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Existence of minimizers for Kohn–Sham models in quantum chemistry

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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.

Keywords: Electronic structure; Density functional theory; Kohn–Sham; Variational methods; Concentration-compactness

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 [12,17], the electronic ground state energy and density of a given molecular system can be obtained by solving a minimization problem of the form

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

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 [13], who introduced the local density approximation (LDA) to DFT. The resulting Kohn–Sham LDA model

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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 [14,23,2,22], 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) construction of the density functional, while the latter is derived from Lieb's (mixed state) construction.

There are three main mathematical difficulties encountered when studying these models from a theoretical point of view: the nonlinearity, the nonconvexity, and the possible loss of compactness at infinity of the models. To our knowledge, very few results on Kohn–Sham LDA and GGA models exist 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 [15]. 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 [26], are not very well known in the mathematical community. The mathematical foundations of DFT are recalled in Section 2.1, and the derivation of the (standard and extended) Kohn–Sham LDA and GGA models is discussed in Section 2.2. We state our main results in Section 3, and postpone the proofs until Section 4.

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 [31], ultrasoft [32], PAW [3]) can be dealt with in a similar way.

2. Mathematical foundations of DFT and Kohn–Sham models

2.1. Density functional theory

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 $z_1, \dots, z_M$ ($z_k \in \mathbb{N} \setminus \{0\}$ in atomic units) and N electrons is the bottom of the spectrum of the electronic hamiltonian

$$H_N^V = -\frac{1}{2}\sum_{i=1}^N \Delta_{\mathbf{r}_i} - \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1}$$

where $\mathbf{r}_i$ and $\mathbf{R}_k$ are the positions in $\mathbb{R}^3$ of the ith electron and the kth nucleus respectively, and V is the electrostatic potential generated by the nuclei defined by

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

The hamiltonian H_N^V acts on electronic wavefunctions $\Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)$, $\sigma_i \in \Sigma := \{|\uparrow\rangle, |\downarrow\rangle\}$ denoting the spin variable of the ith electron, the nuclear coordinates $\{\mathbf{R}_k\}_{1 \leqslant k \leqslant M}$ 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, electronic wavefunctions are antisymmetric with respect to the renumbering of electrons, i.e.

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

where $\epsilon(p)$ is the signature of the permutation p. Note that (in the absence of magnetic fields) $H_N^V \Psi$ is real-valued if Ψ is real-valued. Our purpose being the calculation of the bottom of the spectrum of H_N^V, there is therefore no restriction in considering real-valued wavefunctions only. In other words, H_N^V 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

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

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^V 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 the Zhislin–Sigalov theorem [34,35] that for neutral or positively charged systems ($Z \geqslant N$), H_N^V has an infinite number of negative eigenvalues below the bottom of its essential spectrum. In particular, the electronic ground state energy $I_N(V)$ is an eigenvalue of H_N^V, and more precisely the lowest one.

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

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

Note that it also holds

$$I_N(V) = \inf\{\mathrm{Tr}(H_N^V \Gamma),\ \Gamma \in \mathcal{D}_N\} \tag{3}$$

where $\mathcal{D}_N$ is the set of N-body density matrices defined by

$$\mathcal{D}_N = \{\Gamma \in \mathcal{S}(\mathcal{H}_N)\ |\ 0 \leqslant \Gamma \leqslant 1,\ \mathrm{Tr}(\Gamma) = 1,\ \mathrm{Tr}(-\Delta \Gamma) < \infty\}.$$

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 $0 \leqslant \Gamma \leqslant 1$ stands for $0 \leqslant \langle \Psi | \Gamma | \Psi \rangle \leqslant \|\Psi\|^2_{\mathcal{H}_N}$ 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 $H \geqslant a$.

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 density operator $\Gamma \in \mathcal{D}_N$ can be associated the electronic density

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

(here and below, we use the same notation for an operator and its Green kernel). For an N-electron wavefunction $\Psi \in \mathcal{H}_N$ such that $\|\Psi\|_{\mathcal{H}_N} = 1$, we will denote by $\rho_\Psi := \rho_{|\Psi\rangle\langle\Psi|}$.

Let us now define the interacting free hamiltonian by

$$H_N^0 = -\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{4}$$

It is easy to see that

$$\langle\Psi|H_N^V|\Psi\rangle = \langle\Psi|H_N^0|\Psi\rangle + \int_{\mathbb{R}^3} \rho_\Psi V \quad \text{and} \quad \mathrm{Tr}\big(H_N^V\Gamma\big) = \mathrm{Tr}\big(H_N^0\Gamma\big) + \int_{\mathbb{R}^3} \rho_\Gamma V.$$

Besides, it can be checked that

$$\mathcal{R}_N = \big\{\rho \,\big|\, \exists\Psi \in \mathcal{Q}_N,\ \|\Psi\|_{\mathcal{H}_N} = 1,\ \rho_\Psi = \rho\big\} = \{\rho \mid \exists\Gamma \in \mathcal{D}_N,\ \rho_\Gamma = \rho\}$$
$$= \left\{\rho \geqslant 0 \,\Big|\, \sqrt{\rho} \in H^1\big(\mathbb{R}^3\big),\ \int_{\mathbb{R}^3} \rho = N\right\}.$$

It therefore follows that

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

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

where Levy–Lieb's and Lieb's density functionals [16,17] are respectively defined by

$$F_{\mathrm{LL}}(\rho) = \inf\big\{\langle\Psi|H_N^0|\Psi\rangle,\ \Psi \in \mathcal{Q}_N,\ \|\Psi\|_{\mathcal{H}_N} = 1,\ \rho_\Psi = \rho\big\}, \tag{7}$$

$$F_{\mathrm{L}}(\rho) = \inf\big\{\mathrm{Tr}\big(H_N^0\Gamma\big),\ \Gamma \in \mathcal{D}_N,\ \rho_\Gamma = \rho\big\}. \tag{8}$$

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 [17] that F_{L} is the Legendre transform of the function $V \mapsto I_N(V)$. More precisely, it holds

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

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 ground 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_{LL} nor F_{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 a homogeneous electron gas;
- in Kohn–Sham models (by far the most commonly used), it is a system of N *non-interacting* electrons.

2.2. 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^0 of the physical system (formula (4)) with the hamiltonian of the reference system

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

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

$$\widetilde{T}_{\mathrm{KS}}(\rho) = \inf\big\{\langle\Psi|T_N|\Psi\rangle,\ \Psi \in \mathcal{Q}_N,\ \|\Psi\|_{\mathcal{H}_N} = 1,\ \rho_\Psi = \rho\big\}, \tag{10}$$

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

$$T_{\mathrm{J}}(\rho) = \inf\bigl\{\mathrm{Tr}(T_N\Gamma),\ \Gamma \in \mathcal{D}_N,\ \rho_\Gamma = \rho\bigr\}.$$

Let Γ be in the above minimization set. The energy $\mathrm{Tr}(T_N\Gamma)$ 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

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

Indeed, a simple calculation yields $\mathrm{Tr}(T_N\Gamma) = \mathrm{Tr}(-\frac{1}{2}\Delta_{\mathbf{r}}\Upsilon_\Gamma)$, 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. [6]) that

$$\{\Upsilon \mid \exists\Gamma \in \mathcal{D}_N,\ \rho_\Gamma = \rho\} = \{\Upsilon \in \mathcal{RD}_N \mid \rho_\Upsilon = \rho\}, \tag{11}$$

where

$$\mathcal{RD}_N = \bigl\{\Upsilon \in \mathcal{S}\bigl(L^2\bigl(\mathbb{R}^3_\Sigma\bigr)\bigr) \bigm| 0 \leqslant \Upsilon \leqslant 1,\ \mathrm{Tr}(\Upsilon) = N,\ \mathrm{Tr}(-\Delta_{\mathbf{r}}\Upsilon) < \infty\bigr\}$$

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

$$T_{\mathrm{J}}(\rho) = \inf\left\{\mathrm{Tr}\left(-\frac{1}{2}\Delta_{\mathbf{r}}\Upsilon\right),\ \Upsilon \in \mathcal{RD}_N,\ \rho_\Upsilon = \rho\right\}. \tag{12}$$

It is to be noticed that no such simple expression for $\widetilde{T}_{\mathrm{KS}}(\rho)$ 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, $\widetilde{T}_{\mathrm{KS}}(\rho)$ is replaced with the Kohn–Sham kinetic energy functional

$$T_{\mathrm{KS}}(\rho) = \inf\bigl\{\langle\Psi|T_N|\Psi\rangle,\ \Psi \in \mathcal{Q}_N,\ \Psi \text{ is a Slater determinant},\ \rho_\Psi = \rho\bigr\}, \tag{13}$$

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

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

It is then easy to check that

$$T_{\mathrm{KS}}(\rho) = \inf\left\{\frac{1}{2}\sum_{i=1}^N \int\limits_{\mathbb{R}^3_\Sigma} \bigl|\nabla\phi_i(\mathbf{x})\bigr|^2\,d\mathbf{x},\ \Phi = (\phi_1,\dots,\phi_N) \in \mathcal{W}_N,\ \rho_\Phi = \rho\right\}, \tag{14}$$

where we have set

$$\mathcal{W}_N = \left\{\Phi = (\phi_1,\dots,\phi_N) \bigm| \phi_i \in H^1\bigl(\mathbb{R}^3_\Sigma\bigr),\ \int\limits_{\mathbb{R}^3_\Sigma} \phi_i(\mathbf{x})\phi_j(\mathbf{x})\,d\mathbf{x} = \delta_{ij}\right\}$$

and

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

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

$$T_{\mathrm{J}}(\rho) \leqslant \widetilde{T}_{\mathrm{KS}}(\rho) \leqslant T_{\mathrm{KS}}(\rho).$$

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 $\Phi = (\phi_1,\dots,\phi_N) \in \mathcal{W}_N$, Φ being then a minimizer of (13) and $T_{\mathrm{KS}}(\rho) = T_{\mathrm{J}}(\rho)$. Otherwise, $T_{\mathrm{KS}}(\rho) > T_{\mathrm{J}}(\rho)$.

