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EXISTENCE OF A TYPE OF OPTIMAL NORM-CONSERVING PSEUDOPOTENTIALS FOR KOHN–SHAM MODELS*

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Abstract. In this article, we clarify the mathematical framework underlying the construction of norm-conserving semilocal pseudopotentials for Kohn–Sham models, and prove the existence of optimal pseudopotentials for a family of optimality criteria. Most of our results are proved for the Hartree (also called reduced Hartree–Fock) model, obtained by setting the exchange-correlation energy to zero in the Kohn–Sham energy functional. Extensions to the Kohn–Sham LDA (local density approximation) model are discussed.

Key words. Density functional theory, self-consistent-field methods, Kohn–Sham model, pseudopotential, perturbation theory.

AMS subject classifications. 35Q40, 35Q55, 47H14, 81Q15.

1. Introduction

It is a well-known theoretical and experimental fact that the core electrons of an atom are hardly affected by the chemical environment experienced by this atom. Pseudopotential methods are efficient model reduction techniques relying on this observation, which are widely used in electronic structure calculation, especially in solid state physics and materials science, as well as for the simulation of molecular systems containing heavy atoms. In pseudopotential methods, the original all-electron model is replaced by a reduced model explicitly dealing with valence electrons only, while core electrons are frozen in some reference state. The valence electrons are described by valence pseudo-orbitals, and the interaction between the valence electrons and the ionic cores (an ionic core consists of a nucleus and of the associated core electrons) is modeled by a nonlocal operator called a pseudopotential, constructed once and for all from single-atom reference calculations. The reduction of dimensionality obtained by eliminating the core electrons from the explicit calculation results in a much less computationally expensive approach. The pseudopotential has the property that, for isolated atoms, the valence pseudo-orbitals differ from the valence orbitals in the vicinity of the nucleus, *i.e.* in the so-called core region, but coincide with the valence orbitals out of the core region, *i.e.* in the region where the influence of the chemical environment is important. In addition to the reduction of dimensionality mentioned above, an advantage of pseudopotential models is that pseudopotentials are constructed in such a way that the valence pseudo-orbitals oscillate much less than the valence orbitals in the core region, hence can be approximated using smaller planewave bases, or discretized on coarser grids. In addition, pseudopotentials can be used to incorporate relativistic effects in non-relativistic calculations. This is of major interest for the simulation of heavy atoms with relativistic core electrons. While pseudopotentials are constructed from single-atom calculations only, they are meant to be used in the simulation of molecular systems. The ability of a pseudopotential to provide accurate results for a large variety of molecular systems

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and simulation settings (high temperature or pressure, charge transfer, bond breaking, ionization, etc.) is called its transferability.

The concept of pseudopotential was first introduced by Hellmann [14] as early as in 1934. Several variants of the pseudopotential method were then developed over the years. Let us mention in particular Kerker's pseudopotentials [17], Troullier–Martins [28] and Kleinman–Bylander [18] norm-conserving pseudopotentials, Vanderbilt ultrasoft pseudopotentials [29], and Goedecker pseudopotentials [10]. Blochl's projected augmented wave (PAW) method [3] can also be interpreted, to some extend, as a pseudopotential method. Although existing pseudopotential methods can be justified by convincing chemical arguments and work satisfactorily in practice, they are obtained by ad hoc procedures, so that the error introduced by the pseudopotential approximation is difficult to quantify *a priori*.

The purpose of this article is to clarify the mathematical framework underlying the construction of semilocal norm-conserving pseudopotentials for Kohn–Sham calculations, and to prove the existence of optimal pseudopotentials for a natural family of optimality criteria. We focus here on theoretical issues; the practical interest of this approach will be investigated in future works. In Section 2, we recall the mathematical structures of all-electron and norm-conserving pseudopotential Kohn–Sham models. In Section 3.2, we provide some results on the spectra of Hartree Hamiltonians for neutral atoms upon which the construction of pseudopotentials is based. Recall that the Hartree model is obtained from the exact Kohn–Sham model by discarding the exchange-correlation energy functional. We then define and analyze in sections 3.3 to 3.5 sets of semilocal norm-conserving pseudopotentials satisfying all the requested properties (listed in Section 3.5), leaving aside transferability issues. These sets of admissible pseudopotentials, denoted by $\mathcal{M}_{z,\Delta E,r_c,s}$, depend on four pieces of data: (i) the atomic number z of the atom, (ii) an energy window $\Delta E=(E_-,E_+)\subset\mathbb{R}_-$ defining a partition between core and valence electrons, (iii) the radius r_c of the core region, (iv) a Sobolev exponent s characterizing the way the regularity of the pseudopotential, hence of the valence pseudo-orbitals, is measured. We prove that, at least for most atoms of the first four rows (see Remark 3.4), there exists an energy window ΔE and a critical cut-off radius $r^0_{z,\Delta E,c}$ such that for all $r_c>r^0_{z,\Delta E,c}$ and all $s>0$, the set $\mathcal{M}_{z,\Delta E,r_c,s}$ is not empty and has nice topological properties.

After establishing in Section 3.6 some stability results of the Hartree ground state with respect to both external perturbations and small variations of the pseudopotential, we propose in Section 3.7 a new way to construct pseudopotentials, consisting of choosing the best candidate in some set $\mathcal{M}_{z,\Delta E,r_c,s}$ for a given optimality criterion, based on physical insight and balancing smoothness and transferability requirements. Many optimality criteria can be considered. We focus here in particular on a specific one involving the response of the isolated atom to an external uniform electric field (Stark effect). Most of our results are concerned with the Hartree model. Extensions to the LDA (local density approximation) model are discussed in Section 4. All the proofs are collected in Section 5, and a list of the main symbols used throughout the article is given in Appendix.

2. Kohn–Sham models

Throughout this article, we use atomic units, in which $\hbar=1$, $m_e=1$, $e=1$, and $4\pi\epsilon_0=1$, where $\hbar$ is the reduced Planck constant, m_e the electron mass, e the elementary charge, and ϵ_0 the dielectric permittivity of the vacuum. For simplicity, we only consider here restricted spin-collinear Kohn–Sham models (see [11] for a mathematical analysis of unrestricted and spin-noncollinear Kohn–Sham models) in which the diag-

onal components $\gamma^{\uparrow\uparrow}$ and $\gamma^{\downarrow\downarrow}$ of the spin-dependent density matrix are equal, and the off-diagonal components $\gamma^{\uparrow\downarrow}$ and $\gamma^{\downarrow\uparrow}$ are both equal to zero. A Kohn–Sham state can therefore be described by a density matrix

$$\gamma = \gamma^{\uparrow\uparrow} + \gamma^{\downarrow\downarrow} = 2\gamma^{\uparrow\uparrow} = 2\gamma^{\downarrow\downarrow}$$

satisfying the following properties:

- $\gamma \in \mathcal{S}(L^2(\mathbb{R}^3))$, where $\mathcal{S}(L^2(\mathbb{R}^3))$ denotes the space of the bounded self-adjoint operators on $L^2(\mathbb{R}^3)$;
- $0 \le \gamma \le 2$, which means $0 \le (\phi, \gamma\phi)_{L^2} \le 2\|\phi\|_{L^2}^2$ for all $\phi \in L^2(\mathbb{R}^3)$;
- $\mathrm{Tr}(\gamma)$ equals the number of electrons in the system.

As we do not consider here molecular models with magnetic fields, we can work in the space $L^2(\mathbb{R}^3)$ of *real-valued* square integrable functions on $\mathbb{R}^3$.

2.1. All electron Kohn–Sham models. Consider a molecular system with N electrons and K point-like nuclei of charges $Z = (z_1, \dots, z_K) \in \mathbb{N}^K$, located at positions $\mathbf{R} = (\mathbf{R}_1, \dots, \mathbf{R}_K) \in (\mathbb{R}^3)^K$. The Kohn–Sham ground state of the system is obtained by solving the minimization problem

$$I_{Z,\mathbf{R}} = \inf\{E_{Z,\mathbf{R}}(\gamma), \gamma \in \mathcal{K}_N\}, \tag{2.1}$$

where

$$E_{Z,\mathbf{R}}(\gamma) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta - \sum_{k=1}^{K} z_k |\cdot - \mathbf{R}_k|^{-1}\right)\gamma\right) + \frac{1}{2}D(\rho_\gamma, \rho_\gamma) + E_{\mathrm{xc}}(\rho_\gamma), \tag{2.2}$$

and

$$\mathcal{K}_N := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \,|\, 0 \le \gamma \le 2, \mathrm{Tr}(\gamma) = N, \mathrm{Tr}(-\Delta\gamma) < \infty\right\},$$

where $\mathrm{Tr}(-\Delta\gamma) := \mathrm{Tr}(|\nabla|\gamma|\nabla|)$, with $|\nabla| := (-\Delta)^{1/2}$. Recall that any $\gamma \in \mathcal{K}_N$ has a density $\rho_\gamma \in L^1(\mathbb{R}^3)$, defined by

$$\forall W \in L^\infty(\mathbb{R}^3), \quad \mathrm{Tr}(\gamma W) = \int_{\mathbb{R}^3} \rho_\gamma W,$$

which satisfies $\rho_\gamma \ge 0$ in $\mathbb{R}^3$ and $\sqrt{\rho}_\gamma \in H^1(\mathbb{R}^3)$, so that $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. In particular,

$$\mathrm{Tr}\left(\left(-\frac{1}{2}\Delta - \sum_{k=1}^{K} z_k |\cdot - \mathbf{R}_k|^{-1}\right)\gamma\right) = \frac{1}{2}\mathrm{Tr}(-\Delta\gamma) - \sum_{k=1}^{K} z_k \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|}\, d\mathbf{r},$$

where the second term of the right-hand side is well-defined by virtue of Hardy and Hoffmann-Ostenhof inequalities [15]

$$0 \le \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|}\, d\mathbf{r} \le 2N^{1/2}\|\nabla\sqrt{\rho}_\gamma\|_{L^2} \le 2N^{1/2}\mathrm{Tr}(-\Delta\gamma)^{1/2} < \infty.$$

The bilinear form $D(\cdot,\cdot)$ in (2.2) is the Coulomb interaction defined for all $(f,g) \in L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$ by

$$D(f,g) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{f(\mathbf{r})\, g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}'. \tag{2.3}$$

Lastly, the exchange-correlation energy functional $E_{\rm xc}$ depends on the Kohn–Sham model under consideration. We will restrict ourselves to two different Kohn–Sham models, namely the Hartree model, also called the reduced Hartree–Fock model, for which

$$E_{\rm xc}^{\rm Hartree}(\rho)=0,$$

and the Kohn–Sham LDA (local density approximation) model [19], for which

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

where for each $\overline{\rho}\in\mathbb{R}_+$, $\epsilon_{\rm xc}(\overline{\rho})\in\mathbb{R}_-$ is the exchange-correlation energy density of the homogeneous electron gas with uniform density $\overline{\rho}$. The function $\overline{\rho}\mapsto\epsilon_{\rm xc}(\overline{\rho})$ does not have a simple explicit expression, but it has the same mathematical properties as the exchange energy density of the homogeneous electron gas given by $\epsilon_{\rm x}(\overline{\rho})=-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\overline{\rho}^{4/3}$.

We are now going to recall some existence and uniqueness results for the Hartree model proved in [5, 25]. Although general results for neutral and positively charged molecular systems are available, we focus here on the case of a single neutral atom, which is of particular interest for the study of pseudopotentials. Weaker results have been obtained for the Kohn–Sham LDA model [1] (see also Section 4).

For convenience, we will call *atom z* the neutral atom with atomic number z.

PROPOSITION 2.1 (All-electron Hartree model for neutral atoms [5, 25]). *Let $z\in\mathbb{N}^*$. The all-electron Hartree model for atom z*

$$I_z^{\rm AA}:=\inf\left\{E_z^{\rm AA}(\gamma),\gamma\in\mathcal{K}_z\right\},\tag{2.4}$$

where

$$E_z^{\rm AA}(\gamma)=\mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right)-z\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r}|}\,d\mathbf{r}+\frac{1}{2}D\left(\rho_\gamma,\rho_\gamma\right),$$

has a minimizer γ_z^0, and all the minimizers of (2.4) share the same density ρ_z^0. In addition,

1. *the ground state density ρ_z^0 is a radial positive function belonging to $H^2(\mathbb{R}^3)\cap C^{0,1}(\mathbb{R}^3)\cap C^\infty(\mathbb{R}^3\setminus\{0\})$ (hence vanishing at infinity);*
2. *the Hartree Hamiltonian*

$$H_z^{\rm AA}=-\frac{1}{2}\Delta+W_z^{\rm AA},\quad \textit{where}\quad W_z^{\rm AA}=-\frac{z}{|\cdot|}+\rho_z^0\star|\cdot|^{-1},$$

is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and such that $\sigma_{\rm ess}(H_z^{\rm AA})=[0,+\infty)$;

3. *the minimizers γ_z^0 satisfy the first-order optimality condition*

$$\gamma_z^0=2\mathbb{1}_{(-\infty,\epsilon_{z,\rm F}^0)}(H_z^{\rm AA})+\delta,$$

where $\epsilon_{z,\rm F}^0\le 0$ is the Fermi level (that is the Lagrange multiplier of the constraint $\mathrm{Tr}(\gamma)=z$), and where δ is a finite-rank operator such that $0\le\delta\le 2$ and $\mathrm{Ran}(\delta)\subset\mathrm{Ker}(H_z^{\rm AA}-\epsilon_{z,\rm F}^0)$;

4. *if $\epsilon^0_{z,\mathrm{F}}$ is negative and is not an accidentally degenerate eigenvalue of H^{AA}_z, then the minimizer γ^0_z of (2.4) is unique.*

REMARK 2.2 (on the Fermi level). Consider, for each $j \in \mathbb{N}^*$, the real number

$$\varepsilon_{z,j} := \inf_{X_j \in \mathcal{X}_j} \sup_{\phi \in X_j \setminus \{0\}} \frac{\langle \phi | H^{\mathrm{AA}}_z | \phi \rangle}{\|\phi\|^2_{L^2}}, \tag{2.5}$$

where $\mathcal{X}_j$ is the set of the vector subspaces of $H^1(\mathbb{R}^3)$ of dimension j and $\langle \phi | H^{\mathrm{AA}}_z | \phi \rangle$ the quadratic form associated with the self-adjoint operator H^{AA}_z (whose form domain is $H^1(\mathbb{R}^3)$). According to the minmax principle [22, Theorem XIII.1], $\varepsilon_{z,j}$ is equal to the jth lowest eigenvalue of H^{AA}_z (counting multiplicities) if H^{AA}_z has at least j nonpositive eigenvalues (still counting multiplicities), and to $\min(\sigma_{\mathrm{ess}}(H^{\mathrm{AA}}_z)) = 0$ otherwise. If z is odd, then $\epsilon^0_{z,\mathrm{F}} = \varepsilon_{z,(z+1)/2}$. If z is even, that is if $z = 2N_{\mathrm{p}}$, where N_{p} is the number of electron pairs, two cases can be distinguished: if $\varepsilon_{z,N_{\mathrm{p}}} = \varepsilon_{z,N_{\mathrm{p}}+1}$, then $\epsilon^0_{z,\mathrm{F}} = \varepsilon_{z,N_{\mathrm{p}}}$, otherwise, any number in the interval $(\varepsilon_{z,N_{\mathrm{p}}}, \varepsilon_{z,N_{\mathrm{p}}+1})$ is an admissible Lagrange multiplier of the constraint $\mathrm{Tr}(\gamma) = z$.

REMARK 2.3 (on essential and accidental degeneracies). Let us clarify the meaning of the last statement of Proposition 2.1. The mean-field operator H^{AA}_z being invariant with respect to rotations, some of its eigenvalues may be degenerate. More precisely, all its eigenvalues corresponding to p, d, f, etc. shells (see Section 3.2) are degenerate, and only those corresponding to s shells are (in general) non-degenerate. Eigenvalue degeneracies due to symmetries are called essential. By contrast, eigenvalues degeneracies of H^{AA}_z which are not due to rotational symmetry are called accidental. For instance, the fact that the 2s and 2p shells of the Hamiltonian $H = -\frac{1}{2}\Delta - \frac{1}{|\cdot|}$ (hydrogen atom) both correspond to the eigenvalue $-1/8$ is an accidental degeneracy. We have checked numerically that $\epsilon^0_{z,\mathrm{F}}$ is negative and is not an accidentally degenerate eigenvalue for any $1 \le z \le 20$. On the other hand, for $z = 21$, $\epsilon^0_{z,\mathrm{F}}$ is very close or equal to zero (see [6]).

2.2. Kohn–Sham models with norm-conserving pseudopotentials. In pseudopotential calculations, the electrons of each chemical element are partitioned into two categories, core electrons on the one hand and valence electrons on the other hand, according to the procedure detailed in Section 3.4 below. We denote by $N_{z,\mathrm{c}}$ the number of core electrons in atom z, and by $N_{z,\mathrm{v}} = z - N_{z,\mathrm{c}}$ the number of valence electrons. Each chemical element is associated with a bounded nonlocal rotation-invariant self-adjoint operator V^{PP}_z, called the atomic pseudopotential, a core pseudo-density $\widetilde{\rho}^0_{z,\mathrm{c}} \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$, and a core energy $E_{z,\mathrm{c}} \in \mathbb{R}$ which will be precisely defined in Section 3.5. Only valence electrons are explicitly dealt with in pseudopotential calculations. For the molecular system considered in Section 2.1, the pseudopotential approximation of the ground state energy is given by

$$I^{\mathrm{PP}}_{Z,\mathbf{R}} = \inf\left\{ E^{\mathrm{PP}}_{Z,\mathbf{R}}(\widetilde{\gamma}), \widetilde{\gamma} \in \mathcal{K}_{N_{\mathrm{v}}} \right\} + \sum_{k=1}^{K} E_{z_k,\mathrm{c}}, \tag{2.6}$$

where

$$N_{\mathrm{v}} = N - \sum_{k=1}^{K} N_{z_k,\mathrm{c}}$$

is the total number of valence electrons in the system ($N_{\rm v} = \sum_{k=1}^{K} N_{z_k,v}$ if the system is electrically neutral). The Kohn–Sham pseudo-energy functional is

$$E^{\rm PP}_{Z,\mathbf{R}}(\widetilde{\gamma}) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + \sum_{k=1}^{K} \tau_{\mathbf{R}_k} V^{\rm PP}_{z_k} \tau_{-\mathbf{R}_k}\right)\widetilde{\gamma}\right) + \frac{1}{2} D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}) + E_{\rm xc}\left(\rho_{\widetilde{\gamma}} + \sum_{k=1}^{K} \tau_{\mathbf{R}_k}(\widetilde{\rho}^0_{z_k,\rm c})\right),$$

where for all $\mathbf{R} \in \mathbb{R}^3$, $\tau_{\mathbf{R}}$ is the translation operator defined on $L^2(\mathbb{R}^3)$ by $(\tau_{\mathbf{R}}\phi)(\mathbf{r}) = \phi(\mathbf{r}-\mathbf{R})$.

