r}) w(\mathbf{r}) + \nabla v(\mathbf{r}) \cdot \nabla w(\mathbf{r}))\, d\mathbf{r}.$$

Multiplying (84) by $\phi e^{2\gamma|\cdot|}$ with $\phi \in \mathcal{D}(B_R^c)$ and integrating by parts, we obtain

$$\int_{B_R^c} A\nabla w \cdot \nabla(\phi e^{2\gamma|\mathbf{r}|}) + \int_{B_R^c} (\mathcal{V}+\theta) w \phi e^{2\gamma|\mathbf{r}|} = -\int_{B_R^c} A\nabla\tilde{u} \cdot \nabla(\phi e^{2\gamma|\mathbf{r}|}) - \int_{B_R^c} (\mathcal{V}+\theta)\tilde{u}\phi e^{2\gamma|\mathbf{r}|}$$

and then

$$\begin{aligned} &\int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla w \cdot e^{\gamma|\mathbf{r}|}\nabla\phi + 2\gamma \int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla w \cdot \frac{\mathbf{r}}{|\mathbf{r}|} e^{\gamma|\mathbf{r}|}\phi + \int_{B_R^c} (\mathcal{V}+\theta) e^{\gamma|\mathbf{r}|} w e^{\gamma|\mathbf{r}|}\phi \\ &= -\int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla\tilde{u} \cdot e^{\gamma|\mathbf{r}|}\nabla\phi - 2\gamma \int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla\tilde{u} \cdot \frac{\mathbf{r}}{|\mathbf{r}|} e^{\gamma|\mathbf{r}|}\phi - \int_{B_R^c} (\mathcal{V}+\theta) e^{\gamma|\mathbf{r}|}\tilde{u} e^{\gamma|\mathbf{r}|}\phi. \end{aligned} \tag{85}$$

Due to the definitions of $W_0^\gamma(B_R^c)$ and $\tilde{u}$, (85) actually holds for $(w,\phi) \in W_0^\gamma(B_R^c) \times W_0^\gamma(B_R^c)$, and it is straightforward to see that (85) is a variational formulation equivalent to (84).
It is also easy to check that the right-hand-side in (85) is a continuous form on $W_0^\gamma(B_R^c)$, so that we only have to prove the coercivity of the bilinear form in the left-hand-side of (85) to be able to apply Lax-Milgram lemma. We have for $v \in W_0^\gamma(B_R^c)$

$$
\begin{aligned}
&\int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla v \cdot e^{\gamma|\mathbf{r}|}\nabla v + 2\gamma \int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla v \cdot \frac{\mathbf{r}}{|\mathbf{r}|} e^{\gamma|\mathbf{r}|} v + \int_{B_R^c} (\mathcal{V}+\theta) e^{\gamma|\mathbf{r}|} v e^{\gamma|\mathbf{r}|} v \\
&\geq \lambda \int_{B_R^c} \left| e^{\gamma|\mathbf{r}|}\nabla v \right|^2 - 2\Lambda\gamma \int_{B_R^c} \left| e^{\gamma|\mathbf{r}|}\nabla v \right| \left| e^{\gamma|\mathbf{r}|} v \right| + \frac{\theta}{2} \int_{B_R^c} \left| e^{\gamma|\mathbf{r}|} v \right|^2 \\
&\geq \lambda \left\| e^{\gamma|\mathbf{r}|}\nabla v \right\|_{L^2(B_R^c)}^2 - 2\Lambda\gamma \left\| e^{\gamma|\mathbf{r}|}\nabla v \right\|_{L^2(B_R^c)} \left\| e^{\gamma|\mathbf{r}|} v \right\|_{L^2(B_R^c)} + \frac{\theta}{2} \left\| e^{\gamma|\mathbf{r}|} v \right\|_{L^2(B_R^c)}^2 \\
&\geq (\lambda - \Lambda\gamma) \left\| e^{\gamma|\mathbf{r}|}\nabla v \right\|_{L^2(B_R^c)}^2 + \left(\frac{\theta}{2} - \Lambda\gamma\right) \left\| e^{\gamma|\mathbf{r}|} v \right\|_{L^2(B_R^c)}^2 .
\end{aligned}
$$

Thus the bilinear form is clearly coercive if $\gamma < \min(\frac{\lambda}{\Lambda}, \frac{\theta}{2\Lambda})$, and there is a unique w solution of (84) in $W_0^\gamma(B_R^c)$ for such a γ. Now since $u = w + \tilde{u}$, it is clear that $e^{\gamma|\cdot|}u \in H^1(B_R^c)$, and then $e^{\gamma|\cdot|}u \in H^1(\mathbb{R}^3)$. $\square$

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