The density functionals T_{KS} and T_{J} associated with the non-interacting hamiltonian T_N 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

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

or

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

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

$$I_N^{\mathrm{KS}}(V)=\inf\left\{\frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3_\Sigma}\left|\nabla\phi_i(\mathbf{x})\right|^2d\mathbf{x}+\int_{\mathbb{R}^3}\rho_\Phi V+J(\rho_\Phi)+E_{\mathrm{xc}}(\rho_\Phi),\ \Phi=(\phi_1,\dots,\phi_N)\in\mathcal{W}_N\right\}, \tag{17}$$

and

$$I_N^{\mathrm{EKS}}(V)=\inf\left\{\mathrm{Tr}\left(-\frac{1}{2}\Delta_{\mathbf{r}}\Upsilon\right)+\int_{\mathbb{R}^3}\rho_\Upsilon V+J(\rho_\Upsilon)+E_{\mathrm{xc}}(\rho_\Upsilon),\ \Upsilon\in\mathcal{RD}_N\right\}. \tag{18}$$

Up to now, no approximation has been made, in such a way that for the exact exchange-correlation functionals ((15) or (16)), $I_N^{\mathrm{KS}}(V)=I_N^{\mathrm{EKS}}(V)=I_N(V)$ for any molecular system containing N electrons. Unfortunately, there is no tractable expression of $E_{\mathrm{xc}}(\rho)$ 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

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

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

$$I_N^{\mathrm{RKS}}(V)=\inf\left\{\sum_{i=1}^{N_p}\int_{\mathbb{R}^3}|\nabla\phi_i|^2+\int_{\mathbb{R}^3}\rho_\Phi V+J(\rho_\Phi)+E_{\mathrm{xc}}(\rho_\Phi),\ \Phi=(\phi_1,\dots,\phi_{N_p})\in\left(H^1(\mathbb{R}^3)\right)^{N_p},\right.$$
$$\left.\int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij},\ \rho_\Phi=2\sum_{i=1}^{N_p}|\phi_i|^2\right\}, \tag{19}$$

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

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

where

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

and

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

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

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

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

$$I_N^{\mathrm{RKS}}(V) = \inf\{\mathcal{E}(\gamma),\ \gamma \in \mathcal{P}_{N_p}\} \tag{20}$$

where

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

is 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's. 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 article [13], Kohn and Sham proposed to use an approximate exchange-correlation functional of the form

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

where $\rho^{-1}g(\rho)$ is the exchange-correlation energy 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. [7]) and accurate quantum Monte Carlo evaluations of $g(\rho)$ for a small number of values of ρ [5]. Several interpolation formulae are available [25,24,33], 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

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

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 definitive 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

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

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

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, $r_\rho(\mathbf{r}) = (\frac{4}{3}\pi\rho(\mathbf{r}))^{-\frac{1}{3}}$ is the Wigner–Seitz radius, $s_\rho(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}}\frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}}$ is the (non-dimensional) reduced density gradient, $t_\rho(\mathbf{r}) = \frac{1}{4(3\pi^{-1})^{1/6}}\frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{7/6}}$ 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 [22], for which

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

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

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.

3. 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

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

$$g' \leqslant 0, \tag{26}$$

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

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

- 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

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

$$\frac{\partial h}{\partial \rho} \leqslant 0, \tag{30}$$

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

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

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

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

Conditions (25)–(28) on the LDA exchange-correlation energy are not restrictive. They are obviously fulfilled by the LDA exchange functional ($g_x^{\mathrm{LDA}}(\rho) = -\frac{3}{4}(\frac{3}{\pi})^{\frac{1}{3}}\rho^{\frac{4}{3}}$), and are also satisfied by all the approximate LDA correlation functionals currently used in practice (with $\alpha = \frac{4}{3}$ and $\beta_- = \beta^+ = \frac{1}{3}$). Besides, it is easy to see that the set of functions satisfying assumptions (29)–(34) is nonempty, and we have checked numerically that assumptions (29)–(34) are actually satisfied for the PBE exchange-correlation functional (see Remark 1), when the LDA correlation energy density $\epsilon_c(r)$ is given by the PZ81 formula [25].

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

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

and

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

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

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

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

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

and introduce the problem at infinity

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

where

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

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

Lemma 1. *Consider* (35) *and* (36) *with* E_{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* $0<\mu<\lambda$,

$$I_\lambda \leqslant I_\mu + I_{\lambda-\mu}^\infty. \tag{37}$$

Inequalities (37) in Lemma 1 are classical concentration-compactness type inequalities [20].

Our main results are the following two theorems.

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

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

for some $\epsilon_{\mathrm{F}} \leqslant 0$, where

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

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

Theorem 2 *(Extended KS-GGA model for two-electron systems). Assume that $Z \geqslant N = 2N_p = 2$ (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_{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*

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

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

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

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_{xc} given by (22) do not have a simple structure for $N_p \geqslant 2$ (see Remark 4 for further details).

Remark 3. Let us explain as of now the usefulness of properties (33) and (34) in the proof of Theorem 2:

- (33) is necessary to make the operator appearing in the Euler–Lagrange equation (39) elliptic;
- (34) implies that the Kohn–Sham energy functional, considered as a function of ρ and $\kappa = |\nabla\sqrt{\rho}|^2$, is convex w.r.t. κ, and thus ensures some lower semicontinuity property of the gradient terms of the energy for the weak topology of $H^1(\mathbb{R}^3)$.

Remark 4. (On the difficulties in extending the results of Theorem 2 to the general case of $N_p > 1$ electron pairs.) Consider the pure-state Kohn–Sham GGA model (19) for the sake of simplicity. Under assumptions (29) to (34), it is easy to see that the equivalent of Lemma 8 with $N = 2N_p > 2$ electrons still holds. The main argument is that, using [10, Theorem 2.5], the condition (34) still ensures the lower semicontinuity of the energy w.r.t. $|\nabla\sqrt{\rho}|^2$ for the weak topology of $H^1(\mathbb{R}^3; \mathbb{R}^{N_p})$. Therefore, for all $N_p \in \mathbb{N}^*$, if a minimizing sequence $(\Phi_n)_{n\in\mathbb{N}}$ is compact in $L^2(\mathbb{R}^3; \mathbb{R}^{N_p})$, then its limit is a minimizer of the problem.

In our proof of compactness in the case $N_p = 1$, we use in a crucial way the properties of the solutions of the Euler equation (39), among which boundedness in $L^\infty(\mathbb{R}^3)$ and exponential decay at infinity. When $N_p > 1$, denoting the state vector by $\Phi = (\phi_1, \dots, \phi_{N_p})$ and assuming that the energy is differentiable, the Euler–Lagrange optimality conditions turn into the following system: $\forall i \in [\![1, N_p]\!]$,

$$\begin{aligned}
&-\frac{1}{2}\operatorname{div}\left(\nabla\phi_i + \frac{\partial h}{\partial \kappa}\left(\rho_\Phi, \frac{1}{2}|\nabla\sqrt{\rho_\Phi}|^2\right)\frac{\sum_k \phi_k\nabla\phi_k}{\sum_k \phi_k^2}\phi_i\right) + \frac{1}{2}\frac{\partial h}{\partial \kappa}\left(\rho_\Phi, \frac{1}{2}|\nabla\sqrt{\rho_\Phi}|^2\right)\frac{\sum_k \phi_k\nabla\phi_k}{\sum_k \phi_k^2}\cdot\nabla\phi_i \\
&\quad - \frac{1}{2}\frac{\partial h}{\partial \kappa}\left(\rho_\Phi, \frac{1}{2}|\nabla\sqrt{\rho_\Phi}|^2\right)\left|\frac{\sum_k \phi_k\nabla\phi_k}{\sum_k \phi_k^2}\right|^2\phi_i + \left(V + \rho_\Phi \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial \rho}\left(\rho_\Phi, \frac{1}{2}|\nabla\sqrt{\rho_\Phi}|^2\right)\right)\phi_i = \epsilon_i\phi_i.
\end{aligned} \tag{40}$$

The study of (40) is much more involved than that of (39). We were not able to prove that solutions of (40) still have the required regularity properties and behaviour at infinity, and thus to extend our proof from the scalar case to the vector case.

4. Proofs

For clarity, we will use the following notation

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

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

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

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

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

4.1. 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. [27]) and introduce the vector space

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

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

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

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

- *Lower bound on the kinetic energy*:

$$\frac{1}{2}\|\nabla\sqrt{\rho_\gamma}\|_{L^2}^2\leqslant\mathrm{Tr}(-\Delta\gamma).\tag{41}$$

- *Upper bound on the Coulomb energy*:

$$0\leqslant J(\rho_\gamma)\leqslant C(\mathrm{Tr}\,\gamma)^{\frac{3}{2}}\big(\mathrm{Tr}(-\Delta\gamma)\big)^{\frac{1}{2}}.\tag{42}$$

- *Bounds on the interaction energy between nuclei and electrons*:

$$-4Z(\mathrm{Tr}\,\gamma)^{\frac{1}{2}}\big(\mathrm{Tr}(-\Delta\gamma)\big)^{\frac{1}{2}}\leqslant\int_{\mathbb{R}^3}\rho_\gamma V\leqslant 0.\tag{43}$$

- *Bounds on the exchange-correlation energy*:

$$-C\Big((\mathrm{Tr}\,\gamma)^{1-\frac{\beta_-}{2}}\big(\mathrm{Tr}(-\Delta\gamma)\big)^{\frac{3\beta_-}{2}}+(\mathrm{Tr}\,\gamma)^{1-\frac{\beta_+}{2}}\big(\mathrm{Tr}(-\Delta\gamma)\big)^{\frac{3\beta_+}{2}}\Big)\leqslant E_{\mathrm{xc}}(\rho_\gamma)\leqslant 0.\tag{44}$$