We will describe the precise nature of the atomic pseudopotentials $V^{\rm PP}_z$ in Section 3.5. Let us just mention at this stage that $V^{\rm PP}_z$ is a rotation-invariant operator of the form

$$V^{\rm PP}_z = V_{z,\rm loc} + \mathcal{V}_{z,\rm nl} \tag{2.7}$$

where $V_{z,\rm loc}$ and $\mathcal{V}_{z,\rm nl}$ are respectively the local and nonlocal parts of the pseudopotential operator $V^{\rm PP}_z$. The operator $V_{z,\rm loc}$ is a multiplication operator by a real-valued radial function $V_{z,\rm loc} \in L^2_{\rm loc}(\mathbb{R}^3)$ satisfying

$$V_{z,\rm loc}(\mathbf{r}) \underset{|\mathbf{r}|\to\infty}{\sim} -\frac{N_{z,\rm v}}{|\mathbf{r}|}. \tag{2.8}$$

The operator $\mathcal{V}_{z,\rm nl}$ is a $-\Delta$-compact, rotation-invariant, bounded self-adjoint operator on $L^2(\mathbb{R}^3)$ such that

$$\forall \phi \in L^2(\mathbb{R}^3), \quad \left(\text{ess-Supp}(\phi) \subset \mathbb{R}^3 \setminus \overline{B}_{r_{\rm c}}\right) \quad \Rightarrow \quad (\mathcal{V}_{z,\rm nl}\phi = 0), \tag{2.9}$$

where $r_{\rm c}$ is a positive real number (depending of z) called the core radius of atom z, and where $\overline{B}_{r_{\rm c}}$ is the closed ball of $\mathbb{R}^3$ centered at the origin, with radius $r_{\rm c}$.

The results below are straightforward extensions of the existence and uniqueness results established in [1, 5, 25]. We skip their proofs for brevity.

PROPOSITION 2.4 (Kohn–Sham models with norm-conserving pseudopotential). *Assume that the molecular system is neutral or positively charged, and that the atomic pseudopotentials satisfy (2.7)–(2.9). Then*

1. *the Hartree model (2.6) with $E_{\rm xc} = E^{\rm Hartree}_{\rm xc} = 0$ has a minimizer and all the minimizers share the same density;*
2. *the Kohn–Sham LDA model (2.6) with $E_{\rm xc} = E^{\rm LDA}_{\rm xc}$ has a minimizer.*

PROPOSITION 2.5 (Hartree model for neutral atoms and norm-conserving pseudopotentials). *Let $z \in \mathbb{N}^*$. If the atomic pseudopotential $V^{\rm PP}_z$ satisfies (2.7)–(2.9), then the Hartree model*

$$\inf\left\{E^{\rm PP}_z(\widetilde{\gamma}), \widetilde{\gamma} \in \mathcal{K}_{N_{z,\rm v}}\right\}, \tag{2.10}$$

where

$$E^{\rm PP}_z(\widetilde{\gamma}) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V^{\rm PP}_z\right)\widetilde{\gamma}\right) + \frac{1}{2} D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}),$$

has a minimizer $\widetilde{\gamma}^0_z$ and all the minimizers share the same density $\widetilde{\rho}^0_z$. In addition,

1. *the pseudo-density $\widetilde{\rho}_z^0$ is a radial positive function belonging to $H^2(\mathbb{R}^3)$ (hence vanishing at infinity);*
2. *the Hartree pseudo-Hamiltonian*

$$H_z^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_z^{\mathrm{PP}}, \quad \text{where} \quad W_z^{\mathrm{PP}} = V_z^{\mathrm{PP}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1}, \tag{2.11}$$

   corresponding to the pseudopotential V_z^{PP}, is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and such that $\sigma_{\mathrm{ess}}(H_z^{\mathrm{PP}}) = [0, +\infty)$;
3. *the minimizers $\widetilde{\gamma}_z^0$ satisfy the first-order optimality condition*

$$\widetilde{\gamma}_z^0 = 2\mathbb{1}_{(-\infty, \widetilde{\epsilon}_{z,\mathrm{F}}^0)}(H_z^{\mathrm{PP}}) + \widetilde{\delta},$$

   where $\widetilde{\epsilon}_{z,\mathrm{F}}^0 \leq 0$ the pseudo Fermi level (the Lagrange multiplier associated with the constraint $\mathrm{Tr}(\widetilde{\gamma}) = N_{z,\mathrm{v}}$), and where $\widetilde{\delta}$ is a finite-rank operator such that $0 \leq \widetilde{\delta} \leq 2$ and $\mathrm{Ran}(\widetilde{\delta}) \subset \mathrm{Ker}(H_z^{\mathrm{PP}} - \widetilde{\epsilon}_{z,\mathrm{F}}^0)$;
4. *if $\widetilde{\epsilon}_{z,\mathrm{F}}^0$ is negative and is not an accidentally degenerate eigenvalue of H_z^{PP}, then the minimizer $\widetilde{\gamma}_z^0$ of (2.4) is unique.*

REMARK 2.6. We will see later that for the class of pseudopotentials constructed in Section 3.5, the Fermi level $\epsilon_{z,\mathrm{F}}^0$ and the pseudo Fermi level $\widetilde{\epsilon}_{z,\mathrm{F}}^0$ can be chosen equal, and that if $\epsilon_{z,\mathrm{F}}^0$ is negative and is not an accidentally degenerate eigenvalue of H_z^{AA}, then $\widetilde{\epsilon}_{z,\mathrm{F}}^0$ is (obviously) negative and is not an accidentally degenerate eigenvalue of H_z^{PP}.

3. Analysis of norm-conserving semilocal pseudopotentials

In this section, we restrict ourselves to the Hartree model. Extensions to the Kohn–Sham LDA model are discussed in Section 4.

3.1. Atomic Hamiltonians and rotational invariance. In both all-electron and pseudopotential calculations, atomic Hartree Hamiltonians are self-adjoint operators on $L^2(\mathbb{R}^3)$ invariant with respect to rotations around the nucleus (assumed located at the origin). These operators are therefore block-diagonal in the decomposition of $L^2(\mathbb{R}^3)$ associated with the eigenspaces of the operator $\mathbf{L}^2$ (the square of the angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (-i\nabla)$). More precisely, the Hilbert space $L^2(\mathbb{R}^3)$ can be decomposed as the direct sum of the pairwise orthogonal subspaces $\mathcal{H}_l := \mathrm{Ker}(\mathbf{L}^2 - l(l+1))$:

$$L^2(\mathbb{R}^3) = \bigoplus_{l \in \mathbb{N}} \mathcal{H}_l. \tag{3.1}$$

It is convenient to introduce the spaces

$$L^2_{\mathrm{o}}(\mathbb{R}) = \left\{ f \in L^2(\mathbb{R}) \,|\, f(-r) = -f(r) \text{ a.e.} \right\}$$

(odd square integrable functions on $\mathbb{R}$) and

$$L^2_{\mathrm{r}}(\mathbb{R}^3) = \left\{ u \in L^2(\mathbb{R}^3) \,|\, u \text{ is radial} \right\}$$

(radial square integrable functions on $\mathbb{R}^3$). To any $u \in L^2_{\mathrm{r}}(\mathbb{R}^3)$ is associated a (unique) function $R_u \in L^2_{\mathrm{o}}(\mathbb{R})$ such that

$$u(\mathbf{r}) = \frac{R_u(|\mathbf{r}|)}{\sqrt{2\pi}|\mathbf{r}|} \quad \text{for a.e. } \mathbf{r} \in \mathbb{R}^3.$$

When there is no ambiguity, we will also denote by

$$u(r) = \frac{R_u(r)}{\sqrt{2\pi} r} \quad \text{for a.e. } r \in \mathbb{R}$$

($r \mapsto u(r)$ then is an even function of r, belonging to the weighted L^2 space $L^2\left(\mathbb{R}, r^2 dr\right)$). It is easily checked that the mapping

$$\mathcal{R} : L^2_{\mathrm{r}}(\mathbb{R}^3) \ni u \mapsto R_u \in L^2_{\mathrm{o}}(\mathbb{R})$$

is unitary. For $s \in \mathbb{R}$, we denote by

$$H^s_{\mathrm{r}}(\mathbb{R}^3) \quad \text{and} \quad H^s_{\mathrm{o}}(\mathbb{R})$$

the subspaces of the Sobolev spaces $H^s(\mathbb{R}^3)$ and $H^s(\mathbb{R})$ consisting of radial, and odd distributions respectively, and, for $s \in \mathbb{R}_+$, we denote by $H^s_{\mathrm{loc,r}}(\mathbb{R}^3)$ the space of radial locally H^s distributions in $\mathbb{R}^3$.

LEMMA 3.1. *For all $s \in \mathbb{R}_+$ and all $u \in H^s_{\mathrm{r}}(\mathbb{R}^3)$, we have that $R_u \in H^s_{\mathrm{o}}(\mathbb{R})$. In addition, the mapping $H^s_{\mathrm{r}}(\mathbb{R}^3) \ni u \mapsto R_u \in H^s_{\mathrm{o}}(\mathbb{R})$ is unitary.*

Denoting by $P_l \in \mathcal{S}(L^2(\mathbb{R}^3))$ the orthogonal projector on $\mathcal{H}_l$, the spaces $\mathcal{H}_l = \mathrm{Ran}(P_l)$ are given by

$$\mathcal{H}_l = \left\{ v_l(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2} v_{l,m}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right) \,\middle|\, v_{l,m} \in L^2_{\mathrm{o}}(\mathbb{R}), \forall -l \le m \le l \right\},$$

where $(\mathcal{Y}_l^m)_{l \ge 0, -l \le m \le l}$ are the real spherical harmonics [31], normalized in such a way that

$$\int_{\mathbb{S}^2} \mathcal{Y}_l^m \mathcal{Y}_{l'}^{m'} = \delta_{ll'} \delta_{mm'},$$

where $\mathbb{S}^2$ is the unit sphere of $\mathbb{R}^3$. Clearly,

$$\forall v_l \in \mathcal{H}_l, \quad \|v_l\|^2_{L^2(\mathbb{R}^3)} = \sum_{m=-l}^{l} \|v_{l,m}\|^2_{L^2(\mathbb{R})}.$$

We also have for all $s \in \mathbb{R}_+$,

$$H^s(\mathbb{R}^3) = \bigoplus_{l \in \mathbb{N}} \left(\mathcal{H}_l \cap H^s(\mathbb{R}^3) \right),$$

$$\mathcal{H}_l \cap H^s(\mathbb{R}^3) = \left\{ v_l(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2} v_{l,m}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right) \,\middle|\, v_{l,m} \in H^s_{\mathrm{o}}(\mathbb{R}), \forall -l \le m \le l \right\},$$

$$\forall v_l \in \mathcal{H}_l \cap H^1(\mathbb{R}^3), \quad \|v_l\|^2_{H^1(\mathbb{R}^3)} = \sum_{m=-l}^{l} \|v_{l,m}\|^2_{H^1(\mathbb{R})} + l(l+1) \sum_{m=-l}^{l} \|r^{-1} v_{l,m}\|^2_{L^2(\mathbb{R})},$$

$$\forall v_l \in \mathcal{H}_l \cap H^2(\mathbb{R}^3), \quad \|v_l\|^2_{H^2(\mathbb{R}^3)} = \sum_{m=-l}^{l} \left\| -v''_{l,m} + l(l+1) r^{-2} v_{l,m} + v_{l,m} \right\|^2_{L^2(\mathbb{R})}.$$

By rotational invariance, any atomic Hamiltonian H_z is block-diagonal in the decomposition (3.1), which we write

$$H_z = \bigoplus_{l \in \mathbb{N}} H_{z,l}. \tag{3.2}$$

3.2. All-electron atomic Hartree Hamiltonians. All-electron atomic Hartree Hamiltonians are Schrödinger operators of the form

$$H_z^{\mathrm{AA}} = -\frac{1}{2}\Delta + W_z^{\mathrm{AA}}, \tag{3.3}$$

where W_z^{AA} is the multiplication operator by the radial function

$$W_z^{\mathrm{AA}}(\mathbf{r}) = -\frac{z}{|\mathbf{r}|} + \left(\rho_z^0 \star |\cdot|^{-1}\right)(\mathbf{r}),$$

where ρ_z^0 is the radial all-electron atomic Hartree ground state density of atom z (see Proposition 2.1). The operator $H_{z,l}^{\mathrm{AA}}$ associated with the decomposition (3.2) is the self-adjoint operator on $\mathcal{H}_l$ with domain $\mathcal{H}_l \cap H^2(\mathbb{R}^3)$ defined for all $v_l \in \mathcal{H}_l \cap H^2(\mathbb{R}^3)$ by

$$(H_{z,l}^{\mathrm{AA}} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|}\left(-\frac{1}{2}v_{l,m}''(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2}v_{l,m}(|\mathbf{r}|) + W_z^{\mathrm{AA}}(|\mathbf{r}|)v_{l,m}(|\mathbf{r}|)\right)\mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right).$$

This leads us to introduce, for each $l \in \mathbb{N}$, the radial Schrödinger equations

$$-\frac{1}{2}R''(r) + \frac{l(l+1)}{2r^2}R(r) + W_z^{\mathrm{AA}}(r)R(r) = \epsilon R(r), \quad R \in H^1_{\mathrm{o}}(\mathbb{R}), \quad \int_{\mathbb{R}} R^2 = 1. \tag{3.4}$$

Recall that, for convenience, we also denote by W_z^{AA} the even function from $\mathbb{R}$ to $\mathbb{R}$ such that for all $\mathbf{r} \in \mathbb{R}^3$, $W_z^{\mathrm{AA}}(\mathbf{r}) = W_z^{\mathrm{AA}}(|\mathbf{r}|)$.

The spectral properties of atomic Hartree Hamiltonians which will be useful to construct atomic pseudopotentials are collected in the following proposition.

PROPOSITION 3.2 (spectrum of atomic Hartree Hamiltonians). *Let $z \in \mathbb{N}^*$ for which $\epsilon_{z,\mathrm{F}}^0 < 0$. The atomic Hartree Hamiltonian H_z^{AA} is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$, and it holds for any $l \in \mathbb{N}$, $\sigma_{\mathrm{ess}}(H_{z,l}^{\mathrm{AA}}) = \sigma_{\mathrm{ess}}(H_z^{\mathrm{AA}}) = [0, +\infty)$. In addition,*

1. *H_z^{AA} has no strictly positive eigenvalues and the set of its non-positive eigenvalues is the union of the non-positive eigenvalues of the operators $H_{z,l}^{\mathrm{AA}}$, which are obtained by solving the one-dimensional spectral problem (3.4);*
2. *for each $l \in \mathbb{N}$, the negative eigenvalues of (3.4), if any, are simple, and the eigenfunctions associated with the nth eigenvalue have exactly $n-1$ nodes on $(0, +\infty)$;*
3. *for each $l \in \mathbb{N}$, (3.4) has at most a finite number $n_{z,l}$ of negative eigenvalues. The sequence $(n_{z,l})_{l\in\mathbb{N}}$ is non-increasing and $n_{z,l} = 0$ for l large enough. We denote by*

$$l_z^+ = \min\{l \in \mathbb{N} \,|\, n_{z,l+1} = 0\};$$

4. *denoting by $(\epsilon_{z,n,l})_{1\le n\le n_{z,l}}$ the negative eigenvalues of (3.4), ranked in increasing order, we have*

$$\forall 0 \le l_1 < l_2 \le l_z^+, \quad \forall n \le n_{z,l_2}, \quad \epsilon_{z,n,l_1} < \epsilon_{z,n,l_2}. \tag{3.5}$$

We denote by $R_{z,n,l}$ the L^2-normalized eigenfunction associated with the (simple) eigenvalue $\epsilon_{z,n,l}$ of (3.4) taking positive values for $r > 0$ large enough:

$$R_{z,n,l} \in H^1_{\mathrm{o}}(\mathbb{R}), \quad -\frac{1}{2}R_{z,n,l}''(r) + \frac{l(l+1)}{2r^2}R_{z,n,l}(r) + W_z^{\mathrm{AA}}(r)R_{z,n,l}(r) = \epsilon_{z,n,l}R_{z,n,l}(r),$$

$$\int_{\mathbb{R}} R_{z,n,l}^2 = 1, \quad R_{z,n,l}(r) > 0 \quad \text{for } r \gg 1.$$

An orthonormal family of eigenfunctions of the negative part of the atomic Kohn–Sham Hamiltonian H_z^{AA} is thus given by

$$\phi_{z,n,l}^m(\mathbf{r}) = \frac{\sqrt{2} R_{z,n,l}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \quad 0 \le l \le l_z^+, 1 \le n \le n_{z,l}, -l \le m \le l.$$

Note that $\phi_{z,n,l}^m \in \mathcal{H}_l \cap H^2(\mathbb{R}^3)$.