- *Lower bound on the energy*:

$$\mathcal{E}(\gamma)\geqslant\frac{1}{2}\Big(\big(\mathrm{Tr}(-\Delta\gamma)\big)^{\frac{1}{2}}-4Z(\mathrm{Tr}\,\gamma)^{\frac{1}{2}}\Big)^2-8Z^2\,\mathrm{Tr}\,\gamma-C\Big((\mathrm{Tr}\,\gamma)^{\frac{2-\beta_-}{2-3\beta_-}}+(\mathrm{Tr}\,\gamma)^{\frac{2-\beta_+}{2-3\beta_+}}\Big).\tag{45}$$

– *Lower bound on the energy at infinity*:

$$\mathcal{E}^\infty(\gamma) \geqslant \frac{1}{2}\operatorname{Tr}(-\Delta\gamma) - C\big((\operatorname{Tr}\gamma)^{\frac{2-\beta_-}{2-3\beta_-}} + (\operatorname{Tr}\gamma)^{\frac{2-\beta_+}{2-3\beta_+}}\big), \tag{46}$$

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. (41) is a straightforward consequence of Cauchy–Schwarz inequality; a proof can be found for instance in [4]. Using Hardy–Littlewood–Sobolev [18], interpolation, and Gagliardo–Nirenberg–Sobolev inequalities, we obtain

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

Hence (42), using (41) and the relation $\|\rho_\gamma\|_{L^1} = 2\operatorname{Tr}(\gamma)$. It follows from Cauchy–Schwarz and Hardy inequalities and from the above estimates that

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

Hence (43). Conditions (25)–(27) for LDA and (29)–(31) for GGA imply that $E_{\rm xc}(\rho) \leqslant 0$ and there exists $1 < p_- < p_+ < \frac{5}{3}$ ($p_\pm = 1 + \beta_\pm$) and some constant $C \in \mathbb{R}_+$ such that

$$\forall \rho \in \mathcal{K}, \quad \big|E_{\rm xc}(\rho)\big| \leqslant C\bigg(\int_{\mathbb{R}^3}\rho^{p_-} + \int_{\mathbb{R}^3}\rho^{p_+}\bigg), \tag{47}$$

from which we deduce (44), using interpolation and Gagliardo–Nirenberg–Sobolev inequalities. Lastly, the estimates (45) and (46) are straightforward consequences of (42)–(44). □

Lemma 3. *$\mathcal{E}$ and $\mathcal{E}^\infty$ are continuous on $\mathcal{H}$.*

Proof. Let $\gamma \in \mathcal{K}_\lambda$ and consider a sequence $(\gamma_n)_{n\in\mathbb{N}}$ converging to γ strongly in $\mathcal{H}$. It is well known that ρ_{γ_n} converges to ρ_γ strongly in $L^p(\mathbb{R}^3)$ and $\sqrt{\rho_{\gamma_n}}$ converges to $\sqrt{\rho_\gamma}$ strongly in $H^1(\mathbb{R}^3)$. Since the linear form $\gamma \mapsto \operatorname{Tr}(-\Delta\gamma)$ is continuous on $\mathcal{H}$ and the functionals $u \mapsto \int_{\mathbb{R}^3} u^2 V$ and $u \mapsto J(u^2) + E_{\rm xc}(u^2)$ are continuous on $H^1(\mathbb{R}^3)$, the continuity of $\mathcal{E}$ and $\mathcal{E}^\infty$ on $\mathcal{H}$ immediately follows. □

4.2. Proof of Lemma 1

Obviously, $I_0 = I_0^\infty = 0$ and $I_\lambda \leqslant I_\lambda^\infty$ 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 $I_\mu \leqslant \mathcal{E}(\gamma) \leqslant I_\mu + \epsilon$. Using Lemma 3, the density of finite-rank operators in $\mathcal{H}$ and the density of $C_c^\infty(\mathbb{R}^3)$ in $L^2(\mathbb{R}^3)$, there is no restriction in choosing γ finite-rank and such that $\operatorname{Ran}(\gamma) \subset C_c^\infty(\mathbb{R}^3)$. Likewise, there exists a finite-rank operator $\gamma' \in \mathcal{K}_{\lambda-\mu}$ such that $\operatorname{Ran}(\gamma') \subset C_c^\infty(\mathbb{R}^3)$ and $I_{\lambda-\mu}^\infty \leqslant \mathcal{E}^\infty(\gamma') \leqslant I_{\lambda-\mu}^\infty + \epsilon$.

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

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

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

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

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 $0 \leqslant \lambda \leqslant 1$, 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 $1 \leqslant \alpha < \frac{3}{2}$, $c > 0$ and $\sigma_0 > 0$ such that for all $0 \leqslant \lambda \leqslant 1$ and all $0 \leqslant \sigma \leqslant \sigma_0$,

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

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 $\lambda > 0$,

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

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* (*see* [20]) *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 I_λ. By contradiction, assume that the sequence ρ_{γ_n} vanishes, i.e.

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

We know from Lemma 2 that γ_n is bounded in $\mathcal{H}$, and thus that ρ_{γ_n} is bounded in $H^1(\mathbb{R}^3)$. According to Lemma I.1 in [20], this and the fact that ρ_{γ_n} is vanishing imply that ρ_{γ_n} converge strongly to 0 in $L^p(\mathbb{R}^3)$ for $1 < p < 3$. In particular, it follows from (47) and from the fact that $V \in L^r(\mathbb{R}^3) + L^q(\mathbb{R}^3)$ for some $\frac{3}{2} < r, q < +\infty$, that

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

As

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

we obtain that $I_\lambda \geqslant 0$. 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 $E_{\mathrm{xc}}(\rho)$. □

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 I_λ^∞. 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

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

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

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

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*

$$\lim_{k\to\infty} \big(E_{\mathrm{xc}}(\alpha_k\rho_k) - E_{\mathrm{xc}}(\rho_k)\big) = 0.$$

Proof. In the LDA setting, we deduce from (27) that there exists $1 < p_- \leqslant p_+ < \frac{5}{3}$ and $C \in \mathbb{R}_+$ such that for k large enough

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

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

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

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 $1 \leqslant p \leqslant 3$ 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.

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

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

For all $k \in \mathbb{N}$, $\gamma_k = \lambda_k \lambda^{-1}\gamma$ is in $\mathcal{K}_{\lambda_k}$ so that $\forall k \in \mathbb{N}$, $I_{\lambda_k} \leqslant \mathcal{E}(\gamma_k)$. Besides, it is easy to see that $\mathcal{E}(\gamma_k)$ tends to $\mathcal{E}(\gamma)$ in virtue of Lemma 5. Thus $I_{\lambda_k} \leqslant I_\lambda + \epsilon$ for k large enough. Now, for each $k \in \mathbb{N}$, we choose $\widetilde{\gamma}_k \in \mathcal{K}_{\lambda_k}$ such that $\mathcal{E}(\widetilde{\gamma}_k) \leqslant I_{\lambda_k} + \frac{1}{k}$. For all $k \in \mathbb{N}$, we set $\overline{\gamma}_k = \lambda\lambda_k^{-1}\widetilde{\gamma}_k$. As $\overline{\gamma}_k \in \mathcal{K}_\lambda$, it holds $I_\lambda \leqslant \mathcal{E}(\overline{\gamma}_k)$. We then deduce from Lemma 5 that $\lim_{k\to\infty}(\mathcal{E}(\widetilde{\gamma}_k) - \mathcal{E}(\overline{\gamma}_k)) = 0$, so that for k large enough we get $I_\lambda - \epsilon \leqslant I_{\lambda_k}$. This proves the continuity of $\lambda \mapsto I_\lambda$ on $\mathbb{R}_+ \setminus \{0\}$. Lastly, it results from the estimates established in Lemma 2 that $\lim_{\lambda\to 0^+} I_\lambda = 0$.

4.3. Proof of Theorem 1

Let us first prove the following lemma, which relies on classical arguments.

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 $1 \leqslant p < 3$ and*

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

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

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

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 [29]), yielding

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

Hence, $(\rho_{\gamma_n})_{n\in\mathbb{N}}$ converges to ρ_γ in $\mathcal{D}'(\mathbb{R}^3)$. As by (41), $(\sqrt{\rho_{\gamma_n}})_{n\in\mathbb{N}}$ 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 $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for all $2 \leqslant p < 6$. 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 $L^2(\mathbb{R}^3)$. Using Hölder's inequality and 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 $2 \leqslant p < 6$, hence that $(\rho_{\gamma_n})_{n\in\mathbb{N}}$ converges to ρ_γ strongly in $L^p(\mathbb{R}^3)$ for all $1 \leqslant p < 3$. This readily implies

$$\lim_{n\to\infty}\int_{\mathbb{R}^3}\rho_{\gamma_n}V = \int_{\mathbb{R}^3}\rho_\gamma V, \qquad \lim_{n\to\infty} J(\rho_{\gamma_n}) = J(\rho_\gamma), \qquad \lim_{n\to\infty} E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_{\gamma_n}) = E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\gamma).$$

Lastly, Fatou's theorem for non-negative trace-class operators yields

$$\mathrm{Tr}\big(|\nabla|\gamma|\nabla|\big) \leqslant \liminf_{n\to\infty} \mathrm{Tr}\big(|\nabla|\gamma_n|\nabla|\big).$$

We thus obtain the desired result. □

We will also need the following result.

Lemma 7. *Consider $\alpha > 0$ and $\beta > 0$ such that $\alpha + \beta \leqslant N_p \leqslant Z/2$. If I_α and I_β^∞ have minimizers, then*

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

Proof. Let γ be a minimizer for I_α. In particular γ satisfies the Euler equation

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

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

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

and where $0 \leqslant \delta \leqslant 1$, $\mathrm{Ran}(\delta) \subset \mathrm{Ker}(H_{\rho_\gamma} - \epsilon_{\mathrm{F}})$. 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,

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

and we know from [19, Lemma II.1] that as $-\sum_{k=1}^M z_k + \int_{\mathbb{R}^3}\rho_\gamma = -Z + 2\alpha < -Z + 2N_p \leqslant 0$, the right-hand side operator has infinitely many negative eigenvalues of finite multiplicities. Therefore, so has H_{ρ_γ}. Eventually, $\epsilon_{\mathrm{F}} < 0$ 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 $0 \leqslant n_i \leqslant 1$ and where

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

$\epsilon_1 < \epsilon_2 \leqslant \epsilon_3 \leqslant \cdots < 0$ 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's, hence ρ_γ, are in $H^2(\mathbb{R}^3)$ and therefore vanish at infinity. Using Lemma 13, all the ϕ_i decay exponentially fast to zero at infinity.