REMARK 3.3. The integers l and m are respectively called the azimuthal and magnetic quantum numbers. With the labeling of the eigenvalues of H_z^{AA} we have chosen, the so-called principal quantum number is equal to $(n+l)$. Thus, the 2p and 4d shells of atom z (see e.g. [8] for a proper mathematical definition of atomic shells) respectively correspond to the eigenvalues $\epsilon_{z,1,1}$ (first eigenvalue of $H_z^{\mathrm{AA}}|_{\mathcal{H}_1}$) and $\epsilon_{z,2,2}$ (second eigenvalue of $H_z^{\mathrm{AA}}|_{\mathcal{H}_2}$).

The ground state density matrix γ_z^0 can be written as

$$\gamma_z^0 = \sum_{l=0}^{l_z^+} \sum_{n=1}^{n_{z,l}} \sum_{m=-l}^{l} p_{z,n,l} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m|, \tag{3.6}$$

where $0 \le p_{z,n,l} \le 2$ is the occupation number of the Kohn–Sham orbital $\phi_{z,n,l}^m$. Note that $p_{z,n,l}$ is independent of the magnetic quantum number m. The occupation numbers are such that

$$p_{z,n,l} = 2 \text{ if } \epsilon_{z,n,l} < \epsilon_{z,\mathrm{F}}^0, \quad 0 \le p_{z,n,l} \le 2 \text{ if } \epsilon_{z,n,l} = \epsilon_{z,\mathrm{F}}^0, \quad p_{z,n,l} = 0 \text{ if } \epsilon_{z,n,l} > \epsilon_{z,\mathrm{F}}^0, \tag{3.7}$$

and

$$\sum_{l=0}^{l_z^+} \sum_{n=1}^{n_{z,l}} (2l+1) p_{z,n,l} = z.$$

We call occupied l-shells of atom z the shells s ($l=0$), p ($l=1$), d ($l=2$), f ($l=3$), etc. for which $n_{z,l} > 0$ and $p_{z,1,l} > 0$. In view of (3.5)–(3.7) if a shell l is occupied, then so are all the shells l' with $l' < l$. Denoting by

$$l_z^- = \max\left\{0 \le l \le l_z^+ \,|\, p_{z,1,l} > 0\right\},$$

we thus obtain that all the shells $l \le l_z^-$ are occupied, and all the shells $l_z^- < l \le l_z^+$ (if any, see Remark 3.4 below) are unoccupied.

It follows from (3.6)–(3.7) that if $\epsilon_{z,\mathrm{F}}^0$ is not an eigenvalue of H_z^{AA} (non-degenerate case in the terminology used in [5]), that is if the highest occupied shell is fully occupied, then the ground state density matrix is unique and is the orthogonal projector

$$\gamma_z^0 = 2 \sum_{n,l,m \,|\, \epsilon_{z,n,l} < \epsilon_{z,\mathrm{F}}^0} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m| \quad \text{(non-degenerate case)}.$$

We also know (see Proposition 2.1 and Remark 2.3) that if $\epsilon_{z,\mathrm{F}}^0$ is an eigenvalue ϵ_{z,n_0,l_0} of H_z^{AA} which is negative (degenerate case in the terminology used in [5]), and is not

accidentally degenerate, then the ground state density matrix is still unique and is given by

$$\gamma_z^0 = 2 \sum_{n,l,m \,|\, \epsilon_{z,n,l} < \epsilon_{z,\mathrm{F}}^0} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m| + \frac{z-N_\mathrm{f}}{2l_0+1} \sum_{m=-l_0}^{l_0} |\phi_{z,n_0,l_0}^m\rangle\langle\phi_{z,n_0,l_0}^m| \quad \text{(degenerate case)},$$

where $N_\mathrm{f} = 2 \sum_{n,l \,|\, \epsilon_{z,n,l} < \epsilon_{z,\mathrm{F}}^0} (2l+1)$ is the number of electrons in the fully occupied shells.

3.3. Atomic semilocal norm-conserving pseudopotentials. Atomic norm-conserving pseudopotentials are operators of the form

$$V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l \mathcal{V}_{z,l} P_l, \qquad \text{for some } l_z^- \le l_z \le l_z^+, \tag{3.8}$$

where $V_{z,\mathrm{loc}} \in H^s_{\mathrm{loc,r}}(\mathbb{R}^3)$ and where we recall that $P_l \in \mathcal{B}(L^2(\mathbb{R}^3))$ is the orthogonal projector on the space $\mathcal{H}_l$. The first term in the right-hand side of (3.8) therefore is a local operator, while the second term is nonlocal. The structure of the operator $\mathcal{V}_{z,l}$ depends on the nature of the pseudopotential under consideration:

- in semilocal pseudopotentials, $\mathcal{V}_{z,l}$ is a multiplication operator by a function $V_{z,l} \in H^s_{\mathrm{r}}(\mathbb{R}^3)$; otherwise stated, $\mathcal{V}_{z,l}$ is a local operator on $\mathcal{H}_l$;
- in Kleinman–Bylander pseudopotentials, $\mathcal{V}_{z,l}$ is a finite-rank rotation-invariant operator.

We restrict our analysis to semilocal pseudopotentials. The case of finite-rank pseudopotentials can be handled as well using the same techniques, *provided the rank of the operator $\mathcal{V}_{z,l}$ is not constrained to be bounded by a fixed integer*. The case of Kleinman–Bylander pseudopotentials, for which the rank of $\mathcal{V}_{z,l}$ is fixed, is more difficult to analyze, due to the possible presence of ghost states [12].

The overall regularity of the pseudopotential is governed by the parameter s. For each $0 \le l \le l_z$, the function $V_{z,l}$ is supported in a ball of radius $r_{\mathrm{c},l}$. The positive number

$$r_\mathrm{c} := \max_{0 \le l \le l_z} r_{\mathrm{c},l}$$

is called the core radius.

The operators $H_{z,l}^{\mathrm{PP}}$ involved in the decomposition (3.2) of the atomic Hartree pseudo-Hamiltonian H_z^{PP} are then given by: for all $0 \le l \le l_z$,

$$(H_{z,l}^{\mathrm{PP}} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v_{l,m}''(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + (W_{z,\mathrm{loc}} + V_{z,l})(\mathbf{r}) v_{l,m}(|\mathbf{r}|) \right) \times \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right),$$

and for all $l > l_z$,

$$(H_{z,l}^{\mathrm{PP}} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v_{l,m}''(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + W_{z,\mathrm{loc}}(\mathbf{r}) v_{l,m}(|\mathbf{r}|) \right) \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right),$$

where

$$W_{z,\mathrm{loc}} = V_{z,\mathrm{loc}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1},$$

$\widetilde{\rho}_z^0$ being the ground state pseudo-density defined in Proposition 2.5.

The mathematical construction of a semilocal pseudopotential for atom z goes as follows:

Step 1: choose an energy window $\Delta E = (E_-, E_+) \subset \mathbb{R}_-$, which, in particular, defines a partition between core and valence electrons;

Step 2: choose the core radius r_c and the Sobolev exponent s, and check that the so-obtained set $\mathcal{M}_{z,\Delta E,r_c,s}$ of admissible pseudopotentials (see Section 3.5) is non-empty;

Step 3: choose the "best" pseudopotential in the set $\mathcal{M}_{z,\Delta E,r_c,s}$.

Steps 1 and 2 are detailed in the next two sections. In Section 3.6, we investigate the stability of the atomic ground state of the pseudopotential model with respect to both external perturbations and variations of the pseudopotential itself. In Section 3.7, we address the existence of optimal pseudopotentials for a variety of optimality criteria.

3.4. Partition between core and valence electrons. As mentioned above, the first task to construct a pseudopotential is to partition the electrons into core and valence electrons. We assume here that $z \in \mathbb{N}^*$ is such that $\epsilon^0_{z,\mathrm{F}} < 0$. This partitioning is made through the choice of an energy window $\Delta E = (E_-, E_+)$, with $-\infty < E_- < E_+ < 0$, containing the Fermi level $\epsilon^0_{z,\mathrm{F}}$ (or *a* Fermi level in the case when the highest occupied energy level is fully occupied, see Remark 2.2) and such that there exists an integer l_z satisfying $l_z^- \le l_z \le l_z^+$ and

$$\forall l \le l_z, \quad \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \Delta E\right) = \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \overline{\Delta E}\right) = 1, \tag{3.9}$$

$$\forall l > l_z, \quad \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \Delta E\right) = 0. \tag{3.10}$$

All the electrons occupying the shells such that $\epsilon_{z,n,l} < E_-$ are considered as core electrons. For each $l \le l_z$, we denote by $n^\star_{z,l}$, the unique non-negative integer such that $\epsilon_{z,n^\star_{z,l},l} \in \Delta E$. The set $\left\{\epsilon_{z,n^\star_{z,l},l}\right\}_{0\le l\le l_z}$ constitute the set of the valence energy levels, which can *a priori* be fully occupied ($E_- < \epsilon_{z,n^\star_{z,l},l} < \epsilon^0_{z,\mathrm{F}}$), partially occupied ($\epsilon_{z,n^\star_{z,l},l} = \epsilon^0_{z,\mathrm{F}}$) or unoccupied ($\epsilon^0_{z,\mathrm{F}} < \epsilon_{z,n^\star_{z,l},l} < E_+$).

Remark 3.4. Let us emphasize that it is not clear *a priori* that one can find energy windows ΔE satisfying (3.9)–(3.10). Here again, we need to rely on numerical simulations to establish that our assumptions make sense and are satisfied in practice, at least for some atoms. In another contribution [6] more focused on numerical simulations, we show in particular that for most atoms of the first four rows of the periodic table, $\epsilon^0_{z,\mathrm{F}} < 0$ and energy windows ΔE satisfying (3.9)–(3.10) do exist. Besides, for most atoms of the first four rows, atomic Hartree Hamiltonians do not seem to have unoccupied energy levels with negative energies, so that for those atoms, $l_z^+ = l_z^-$ and therefore $l_z = l_z^- = l_z^+$. For instance, it can be checked numerically that the Hartree valence energy levels of the copper atom ($z = 29$) are such that

$$l_z = 2, \quad n^\star_{z,0} = 4, \quad n^\star_{z,1} = 2, \quad n^\star_{z,2} = 1, \quad E_- < \epsilon_{z,2,1} < \epsilon_{z,4,0} < \epsilon^0_{z,\mathrm{F}} = \epsilon_{z,1,2} < E_+, \quad \text{(for Cu)}.$$

This is the situation depicted on Figure 3.1. The core and valence configurations are respectively denoted by $1s^2\ 2s^2\ 2p^6\ 3s^2$ and $3p^6\ 4s^2\ 3d^9$ in the chemistry literature. Let us observe that the valence configuration of Cu for the Hartree model differs from the one obtained from the N-body Schrödinger equation with infinitesimal Coulomb repulsion [8], that is $3p^6\ 3d^{10}\ 4s^1$.

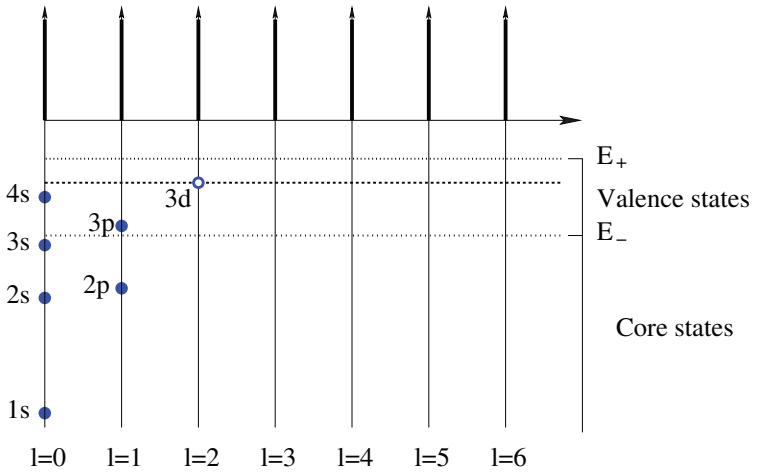

FIG. 3.1. *Sketch of the spectra of the operators* $H_z^{\mathrm{AA}}|_{\mathcal{H}_l}$ *and admissible energy window* $\Delta E = (E_-, E_+)$ *for the copper atom* ($z=29$). *The energy scale is arbitrary. The actual values of the energy levels are the following:* $\epsilon_{z,1,0} \simeq -312.78$ *Ha (1s),* $\epsilon_{z,2,0} \simeq -36.42$ *Ha (2s),* $\epsilon_{z,1,1} \simeq -31.57$ *Ha (2p),* $\epsilon_{z,3,0} \simeq -3.716$ *Ha (3s),* $\epsilon_{z,2,1} \simeq -2.294$ *Ha (3p),* $\epsilon_{z,4,0} \simeq -5.540 \times 10^{-2}$ *Ha (4s),* $\epsilon^0_{z,\mathrm{F}} = \epsilon_{z,1,2} \simeq -1.371 \times 10^{-2}$ *Ha (3d). The self-consistent Hartree Hamiltonian* H_z^{AA} *seems to have no negative eigenvalue above the Fermi level* $\epsilon^0_{z,\mathrm{F}}$.

We therefore have

$$N_{z,\mathrm{c}} = \sum_{n,l\,|\,\epsilon_{z,n,l} \le E_-} (2l+1) p_{z,n,l} \qquad \text{and} \qquad N_{z,\mathrm{v}} = z - N_{z,\mathrm{c}},$$

where we recall that $N_{z,\mathrm{c}}$ and $N_{z,\mathrm{v}}$ respectively denote the numbers of core and valence electrons. We also introduce the core and valence all-electron Hartree ground state densities, respectively defined as

$$\rho^0_{z,\mathrm{c}}(\mathbf{r}) := 2 \sum_{n,l\,|\,\epsilon_{z,n,l} \le E_-} \sum_{m=-l}^{l} |\phi^m_{z,n,l}(\mathbf{r})|^2 \quad \text{and} \quad \rho^0_{z,\mathrm{v}}(\mathbf{r}) := \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\phi^m_{z,n^\star_{z,l},l}(\mathbf{r})|^2.$$

Note that the core density $\rho^0_{z,\mathrm{c}}$ should not be confused with the core pseudo-density $\widetilde{\rho}^0_{z,\mathrm{c}}$ mentioned in Section 2.2 and whose expression will be given below (see (3.21)).

3.5. Admissible pseudopotentials. Let $z \in \mathbb{N}^*$ be such that $\epsilon^0_{z,\mathrm{F}} < 0$, and let $\Delta E = (E_-, E_+)$ be an energy window satisfying the properties (3.9)–(3.10). An admissible semilocal norm-conserving pseudopotential with core radius r_{c} and regularity H^s ($s > 0$) is an operator V_z^{PP} of the form

$$V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l, \qquad \text{for some } l_z^- \le l_z \le l_z^+,$$

for which the radial functions $V_{z,\mathrm{loc}}$ and $V_{z,l}$ satisfy the following properties:

(1) **values out of the core region:**

$$\text{in } \mathbb{R}^3 \setminus B_{r_{\mathrm{c}}}, \quad V_{z,\mathrm{loc}} = -\frac{z}{|\cdot|} + \rho^0_{z,\mathrm{c}} \star |\cdot|^{-1} \quad \text{and} \quad V_{z,l} = 0 \text{ for all } 0 \le l \le l_z; \tag{3.11}$$

(2) H^s**-regularity:**

$$V_{z,\mathrm{loc}} \in H^s_{\mathrm{loc,r}}(\mathbb{R}^3) \quad \text{and for all } 0 \le l \le l_z,\, V_{z,l} \in H^s_{\mathrm{r}}(\mathbb{R}^3); \tag{3.12}$$

(3) **consistency:** the atomic Hartree pseudo-Hamiltonian

$$H_z^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_z^{\mathrm{PP}}, \qquad \text{where} \qquad W_z^{\mathrm{PP}} = W_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l,$$

obtained with the pseudopotential V_z^{PP} (see Proposition 2.5) is such that

$$\mathbb{1}_{(-\infty,E_+)}(H_z^{\mathrm{PP}}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} |\widetilde{\phi}^m_{z,l}\rangle\langle\widetilde{\phi}^m_{z,l}|, \tag{3.13}$$

$$W_{z,\mathrm{loc}} = V_{z,\mathrm{loc}} + \widetilde{\rho}^0_z \star |\cdot|^{-1}, \qquad \widetilde{\rho}^0_z(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\widetilde{\phi}^m_{z,n^\star_{z,l},l}(\mathbf{r})|^2, \tag{3.14}$$

where

$$\widetilde{\phi}^m_{z,l}(\mathbf{r}) = \frac{\sqrt{2}\,\widetilde{R}_{z,l}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}^m_l\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \tag{3.15}$$

with, for each $0 \le l \le l_z$,

$$\widetilde{R}_{z,l} \in H^1_{\mathrm{o}}(\mathbb{R}), \tag{3.16}$$

$$-\frac{1}{2}\widetilde{R}''_{z,l}(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_{z,l}(r) + (W_{z,\mathrm{loc}}(r) + V_{z,l}(r))\,\widetilde{R}_{z,l}(r) = \epsilon_{z,n^\star_{z,l},l}\widetilde{R}_{z,l}(r), \tag{3.17}$$

$$\int_{\mathbb{R}} \widetilde{R}^2_{z,l} = 1, \tag{3.18}$$

$$\widetilde{R}_{z,l} = R_{z,n^\star_{z,l},l} \quad \text{on } (r_{\mathrm{c},l},+\infty) \text{ for some } 0 < r_{\mathrm{c},l} \le r_{\mathrm{c}}, \tag{3.19}$$

$$\widetilde{R}_{z,l} \ge 0 \quad \text{on } (0,+\infty). \tag{3.20}$$

We can therefore define the set of admissible semilocal norm-conserving pseudopotentials with energy window $\Delta E = (E_-, E_+)$, core radius r_{c} and regularity H^s, for the atom z as

$$\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s} := \left\{ V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l \,\middle|\, \text{such that (3.11)–(3.20) hold} \right\}.$$

Several comments are in order:

- condition (3.11) implies conditions (2.8)–(2.9), so that the existence and uniqueness of the atomic ground state valence pseudo-density $\widetilde{\rho}^0_z$ is guaranteed by Proposition 2.5 as soon as (3.11) is satisfied;
- it follows from (3.16)–(3.18) and (3.20) that $\epsilon_{z,n^\star_{z,l},l}$ is the ground state eigenvalue of $H_z^{\mathrm{PP}}|_{\mathcal{H}_l}$ and that the $(2l+1)$ functions $\widetilde{\phi}^m_{z,l}$, $-l \le m \le l$, form an orthonormal basis of associated eigenfunctions;

- by construction (see Section 3.4), the energy window ΔE contains $\epsilon^0_{z,\mathrm{F}}$. In addition, H_z^{AA} and H_z^{PP} have the same spectra in ΔE (including multiplicities), and in both all-electron and pseudopotential models, $N_{z,\mathrm{v}}$ electrons are placed in the energy levels in ΔE, according the *Aufbau* and Pauli principles (that is, occupy the lower energy states with no more than two electrons per state). As a consequence, and as already mentioned in Remark 2.6, the all-electron Fermi level $\epsilon^0_{z,\mathrm{F}}$ and the pseudo Fermi level $\widetilde{\epsilon}^0_{z,\mathrm{F}}$ can be chosen equal, and if $\epsilon^0_{z,\mathrm{F}}$ is not an accidentally degenerate eigenvalue of H_z^{AA}, then $\widetilde{\epsilon}^0_{z,\mathrm{F}} = \epsilon^0_{z,\mathrm{F}}$ cannot be an accidentally degenerate eigenvalue of H_z^{PP};
- it also follows from (3.13) that the $\epsilon_{z,n^\star_{z,l},l}$'s are the only eigenvalues of H_z^{PP} in the energy range $(-\infty, E_+)$. This property is referred to as the *absence of ghost states* in the physics literature;
- out of the core region, (3.11) is compatible with (3.17) and (3.19). Indeed, (3.17) and (3.19) imply that

$$\forall \mathbf{r} \in \mathbb{R}^3 \setminus B_{r_\mathrm{c}}, \quad \widetilde{\rho}^0_z(\mathbf{r}) = \rho^0_{z,\mathrm{v}}(\mathbf{r}) \quad \text{and} \quad W_{z,\mathrm{loc}}(\mathbf{r}) + V_{z,l}(\mathbf{r}) = W_z^{\mathrm{AA}}(\mathbf{r}),$$

  hence, applying Gauss theorem, that $\widetilde{\rho}^0_z \star |\cdot|^{-1} = \rho^0_{z,\mathrm{v}} \star |\cdot|^{-1}$ in $\mathbb{R}^3 \setminus B_{r_\mathrm{c}}$, which finally leads to

$$V_{z,\mathrm{loc}} + V_{z,l} = W_z^{\mathrm{AA}} - \rho^0_{z,\mathrm{v}} \star |\cdot|^{-1} = -\frac{z}{|\cdot|} + \rho^0_{z,\mathrm{c}} \star |\cdot|^{-1} \quad \text{in } \mathbb{R}^3 \setminus B_{r_\mathrm{c}};$$

- the core energies and the core pseudo-densities $\widetilde{\rho}_{0,\mathrm{c}}$ of the atoms appearing in (2.6) are defined in such a way that for an isolated atom, the pseudopotential calculation gives the same energy as the all-electron model. In the Hartree case, the core energy of atom z is therefore given by

$$\begin{aligned} E_{z,\mathrm{c}} &= I_z^{\mathrm{AA}} - \inf\left\{ E_z^{\mathrm{PP}}(\widetilde{\gamma}), \widetilde{\gamma} \in \mathcal{K}_{N_{z,\mathrm{v}}} \right\} \\ &= I_z^{\mathrm{AA}} - \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\mathrm{PP}} \right) \widetilde{\gamma}^0_z \right) - \frac{1}{2} D\left(\widetilde{\rho}^0_z, \widetilde{\rho}^0_z \right) \\ &= I_z^{\mathrm{AA}} - \sum_{l=0}^{l_z} (2l+1) p_{z,n^\star_{z,l},l} \epsilon_{z,n^\star_{z,l},l} + \frac{1}{2} D\left(\widetilde{\rho}^0_z, \widetilde{\rho}^0_z \right). \end{aligned}$$

  The core pseudo-density of atom z is defined by

$$\widetilde{\rho}^0_{z,\mathrm{c}} = \rho^0_z - \widetilde{\rho}^0_z. \tag{3.21}$$

  Note that atomic core pseudo-densities do not play any role in the Hartree model, since they are only involved in the exchange-correlation energy functional.

The rest of this section is devoted to the study of the set $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$. We assume here that $z \in \mathbb{N}^*$ is such that $\epsilon^0_{z,\mathrm{F}} < 0$ and that $\Delta E = (E_-, E_+)$ is a fixed energy window satisfying (3.9)–(3.10). It readily follows from the definition of $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ that

$$\forall 0 < r_\mathrm{c} \le r'_\mathrm{c} < +\infty, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s} \subset \mathcal{M}_{z,\Delta E,r'_\mathrm{c},s}, \tag{3.22}$$

$$\forall 0 \le s \le s' < +\infty, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s'} \subset \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}. \tag{3.23}$$

Let

$$r^-_{z,\Delta E,\mathrm{c}} = \max_{0\le l\le l_z} \left(\max R^{-1}_{z,n^\star_{z,l},l}(0)\right) \ge 0$$

be the maximum over $0\le l\le l_z$ of the largest node of the function $R_{z,n^\star_{z,l},l}$. If $r_\mathrm{c} < r^-_{z,\Delta E,\mathrm{c}}$, then (3.19) and (3.20) are obviously inconsistent, and $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s} = \emptyset$. On the other hand, we are going to see that $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ is not empty, for any $s\ge 0$, as soon as r_c is large enough. To any potential $W \in L^{3/2}_\mathrm{r}(\mathbb{R}^3)$, we associate the function $\mathcal{T}_W : (0,+\infty)\to\mathbb{R}_-$ defined for all $r>0$ by

$$\mathcal{T}_W(r) := \inf_{\substack{\phi\in H^1_0(\overline{B}^\mathrm{c}_r)\\ \|\phi\|_{L^2(\overline{B}^\mathrm{c}_r)}=1}} \int_{\overline{B}^\mathrm{c}_r} \left(\frac{1}{2}|\nabla\phi|^2 + W\phi^2\right),$$

where $\overline{B}^\mathrm{c}_r = \mathbb{R}^3\setminus\overline{B}_r$. We will prove in Section 5.3 that $\mathcal{T}_{W^{\mathrm{AA}}_z}$ is continuous and nondecreasing, and that it maps $(0,+\infty)$ onto $(\varepsilon_{z,1},0]$ (where we recall that $\varepsilon_{z,1}$ is the lowest eigenvalue of H^{AA}_z, see (2.5)).

LEMMA 3.5. *Let $z\in\mathbb{N}^*$ be such that $\epsilon^0_{z,\mathrm{F}}<0$. Let $\Delta E=(E_-,E_+)$ be an energy window satisfying (3.9)–(3.10). The equation $\mathcal{T}_{W^{\mathrm{AA}}_z}(r)=E_+$ has a unique solution $r^+_{z,\Delta E,\mathrm{c}}>0$. In addition, $r^-_{z,\Delta E,\mathrm{c}} < r^+_{z,\Delta E,\mathrm{c}}$ and for all $r_\mathrm{c}\ge r^+_{z,\Delta E,\mathrm{c}}$ and all $s\ge 0$, the set $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ is nonempty.*

We were not able to provide a simple characterization of the critical core radius $r^0_{z,\Delta E,\mathrm{c}}$, $r^-_{z,\Delta E,\mathrm{c}} \le r^0_{z,\Delta E,\mathrm{c}} \le r^+_{z,\Delta E,\mathrm{c}}$, such that for all $s\ge 0$,

$$\forall r_\mathrm{c} < r^0_{z,\Delta E,\mathrm{c}}, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}=\emptyset \quad\text{and}\quad \forall r_\mathrm{c} > r^0_{z,\Delta E,\mathrm{c}}, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}\neq\emptyset.$$

We can only show, using the same regularization argument as in the proof of Lemma 3.5, that $r^0_{z,\Delta E,\mathrm{c}}$ is indeed independent of s.

REMARK 3.6. We have seen that r_c cannot be chosen too small. On the other hand, it should not be chosen too large for transferability issues. In particular, the core regions of the atoms of the molecular system under study should not overlap. In practice, the radius $r_{\mathrm{c},l}$ in (3.19) is chosen by trial and error procedures in the range $(\max R^{-1}_{z,n^*_{z,l},l}(0), \max \frac{dR_{z,n^*_{z,l},l}}{dr}^{-1}(0))$ between the outermost node and the outermost peak of the radial orbital $R_{z,n^*_{z,l},l}$.

REMARK 3.7. The smoothness parameter s affects the numerical properties of the pseudopotential, and more precisely the convergence rate of the numerical solution toward the exact solution of the pseudopotential model with respect to the discretization parameters [4]. For example, Troullier–Martins pseudopotentials [28] are constructed in such a way that the pseudo-orbitals $\widetilde{R}^{\mathrm{TM}}_{z,l}$ are of the form

$$\widetilde{R}^{\mathrm{TM}}_{z,l}(r) = \begin{cases} r^{l+1}\, e^{p_{z,l,r_{\mathrm{c},l}}(r)} & \text{if } 0\le r<r_{\mathrm{c},l},\\ R_{z,n^*_{z,l},l}(r) & \text{if } r\ge r_{\mathrm{c},l}, \end{cases} \tag{3.24}$$

where $p_{z,l,r_{\mathrm{c},l}}$ is an even polynomial of degree 12 whose seven non-zero coefficients are fitted so that $\widetilde{R}^{\mathrm{TM}}_{z,l}$ is L^2-normalized and of class C^4 in the vicinity of $r_{\mathrm{c},l}$. The additional condition allowing one to unambiguously determine the seven non-zero coefficients of $p_{z,l,r_{\mathrm{c},l}}$ is that the second derivative of $(W_{z,\mathrm{loc}}+V_{z,l})$ vanishes at $r=0$. It can

be checked that this implies that Troullier–Martins pseudopotentials are in $\mathcal{M}_{z,\Delta E,r_c,s}$ for all $0<s\leq 7/2$.

Our next results will be established under the following:

Assumption 1: $z\in\mathbb{N}^*$ is such that $\epsilon^0_{z,\mathrm{F}}$ is negative and is not an accidentally degenerate eigenvalue of H_z^{AA}, $\Delta E=(E_-,E_+)$ satisfies (3.9)–(3.10), $r_c>r^0_{z,\Delta E,c}$ and $s>0$.

Consider now the Hilbert space

$$\begin{aligned} X_{z,\Delta E,r_c,s} &= \left\{ v=v_{\mathrm{loc}}+\sum_{l=0}^{l_z} P_l v_l P_l \;\middle|\; (v_{\mathrm{loc}},(v_l)_{0\leq l\leq l_z})\in (H^s_{0,\mathrm{r}}(B_{r_c}))^{l_z+2} \right\} \\ &\equiv (H^s_{0,\mathrm{r}}(B_{r_c}))^{l_z+2}, \end{aligned}$$

where $H^s_{0,\mathrm{r}}(B_{r_c})$ is the closure in $H^s(\mathbb{R}^3)$ of the space of radial, real-valued, C^∞ functions on $\mathbb{R}^3$ with compact supports included in the open ball $B_{r_c}:=\left\{\mathbf{r}\in\mathbb{R}^3\,|\,|\mathbf{r}|<r_c\right\}$, and the affine space

$$\mathcal{X}_{z,\Delta E,r_c,s}=\left\{ V=V_{\mathrm{loc}}+\sum_{l=0}^{l_z} P_l V_l P_l \;\middle|\; \text{such that (3.11)}--\text{(3.12) hold} \right\}.$$

Note that

$$\forall V\in\mathcal{X}_{z,\Delta E,r_c,s},\quad \mathcal{X}_{z,\Delta E,r_c,s}=V+X_{z,\Delta E,r_c,s}.$$

As $\mathcal{M}_{z,\Delta E,r_c,s}$ is a subset of $\mathcal{X}_{z,\Delta E,r_c,s}$, we can endow the former set with the topology of the latter, and say that a sequence $(V^{\mathrm{PP}}_{z,k})_{k\in\mathbb{N}}\in\mathcal{M}_{z,\Delta E,r_c,s}$ of admissible pseudopotentials

- strongly converges to some $V\in\mathcal{X}_{z,\Delta E,r_c,s}$ if (with obvious notation)

$$\|V_{z,\mathrm{loc},k}-V_{\mathrm{loc}}\|^2_{H^s}+\sum_{l=0}^{l_z}\|V_{z,l,k}-V_l\|^2_{H^s}\underset{k\to\infty}{\to}0; \tag{3.25}$$

- weakly converges to some $V\in\mathcal{X}_{z,\Delta E,r_c,s}$ if

$$\forall V'\in X_{z,\Delta E,r_c,s},\quad (V_{z,\mathrm{loc},k}-V_{\mathrm{loc}},V'_{\mathrm{loc}})_{H^s}+\sum_{l=0}^{l_z}(V_{z,l,k}-V_l,V'_l)_{H^s}\underset{k\to\infty}{\to}0. \tag{3.26}$$

THEOREM 3.8 (properties of the set of norm-conserving pseudopotentials). *Under Assumption 1, $\mathcal{M}_{z,\Delta E,r_c,s}$ is a nonempty weakly (hence strongly) closed subset of the affine space $\mathcal{X}_{z,\Delta E,r_c,s}$.*

In practice, some classes of pseudopotentials are constructed by first defining the pseudo-orbitals $\widetilde{R}_{z,l}$, $0\leq l\leq l_z$, and then deducing from these functions the local and nonlocal components of the atomic pseudopotential using the relations

$$\forall\mathbf{r}\in\mathbb{R}^3\setminus\{0\},\quad V_{z,\mathrm{loc}}(\mathbf{r})+V_{z,l}(\mathbf{r})=\epsilon_{z,n^\star_{z,l},l}+\frac{1}{2}\frac{\widetilde{R}''_{z,l}(|\mathbf{r}|)}{\widetilde{R}_{z,l}(|\mathbf{r}|)}-\frac{l(l+1)}{2|\mathbf{r}|^2}-\left(\widetilde{\rho}^0_z\star|\cdot|^{-1}\right)(\mathbf{r}),$$

where $\widetilde{\rho}^0_z$ is defined by (3.14) and (3.15). This is notably the case for the Troullier–Martins pseudopotentials mentioned in Remark 3.7. The reason why pseudopotentials

are usually constructed in this way is that it is easy to enforce the constraints (3.16)–(3.20) when dealing with explicit pseudo-orbitals (as in (3.24)).

The following lemma is useful to select admissible functions $\widetilde{R}_{z,l}$.

LEMMA 3.9. *Let $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ for some $s > \frac{1}{2}$ (so that the functions $V_{z,\rm loc}$ and $V_{z,l}$ are continuous). For each $0 \le l \le l_z$, the radial function $\widetilde{R}_{z,l}$, defined by (3.16)–(3.20) in is $H^{s+2}_{\rm o}(\mathbb{R})$ and*

$$\widetilde{R}_{z,l}(r) = O(r^{l+1}) \quad as \quad r \to 0.$$

One can check that the Troullier–Martins pseudo-orbitals defined in (3.24) indeed satisfy the above property.

3.6. Some stability results. Let $z, \Delta E, r_{\rm c}, s$ satisfy Assumption 1. Let $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ be a reference pseudopotential. It follows from Proposition 2.5 and the definition of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ (see also Remark 2.6) that $\epsilon^0_{z,\rm F}$ is not an accidentally degenerate eigenvalue of $H_z^{\rm PP}$ and that the ground state pseudo-density matrix $\widetilde{\gamma}^0_z$ corresponding to $V_z^{\rm PP}$ is unique.

We can study the sensitivity of $\widetilde{\gamma}^0_z$ with respect to both an external perturbation and the choice of the pseudopotential by considering the minimization problem

$$\mathcal{E}_{V_z^{\rm PP}}(v,W) := \inf\left\{E_{V_z^{\rm PP}}(\widetilde{\gamma},v,W), \widetilde{\gamma} \in \mathcal{K}_{N_{z,\rm v}}\right\}, \tag{3.27}$$

where the energy functional $E_{V_z^{\rm PP}}$ is defined on $\mathcal{K}_{N_{z,\rm v}} \times X_{z,\Delta E,r_{\rm c},s} \times \mathcal{C}'$ by

$$E_{V_z^{\rm PP}}(\widetilde{\gamma},v,W) := \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\rm PP} + v\right)\widetilde{\gamma}\right) + \frac{1}{2}D(\rho_{\widetilde{\gamma}},\rho_{\widetilde{\gamma}}) + \int_{\mathbb{R}^3}\rho_{\widetilde{\gamma}}W,$$

and where we have denoted by

$$\mathcal{C}' = \left\{W \in L^6(\mathbb{R}^3) \,|\, \nabla W \in (L^2(\mathbb{R}^3))^3\right\}$$

the space of potentials with finite Coulomb energies, endowed with the scalar product defined by

$$\forall (W_1,W_2) \in \mathcal{C}' \times \mathcal{C}', \quad (W_1,W_2)_{\mathcal{C}'} = \int_{\mathbb{R}^3} \nabla W_1 \cdot \nabla W_2.$$

For $\eta > 0$ and X a normed vector space, we denote by $B_\eta(X)$ the open ball of X with center 0 and radius η. The following result guarantees the stability of the pseudopotential model with respect to the choice of the pseudopotential.