Now consider γ' a minimizer for I_β^∞. γ' satisfies

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

where

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

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

First consider the case $\epsilon_{F'} < 0$. 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

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

then is in $\mathcal{K}$ and $\mathrm{Tr}(\gamma_n) \leqslant (\alpha + \beta)$, which implies $I_{\alpha+\beta} \leqslant I_{\mathrm{Tr}(\gamma_n)}$ due to Lemma 1. 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

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

Since $2\beta < 2N_p \leqslant Z$, we have for n large enough

$$I_{\alpha+\beta} \leqslant I_{\mathrm{Tr}(\gamma_n)} \leqslant \mathcal{E}^{\mathrm{LDA}}(\gamma_n) < I_\alpha + I_\beta^\infty.$$

Now if $\epsilon_{F'} = 0$, 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 $\mu > 0$. For $0 < \eta < \mu$, $\gamma + \eta|\phi_{m+1}\rangle\langle\phi_{m+1}|$ and $\gamma' - \eta|\psi\rangle\langle\psi|$ are in $\mathcal{K}$ and it is easy to see that

$$\mathcal{E}^{\mathrm{LDA}}\bigl(\gamma + \eta|\phi_{m+1}\rangle\langle\phi_{m+1}|\bigr) = I_\alpha + 2\eta\epsilon_{m+1} + o(\eta)$$

and

$$\mathcal{E}^{\mathrm{LDA},\infty}\bigl(\gamma' - \eta|\psi\rangle\langle\psi|\bigr) = I_\beta^\infty + o(\eta).$$

Since $\mathrm{Tr}(\gamma + \eta|\phi_{m+1}\rangle\langle\phi_{m+1}|) = \alpha + \eta$ and $\mathrm{Tr}(\gamma' - \eta|\psi\rangle\langle\psi|) = \beta - \eta$, we deduce

$$I_{\alpha+\eta} \leqslant I_\alpha + 2\eta\epsilon_{m+1} + o(\eta) \quad \text{and} \quad I^\infty_{\beta-\eta} \leqslant I^\infty_\beta + o(\eta).$$

Then, according to Lemma 1, we obtain for η small enough

$$I_{\alpha+\beta} \leqslant I_{\alpha+\eta} + I^\infty_{\beta-\eta} \leqslant I_\alpha + I^\infty_\beta + 2\eta\epsilon_{m+1} + o(\eta) < I_\alpha + I^\infty_\beta. \qquad \square$$

We are now in position to prove Theorem 1, and even more generally that problem (35) with (21) has a minimizer for $\lambda \leqslant N_p$. Let $(\gamma_n)_{n\in\mathbb{N}}$ be a minimizing sequence for I_λ with $\lambda \leqslant N_p$. 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 $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for all $2 \leqslant p < 6$ and almost everywhere.

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

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

yielding that γ is a minimizer of (35).

The rest of the proof consists in ruling out the eventuality when $\mathrm{Tr}(\gamma) < \lambda$.

Let us first rule out the case $\mathrm{Tr}(\gamma) = 0$. By contradiction, assume that $\mathrm{Tr}(\gamma) = 0$, which implies $\rho_\gamma = 0$. Then ρ_{γ_n} converges to 0 strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for $1 \leqslant p < 6$, from which we deduce

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

Consequently,

$$I^\infty_\lambda \leqslant \lim_{n\to+\infty} \mathcal{E}^{\mathrm{LDA},\infty}(\gamma_n) = \lim_{n\to+\infty} \mathcal{E}^{\mathrm{LDA}}(\gamma_n) = I_\lambda$$

which contradicts the first assertion of Lemma 1.

Let us now set $\alpha = \mathrm{Tr}(\gamma)$ and assume that $0 < \alpha < \lambda$. Following e.g. [9], 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 $\xi(0) = 1$,

$0 \leqslant \xi(x) < 1$ if $|x| > 0$, $\xi(x) = 0$ if $|x| \geqslant 1$, $\|\nabla\xi\|_{L^\infty} \leqslant 2$ and $\|\nabla(1-\xi^2)^{\frac{1}{2}}\|_{L^\infty} \leqslant 2$. We then set $\xi_R(\cdot) = \xi(\frac{\cdot}{R})$. For all $n \in \mathbb{N}$, $R \mapsto \operatorname{Tr}(\xi_R\gamma_n\xi_R)$ is a continuous nondecreasing function which vanishes at $R = 0$ and converges to $\operatorname{Tr}(\gamma_n) = \lambda$ when R goes to infinity. Let $R_n > 0$ be such that $\operatorname{Tr}(\xi_{R_n}\gamma_n\xi_{R_n}) = \alpha$. 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

$$\int_{\mathbb{R}^3} \rho_\gamma(x)\xi_{R^*}^2(x)\,dx = \lim_{k\to\infty}\int_{\mathbb{R}^3} \rho_{\gamma_{n_k}}(x)\xi_{R_{n_k}}^2(x)\,dx = 2\lim_{k\to\infty}\operatorname{Tr}(\xi_{R_{n_k}}\gamma_{n_k}\xi_{R_{n_k}}) = 2\alpha = \int_{\mathbb{R}^3}\rho_\gamma(x)\,dx.$$

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 $0 \leqslant \gamma_{j,n} \leqslant 1$, that $\rho_{\gamma_n} = \rho_{\gamma_{1,n}} + \rho_{\gamma_{2,n}}$ and that $\operatorname{Tr}(\gamma_{1,n}) = \alpha$ while $\operatorname{Tr}(\gamma_{2,n}) = \lambda - \alpha$. 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

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

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 $\phi \in C_c^\infty(\mathbb{R}^3)$,

$$\begin{aligned}\operatorname{Tr}\big(\gamma_{1,n}\big(|\phi\rangle\langle\phi|\big)\big) &= \operatorname{Tr}\big(\gamma_n\big(|\xi_{R_n}\phi\rangle\langle\xi_{R_n}\phi|\big)\big)\\ &= \operatorname{Tr}\big(\gamma_n\big(\big|(\xi_{R_n}-1)\phi\big\rangle\langle\xi_{R_n}\phi|\big)\big) + \operatorname{Tr}\big(\gamma_n\big(|\phi\rangle\big\langle(\xi_{R_n}-1)\phi\big|\big)\big) + \operatorname{Tr}\big(\gamma_n\big(|\phi\rangle\langle\phi|\big)\big)\\ &\xrightarrow[n\to\infty]{} \operatorname{Tr}\big(\gamma\big(|\phi\rangle\langle\phi|\big)\big),\end{aligned}$$

we obtain that $(\gamma_{1,n})_{n\in\mathbb{N}}$ converges to γ for the weak-$*$ topology of $\mathcal{H}$. Since $\operatorname{Tr}(\gamma_{1,n}) = \alpha = \operatorname{Tr}(\gamma)$ 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 $1 \leqslant p < 3$, and that

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

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 $1 \leqslant p < 3$ (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 $1 \leqslant p < 3$). Besides, using again (49), it holds

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

For R large enough, one has on the one hand

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

and on the other hand

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

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

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

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.

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 $\eta>0$, $R>0$ such that for all $n\in\mathbb{N}$, $\int_{y_n+B_R}\rho_{\gamma_{2,n}}\geqslant\eta$ 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 $\mathrm{Tr}(\gamma')\geqslant\eta>0$. Let $\beta=\mathrm{Tr}(\gamma')$. Reasoning as above, one can easily check that γ' is a minimizer for I^∞_β, and that $I_\lambda=I_\alpha+I^\infty_\beta+I^\infty_{\lambda-\alpha-\beta}$. On the other hand, Lemma 7 yields $I_{\alpha+\beta}<I_\alpha+I^\infty_\beta$.

All in all we obtain $I_\lambda>I_{\alpha+\beta}+I^\infty_{\lambda-\alpha-\beta}$, which contradicts Lemma 1. The proof is complete.

4.4. *Proof of Theorem 2*

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

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

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,

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

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

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

Consequently,

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

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 $(\phi, w) \in H^1(\mathbb{R}^3) \times H^1(\mathbb{R}^3)$,

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

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 $0 \leqslant \lambda \leqslant 1$ (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 $0 \leqslant \lambda \leqslant 1$. Let us start with a simple lemma.

Lemma 8. *Let $0 \leqslant \mu \leqslant 1$ 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 $\mathbb{R}^3$ due to (34). Besides the function $t \mapsto t + h(\rho_\phi(x), t)$ is Lipschitz on $\mathbb{R}_+$, uniformly in x due to (33). 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

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

Besides, we deduce from (31) that

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

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,

$$\int_{\mathbb{R}^3} |\nabla\phi|^2 + E_{\mathrm{xc}}^{\mathrm{GGA}}(\rho_\phi) = \int_{\mathbb{R}^3} \big(|\nabla\phi|^2 + h\big(\rho_\phi, |\nabla\phi|^2\big)\big)$$
$$\leqslant \liminf_{n\to\infty} \int_{\mathbb{R}^3} \big(|\nabla\phi_n|^2 + h\big(\rho_\phi, |\nabla\phi_n|^2\big)\big) + \lim_{n\to\infty} \int_{\mathbb{R}^3} \big(h\big(\rho_{\phi_n}, |\nabla\phi_n|^2\big) - h\big(\rho_\phi, |\nabla\phi_n|^2\big)\big)$$
$$= \liminf_{n\to\infty} \int_{\mathbb{R}^3} |\nabla\phi_n|^2 + E_{\mathrm{xc}}^{\mathrm{GGA}}(\rho_{\phi_n}).$$

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 $2 \leqslant p < 6$, 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,

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

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^∞. □

Next, we show that the equivalent of Lemma 7 in the GGA setting holds.