PROPOSITION 3.10. *Let $z, \Delta E, r_{\rm c}, s$ satisfy Assumption 1. Then, for all $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$, there exists $\eta > 0$ such that for all $(v,W) \in B_\eta(X_{z,\Delta E,r_{\rm c},s}) \times B_\eta(\mathcal{C}')$, problem (3.27) has a unique minimizer $\widetilde{\gamma}_{v,W}(V_z^{\rm PP})$. Moreover, for each $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$, the function $(v,W) \mapsto \widetilde{\gamma}_{v,W}(V_z^{\rm PP})$ is real analytic from $B_\eta(X_{z,\Delta E,r_{\rm c},s}) \times B_\eta(\mathcal{C}')$ to the space*

$$\mathfrak{S}_{1,1} := \left\{T \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) \cap \mathcal{S}(L^2(\mathbb{R}^3)) \,|\, |\nabla|T|\nabla| \in \mathfrak{S}_1(L^2(\mathbb{R}^3))\right\},$$

$\mathfrak{S}_1(L^2(\mathbb{R}^3))$ denoting the space of the trace-class operators on $L^2(\mathbb{R}^3)$. For all $v \in X_{z,\Delta E,r_{\rm c},s}$, all $W \in \mathcal{C}'$, and all real numbers α and β such that

$$-\eta\|v\|^{-1}_{X_{z,\Delta E,r_{\rm c},s}} < \alpha < \eta\|v\|^{-1}_{X_{z,\Delta E,r_{\rm c},s}} \text{ and } -\eta\|W\|^{-1}_{\mathcal{C}'} < \beta < \eta\|W\|^{-1}_{\mathcal{C}'},$$

we have

$$\widetilde{\gamma}_{\alpha v,\beta W}(V_z^{\mathrm{PP}}) = \widetilde{\gamma}_z^0 + \sum_{(j,k)\in(\mathbb{N}\times\mathbb{N})\setminus\{(0,0)\}} \alpha^j \beta^k \widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\mathrm{PP}}), \tag{3.28}$$

where $\widetilde{\gamma}_z^0$ *is the ground state density matrix for the pseudopotential* V_z^{PP}*, where the coefficients* $\widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\mathrm{PP}})$ *of the expansion are uniquely defined in* $\mathfrak{S}_{1,1}$*, and the series is absolutely convergent in* $\mathfrak{S}_{1,1}$*.*

In the next section, we will define optimality criteria based on first-order perturbation method for choosing the "best" pseudopotential in the class $\mathcal{M}_{z,\Delta E,r_c,s}$. These criteria will involve the difference between the first-order response of the all-electron model and that of the pseudopotential model to a given external perturbation W. A natural external perturbation is the one obtained by subjecting the atom to an external uniform electric field (Stark effect):

$$W^{\mathrm{Stark}}(\mathbf{r}) = -\mathbf{r}\cdot\mathbf{e}, \tag{3.29}$$

where $\mathbf{e}$ is the unit vector of the vertical axis of the reference frame. As the unperturbed system is rotation-invariant, the direction of the electric field is unimportant. So is its magnitude since we only consider here first-order perturbations (linear responses).

Note that it is not possible to apply the results in Proposition 3.10 to the perturbation (3.29) since W^{Stark} is not in $\mathcal{C}'$. In the framework of the linear Schrödinger equation (see e.g. [22] for a detailed analysis of the case of the Hydrogen atom), the spectrum of a molecular Stark Hamiltonian is purely absolutely continuous and equal to $\mathbb{R}$ for all non-zero values of the electric field. The eigenstates of the unperturbed Hamiltonian turn into resonances. On the other hand, the perturbation series is well-defined; its convergence radius is equal to zero, but the energies and widths of the resonances can nonetheless be computed from the perturbation expansion using Borel summation techniques.

For the atomic Hartree model under consideration here, the perturbed energy functional has no minimizer: for all $\beta \neq 0$,

$$\inf\left\{ E_z^{\mathrm{AA}}(\gamma) - \beta \int_{\mathbb{R}^3} \rho_\gamma(\mathbf{r}\cdot\mathbf{e}),\, \gamma \in \mathcal{K}_z \right\} = -\infty.$$

The same holds true for the corresponding pseudopotential model for any $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_c,s}$. Physically, this corresponds to the fact that the infimum of the energy is obtained by allowing the electrons to go to infinity towards the regions where $W(\mathbf{r}) = -\beta\mathbf{r}\cdot\mathbf{e}$ goes to $-\infty$. As in the linear framework, each term of the perturbation series is well-defined, but the convergence radius of the series is equal to zero. We will only prove here the part of this result we need, namely that the first-order term of the perturbation expansion is well-defined, and, in the pseudopotential case, that the linear response is continuous with respect to the choice of the pseudopotential (see Theorem 3.11 below). We are not aware of an extension of the theory of resonances to nonlinear mean-field models of Kohn–Sham type.

For $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_c,s}$ and $W \in \mathcal{C}'$, we denote by $\widetilde{\gamma}_W^{(k)}(V_z^{\mathrm{PP}}) := \widetilde{\gamma}_{0,W}^{(0,k)}(V_z^{\mathrm{PP}})$, where the right-hand side is defined in Proposition 3.10. We also denote by $\gamma_{z,W}^{(k)}$ the kth-order perturbation of the all-electron ground state γ_z^0 when atom z is subjected to an

external potential $W \in \mathcal{C}'$. A consequence of [5, Theorems 5 and 12] and of the above Proposition 3.10 is that the linear maps

$$\mathcal{C}' \ni W \mapsto \gamma^{(1)}_{z,W} \in \mathfrak{S}_{1,1} \quad \text{and} \quad \mathcal{C}' \ni W \mapsto \widetilde{\gamma}^{(1)}_{W}(V_z^{\mathrm{PP}}) \in \mathfrak{S}_{1,1}, \quad V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}, \quad (3.30)$$

are continuous.

THEOREM 3.11 (Stark effect). *Let $z, \Delta E, r_{\mathrm{c}}, s$ satisfying Assumption 1. The continuous linear maps defined by (3.30) can be extended in a unique way to continuous linear maps*

$$\mathcal{Y}_z \ni W \mapsto \gamma^{(1)}_{W} \in \mathfrak{S}_{1,1} \quad \textit{and} \quad \mathcal{Y}_z \ni W \mapsto \widetilde{\gamma}^{(1)}_{W}(V_z^{\mathrm{PP}}) \in \mathfrak{S}_{1,1}, \quad V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}, \quad (3.31)$$

where $\mathcal{Y}_z$ is the Banach space

$$\mathcal{Y}_z := \mathcal{C}' + L^2_{\mathrm{w}} \quad \textit{where} \quad L^2_{\mathrm{w}} := \left\{ W \in L^2_{\mathrm{loc}}(\mathbb{R}^3) \,|\, \int_{\mathbb{R}^3} |W(\mathbf{r})|^2 e^{-\sqrt{|\epsilon^0_{z,\mathrm{F}}|}|\mathbf{r}|}\, d\mathbf{r} < \infty \right\}.$$

In addition, $W^{\mathrm{Stark}} \in \mathcal{Y}_z$ and the mapping $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s} \ni V_z^{\mathrm{PP}} \mapsto \widetilde{\gamma}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}}) \in \mathfrak{S}_{1,1}$ is compact.

3.7. Optimization of norm-conserving pseudopotentials. A natural way to choose a pseudopotential in the class $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ is to optimize some criterion $J(V_z^{\mathrm{PP}})$ combining the two requirements that the pseudopotential must be as smooth as possible and as transferable as possible. The smoothness requirement leads us to introduce the criterion

$$J_{\mathrm{s}}(V_z^{\mathrm{PP}}) := \frac{1}{2}\|W_z^{\mathrm{PP}}\|^2_{H^s} := \frac{1}{2}\left(\|W_{z,\mathrm{loc}}\|^2_{H^s} + \sum_{l=0}^{l_z} \|V_{z,l}\|^2_{H^s} \right), \quad (3.32)$$

where W_z^{PP} is the self-consistent pseudopotential corresponding to the pseudopotential V_z^{PP} (see Proposition 2.5). Note that it is natural to use the self-consistent pseudopotential W_z^{PP} rather than V_z^{PP} in the right-hand side of (3.32) since the smoothness of the Kohn–Sham pseudo-orbitals is controlled by W_z^{PP}. Let us first state a general result.

THEOREM 3.12. *Let $z, \Delta E, r_{\mathrm{c}}, s$ satisfying Assumption 1. Consider the criterion*

$$J(V_z^{\mathrm{PP}}) = \alpha J_{\mathrm{s}}(V_z^{\mathrm{PP}}) + J_{\mathrm{t}}(V_z^{\mathrm{PP}}),$$

where the smoothness criterion J_{s} is defined by (3.32), where the transferability criterion $J_{\mathrm{t}} : \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s} \to \mathbb{R}$ is a bounded below weakly lower-semicontinuous function, and where $\alpha > 0$ is a parameter allowing one to balance the smoothness and transferability requirements. Then, the optimization problem

$$\inf\left\{ J(V_z^{\mathrm{PP}}), V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s} \right\} \quad (3.33)$$

has a minimizer.

Many different transferability criteria J_{t}, based on various physical and chemical properties, can be considered. A natural choice is the criterion

$$J^{\mathrm{Stark}}_{\mathrm{t}}(V_z^{\mathrm{PP}}) := \frac{1}{2}\left\| \mathbb{1}_{\mathbb{R}^3 \setminus B_{r_{\mathrm{c}}}} \left(\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}}) - \rho^{(1)}_{z,W^{\mathrm{Stark}}} \right) \right\|^2_{\mathcal{C}}, \quad (3.34)$$

where $\rho^{(1)}_{z,W^{\mathrm{Stark}}} = \rho_{\gamma^{(1)}_{z,W^{\mathrm{Stark}}}}$ and $\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}}) = \rho_{\widetilde{\gamma}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}})}$ are respectively the first-order perturbations of the all-electron and pseudo densities of atom z, when the latter is submitted to the Stark potential (3.29). The Coulomb space $\mathcal{C}$ is defined as

$$\mathcal{C} = \left\{ \rho \in \mathcal{S}'(\mathbb{R}^3) \,|\, \widehat{\rho} \in L^1_{\mathrm{loc}}(\mathbb{R}^3),\, \|\rho\|_{\mathcal{C}}^2 := D(\rho,\rho) < \infty \right\},$$

where

$$D(f,g) := 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{f}(\mathbf{k})}\,\widehat{g}(\mathbf{k})}{|\mathbf{k}|^2}\, d\mathbf{k}. \tag{3.35}$$

Let us recall that $L^{6/5}(\mathbb{R}^3) \subset \mathcal{C}$, that the definitions (2.3) and (3.35) agree for $(f,g) \in L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$, and that $\mathcal{C}$ is therefore the space of all charge distributions ρ with finite Coulomb energy.

The following lemma shows that the transferability criterion $J_{\mathrm{t}}^{\mathrm{Stark}}$ is well-defined and falls into the scope of Theorem 3.12.

LEMMA 3.13. *Let $z, \Delta E, r_{\mathrm{c}}, s$ satisfying Assumption 1. Then, $J_{\mathrm{t}}^{\mathrm{Stark}}$ is a well-defined bounded below weakly continuous mapping from $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ to $\mathbb{R}_+$.*

4. Extensions to the Kohn–Sham LDA model

It is probably quite difficult to extend to the LDA model the results established above for the Hartree model. As usual in the mathematical analysis of Kohn–Sham models, the main obstacle is that we do not know whether the atomic ground state density of atom z is unique. We will therefore limit ourselves to comment on the extensions of our main results under some additional assumptions on the Kohn–Sham LDA ground state.

Assuming that the LDA ground state density ρ_z^0 of atom z is unique, hence radial, and that the LDA Fermi level of atom z is negative, it is then easy to show that the properties of the ground state density and of the atomic Hamiltonian listed in propositions 1 and 8, as well as the result of uniqueness of the ground state density matrix, still hold for the all-electron Kohn–Sham LDA model. Likewise, the results in Proposition 5 are still valid for the LDA model under the assumption that the ground state pseudo-density $\widetilde{\rho}_z^0$ of atom z is unique. Note that the self-consistent potentials are then given, in the all-electron setting, by

$$W_z^{\mathrm{AA}} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1} + v_{\mathrm{xc}}(\rho_z^0),$$

where $v_{\mathrm{xc}}(\rho_z^0) = \frac{d\epsilon_{\mathrm{xc}}}{d\rho}(\rho_z^0)$ is the exchange-correlation potential, and, in the pseudopotential setting, by

$$W_z^{\mathrm{PP}} = V_z^{\mathrm{PP}} + \widetilde{\rho_z^0} \star |\cdot|^{-1} + v_{\mathrm{xc}}(\widetilde{\rho}^0_{z,\mathrm{c}} + \widetilde{\rho}_z^0).$$

Still under the above assumptions, Lemma 11 (nonemptyness of the set $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ of admissible pseudopotentials), Theorem 11 ($\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ is a weakly closed subset of the affine space $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$), and Theorem 16 (existence of an optimal pseudopotential in an abstract framework) can all be extended to the LDA setting.

Note that, in practice, the calibration of pseudopotentials is made under the assumption that the LDA ground state density (with or without pseudopotential) is radial. The calculations then boil down to solving coupled systems of radial Schrödinger equations

(see [6, 18, 28] for details). To the best of our knowledge, no numerical evidence that the radial LDA ground state of an atom might not be unique has been published so far.

The extensions of our results involving nonlinear perturbation theory (Proposition 14, Theorem 15, and Lemma 17) require, on top of the above assumptions, an additional assumption on the uniform coercivity of the Hessian of the energy functional at the unperturbed local minimizer. As the exchange-correlation energy density is not twice differentiable at 0 (it behaves as the function $\mathbb{R}_+ \ni \rho \mapsto -\rho^{4/3} \in \mathbb{R}_-$), it is not clear that such an assumption is satisfied. As already mentioned in [5, Section 5], this technical problem is not encountered in Kohn–Sham calculations with periodic boundary conditions due to the fact that the ground state density then is both bounded and bounded away from zero.

5. Proofs

5.1. Proof of Lemma 3.1. The three-dimensional Fourier transform of a radial function $u \in L^2_{\mathrm{r}}(\mathbb{R}^3)$ is related to the one-dimensional Fourier transform of the function $R_u = \mathcal{R}(u)$ by the simple relation

$$\mathcal{F}_3(u)(\mathbf{k}) = \frac{i}{\sqrt{2\pi}|\mathbf{k}|}\mathcal{F}_1(R_u)(|\mathbf{k}|).$$

The above expression is a special case of the Grafakos–Teschl recursion formula [13]. We therefore have

$$\begin{aligned}\|u\|^2_{H^s(\mathbb{R}^3)} &= \int_{\mathbb{R}^3}(1+|\mathbf{k}|^2)^s|\mathcal{F}_3(u)(\mathbf{k})|^2\,d\mathbf{k} = \frac{1}{2\pi}\int_{\mathbb{R}^3}\frac{(1+|\mathbf{k}|^2)^s}{|\mathbf{k}|^2}|\mathcal{F}_1(R_u)(|\mathbf{k}|)|^2\,d\mathbf{k}\\ &= 2\int_0^\infty (1+k^2)^s|\mathcal{F}_1(R_u)(k)|^2\,dk = \int_{-\infty}^{+\infty}(1+k^2)^s|\mathcal{F}_1(R_u)(k)|^2\,dk = \|R_u\|^2_{H^s(\mathbb{R})}.\end{aligned}$$

5.2. Proof of Proposition 3.2. The proof of Proposition 3.2 is based on the following observation.

LEMMA 5.1. *Let $z \in \mathbb{N}^*$ such that $\epsilon^0_{z,\mathrm{F}} < 0$. The Hartree potential W^{AA}_z is a radial increasing negative function of $L^2_{\mathrm{r}}(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{0\})$ converging exponentially fast to* 0.

Proof. The Hartree potential W^{AA}_z satisfies $-\Delta W^{\mathrm{AA}}_z = 4\pi(\rho^0_z - z\delta_0)$, where the ground state density ρ^0_z is in $\mathcal{C}$ and satisfies $\int_{\mathbb{R}^3}\rho^0_z = z$. We also know from Proposition 2.1 that ρ^0_z is a radial positive function belonging to $C^\infty(\mathbb{R}^3 \setminus \{0\})$. Therefore, W^{AA}_z is radial and belongs to $C^\infty(\mathbb{R}^3 \setminus \{0\})$, and we infer from Gauss theorem that for all $r > 0$,

$$4\pi r^2 \frac{dW^{\mathrm{AA}}_z}{dr}(r) = -4\pi\left(-z + \int_{B_r}\rho^0_z\right) = 4\pi\int_{\mathbb{R}^3\setminus B_r}\rho^0_z > 0,$$

where B_r is the ball of $\mathbb{R}^3$ with center 0 and radius r. Hence, W^{AA}_z is a radial increasing function. Its limit at infinity is necessarily equal to zero since $W^{\mathrm{AA}}_z = -\frac{z}{|\cdot|} + \rho^0_z \star |\cdot|^{-1}$ with $\rho^0_z \star |\cdot|^{-1} \in \mathcal{C}' \subset L^6(\mathbb{R}^3)$. As $\epsilon^0_{z,\mathrm{F}} < 0$, the ground state density of the atom z is of the form

$$\rho^0_z(\mathbf{r}) = \sum_{i=1}^n p_i|\phi_i(\mathbf{r})|^2,$$

where the occupation numbers p_i are such that $0 \le p_i \le 2$ and $\sum_{i=1}^n p_i = z$, and where the orbitals ϕ_i satisfy

$$\phi_i \in H^2(\mathbb{R}^3), \quad -\frac{1}{2}\Delta\phi_i + W_z^{\mathrm{AA}}\phi_i = \epsilon_i\phi_i, \quad \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}.$$

As $\epsilon_i \le \epsilon^0_{z,\mathrm{F}} < 0$ and W_z^{AA} goes to zero at infinity, we deduce from the maximum principle for second-order elliptic equations (see e.g. [9]) that for each $1 \le i \le n$, $\phi_i\, e^{\sqrt{|\epsilon^0_{z,\mathrm{F}}|}|\cdot|/2} \in L^\infty(\mathbb{R}^3)$. Therefore, there exists $C_z \in \mathbb{R}_+$ such that

$$\forall \mathbf{r} \in \mathbb{R}^3, \quad 0 < \rho_z^0(\mathbf{r}) \le C_z\, e^{-\sqrt{|\epsilon^0_{z,\mathrm{F}}|}|\mathbf{r}|}. \tag{5.1}$$

Hence,

$$\forall r > 0, \quad 0 \le \frac{dW_z^{\mathrm{AA}}}{dr}(r) = \frac{1}{r^2}\int_{\mathbb{R}^3\setminus B_r} \rho_z^0 \le \frac{C_z}{r^2}\int_{\mathbb{R}^3\setminus B_r} e^{-\sqrt{|\epsilon^0_{z,\mathrm{F}}|}|\mathbf{r}'|}\, d\mathbf{r}'.$$

Integrating the above inequality leads to

$$\forall r \ge \frac{2}{\sqrt{|\epsilon^0_{z,\mathrm{F}}|}}, \quad 0 \ge W_z^{\mathrm{AA}}(r) \ge -\frac{4\pi r^2 C_z}{\sqrt{|\epsilon^0_{z,\mathrm{F}}|}}\, e^{-\sqrt{|\epsilon^0_{z,\mathrm{F}}|}r}.$$

Together with the fact that $W_z^{\mathrm{AA}} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)$, this bound implies that $W_z^{\mathrm{AA}} \in L^2_{\mathrm{r}}(\mathbb{R}^3)$. ∎

The proof of Proposition 3.2 then follows from classical results on the spectra of rotation-invariant Schrödinger operators (see e.g. [22]), which we recall here for completeness. First, as the function W_z^{AA} is in $L^2_{\mathrm{r}}(\mathbb{R}^3)$, the operator $W_z^{\mathrm{AA}}(1-\Delta)^{-1}|_{\mathcal{H}_l} = (W_z^{\mathrm{AA}}(1-\Delta)^{-1})|_{\mathcal{H}_l}$ is Hilbert–Schmidt for each $l \in \mathbb{N}$ by the Kato–Seiler–Simon inequality [23] and the continuity of P_l. Therefore, W_z^{AA} is a compact perturbation of the operator $-\frac{1}{2}\Delta|_{\mathcal{H}_l}$, and we deduce from Weyl's theorem that $\sigma_{\mathrm{ess}}(H^{\mathrm{AA}}_{z,l}) = \sigma_{\mathrm{ess}}(-\frac{1}{2}\Delta|_{\mathcal{H}_l}) = [0,+\infty)$.