Lemma 9. *Consider $\alpha > 0$ and $\beta > 0$ such that $\alpha + \beta \leqslant 1$. If J_α and J_β^∞ have minimizers, then*

$$J_{\alpha+\beta} < J_\alpha + J_\beta^\infty.$$

Proof. Let u and v be minimizers for J_α and J_β^∞ respectively. Since $E(\phi) = E(|\phi|)$ $\forall\phi \in H^1(\mathbb{R}^3)$, we can assume that u and v are non-negative. u satisfies the Euler equation

$$-\frac{1}{2}\,\mathrm{div}\left(\left(1 + \frac{\partial h}{\partial\kappa}\big(\rho_u, |\nabla u|^2\big)\right)\nabla u\right) + \left(V + \rho_u \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial\rho}\big(\rho_u, |\nabla u|^2\big)\right)u + \theta_1 u = 0 \tag{54}$$

and v satisfies the Euler equation

$$-\frac{1}{2}\,\mathrm{div}\left(\left(1 + \frac{\partial h}{\partial\kappa}\big(\rho_v, |\nabla v|^2\big)\right)\nabla v\right) + \left(\rho_v \star |\mathbf{r}|^{-1} + \frac{\partial h}{\partial\rho}\big(\rho_v, |\nabla v|^2\big)\right)v + \theta_2 v = 0 \tag{55}$$

where θ_1 and θ_2 are two Lagrange multipliers.

Using properties (31) and (33) and classical elliptic regularity arguments [11] (see also the proof of Lemma 13 below), we obtain that both u and v are in $C^{0,\alpha}(\mathbb{R}^3)$ for some $0 < \alpha < 1$ and vanish at infinity.

Using again (31), this implies that $\frac{\partial h}{\partial\rho}(\rho_u, |\nabla u|^2)u$ vanishes at infinity. Since it is a non-positive function, applying Lemma 12 (proved in Appendix A) to (54) then yields $\theta_1 > 0$.

Moreover, the function $\lambda \mapsto J_\lambda^\infty$ being decreasing on [0, 1], θ_2 is non-negative.

Let us first assume $\theta_2 > 0$. Applying Lemma 13, 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

$$u = e^{-\gamma|\cdot|} f_1, \qquad v = e^{-\gamma|\cdot|} f_2, \qquad \nabla u = e^{-\gamma|\cdot|} g_1, \qquad \nabla v = e^{-\gamma|\cdot|} g_2. \tag{56}$$

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

$$w_t(\mathbf{r}) = \alpha_t\big(u(\mathbf{r}) + v(\mathbf{r} - t\mathbf{e})\big) \quad \text{where } \alpha_t = (\alpha+\beta)^{\frac{1}{2}} \big\|u + v(\cdot - t\mathbf{e})\big\|_{L^2}^{-1}.$$

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

$$E(w_t) \geqslant J_{\alpha+\beta}. \tag{57}$$

Besides, a little calculation (see [1] for details) shows that

$$E(w_t) = J_\alpha + J_\beta^\infty + \int_{\mathbb{R}^3} V\big|v(\cdot - t\mathbf{e})\big|^2 + D(\rho_u, \rho_{v(\cdot - t\mathbf{e})}) + O\big(e^{-\gamma t}\big),$$

the main difficulty being to verify that (31), (33), (56) and the boundedness of u and v in $L^\infty(\mathbb{R}^3)$ yield

$$\left|\int_{\mathbb{R}^3} h\big(\rho_{w_t}, |\nabla w_t|^2\big) - h\big(\rho_u, |\nabla u|^2\big) - h\big(\rho_{v(\cdot - t\mathbf{e})}, \big|\nabla v(\cdot - t\mathbf{e})\big|^2\big)\right| = O\big(e^{-\gamma t}\big).$$

Next, using (56), we get

$$\int_{\mathbb{R}^3} V\rho_{v(\cdot - t\mathbf{e})} + D(\rho_u, \rho_{v(\cdot - t\mathbf{e})}) = -Zt^{-1}\int_{\mathbb{R}^3}\rho_u + t^{-1}\int_{\mathbb{R}^3}\rho_v\int_{\mathbb{R}^3}\rho_u + o\big(t^{-1}\big)$$
$$= -2\alpha(Z - 2\beta)t^{-1} + o\big(t^{-1}\big).$$

Finally, for t large enough and since $2\beta < 2 \leqslant Z$,

$$J_{\alpha+\beta} \leqslant E(w_t) \leqslant J_\alpha + J_\beta^\infty - 2\alpha(Z - 2\beta)t^{-1} + o\big(t^{-1}\big) < J_\alpha + J_\beta^\infty.$$

Let us now assume that $\theta_2 = 0$. Using (54) and (55), we easily get that for $\eta > 0$ small enough,

$$J_{(1+\eta)^2\alpha} \leqslant E(u + \eta u) = E(u) - \eta\theta_1\alpha + o(\eta) = J_\alpha - \eta\theta_1\alpha + o(\eta)$$

while

$$J^\infty_{(1-2\frac{\alpha}{\beta}\eta)^2\beta} \leqslant E^\infty\left(v - 2\frac{\alpha}{\beta}\eta v\right) = E^\infty(v) + o(\eta) = J_\beta^\infty + o(\eta).$$

Lemma 1 then yields

$$J_{(1+\eta)^2\alpha + (1-2\frac{\alpha}{\beta}\eta)^2\beta} \leqslant J_{(1+\eta)^2\alpha} + J^\infty_{(1-2\frac{\alpha}{\beta}\eta)^2\beta} \leqslant J_\alpha + J_\beta^\infty - \eta\theta_1\alpha + o(\eta),$$

and for η small enough, it holds $(1+\eta)^2\alpha + (1 - 2\frac{\alpha}{\beta}\eta)^2\beta \leqslant \alpha + \beta$ so that

$$J_{\alpha+\beta} \leqslant J_{(1+\eta)^2\alpha + (1-2\frac{\alpha}{\beta}\eta)^2\beta} \leqslant J_\alpha + J_\beta^\infty - \eta\theta_1\alpha + o(\eta) < J_\alpha + J_\beta^\infty. \qquad \square$$

In order to prove that the minimizing sequences for J_λ (or at least some of them) are indeed precompact in $L^2(\mathbb{R}^3)$ and to apply Lemma 8, we will use the concentration-compactness method due to P.-L. Lions [20], for the simpler method used in the LDA setting does not seem to work anymore. Consider an Ekeland sequence $(\phi_n)_{n\in\mathbb{N}}$ for (52), that is [8] a sequence $(\phi_n)_{n\in\mathbb{N}}$ such that

$$\forall n \in \mathbb{N}, \quad \phi_n \in H^1\big(\mathbb{R}^3\big) \quad \text{and} \quad \int_{\mathbb{R}^3}\phi_n^2 = \lambda, \tag{58}$$

$$\lim_{n\to+\infty} E(\phi_n) = J_\lambda, \tag{59}$$

$$\lim_{n\to+\infty} E'(\phi_n) + \theta_n\phi_n = 0 \quad \text{in } H^{-1}\big(\mathbb{R}^3\big) \tag{60}$$

for some sequence $(\theta_n)_{n\in\mathbb{N}}$ of real numbers. As in the proof of Lemma 9, we can assume that

$$\forall n \in \mathbb{N}, \quad \phi_n \geqslant 0 \quad \text{a.e. on } \mathbb{R}^3 \quad \text{and} \quad \theta_n \geqslant 0. \tag{61}$$

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

$$\phi_n \rightharpoonup \phi \quad \text{weakly in } H^1\big(\mathbb{R}^3\big), \tag{62}$$

$$\phi_n \to \phi \quad \text{strongly in } L^p_{\mathrm{loc}}\big(\mathbb{R}^3\big) \text{ for all } 2 \leqslant p < 6, \tag{63}$$

$$\phi_n \to \phi \quad \text{a.e. in } \mathbb{R}^3, \tag{64}$$

$$\theta_n \to \theta \quad \text{in } \mathbb{R}, \tag{65}$$

and it follows from (61) that $\phi \geqslant 0$ a.e. on $\mathbb{R}^3$ and $\theta \geqslant 0$. Note that the Ekeland condition (60) also reads

$$-\frac{1}{2}\operatorname{div}\left(\left(1+\frac{\partial h}{\partial \kappa}\big(\rho_{\phi_n}, |\nabla\phi_n|^2\big)\right)\nabla\phi_n\right)+\left(V+\rho_{\phi_n}\star|\mathbf{r}|^{-1}+\frac{\partial h}{\partial\rho}\big(\rho_{\phi_n}, |\nabla\phi_n|^2\big)\right)\phi_n+\theta_n\phi_n=\eta_n$$
$$\text{with } \eta_n \xrightarrow[n\to 0]{} 0 \text{ in } H^{-1}\big(\mathbb{R}^3\big). \tag{66}$$

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

Lemma 10. *Consider $(\phi_n)_{n\in\mathbb{N}}$ satisfying* (58)–(65). *Then, using the terminology introduced in the concentration-compactness lemma in* [20],

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 $2 \leqslant p < 6$;*
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 $2 \leqslant p < 6$. It follows that ϕ is a minimizer to (52).

Proof of the first two assertions of Lemma 10. 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

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

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

$$\lim_{k\to\infty}\int\limits_{\mathbb{R}^3}\phi_{n_k}^2 V = 0.$$

Hence

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

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 $L^2_{\mathrm{loc}}(\mathbb{R}^3)$, that

$$\int\limits_{\mathbb{R}^3}\phi^2 \geqslant \int\limits_{y+B_R}\phi^2 \geqslant \lambda-\epsilon,$$

where y is the limit of some converging subsequence of $(y_k)_{k\in\mathbb{N}}$. This implies that $\|\phi\|_{L^2}^2 = \lambda$, 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 $2 \leqslant p < 6$.

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 10. Let us first introduce two functions ξ and χ in $\mathcal{C}^\infty(\mathbb{R}^3)$ such that $0 \leqslant \xi, \chi \leqslant 1$, $\xi(x) = 1$ if $|x| \leqslant 1$, $\xi(x) = 0$ if $|x| \geqslant 2$, $\chi(x) = 0$ if $|x| \leqslant 1$, $\chi(x) = 1$ if $|x| \geqslant 2$, $\|\nabla\chi\|_{L^\infty} \leqslant 2$ and $\|\nabla\xi\|_{L^\infty} \leqslant 2$. For $R > 0$, we denote by $\xi_R(\cdot) = \xi(\frac{\cdot}{R})$ and $\chi_R(\cdot) = \chi(\frac{\cdot}{R})$.

Replacing $(\phi_n)_{n\in\mathbb{N}}$ with a subsequence and using the detailed construction of the dichotomy case given in [20], we can assume that in addition to (58)–(65), there exist

- $\delta \in]0, \lambda[$,
- 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

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

such that the sequences $\phi_{1,n} = \xi_{R_{1,n}}(\cdot - y_n)\phi_n$ and $\phi_{2,n=}\chi_{R_{2,n}/2}(\cdot - y_n)\phi_n$ satisfy

$$\begin{cases} \phi_n = \phi_{1,n} \quad \text{on } y_n + B_{R_{1,n}}, \\ \phi_n = \phi_{2,n} \quad \text{on } \mathbb{R}^3 \setminus (y_n + B_{R_{2,n}}), \\ \lim_{n\to\infty} \int_{\mathbb{R}^3} \phi_{1,n}^2 = \delta, \qquad \lim_{n\to\infty} \int_{\mathbb{R}^3} \phi_{2,n}^2 = \lambda - \delta, \\ \lim_{n\to\infty} \|\phi_n - (\phi_{1,n} + \phi_{2,n})\|_{L^p(\mathbb{R}^3)} = 0 \quad \text{for all } 2 \leqslant p < 6, \\ \lim_{n\to\infty} \|\phi_n\|_{L^p(y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}}))} = 0 \quad \text{for all } 2 \leqslant p < 6, \\ \lim_{n\to\infty} \operatorname{dist}(\operatorname{Supp}\phi_{1,n}, \operatorname{Supp}\phi_{2,n}) = \infty, \\ \liminf_{n\to\infty} \int_{\mathbb{R}^3} \left(|\nabla\phi_n|^2 - |\nabla\phi_{1,n}|^2 - |\nabla\phi_{2,n}|^2\right) \geqslant 0. \end{cases}$$

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

$$\forall n \in \mathbb{N}, \quad \phi_{1,n} \geqslant 0 \quad \text{and} \quad \phi_{2,n} \geqslant 0 \quad \text{a.e. on } \mathbb{R}^3. \tag{67}$$

A straightforward calculation leads to

$$\begin{aligned} E(\phi_n) = {} & E^\infty(\phi_{1,n}) + \int_{\mathbb{R}^3} \rho_{\phi_{1,n}} V + E^\infty(\phi_{2,n}) + \int_{\mathbb{R}^3} \rho_{\phi_{2,n}} V + \int_{\mathbb{R}^3} \left(|\nabla\phi_n|^2 - |\nabla\phi_{1,n}|^2 - |\nabla\phi_{2,n}|^2\right) + \int_{\mathbb{R}^3} \widetilde{\rho}_n V \\ & + D(\rho_{\phi_{1,n}}, \rho_{\phi_{2,n}}) + D(\widetilde{\rho}_n, \rho_{\phi_{1,n}} + \rho_{\phi_{2,n}}) + \frac{1}{2} D(\widetilde{\rho}_n, \widetilde{\rho}_n) \\ & + \int_{\mathbb{R}^3} \left(h\left(\rho_{\phi_n}, |\nabla\phi_n|^2\right) - h\left(\rho_{\phi_{1,n}}, |\nabla\phi_{1,n}|^2\right) - h\left(\rho_{\phi_{2,n}}, |\nabla\phi_{2,n}|^2\right)\right), \end{aligned} \tag{68}$$

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

$$|\widetilde{\rho}_n| \leqslant 3\mathbb{1}_{y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}})} |\phi_n|^2,$$

where $\mathbb{1}_{y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}})}$ is the characteristic function of $y_n + (B_{R_{2,n}} \setminus \overline{B}_{R_{1,n}})$, the sequence $(\widetilde{\rho}_n)_{n\in\mathbb{N}}$ goes to zero in $L^p(\mathbb{R}^3)$ for all $1 \leqslant p < 3$, yielding

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

Besides,

$$D(\rho_{\phi_{1,n}}, \rho_{\phi_{2,n}}) \leqslant 4 \operatorname{dist}(\operatorname{Supp}\phi_{1,n}, \operatorname{Supp}\phi_{2,n})^{-1} \|\phi_{1,n}\|_{L^2}^2 \|\phi_{2,n}\|_{L^2}^2 \xrightarrow[n\to\infty]{} 0$$

and

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

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

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

It therefore follows from (68) 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

$$J_\lambda \geqslant J_\delta + J_{\lambda-\delta}^\infty \quad \text{(case 1)} \quad \text{or} \quad J_\lambda \geqslant J_\delta^\infty + J_{\lambda-\delta} \quad \text{(case 2)}. \tag{69}$$

As the opposite inequalities are always satisfied, we obtain

$$J_\lambda = J_\delta + J_{\lambda-\delta}^\infty \quad \text{(case 1)} \quad \text{or} \quad J_\lambda = J_\delta^\infty + J_{\lambda-\delta} \quad \text{(case 2)} \tag{70}$$

and (still up to extraction)

$$\begin{cases} \lim\limits_{n\to\infty} E(\phi_{1,n}) = J_\delta, \\ \lim\limits_{n\to\infty} E^\infty(\phi_{2,n}) = J_{\lambda-\delta}^\infty \end{cases} \quad \text{(case 1)} \quad \text{or} \quad \begin{cases} \lim\limits_{n\to\infty} E^\infty(\phi_{1,n}) = J_\delta^\infty, \\ \lim\limits_{n\to\infty} E(\phi_{2,n}) = J_{\lambda-\delta} \end{cases} \quad \text{(case 2)}. \tag{71}$$

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 (66) as

$$-\operatorname{div}(a_n \nabla\phi_n) + V\phi_n + \left(\rho_{\phi_n} \star |\mathbf{r}|^{-1}\right)\phi_n + V_n^- \phi_n^{1+2\beta_-} + V_n^+ \phi_n^{1+2\beta_+} + \theta_n\phi_n = \eta_n \tag{72}$$

where

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

Due to assumption (32), V_n^- and V_n^+ are bounded in $L^\infty(\mathbb{R}^3)$.

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 (72) 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 $0 \leqslant e_n \leqslant 1$ 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

$$0 < \frac{a}{2} \leqslant a_n = \frac{1}{2}\left(1 + \frac{\partial h}{\partial \kappa}\left(\rho_{\phi_n}, |\nabla\phi_n|^2\right)\right) \leqslant \frac{b}{2} < \infty \quad \text{a.e. on } \mathbb{R}^3 \tag{73}$$

and $0 \leqslant e_n^2 \leqslant e_n \leqslant 1$, 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 $L^2(\mathbb{R}^3)$. Plugging this information in (72) 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

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

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 ϕ_1 and ϕ_2 weakly in $H^1(\mathbb{R}^3)$, strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for all $2\leqslant p<6$ and a.e. in $\mathbb{R}^3$. In virtue of (67), we also have $\phi_1\geqslant 0$ and $\phi_2\geqslant 0$ a.e. on $\mathbb{R}^3$. To pass to the limit in the above equations, we use a H-convergence result proved in Appendix A (Lemma 11). The sequence $(a_n)_{n\in\mathbb{N}}$ satisfying (73), there exists $a_\infty\in L^\infty(\mathbb{R}^3)$ such that $\frac{a}{2}\leqslant a_\infty\leqslant\frac{b^2}{2a}$ and (up to extraction) $a_nI_3\rightharpoonup_H a_\infty I_3$ (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 $j\in[\![1,2]\!]$ (and up to extraction)

$$\begin{cases} V\phi_{j,n}\xrightarrow[n\to\infty]{}V\phi_j\quad\text{strongly in }H^{-1}(\mathbb{R}^3),\\ V_n^\pm\phi_{j,n}^{1+2\beta_\pm}\underset{n\to\infty}{\rightharpoonup}V^\pm\phi_j^{1+2\beta_\pm}\quad\text{weakly in }L^2_{\mathrm{loc}}(\mathbb{R}^3),\\ \left(\rho_{\phi_{j,n}}\star|\mathbf{r}|^{-1}\right)\phi_{j,n}+\theta_n\phi_{j,n}\xrightarrow[n\to\infty]{}\left(\rho_{\phi_j}\star|\mathbf{r}|^{-1}\right)\phi_j+\theta\phi_j\quad\text{strongly in }L^2_{\mathrm{loc}}(\mathbb{R}^3).\end{cases}$$

We end up, for $j\in[\![1,2]\!]$, with

$$-\operatorname{div}(a_\infty\nabla\phi_j)+V\phi_j+\left(\rho_{\phi_j}\star|\mathbf{r}|^{-1}\right)\phi_j+V^-\phi_j^{1+2\beta_-}+V^+\phi_j^{1+2\beta_+}+\theta\phi_j=0.\tag{74}$$

Remark 5. The elliptic operator involved in Eq. (72) being monotone, it appears that we could also pass to the limit using Leray–Lions theory instead of H-convergence. Since we are not interested in the very precise structure of the limit equation, we chose not to follow that way.

By classical elliptic regularity arguments already stated in the proof of Lemma 9, both ϕ_1 and ϕ_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 ϕ_1 and ϕ_2 is different from zero. Indeed, if both ϕ_1 and ϕ_2 were equal to zero, then we would have $\phi=0$, an eventuality that we have already excluded in the proof of the first two assertions of Lemma 10. On the other hand, as $\operatorname{dist}(\operatorname{Supp}\phi_{1,n},\operatorname{Supp}\phi_{2,n})\to\infty$, at least one of the functions ϕ_1 and ϕ_2 is equal to zero.