The absence of strictly positive eigenvalues of H_z^{AA} is a consequence of Lemma 5.1 and [22, Theorem XIII.56]. The set of the negative eigenvalues of H_z^{AA} is the union of the sets of the negative eigenvalues of (3.4) for $l \in \mathbb{N}$; this is a straightforward consequence of the decomposition (3.2).

The fact that for each $l \in \mathbb{N}$, the negative eigenvalues of (3.4), if any, are simple and that the eigenfunctions associated with the nth eigenvalue have exactly $n-1$ nodes on $(0,+\infty)$ is a standard result on one-dimensional Schrödinger equations (Sturm's oscillation theory), which can be read in [7, 16] for instance.

Lemma 5.1, together with [22, Theorem XIII.9], implies that for each $l \in \mathbb{N}$, (3.4) has at most $(2l+1)^{-1}\int_0^{+\infty} r|W_z^{\mathrm{AA}}(r)|\,dr < \infty$ negative eigenvalues. Since this number is lower than 1 for l large enough, $H^{\mathrm{AA}}_{z,l}$ has no negative eigenvalue for l large enough. The monotonicity of the sequence $(n_{z,l})_{l\in\mathbb{N}}$ readily follows from the minmax principle. So does the last assertion.

5.3. Proof of Lemma 3.5. Let us first establish a couple of intermediate results.

LEMMA 5.2. *Let $W \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$. We denote by $\overline{B}^{\mathrm{c}}_r = \mathbb{R}^3 \setminus \overline{B}_r$, by $T_{W,r}$ the self-adjoint operator on $L^2(\overline{B}^{\mathrm{c}}_r)$ with domain $H^1_0(\overline{B}^{\mathrm{c}}_r) \cap H^2(\overline{B}^{\mathrm{c}}_r)$ defined by $T_{W,r}\phi = -\frac{1}{2}\Delta\phi + W\phi$ for all $\phi \in H^1_0(\overline{B}^{\mathrm{c}}_r) \cap H^2(\overline{B}^{\mathrm{c}}_r)$, and by*

$$\mathcal{T}_W(r) := \min(\sigma(T_{W,r})) = \inf_{\substack{\phi \in H^1_0(\overline{B}^{\mathrm{c}}_r) \\ \|\phi\|_{L^2(\overline{B}^{\mathrm{c}}_r)} = 1}} \int_{\overline{B}^{\mathrm{c}}_r} \left(\frac{1}{2}|\nabla\phi|^2 + W\phi^2 \right).$$

We also introduce the self-adjoint operator $T_{W,0}$ on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ defined by $T_{W,0}\phi = -\frac{1}{2}\Delta\phi + W\phi$ for all $\phi \in H^2(\mathbb{R}^3)$. Then, two situations may occur:

- *either $\min(\sigma(T_{W,0})) = 0$, in which case the function $\mathcal{T}_W$ is identically equal to zero on $(0,+\infty)$;*
- *or $\min(\sigma(T_{W,0})) < 0$, in which case there exists $\widetilde{r}_{\mathrm{c}} \in (0,+\infty)$ such that the function $\mathcal{T}_W$ is differentiable, strictly increasing, and bijective from $(0,\widetilde{r}_{\mathrm{c}})$ to $(\min(\sigma(T_{W,0})),0)$, and identically equal to zero on $(\widetilde{r}_{\mathrm{c}},+\infty)$.*

Proof. Let $W \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$. Since for any $0 < r < r' < \infty$, we have $\overline{B}^{\mathrm{c}}_{r'} \subset \overline{B}^{\mathrm{c}}_r$, the function $\mathcal{T}_W$ is non-decreasing on $(0,+\infty)$. As $\sigma_{\mathrm{ess}}(T_{W,r}) = [0,+\infty)$, we have for all $0 < r < \infty$,

$$0 \geq \mathcal{T}_W(r) \geq \inf_{\phi \in H^1(\mathbb{R}^3) \,|\, \|\phi\|_{L^2} = 1} \int_{\mathbb{R}^3} \left(\frac{1}{2}|\nabla\phi|^2 + \mathbb{1}_{\overline{B}^{\mathrm{c}}_r} W|\phi|^2 \right),$$

and it follows from [22, Theorem XIII.9] that the right-hand side is equal to zero for r large enough.

It also holds that $\sigma_{\mathrm{ess}}(T_{W,0}) = [0,+\infty)$. If $T_{W,0}$ has no negative eigenvalue, then the function $\mathcal{T}_W$ is identically equal to zero by the minmax principle. Otherwise, denoting by ϵ_1 the lowest negative eigenvalue of $T_{W,0}$, we have

$$\lim_{r \to 0} \mathcal{T}_W(r) = \epsilon_1.$$

This follows from the fact that $C^\infty_{\mathrm{c}}(\mathbb{R}^3 \setminus \{0\})$ is dense in $H^1(\mathbb{R}^3)$.

Lastly, for any $r \in (0,+\infty)$ such that $\mathcal{T}_W(r) < 0$, the operator $T_{W,r}$ has a negative non-degenerate ground state eigenvalue and a radial ground state $\phi_{W,r} \in H^1_0(\overline{B}^{\mathrm{c}}_r) \cap H^2(\overline{B}^{\mathrm{c}}_r)$ such that $\|\phi_{W,r}\|_{L^2(\overline{B}^{\mathrm{c}}_r)} = 1$ and $\phi_{W,r} > 0$ in $\overline{B}^{\mathrm{c}}_r$. By the Hopf's maximum principle for second-order linear elliptic equations [9], $\frac{\partial \phi_{W,r}}{\partial r} > 0$ on $\partial\overline{B}^{\mathrm{c}}_r = \partial B_r$. It is then well-known [24] that $\mathcal{T}_W$ is differentiable at r and that

$$\mathcal{T}'_W(r) = -\int_{\partial\overline{B}^{\mathrm{c}}_r} \frac{\partial \phi_{W,r}}{\partial n} = \int_{\partial B_r} \frac{\partial \phi_{W,r}}{\partial r} > 0.$$

Therefore, if $T_{W,0}$ has a negative eigenvalue, then the function $\mathcal{T}_W$ is continuous, there exists $0 < \widetilde{r}_{\mathrm{c}} < +\infty$ such that $\mathcal{T}_W$ is differentiable and strictly increasing on $(0,\widetilde{r}_{\mathrm{c}})$, and identically equal to zero on $[\widetilde{r}_{\mathrm{c}},+\infty)$, and $\mathcal{T}_W$ maps $(0,+\infty)$ onto $(\epsilon_1,0]$. ∎

It follows in particular from Lemma 5.2 that, since $W^{\mathrm{AA}}_z \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$ by Lemma 5.1, and $\varepsilon_{z,1} = \min(\sigma(H^{\mathrm{AA}}_z)) < E_+ < 0$, $\mathcal{T}_{W^{\mathrm{AA}}_z}$ maps $(0,+\infty)$ onto $(\varepsilon_{z,1},0]$ and the equation $\mathcal{T}_{W^{\mathrm{AA}}_z}(r) = E_+$ has a unique solution $r^+_{z,\Delta E,\mathrm{c}}$.

The second intermediate result we need is the following.

LEMMA 5.3. *Let $l\in\mathbb{N}$, $s\in\mathbb{R}_+$, $E_+<0$ and $W\in L^{3/2}_{\rm r}(\mathbb{R}^3)$ vanishing at infinity and such that $W\in H^s(\overline{B}^{\rm c}_\varepsilon)$, for any $\varepsilon>0$. Let $R_l\in H^2_{\rm o}(\mathbb{R})$ and $\epsilon_l<E_+$ be such that*

$$-\frac{1}{2}R_l''(r)+\frac{l(l+1)}{2r^2}R_l(r)+W(r)R_l(r)=\epsilon_l R_l(r),\quad \int_{\mathbb{R}}R_l^2=1.$$

Let $r_{\rm c}^+$ be the unique positive real number such that $\mathcal{T}_W(r_{\rm c}^+)=E_+$. Then, for all $r_{\rm c}>r_{\rm c}^+$, there exists $\widetilde{W}\in H^s_{\rm r}(\mathbb{R}^3)$ such that

$$\widetilde{R}_l\in H^1_{\rm o}(\mathbb{R}), \tag{5.2}$$

$$-\frac{1}{2}\widetilde{R}_l''(r)+\frac{l(l+1)}{2r^2}\widetilde{R}_l(r)+\widetilde{W}(r)\widetilde{R}_l(r)=\epsilon_l\widetilde{R}_l(r), \tag{5.3}$$

$$\int_{\mathbb{R}}\widetilde{R}_l^2=1, \tag{5.4}$$

$$\widetilde{R}_l=R_l\quad \text{on } (r_{\rm c},+\infty), \tag{5.5}$$

$$\widetilde{R}_l\geq 0\quad \text{on } (0,+\infty), \tag{5.6}$$

$$\sigma\left(\left(-\frac{1}{2}\Delta+\widetilde{W}\right)\Big|_{\mathcal{H}_l}\right)\setminus\{\epsilon_l\}\subset[E_+,+\infty). \tag{5.7}$$

Proof. Using the notation and the results in Lemma 5.2, we see that ϵ_l is an eigenvalue of $(T_{W,0})|_{\mathcal{H}_l}$, so that $E_+\in(\min(\sigma(T_{W,0})),0)$, which implies that there exists a unique positive real number $r_{\rm c}^+$ such that $\mathcal{T}_W(r_{\rm c}^+)=E_+$.

The rest of the proof is dedicated to constructing an explicit solution to (5.2)–(5.7). Let $r_{\rm c}>r_{\rm c}^+$ and $m_{\rm c}=\int_0^{r_{\rm c}}R_l^2$. We denote by R the unique odd function in $H^1(-r_c,r_c)$ such that

$$-\frac{1}{2}R''+\frac{l(l+1)}{2r^2}R-\epsilon_l R=0,\quad R(r_{\rm c})=1,$$

and by

$$F(d)=\int_0^{r_c-d}R^2(r)dr.$$

Note that the function $u(\mathbf{r})=\frac{r_{\rm c}R(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}_l^m(\frac{\mathbf{r}}{|\mathbf{r}|})$ is the unique solution in $H^1(B_{r_c})$ to the boundary value problem $-\frac{1}{2}\Delta u-\epsilon_l u=0$ in B_{r_c}, $u|_{\partial B_{r_c}}=\mathcal{Y}_l^m$, and that $F(d)=r_{\rm c}^{-2}\int_{B_{r_c-d}}|u|^2$. For all $0<\alpha\ll 1\ll A<\infty$, we introduce

$$\theta^-_{\alpha,A}=\arcsin(\alpha/A),\quad \theta^+_{\alpha,A}=\pi-\arcsin(R_l(r_{\rm c})/A)-\theta^-_{\alpha,A},$$

$d_{\alpha,A}$ the unique solution in $(0,r_{\rm c})$ of

$$\alpha^2F(d)+A^2\frac{d}{2}\left(1-\frac{\sin(2(\theta^+_{\alpha,A}+\theta^-_{\alpha,A}))-\sin(2\theta^-_{\alpha,A})}{2\theta^+_{\alpha,A}}\right)=m_{\rm c},$$

$$k_{\alpha,A}=\frac{\theta^+_{\alpha,A}}{d_{\alpha,A}},\quad v_{\alpha,A}=\epsilon_l-\frac{k^2_{\alpha,A}}{2},$$

$$\beta^-_{\alpha,A}=\frac{k_{\alpha,A}A\cos(\theta^-_{\alpha,A})}{2\alpha}-\frac{R'(r_c-d_{\alpha,A})}{2R(r_c-d_{\alpha,A})},\quad \beta^+_{\alpha,A}=\frac{R_l'(r_c)-k_{\alpha,A}A\cos(\theta^+_{\alpha,A}+\theta^-_{\alpha,A})}{2R_l(r_c)}.$$

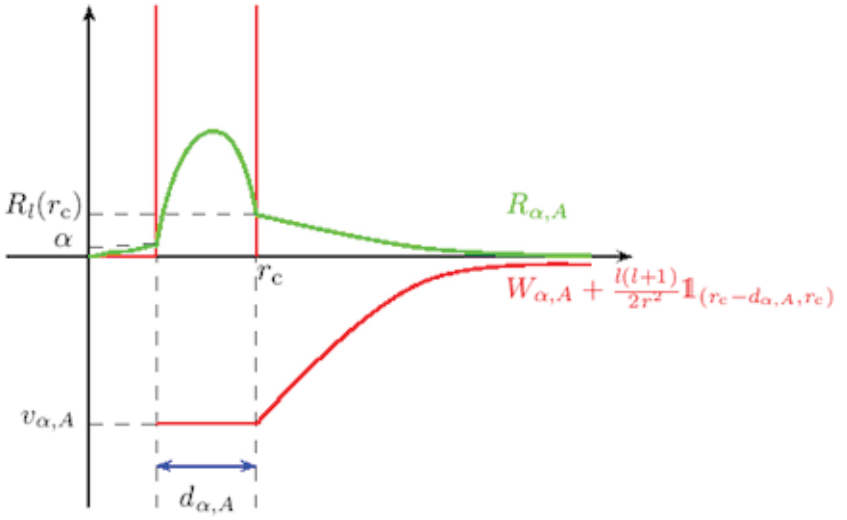

FIG. 5.1. *Sketch of the function $R_{\alpha,A}$ (green) and of the potential $W_{\alpha,A}+\frac{l(l+1)}{2r^2}\mathbb{1}_{(r_c-d_{\alpha,A},r_c)}$ (red).*

When $\alpha\to 0^+$ and $A\to+\infty$, the above quantities behave as follows

$$\theta^-_{\alpha,A}\to 0^+,\quad \theta^+_{\alpha,A}\to\pi^-,\quad d_{\alpha,A}\sim\frac{2m_c}{A^2},\quad k_{\alpha,A}\sim\frac{\pi A^2}{2m_c},\quad v_{\alpha,A}\sim-\frac{\pi^2A^4}{8m_c^2},$$
$$\beta^-_{\alpha,A}\sim\frac{\pi A^3}{4m_c\alpha},\quad \beta^+_{\alpha,A}\sim\frac{\pi A^3}{4m_cR_l(r_c)}. \tag{5.8}$$

Consider the function $R_{\alpha,A}\in H^1_o(\mathbb{R})$ defined on $(0,+\infty)$ by

$$R_{\alpha,A}=\alpha\frac{R}{R(r_c-d_{\alpha,A})}\mathbb{1}_{(0,r_c-d_{\alpha,A})}+A\sin\left(k_{\alpha,A}(r-r_c)+\theta^-_{\alpha,A}+\theta^+_{\alpha,A}\right)\mathbb{1}_{(r_c-d_{\alpha,A},r_c)}$$
$$+R_l\mathbb{1}_{(r_c,+\infty)}.$$

It is easily checked that $\widetilde{R}_l=R_{\alpha,A}$ is solution of (5.2)–(5.6) for $\widetilde{W}=W_{\alpha,A}\in H^{-1}_r(\mathbb{R}^3)$, with radial representation given by

$$W_{\alpha,A}=\beta^-_{\alpha,A}\delta_{r_c-d_{\alpha,A}}+\left(v_{\alpha,A}-\frac{l(l+1)}{2r^2}\right)\mathbb{1}_{(r_c-d_{\alpha,A},r_c)}+\beta^+_{\alpha,A}\delta_{r_c}+W\mathbb{1}_{(r_c,+\infty)}.$$

Denoting by

$$H_{\alpha,A}=-\frac{1}{2}\Delta+W_{\alpha,A},$$

we are going to show that for $\alpha>0$ small enough and $A<+\infty$ large enough

$$\sigma\left(H_{\alpha,A}\Big|_{\mathcal{H}_l}\right)\setminus\{\epsilon_l\}\subset(E_+,+\infty).$$