We only consider here the case when $\phi_2=0$, corresponding to case 1 in (69)–(71), since the other case can be dealt with the same arguments. A key point of the proof consists in noticing, as in the proof of Lemma 9, that applying Lemma 12 to (74) (note that $W=V^-\phi_1^{\beta_-}+V^+\phi_1^{\beta_+}$ is non-positive and goes to zero at infinity) yields

$$\theta>0.\tag{75}$$

Consider now the sequence $(\widetilde{\phi}_{1,n})_{n\in\mathbb{N}}$ defined by $\widetilde{\phi}_{1,n}=\delta^{\frac12}\phi_{1,n}\|\phi_{1,n}\|_{L^2}^{-1}$. It is easy to check that

$$\begin{cases}\forall n\in\mathbb{N},\quad\widetilde{\phi}_{1,n}\in H^1(\mathbb{R}^3),\quad\displaystyle\int_{\mathbb{R}^3}\widetilde{\phi}_{1,n}^2=\delta\quad\text{and}\quad\widetilde{\phi}_{1,n}\geqslant 0\quad\text{a.e. on }\mathbb{R}^3,\\ \displaystyle\lim_{n\to+\infty}E(\widetilde{\phi}_{1,n})=J_\delta,\\ -\operatorname{div}(a_{1,n}\nabla\widetilde{\phi}_{1,n})+V\widetilde{\phi}_{1,n}+\left(\rho_{\widetilde{\phi}_{1,n}}\star|\mathbf{r}|^{-1}\right)\widetilde{\phi}_{1,n}+V_{1,n}^-\widetilde{\phi}_{1,n}^{1+2\beta_-}+V_{1,n}^+\widetilde{\phi}_{1,n}^{1+2\beta_+}+\theta_n\widetilde{\phi}_{1,n}\xrightarrow[n\to\infty]{H^{-1}}0,\\ (\widetilde{\phi}_{1,n})_{n\in\mathbb{N}}\text{ converges to }\widetilde{\phi}_1\neq 0\text{ weakly in }H^1,\text{ strongly in }L^p_{\mathrm{loc}}\text{ for }2\leqslant p<6\text{ and a.e. on }\mathbb{R}^3\end{cases}$$

(with in fact $\widetilde{\phi}_1=\phi$). Likewise, the sequence $((\lambda-\delta)^{\frac12}\|\phi_{2,n}\|_{L^2}^{-1}\phi_{2,n})_{n\in\mathbb{N}}$ being a minimizing sequence for $J^\infty_{\lambda-\delta}$, 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 $\int_{x_n+B_R}|\phi_{2,n}|^2\geqslant\gamma$. Then, defining $\widetilde{\phi}_{2,n}=(\lambda-\delta)^{\frac12}\|\phi_{2,n}\|_{L^2}^{-1}\phi_{2,n}(\cdot-x_n)$,

$$\begin{cases}\forall n\in\mathbb{N},\quad\widetilde{\phi}_{2,n}\in H^1(\mathbb{R}^3),\quad\displaystyle\int_{\mathbb{R}^3}\widetilde{\phi}_{2,n}^2=\lambda-\delta\quad\text{and}\quad\widetilde{\phi}_{2,n}\geqslant 0\quad\text{a.e. on }\mathbb{R}^3,\\ \displaystyle\lim_{n\to+\infty}E^\infty(\widetilde{\phi}_{2,n})=J^\infty_{\lambda-\delta},\\ -\operatorname{div}(a_{2,n}\nabla\widetilde{\phi}_{2,n})+\left(\rho_{\widetilde{\phi}_{2,n}}\star|\mathbf{r}|^{-1}\right)\widetilde{\phi}_{2,n}+V_{2,n}^-\widetilde{\phi}_{2,n}^{1+2\beta_-}+V_{2,n}^+\widetilde{\phi}_{2,n}^{1+2\beta_+}+\theta_n\widetilde{\phi}_{2,n}\xrightarrow[n\to\infty]{H^{-1}}0,\\ (\widetilde{\phi}_{2,n})_{n\in\mathbb{N}}\text{ converges to }\widetilde{\phi}_2\neq 0\text{ weakly in }H^1,\text{ strongly in }L^p_{\mathrm{loc}}\text{ for }2\leqslant p<6\text{ and a.e. on }\mathbb{R}^3.\end{cases}$$

It is important to note that the sequences $(a_{j,n})_{n\in\mathbb{N}}$ and $(V^{\pm}_{j,n})_{n\in\mathbb{N}}$ for $j \in [\![1,2]\!]$, which we do not detail for their exact expression is not of use, are such that

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

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 these sequences cannot vanish, they are either compact or split 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 $k \in \mathbb{N}$

$$\begin{cases} \forall n \in \mathbb{N}, \quad \widetilde{\psi}_{k,n} \in H^1(\mathbb{R}^3), \quad \displaystyle\int_{\mathbb{R}^3} \widetilde{\psi}^2_{k,n} = \delta_k \quad \text{and} \quad \widetilde{\psi}_{k,n} \geqslant 0 \quad \text{a.e. on } \mathbb{R}^3, \\ -\operatorname{div}(\widetilde{a}_{k,n}\nabla\widetilde{\psi}_{k,n}) + (\rho_{\widetilde{\psi}_{k,n}} \star |\mathbf{r}|^{-1})\widetilde{\psi}_{k,n} + \widetilde{V}^-_{k,n}\widetilde{\psi}^{1+2\beta_-}_{k,n} + \widetilde{V}^+_{k,n}\widetilde{\psi}^{1+2\beta_+}_{k,n} + \theta_n\widetilde{\psi}_{k,n} \xrightarrow[n\to\infty]{H^{-1}} 0, \\ (\widetilde{\psi}_{k,n})_{n\in\mathbb{N}} \text{ converges to } \widetilde{\psi}_k \neq 0 \text{ weakly in } H^1, \text{ strongly in } L^p_{\text{loc}} \text{ for } 2 \leqslant p < 6 \text{ and a.e. on } \mathbb{R}^3, \end{cases}$$

with

$$\sum_{k\in\mathbb{N}} \delta_k \leqslant \lambda, \tag{76}$$

and $\forall k \in \mathbb{N}$, $\forall n \in \mathbb{N}$,

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

Using Lemma 11 to pass to the limit with respect to n in the equation satisfied by $\widetilde{\psi}_{k,n}$, we obtain

$$-\operatorname{div}(\widetilde{a}_k\nabla\widetilde{\psi}_k) + (\rho_{\widetilde{\psi}_k} \star |\mathbf{r}|^{-1})\widetilde{\psi}_k + \widetilde{V}^-_k\widetilde{\psi}^{1+2\beta_-}_k + \widetilde{V}^+_k\widetilde{\psi}^{1+2\beta_+}_k + \theta\widetilde{\psi}_k = 0, \tag{77}$$

with

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

Besides, we infer from (76) that $\sum_{k\in\mathbb{N}} \|\widetilde{\psi}_k\|^2_{L^2} \leqslant \lambda$, hence that

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

It then easily follows from (77) that

$$\lim_{k\to\infty} \|\operatorname{div}(\widetilde{a}_k\nabla\widetilde{\psi}_k)\|_{L^2} = 0.$$

We can now make use of the elliptic regularity result [11] (see also the proof of Lemma 13) stating that there exists a constant C, depending only on the positive constants a and b, such that for all $k \in \mathbb{N}$

$$\|\widetilde{\psi}_k\|_{L^\infty} \leqslant C(\|\widetilde{\psi}_k\|_{L^2} + \|\operatorname{div}(\widetilde{a}_k\nabla\widetilde{\psi}_k)\|_{L^2})$$

and obtain

$$\lim_{k\to\infty} \|\widetilde{\psi}_k\|_{L^\infty} = 0.$$

Lastly, we deduce from (77) that

$$\theta\|\widetilde{\psi}_k\|^2_{L^2} \leqslant C(\|\widetilde{\psi}_k\|^{2\beta_-}_{L^\infty} + \|\widetilde{\psi}_k\|^{2\beta_+}_{L^\infty})\|\widetilde{\psi}_k\|^2_{L^2}.$$

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

$$\theta \leqslant C(\|\widetilde{\psi}_k\|^{2\beta_-}_{L^\infty} + \|\widetilde{\psi}_k\|^{2\beta_+}_{L^\infty}) \xrightarrow[k\to\infty]{} 0,$$

which obviously contradicts (75). We therefore conclude from this analysis that, if dichotomy occurs, $(\phi_n)_{n\in\mathbb{N}}$ splits in a finite number, say K, of compact bits having mass $\delta_k > 0$ with $\sum_{k=1}^{K} \delta_k = \lambda$. We are now going to prove that this cannot be.

If this was the case, there would exist two sequences $(u_{1,n})_{n\in\mathbb{N}}$ and $(u_{2,n})_{n\in\mathbb{N}}$ such that

$$\begin{cases} \forall n \in \mathbb{N}, \quad u_{1,n} \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} |u_{1,n}|^2 = \delta_1, \quad u_1 \geqslant 0 \quad \text{a.e. on } \mathbb{R}^3, \\ \lim_{n\to\infty} E(u_{1,n}) = J_{\delta_1} \end{cases}$$

and

$$\begin{cases} \forall n \in \mathbb{N}, \quad u_{2,n} \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} |u_{2,n}|^2 = \delta_2, \quad u_2 \geqslant 0 \quad \text{a.e. on } \mathbb{R}^3, \\ \lim_{n\to\infty} E^\infty(u_{2,n}) = J_{\delta_2} \end{cases}$$

and converging weakly in $H^1(\mathbb{R}^3)$ to u_1 and u_2 respectively, with $\|u_1\|_{L^2}^2 = \delta_1$ and $\|u_2\|_{L^2}^2 = \delta_2$ (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 8 that u_1 and u_2 are minimizers for J_{δ_1} and $J_{\delta_2}^\infty$, and from Lemma 9 that $J_{\delta_1+\delta_2} < J_{\delta_1} + J_{\delta_2}^\infty$.