Let $\mu_{\alpha,A} = \min\left(\sigma\left(H_{\alpha,A}\Big|_{\mathcal{H}_l}\right)\setminus\{\epsilon_l\}\right)$. Assume that $\mu_{\alpha,A} \le E_+$. As $\sigma_{\rm ess}(H_{\alpha,A}|_{\mathcal{H}_l}) = \mathbb{R}_+$, $\mu_{\alpha,A}$ is a discrete eigenvalue of $H_{\alpha,A}|_{\mathcal{H}_l}$. We denote by $U_{\alpha,A}$ an associated normalized eigenfunction and by $u_{\alpha,A} \in H^1_{\rm o}(\mathbb{R})$ the odd extension of its radial component multiplied by r. As $\mu_{\alpha,A}$ is in fact the second lowest eigenvalue of $H_{\alpha,A}|_{\mathcal{H}_l}$ (counting multiplicities), the function $u_{\alpha,A}$ satisfies

$$-\frac{1}{2}u''_{\alpha,A} + \frac{l(l+1)}{2r^2}u_{\alpha,A} + W_{\alpha,A}u_{\alpha,A} = \mu_{\alpha,A}u_{\alpha,A},$$

and has exactly one node $r^0_{\alpha,A}$ in $(0,+\infty)$. This node cannot lay in the interval $[r_{\rm c},+\infty)$; otherwise, the function $\phi(\mathbf{r}) = U_{\alpha,A}(\mathbf{r})\mathbb{1}_{[r^0_{\alpha,A},+\infty)}(|\mathbf{r}|)\mathcal{Y}^0_l\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right)$ would belong to $H^1_0(\overline{B}^{\rm c}_{r^0_{\alpha,A}})\setminus\{0\}$ and we would have

$$E_+ = \mathcal{T}_W(r_{\rm c}^+) < \mathcal{T}_W(r^0_{\alpha,A}) \le \frac{\langle\phi|T_{W,r^0_{\alpha,A}}|\phi\rangle}{\langle\phi|\phi\rangle} = \mu_{\alpha,A},$$

which contradicts the assumption that $\mu_{\alpha,A} \le E_+$. It cannot either lay in the interval $(0, r_{\rm c} - d_{\alpha,A}]$; otherwise, as the potential $W_{\alpha,A}$ is equal to zero on this interval, we would have

$$\frac{1}{2}\int_0^{r^0_{\alpha,A}} |u'_{\alpha,A}|^2 + \frac{l(l+1)}{2}\int_0^{r^0_{\alpha,A}} \frac{|u_{\alpha,A}(r)|^2}{r^2}\,dr = \mu_{\alpha,A}\int_0^{r^0_{\alpha,A}} |u_{\alpha,A}|^2 < 0,$$

which is obviously not possible. We therefore have $r_{\alpha,A} \in (r_{\rm c} - d_{\alpha,A}, r_{\rm c})$, and without loss of generality, we can assume that $u_{\alpha,A}$ is positive in the neighborhood of $+\infty$. As $W_{\alpha,A}$ is equal to zero on $(0, r_{\rm c} - d_{\alpha,A})$, $u_{\alpha,A}$ is negative and concave on this interval, so that $u_{\alpha,A}(r_{\rm c} - d_{\alpha,A}) < 0$ and $u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+) < u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^-) < 0$. We therefore have

$$\forall r \in [r_{\rm c} - d_{\alpha,A}, r_{\rm c}], \quad u_{\alpha,A} = \widetilde{A}_{\alpha,A}\sin\left(\widetilde{k}_{\alpha,A}(r - (r_{\rm c} - d_{\alpha,A})) + \widetilde{\theta}_{\alpha,A}\right),$$

with $\widetilde{A}_{\alpha,A} < 0$, $\widetilde{k}_{\alpha,A} = \sqrt{2(\mu_{\alpha,A} - v_{\alpha,A})}$, $0 < \widetilde{\theta}_{\alpha,A} < \pi/2$, and $\pi < \widetilde{k}_{\alpha,A}d_{\alpha,A} + \widetilde{\theta}_{\alpha,A} < 2\pi$. It follows from the jump condition at $r_{\rm c} - d_{\alpha,A}$ and from the fact that $u_{\alpha,A}$ is negative and concave on $(0, r_{\rm c} - d_{\alpha,A})$ that

$$\frac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{\theta}_{\alpha,A})} = \frac{u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+)}{u_{\alpha,A}(r_{\rm c} - d_{\alpha,A})} \ge \frac{u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+) - u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^-)}{u_{\alpha,A}(r_{\rm c} - d_{\alpha,A})} = \beta^-_{\alpha,A}.$$

Thus,

$$\tan(\widetilde{\theta}_{\alpha,A}) \le \frac{\widetilde{k}_{\alpha,A}}{\beta^-_{\alpha,A}} \le \frac{2\pi}{\beta^-_{\alpha,A}d_{\alpha,A}} \sim \frac{4\alpha}{A}, \quad \text{when } \alpha \to 0^+ \text{ and } A \to +\infty. \tag{5.9}$$

We can distinguish two cases:

- case 1: $u'_{\alpha,A}(r_c - 0) < 0$. In this case, $\widetilde{k}_{\alpha,A}d_{\alpha,A} + \widetilde{\theta}_{\alpha,A} > \frac{3\pi}{2}$, which, together with (5.9), implies that for $\alpha > 0$ small enough and $A > 0$ large enough,

  $$\widetilde{k}_{\alpha,A} \ge \frac{5}{4}k_{\alpha,A} \quad \text{or equivalently} \quad \mu_{\alpha,A} \ge \epsilon_l - \frac{9}{16}v_{\alpha,A} \sim \frac{9\pi^2A^4}{128m_{\rm c}^2},$$

  which contradicts the assumption that $\mu_{\alpha,A} \le E_+$;

- case 2: $u'_{\alpha,A}(r_c-0)\geq 0$. In this case, the function $u_{\alpha,A}$ is positive on $(r_{\rm c},+\infty)$ and the pair $(u_{\alpha,A},\mu_{\alpha,A})$ is solution to the spectral problem on $(r_{\rm c},+\infty)$ with Robin boundary conditions

$$\begin{cases} -\dfrac{1}{2}u''_{\alpha,A}(r)+\dfrac{l(l+1)}{2r^2}u_{\alpha,A}(r)+Wu_{\alpha,A}(r)=\mu_{\alpha,A}u_{\alpha,A}(r), \quad r\in(r_{\rm c},+\infty) \\ \\ u'_{\alpha,A}(r_c+0)=\left(\dfrac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{k}_{\alpha,A}d_{\alpha,A}+\widetilde{\theta}_{\alpha,A})}+\beta^+_{\alpha,A}\right)u_{\alpha,A}(r_c). \end{cases} \tag{5.10}$$

  When $\alpha\to 0^+$ and $A\to+\infty$, the parameter $\frac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{k}_{\alpha,A}d_{\alpha,A}+\widetilde{\theta}_{\alpha,A})}+\beta^+_{\alpha,A}$ goes to $+\infty$, so that $\mu_{\alpha,A}$ converges to the ground state eigenvalue of $T_{W,r_c}|_{\mathcal{H}_l}$, which implies

$$\lim_{\alpha\downarrow 0,\,A\to+\infty}\mu_{\alpha,A}=\mathcal{T}_W(r_c)>\mathcal{T}_W(r_c^+)=E_+.$$

  Choosing $\alpha>0$ small enough and A large enough, we obtain a contradiction with the assumption that $\mu_{\alpha,A}\leq E_+$.

We therefore have obtained a function $\widetilde{R}_l=R_{\alpha,A}\in H^1_{\rm o}(\mathbb{R})$ and a potential $\widetilde{W}=W_{\alpha,A}\in H^{-1}_{\rm r}(\mathbb{R}^3)$ such that (5.2)–(5.7) are satisfied. As $R_{\alpha,A}$ is in $C^\infty(\mathbb{R}\setminus\{\pm(r_{\rm c}-d_{\alpha,A}),\pm r_{\rm c}\})$ and is positive on $(0,+\infty)$, we can construct a sequence $(\widetilde{R}_{l,n})_{n\in\mathbb{N}}$ of odd functions of $C^\infty(\mathbb{R})\cap H^1_{\rm o}(\mathbb{R})$ positive on $(0,+\infty)$ and converging in $H^1_{\rm o}(\mathbb{R})$ to $R_{\alpha,A}$, such that $\widetilde{R}_{l,n}=R_{\alpha,A}=R_l$ on $(r_{\rm c},+\infty)$, $\widetilde{R}_{l,n}=R_{\alpha,A}$ on $(0,r_{\rm c}-d_{\alpha,A})$ and $\int_{\mathbb{R}}|\widetilde{R}_{l,n}|^2=1$. Consider the sequence of radial potentials defined by

$$\forall n\in\mathbb{N},\,\forall r\in(0,+\infty),\quad \widetilde{W}_n(r)=\epsilon_l+\frac{1}{2}\frac{\widetilde{R}''_{l,n}(r)}{\widetilde{R}_{l,n}(r)}-\frac{l(l+1)}{2r^2}.$$

As $\widetilde{R}_{l,n}(r)$ is bounded away from zero on the interval $[(r_c-d_{\alpha,A})/2,r_c+1]$ uniformly in n, each $\widetilde{W}_n$ is in $H^s_{\rm r}(\mathbb{R}^3)$ for all $s\geq 0$, and the sequence $(\widetilde{W}_n)_{n\in\mathbb{N}}$ converges to $W_{\alpha,A}$ in $H^{-1}_{\rm r}(\mathbb{R}^3)$. Consequently, the Rayleigh quotients $\mathbf{R}_n(\phi)=\dfrac{\langle\phi|-\frac{1}{2}\Delta+\widetilde{W}_n|\phi\rangle}{\|\phi\|^2}$ converge to $\mathbf{R}(\phi)=\dfrac{\langle\phi|-\frac{1}{2}\Delta+\widetilde{W}|\phi\rangle}{\|\phi\|^2}$ for any $\phi\in\mathcal{H}_l\cap H^1(\mathbb{R}^3)$, which implies, by the minmax principle, that the kth negative eigenvalue of $\left(-\frac{1}{2}\Delta+\widetilde{W}_n\right)\Big|_{\mathcal{H}_l}$ converges to the kth negative eigenvalue of $\left(-\frac{1}{2}\Delta+W_{\alpha,A}\right)\big|_{\mathcal{H}_l}$ when n goes to infinity. Therefore, for n large enough, conditions (5.2)–(5.7) are satisfied for $\widetilde{W}=\widetilde{W}_n$. ∎

We are now in a position to prove the non-emptiness of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ under the assumptions of Lemma 3.5. Applying Lemma 5.3 successively for each $0\leq l\leq l_z$ with $W=W_z^{\rm AA}$, $R_l=R_{z,n^\star_{z,l},l}$, $\epsilon_l=\epsilon_{z,n^\star_{z,l},l}$, and $r_{\rm c}>r^+_{z,{\rm c}}$, we obtain l_z+1 functions $\widetilde{W}_l\in H^s_{\rm r}(\mathbb{R}^3)$ and l_z+1 functions $\widetilde{R}_l$, satisfying for each $0\leq l\leq l_z$,

$$\widetilde{R}_l\in H^1_{\rm o}(\mathbb{R}), \tag{5.11}$$

$$-\frac{1}{2}\widetilde{R}''_l(r)+\frac{l(l+1)}{2r^2}\widetilde{R}_l(r)+\widetilde{W}_l\widetilde{R}_l(r)=\epsilon_{z,n^\star_{z,l},l}\widetilde{R}_l(r), \tag{5.12}$$

$$\int_{\mathbb{R}} \widetilde{R}_l^2 = 1, \tag{5.13}$$

$$\widetilde{R}_l = R_{z,n^\star_{z,l},l} \quad \text{and} \quad \widetilde{W}_l = W_z^{\mathrm{AA}} \quad \text{on } (r_{\mathrm{c}},+\infty), \tag{5.14}$$

$$\widetilde{R}_l \geq 0 \quad \text{on } (0,+\infty). \tag{5.15}$$

We then introduce the functions

$$\widetilde{\phi}_l^m(\mathbf{r}) = \frac{\sqrt{2}\,\widetilde{R}_l(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \qquad -l \leq m \leq l, \tag{5.16}$$

and the density

$$\widetilde{\rho}^0(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\widetilde{\phi}_l^m(\mathbf{r})|^2,$$

and we consider a sequence $(W_{\mathrm{loc},k})_{k\geq 1}$ of local potentials in the class $H^s_{\mathrm{r}}(\mathbb{R}^3)$ such that $W_{\mathrm{loc},k} \geq W_z^{\mathrm{AA}}$ on $\mathbb{R}^3$, $W_{\mathrm{loc},k} = W_z^{\mathrm{AA}}$ in $\overline{B}^{\mathrm{c}}_{r_{\mathrm{c}}}$, and $W_{\mathrm{loc},k} = k$ on $B_{r_{\mathrm{c}}-1/k}$. We finally set

$$V_{\mathrm{loc},k} = W_{\mathrm{loc},k} - \widetilde{\rho}^0 \star |\cdot|^{-1} \quad \text{and} \quad \forall 0 \leq l \leq l_z, \quad V_{l,k} = \widetilde{W}_l - W_{\mathrm{loc},k},$$

and

$$V_k = V_{\mathrm{loc},k} + \sum_{l=0}^{l_z} P_l V_{l,k} P_l.$$

By construction, the self-adjoint operator

$$H_k = -\frac{1}{2}\Delta + V_k + \widetilde{\rho}^0 \star |\cdot|^{-1},$$

on $L^2(\mathbb{R}^3)$ is rotation-invariant, and for all $0 \leq l \leq l_z$,

$$\mathbb{1}_{(-\infty,E_+)}(H_k|_{\mathcal{H}_l}) = \mathbb{1}_{(-\infty,E_+)}\left(\left(-\frac{1}{2}\Delta + \widetilde{W}_l\right)\Big|_{\mathcal{H}_l}\right) = \sum_{m=-l}^{l} |\widetilde{\phi}_l^m\rangle\langle\widetilde{\phi}_l^m|.$$

Lastly, for all $l > l_z$,

$$\min\sigma(H_k|_{\mathcal{H}_l}) \geq \min\sigma\left(-\frac{1}{2}\Delta + W_{\mathrm{loc},k}\right) \underset{k\to\infty}{\longrightarrow} \mathcal{T}_{W_z^{\mathrm{AA}}}(r_{\mathrm{c}}) > \mathcal{T}_{W_z^{\mathrm{AA}}}(r^+_{z,\mathrm{c}}) = E_+.$$

Therefore, for k large enough, $V_k \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$.

5.4. Proof of Theorem 3.8. Let us prove that $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ is weakly closed in the affine space $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$. For this purpose, we consider a sequence $(V_{z,k}^{\mathrm{PP}})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ weakly converging to some V_z^{PP} in $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$. We denote by $H_{z,k}^{\mathrm{PP}}$ the Hartree pseudo-Hamiltonian obtained with the pseudopotential $V_{z,k}^{\mathrm{PP}}$ and by $\widetilde{\phi}_{z,l,k}^m$ its eigenfunctions of the form (3.15). We have for all $k \in \mathbb{N}$,

$$H_{z,k}^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_k, \qquad H_{z,k}^{\mathrm{PP}} \widetilde{\phi}_{z,l,k}^m = \epsilon_{z,n^\star_{z,l},l} \widetilde{\phi}_{z,l,k}^m, \qquad \|\widetilde{\phi}_{z,l,k}^m\|_{L^2} = 1, \tag{5.17}$$

$$\widetilde{\rho}_k(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\widetilde{\phi}^m_{z,l,k}(\mathbf{r})|^2, \qquad v_k = \widetilde{\rho}_k \star |\cdot|^{-1},$$

$$W_k = V_{z,\mathrm{loc},k} + v_k + \sum_{l=0}^{l_z} P_l V_{z,l,k} P_l.$$

Note that for all $0 \le l \le l_z$, $-l \le m \le l$, and $k \in \mathbb{N}$, we have $\widetilde{\phi}^m_{z,l,k} = \phi^m_{z,n^\star_{z,l},l}$ on $\mathbb{R}^3 \setminus B_{r_\mathrm{c}}$ and

$$(W_k \widetilde{\phi}^m_{z,l,k})(\mathbf{r}) = \begin{cases} W^{\mathrm{AA}}_z(\mathbf{r}) \phi^m_{z,n^\star_{z,l},l}(\mathbf{r}) & \text{if } |\mathbf{r}| \ge r_\mathrm{c}, \\ (V_{z,\mathrm{loc},k}(\mathbf{r}) + v_k(\mathbf{r}) + V_{z,l,k}(\mathbf{r})) \widetilde{\phi}^m_{z,l,k}(\mathbf{r}) & \text{if } |\mathbf{r}| < r_\mathrm{c}. \end{cases}$$