Applying (70) twice, we also have $J_\lambda = J_{\delta_1} + J_{\delta_2}^\infty + J_{\lambda-\delta_1-\delta_2}^\infty$, so that we infer $J_\lambda > J_{\delta_1+\delta_2} + J_{\lambda-\delta_1-\delta_2}^\infty$ which is a contradiction to Lemma 1. □

End of the proof of Lemma 10. As a consequence of the concentration-compactness lemma and of the first three assertions of Lemma 10, 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 $2 \leqslant p < 6$. In particular,

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

It follows from Lemma 8 that ϕ is a minimizer to (52). □

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Appendix A

In this appendix, we state 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 $-\operatorname{div}(A\nabla\cdot)$. 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 $0 < \lambda \leqslant \Lambda < \infty$, we denote by $M^s(\lambda, \Lambda, \Omega)$ the closed convex subset of $L^\infty(\Omega, \mathbb{R}^{3\times 3})$ consisting of the symmetric matrix fields $A \in L^\infty(\Omega, \mathbb{R}^{3\times 3})$ such that for almost all $x \in \Omega$,

$$\lambda \leqslant A(x) \leqslant \Lambda.$$

The first lemma is a H-convergence result which allows to pass to the limit in the Ekeland condition (66). We shall not give the proof, for it is very similar to the proofs that can be found in the original article by Murat and Tartar [21]. Recall that a sequence $(A_n)_{n\in\mathbb{N}}$ of elements of $M^s(\lambda, \Lambda, \Omega)$ is said to H-converge to some $A \in M^s(\lambda', \Lambda', \Omega)$, which is denoted by $A_n \rightharpoonup_H A$, if for every $\omega \Subset \Omega$ the following property holds: $\forall f \in H^{-1}(\omega)$, the sequence $(u_n)_{n\in\mathbb{N}}$ of the elements of $H_0^1(\omega)$ such that $-\operatorname{div}(A_n \nabla u_n) = f|_\omega$ in $H^{-1}(\omega)$, satisfies

$$\begin{cases} u_n \rightharpoonup u \quad \text{weakly in } H_0^1(\omega), \\ A_n \nabla u_n \rightharpoonup A\nabla u \quad \text{weakly in } L^2(\omega) \end{cases}$$

where u is the solution in $H_0^1(\omega)$ to $-\operatorname{div}(A\nabla u) = f|_\omega$. It is known [21] that from any bounded sequence $(A_n)_{n\in\mathbb{N}}$ in $M^s(\lambda, \Lambda, \Omega)$ one can extract a subsequence which H-converges to some $A \in M^s(\lambda, \lambda^{-1}\Lambda^2, \Omega)$.

Lemma 11. *Let Ω be an open subset of $\mathbb{R}^3$, $0 < \lambda \leqslant \Lambda < \infty$, $0 < \lambda' \leqslant \Lambda' < \infty$, and $(A_n)_{n\in\mathbb{N}}$ a sequence of elements of $M^s(\lambda, \Lambda, \Omega)$ which H-converges to some $A \in M^s(\lambda', \Lambda', \Omega)$. 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*

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

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

The second lemma is an extension of [19, Lemma II.1] and of a classical result on the ground state of Schrödinger operators [28]. Recall that

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

Lemma 12. *Let $0 < \lambda \leqslant \Lambda < \infty$, $A \in M^s(\lambda, \Lambda, \mathbb{R}^3)$, $W \in L^2(\mathbb{R}^3) + L^\infty_\epsilon(\mathbb{R}^3)$ 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,*

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

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

$$D(H) = \{u \in H^1(\mathbb{R}^3) \mid \operatorname{div}(A\nabla u) \in L^2(\mathbb{R}^3)\}.$$

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, $\sigma_{\mathrm{ess}}(H) \subset [0, \infty)$ 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 $w \geqslant 0$ 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 13. *Let $0 < \lambda \leqslant \Lambda < \infty$, $A \in M^s(\lambda, \Lambda, \mathbb{R}^3)$, $\mathcal{V}$ a function of $L^{\frac{6}{5}}_{\mathrm{loc}}(\mathbb{R}^3)$ which vanishes at infinity, $\theta > 0$ and $u \in H^1(\mathbb{R}^3)$ such that*

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

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

Proof of Lemma 12. 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 $D(H_0) = \{u \in H^1(\mathbb{R}^3) \mid \operatorname{div}(A\nabla u) \in L^2(\mathbb{R}^3)\}$ and that $\forall u \in D(H_0)$,

$H_0 u = -\operatorname{div}(A\nabla u)$. Using classical elliptic regularity results [11], we obtain that there exist two constants $0 < \alpha < 1$ and $C \in \mathbb{R}_+$ (depending on λ and Λ) such that for all regular bounded domains $\Omega \Subset \mathbb{R}^3$, and all $v \in H^1(\Omega)$ such that $\operatorname{div}(A\nabla v) \in L^2(\Omega)$,

$$\|v\|_{C^{0,\alpha}(\overline{\Omega})} := \sup_{\Omega}|v| + \sup_{(\mathbf{r},\mathbf{r}')\in\Omega\times\Omega} \frac{|v(\mathbf{r}) - v(\mathbf{r}')|}{|\mathbf{r}-\mathbf{r}'|^\alpha} \leqslant C\big(\|v\|_{L^2(\Omega)} + \big\|\operatorname{div}(A\nabla v)\big\|_{L^2(\Omega)}\big).$$

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

$$\forall u \in D(H_0), \quad \|u\|_{L^\infty(\mathbb{R}^3)} + \sup_{(\mathbf{r},\mathbf{r}')\in\mathbb{R}^3\times\mathbb{R}^3} \frac{|v(\mathbf{r}) - v(\mathbf{r}')|}{|\mathbf{r}-\mathbf{r}'|^\alpha} \leqslant C\big(\|u\|_{L^2} + \|H_0 u\|_{L^2}\big), \tag{78}$$

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:

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

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 $\|\mathcal{W}_\infty\|_{L^\infty} \leqslant \epsilon$ and $\mathcal{W} = \mathcal{W}_2 + \mathcal{W}_\infty$. On the one hand, $\|\mathcal{W}_\infty(u_n - u)\|_{L^2} \leqslant 2\epsilon \sup_{n\in\mathbb{N}}\|u_n\|_{H_0}$, 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 (78) 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 form an increasing sequence converging to zero. First, H is bounded below since for all $v \in D(H)$ such that $\|v\|_{L^2} = 1$,

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

In order to prove that H has at least N negative eigenvalues, including multiplicities, first notice that we have

$$H \leqslant -\Lambda\Delta + V + \mu \star |\mathbf{r}|^{-1} + W_+ \tag{79}$$

with $W_+ \in L^2(\mathbb{R}^3) + L^3(\mathbb{R}^3)$. It is proven in [19, Lemma II.1] that the operator in the right-hand side of (79) has infinitely many eigenvalues including multiplicities. Therefore by the minimax principle, H also has infinitely many negative eigenvalues, including multiplicities.

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

$$\mu_1 = \inf\left\{ \int_{\mathbb{R}^3} A\nabla u \cdot \nabla u + \int_{\mathbb{R}^3} \mathcal{W}|u|^2,\ u \in H^1(\mathbb{R}^3),\ \|u\|_{L^2} = 1 \right\}, \tag{80}$$

and the minimizers of (80) are exactly the set of the normalized eigenvectors of H associated with μ_1. Let u_1 be a minimizer (80). As for all $u \in H^1(\mathbb{R}^3)$, $|u| \in H^1(\mathbb{R}^3)$ and $\nabla|u| = \operatorname{sgn}(u)\nabla u$ a.e. on $\mathbb{R}^3$, $|u_1|$ also is a minimizer to (80). Up to replacing u_1 with $|u_1|$, there is therefore no restriction in assuming that $u_1 \geqslant 0$ on $\mathbb{R}^3$. We thus have

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

with $g = \mathcal{W} - \mu_1 \in L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for some $p > \frac{3}{2}$ (take $p = 2$). A Harnack-type inequality due to Stampacchia [30] 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 $\mathbb{R}^3$. Using classical arguments (see e.g. [28]), it is then not difficult to prove that μ_1 is simple. The proof of the third assertion of the lemma then is straightforward. □

Proof of Lemma 13. Consider $R > 0$ large enough to ensure that $\frac{\theta}{2} \leqslant \mathcal{V}(\mathbf{r}) + \theta \leqslant \frac{3\theta}{2}$ 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

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

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

$$\begin{cases} -\operatorname{div}(A\nabla w) + \mathcal{V}w + \theta w = \operatorname{div}(A\nabla\tilde{u}) - \mathcal{V}\tilde{u} - \theta\tilde{u} & \text{in } B_R^c, \\ w = 0 & \text{on } \partial B_R. \end{cases} \tag{81}$$

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

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

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

$$\begin{aligned} &\int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla w \cdot e^{\gamma|\mathbf{r}|}\nabla\phi + 2\gamma \int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla w \cdot \frac{\mathbf{r}}{|\mathbf{r}|} e^{\gamma|\mathbf{r}|}\phi + \int_{B_R^c} (\mathcal{V} + \theta) e^{\gamma|\mathbf{r}|} w e^{\gamma|\mathbf{r}|}\phi \\ &\quad = -\int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla\tilde{u} \cdot e^{\gamma|\mathbf{r}|}\nabla\phi - 2\gamma \int_{B_R^c} A e^{\gamma|\mathbf{r}|}\nabla\tilde{u} \cdot \frac{\mathbf{r}}{|\mathbf{r}|} e^{\gamma|\mathbf{r}|}\phi - \int_{B_R^c} (\mathcal{V} + \theta) e^{\gamma|\mathbf{r}|}\tilde{u} e^{\gamma|\mathbf{r}|}\phi. \end{aligned} \tag{82}$$

Due to the definitions of $W_0^\gamma(B_R^c)$ and $\tilde{u}$, (82) 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 (82) is a variational formulation equivalent to (81). It is also easy to check that the right-hand side in (82) 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 (82) to be able to apply Lax–Milgram lemma. We have for $v \in W_0^\gamma(B_R^c)$

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

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 (81) 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 $e^{\gamma|\cdot|}u \in H^1(\mathbb{R}^3)$. □

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