As $\epsilon_{z,n^\star_{z,l},l} < 0$, $v_k \ge 0$ in $\mathbb{R}^3$, and $\|\widetilde{\phi}^m_{z,l,k}\|_{L^2} = 1$ we obtain, using the Sobolev inequality in $\mathbb{R}^3$, the boundedness of the sequence $(\|V_{z,l,k}\|_{L^2})_{k\in\mathbb{N}}$, and Lemma 5.1, that for all $k \in \mathbb{N}$,

$$\begin{aligned} \frac{1}{2}\|\nabla \widetilde{\phi}^m_{z,l,k}\|^2_{L^2} &= -\langle \widetilde{\phi}^m_{z,l,k} | W_k | \widetilde{\phi}^m_{z,l,k} \rangle + \epsilon_{z,n^\star_{z,l},l} \\ &\le -\int_{B_{r_\mathrm{c}}} (V_{z,\mathrm{loc},k} + V_{z,l,k}) |\widetilde{\phi}^m_{z,l,k}|^2 - \int_{\mathbb{R}^3 \setminus B_{r_\mathrm{c}}} W^{\mathrm{AA}}_z |\phi^m_{z,n^\star_{z,l},l}|^2 \\ &\le \left(\|V_{z,\mathrm{loc},k} + V_{z,l,k}\|_{L^2} \|\widetilde{\phi}^m_{z,l,k}\|^{1/2}_{L^2} \|\widetilde{\phi}^m_{z,l,k}\|^{3/2}_{L^6} + \|W^{\mathrm{AA}}_z\|_{L^\infty(\mathbb{R}^3\setminus B_{r_\mathrm{c}})} \right) \\ &\le C(1 + \|\nabla \widetilde{\phi}^m_{z,l,k}\|^{3/2}_{L^2}), \end{aligned}$$

where the constant C is independent of k. This implies that for all $0 \le l \le l_z$ and all $-l \le m \le l$, the sequence $(\widetilde{\phi}^m_{z,l,k})_{k\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$. We can therefore extract from $(\widetilde{\phi}^m_{z,l,k})_{k\in\mathbb{N}}$ a subsequence $(\widetilde{\phi}^m_{z,l,k_n})_{n\in\mathbb{N}}$ which weakly converges in $H^1(\mathbb{R}^3)$ to some function $\widetilde{\phi}^m_{z,l} \in H^1(\mathbb{R}^3) \cap \mathcal{H}_l$. As for all $k \in \mathbb{N}$, $\widetilde{\phi}^m_{z,l,k} = \phi^m_{z,n^\star_{z,l},l}$ in $\mathbb{R}^3 \setminus B_{r_\mathrm{c}}$, we can assume, without loss of generality, that the convergence of $(\widetilde{\phi}^m_{z,l,k_n})_{n\in\mathbb{N}}$ to $\widetilde{\phi}^m_{z,l}$ also holds strongly in $L^p(\mathbb{R}^3)$ for all $1 \le p < 6$ and almost everywhere in $\mathbb{R}^3$. In particular,

$$\forall 0 \le l, l' \le l_z, \quad \forall -l \le m \le l, \quad \forall -l' \le m' \le l', \quad \int_{\mathbb{R}^3} \widetilde{\phi}^m_{z,l} \widetilde{\phi}^{m'}_{z,l'} = \delta_{ll'} \delta_{mm'},$$

and the associated functions $\widetilde{R}_{z,l}$ defined by (3.15) satisfy (3.16) and (3.18)–(3.20). We also infer from the strong convergence of $(\widetilde{\phi}^m_{z,l,k_n})_{n\in\mathbb{N}}$ to $\widetilde{\phi}^m_{z,l}$ in $L^2(\mathbb{R}^3) \cap L^4(\mathbb{R}^3)$ that the sequence $(\widetilde{\rho}_{k_n})_{n\in\mathbb{N}}$ strongly converges in $L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$, hence in $L^{6/5}(\mathbb{R}^3)$ to the function $\widetilde{\rho}$ defined by

$$\widetilde{\rho}(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\widetilde{\phi}^m_{z,l}(\mathbf{r})|^2,$$

which, in turn, implies that the sequence $(v_{k_n})_{n\in\mathbb{N}}$ strongly converges in $\mathcal{C}'$, hence in $L^6(\mathbb{R}^3)$, to the function $v = \widetilde{\rho} \star |\cdot|^{-1}$. Lastly, as $(V_{z,l,k_n})_{n\in\mathbb{N}}$ weakly converges to $V_{z,l}$ in $H^s_{0,r}(B_{r_c})$ for $s > 0$, we can assume without loss of generality that the sequence $(V_{z,l,k_n})_{k_n\in\mathbb{N}}$ strongly converges to $V_{z,l}$ in $L^2(B_{r_\mathrm{c}})$. Passing to the limit in (5.17), we obtain that the functions $\widetilde{R}_{z,l}$ satisfy

$$-\frac{1}{2}\widetilde{R}''_{z,l}(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_{z,l}(r) + (v(r) + V_{z,l}(r))\widetilde{R}_{z,l}(r) = \epsilon_{z,n^\star_{z,l},l}\widetilde{R}_{z,l}(r).$$

To conclude that $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s}$, we just need to show that

$$\mathbb{1}_{(-\infty,E_+)}(H_z^{\rm PP}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} |\widetilde{\phi}_{z,l}^m\rangle\langle\widetilde{\phi}_{z,l}^m|, \tag{5.18}$$

where $H_z^{\rm PP} = -\frac{1}{2}\Delta + V_z^{\rm PP} + v$. If this was not the case, there would exists $\lambda < E_+$ and

$$\phi \in H^2(\mathbb{R}^3) \cap \left(\mathrm{Span}\left\{\widetilde{\phi}_{z,l}^m, 0 \le l \le l_z, -l \le m \le l\right\}\right)^{\perp}$$

such that $\|\phi\|_{L^2} = 1$ and $H_z^{\rm PP}\phi = \lambda\phi$. Consider, for n large enough, the function

$$\phi_n = \frac{\phi - \displaystyle\sum_{l=0}^{l_z}\sum_{m=-l}^{l} (\widetilde{\phi}_{z,l,k_n}^m, \phi)_{L^2}\widetilde{\phi}_{z,l,k_n}^m}{\left\|\phi - \displaystyle\sum_{l=0}^{l_z}\sum_{m=-l}^{l} (\widetilde{\phi}_{z,l,k_n}^m, \phi)_{L^2}\widetilde{\phi}_{z,l,k_n}^m\right\|_{L^2}}.$$

We have

$$\phi_n \in H^2(\mathbb{R}^3) \cap \left(\mathrm{Span}\left\{\widetilde{\phi}_{z,l,k_n}^m, 0 \le l \le l_z, -l \le m \le l\right\}\right)^{\perp}, \qquad \|\phi_n\|_{L^2} = 1, \tag{5.19}$$

and

$$\begin{aligned}\langle\phi_n|H_{z,k_n}^{\rm PP}|\phi_n\rangle = \left\|\phi - \sum_{l=0}^{l_z}\sum_{m=-l}^{l} (\widetilde{\phi}_{z,l,k_n}^m, \phi)_{L^2}\widetilde{\phi}_{z,l,k_n}^m\right\|_{L^2}^{-2} \Bigg(\lambda + \langle\phi|V_{z,k_n}^{\rm PP} - V_z^{\rm PP}|\phi\rangle \\ + \int_{\mathbb{R}^3}(v_{k_n} - v)\phi^2 - \sum_{l=0}^{l_z}\sum_{m=-l}^{l} \epsilon_{z,n_{z,l}^\star,l}|(\widetilde{\phi}_{z,l,k_n}^m, \phi)_{L^2}|^2\Bigg).\end{aligned}$$

Using the weak convergence of $V_{z,k_n}^{\rm PP}$ to $V_z^{\rm PP}$ in $\mathcal{X}_{z,\Delta E,r_c,s}$, the strong convergence of v_{k_n} to v in $L^2(\mathbb{R}^3)$ and the strong convergence of $\widetilde{\phi}_{z,l,k_n}^m$ to $\widetilde{\phi}_{z,l}^m$ in $L^2(\mathbb{R}^3)$, we obtain that

$$\lim_{n\to\infty} \langle\phi_n|H_{z,k_n}^{\rm PP}|\phi_n\rangle = \lambda.$$

Together with (5.17) and (5.19), this implies that for n large enough, $H_{z,k_n}^{\rm PP}$ has at least $(l_z+1)^2+1$ eigenvalues in $(-\infty, E_+)$, which contradicts the fact that $V_{z,k_n}^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s}$. Therefore, $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s}$, which proves that $\mathcal{M}_{z,\Delta E,r_c,s}$ is weakly closed in $\mathcal{X}_{z,\Delta E,r_c,s}$.

5.5. Proof of Lemma 3.9. The function $\widetilde{\phi}_{z,l,m}$ is an eigenfunction of the Schrödinger operator $-\frac{1}{2}\Delta + W_{z,\rm loc} + V_{z,l}$ on $L^2(\mathbb{R}^3)$, with $W_{z,\rm loc} + V_{z,l} \in H_{\rm r}^s(\mathbb{R}^3)$. By elliptic regularity, $\widetilde{\phi}_{z,n,l} \in H^{s+2}(\mathbb{R}^3)$, and therefore $\widetilde{R}_{z,l} \in H_{\rm o}^{s+2}(\mathbb{R})$ in view of Lemma 3.1. It follows from the unique continuation principle for nonnegative solutions of second-order ordinary differential equations that $\widetilde{R}_{z,l} > 0$ on $(0,+\infty)$. The function $\widetilde{R}_{z,l}$ is an odd function which solves a differential equation, with regular singular point, of the form

$$r^2 y'' - l(l+1)y + V_l(r)y = 0, \quad \text{with} \quad V_l(0) = 0. \tag{5.20}$$

Its indicial equation is

$$s(s-1)-l(l+1)=0,$$

with roots $s_1=l+1$ and $s_2=-l$. Since $s_1-s_2=2l+1$ is an integer, Fuchs' theorem [16, 30] states that the fundamental system of solutions of (5.20) is

$$\begin{cases} y_1(r)=r^{s_1}p(r) \\ y_2(r)=cp(r)r^{s_1}\ln(r)+r^{s_2}q(r), \end{cases}$$

where $p(0)\neq 0$, $q(0)\neq 0$, and c is a constant. As y_2 does not vanish at zero, $\widetilde{R}_{z,l}$ is proportional to y_1.

5.6. Proof of Proposition 3.10. Observing that

$$E_{V_z^{\mathrm{PP}}}(\widetilde{\gamma},v,W)=\mathrm{Tr}\left(\left(-\frac{1}{2}\Delta+V_z^{\mathrm{PP}}\right)\widetilde{\gamma}\right)+\frac{1}{2}D(\rho_{\widetilde{\gamma}},\rho_{\widetilde{\gamma}})+\mathrm{Tr}\left(\widetilde{\gamma}(v+W)\right)$$

allows us to follow the same lines as in the proofs of [5, theorems 5 and 12] (see also the first point in [5, Section 5]). Indeed, the operator H_z^{PP} has the same spectral properties as the operator H_0 in [5], and the key property on the perturbation that we need to proceed as in [5] is that there exists a constant $C\in\mathbb{R}_+$ such that

$$|\mathrm{Tr}\left(\widetilde{\gamma}(v+W)\right)|\leq C\left(\|v\|_{X_{z,\Delta E,r_c,s}}+\|W\|_{\mathcal{C}'}\right)\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}, \tag{5.21}$$

for all $(\widetilde{\gamma},v,W)\in\mathfrak{S}_{1,1}\times X_{z,\Delta E,r_c,s}\times\mathcal{C}'$. Let us prove that (5.21) actually holds true. On the one hand, we have for all $(\widetilde{\gamma},W)\in\mathfrak{S}_{1,1}\times\mathcal{C}'$,

$$\begin{aligned} |\mathrm{Tr}\left(\widetilde{\gamma}W\right)| &= \left|\mathrm{Tr}\left((1-\Delta)^{-1/2}(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}(1-\Delta)^{-1/2}W\right)\right| \\ &\leq \|(1-\Delta)^{-1/2}\|\,\|(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\|_{\mathfrak{S}_1}\|(1-\Delta)^{-1/2}W\| \\ &\leq \|(1-\Delta)^{-1/2}\|\,\|(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\|_{\mathfrak{S}_1}\|(1-\Delta)^{-1/2}W\|_{\mathfrak{S}_6} \\ &\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\|W\|_{L^6}\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\|W\|_{\mathcal{C}'}, \end{aligned}$$

where we have used the Kato–Seiler–Simon inequality [23] in the Schatten class $\mathfrak{S}_6(L^2(\mathbb{R}^3)):=\left\{T\in\mathcal{B}(L^2(\mathbb{R}^3))\,|\,\|T\|_{\mathfrak{S}_6}:=\mathrm{Tr}\,(|T|^6)^{1/6}<\infty\right\}$. Likewise, we have for all $(\widetilde{\gamma},v)\in\mathfrak{S}_{1,1}\times X_{z,\Delta E,r_c,s}$,

$$\begin{aligned} |\mathrm{Tr}\left(\widetilde{\gamma}v\right)| &= \left|\mathrm{Tr}\left(\left(v_{\mathrm{loc}}+\sum_{l=0}^{l_z}P_lv_lP_l\right)\widetilde{\gamma}\right)\right| \\ &\leq \left|\mathrm{Tr}\left((1-\Delta)^{-1/2}v_{\mathrm{loc}}(1-\Delta)^{-1/2}(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\right)\right| \\ &\quad+\sum_{l=0}^{l_z}\left|\mathrm{Tr}\left(P_l(1-\Delta)^{-1/2}v_l(1-\Delta)^{-1/2}P_l(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\right)\right| \\ &\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\left(\|v_{\mathrm{loc}}\|_{L^2}+\sum_{l=0}^{l_z}\|v_l\|_{L^2}\right)\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\|v\|_{X_{z,\Delta E,r_c,s}}, \end{aligned}$$

where we have used that the P_l's commute with the Laplace operator and the fact that for all $w\in L^2(\mathbb{R}^3)$,

$$\|(1-\Delta)^{-1/2}w(1-\Delta)^{-1/2}\|\leq\||w|^{1/2}(1-\Delta)^{-1/2}\|^2\leq\||w|^{1/2}(1-\Delta)^{-1/2}\|_{\mathfrak{S}_4}^2\leq C\|w\|_{L^2},$$

by the Kato–Seiler–Simon inequality for $p=4$.

Proceeding as in the proofs of theorems 5 (non-degenerate case) and 12 (degenerate case) in [5], we obtain that there exists $\eta>0$ such that for all $(v,W)\in B_\eta(X_{z,\Delta E,r_c,s})\times B_\eta(\mathcal{C}')$, problem (3.27) has a unique minimizer $\widetilde{\gamma}_{v+W}(V_z^{\rm PP})$ and that, for each $V_z^{\rm PP}\in\mathcal{M}_{z,\Delta E,r_c,s}$, the function $(v+W)\mapsto\widetilde{\gamma}_{v+W}(V_z^{\rm PP})$ is real analytic from $B_\eta(X_{z,\Delta E,r_c,s})+B_\eta(\mathcal{C}')$ to $\mathfrak{S}_{1,1}$. Expanding $\alpha\mapsto\widetilde{\gamma}_{\alpha(v+W)}(V_z^{\rm PP})$ as

$$\widetilde{\gamma}_{\alpha(v+W)}(V_z^{\rm PP})=\widetilde{\gamma}_z^0+\sum_{k=1}^{+\infty}\alpha^k\gamma_{v+W}^{(k)}(V_z^{\rm PP}),$$

the coefficients $\widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\rm PP})$ in (3.28) are connected to the coefficients $\gamma_{v+W}^{(k)}(V_z^{\rm PP})$ in the above expansion by the relation

$$\gamma_{\alpha v+\beta W}^{(k)}(V_z^{\rm PP})=\sum_{j=0}^{k}\alpha^j\beta^{k-j}\widetilde{\gamma}_{v,W}^{(j,k-j)}(V_z^{\rm PP}).$$

5.7. Proof of Theorem 3.11. It suffices to prove the results in the degenerate case, since, in this setting, the non-degenerate case can be seen as a special case of the degenerate case (take $N_{\rm p}=0$ in [5, Section 4]). We can also restrict ourselves to the pseudopotential case, as the all-electron case works the same.

Let $V_{\rm ref}\in\mathcal{M}_{z,\Delta E,r_c,s}$ be a reference pseudopotential fixed once and for all and $M\in\mathbb{R}_+$. We are going to establish a series of uniform bounds valid for all $V_z^{\rm PP}\in\mathcal{M}_{z,\Delta E,r_c,s}$ satisfying

$$\|V_z^{\rm PP}-V_{\rm ref}\|_{X_{z,\Delta E,r_c,s}}\le M. \tag{5.22}$$

In the sequel, we will denote by C_M constants depending on z, $V_{\rm ref}$, and M, but not on $V_z^{\rm PP}$. It follows from the arguments used in Section 5.4 that the pseudo-orbitals associated with $V_z^{\rm PP}$ satisfy

$$\max_{0\le l\le l_z}\max_{|m|\le l}\|\widetilde{\phi}_{z,l}^m\|_{H^1}\le C_M,$$

which implies that $\|\widetilde{\rho}_z^0\|_{L^1\cap L^3}\le C_M$, and therefore that $\|\widetilde{\rho}_z^0\star|\cdot|^{-1}\|_{L^\infty}\le C_M$, from which we infer that

$$\max_{0\le l\le l_z}\|W_{z,\rm loc}+V_{z,l}\|_{L^{3/2}}\le C_M. \tag{5.23}$$

Finally, using the Sobolev embedding $H^2(\mathbb{R}^3)\hookrightarrow L^\infty(\mathbb{R}^3)$, and the fact that for all $\phi\in H^2(\mathbb{R}^3)$, $\|\phi\|_{L^\infty}\le\|\phi\|_{H^2}$, we obtain

$$\max_{0\le l\le l_z}\max_{|m|\le l}\|\widetilde{\phi}_{z,l}^m\|_{L^\infty}\le\max_{0\le l\le l_z}\max_{|m|\le l}\|\widetilde{\phi}_{z,l}^m\|_{H^2}\le C_M. \tag{5.24}$$

Using the fact that $W_z^{\rm PP}=W_z^{\rm AA}$ in $\overline{B}_{r_c}^{\rm c}$ and the maximum principle for second-order elliptic equations [9], we obtain that

$$\max_{0\le l\le l_z}\max_{|m|\le l}\|\widetilde{\phi}_{z,l}^m e^{\sqrt{|\epsilon_{z,\rm F}^0|}|\cdot|/2}\|_{L^\infty}\le C_M. \tag{5.25}$$

As in [5], we decompose $L^2(\mathbb{R}^3)$ as the orthogonal sum of the fully occupied, partially occupied, and unoccupied spaces

$$L^2(\mathbb{R}^3):=\mathcal{H}_{\rm f}\oplus\mathcal{H}_{\rm p}\oplus\mathcal{H}_{\rm u}, \tag{5.26}$$

where $\mathcal{H}_{\rm f} = {\rm Ran}(\mathbb{1}_{(-\infty,\epsilon^0_{z,{\rm F}})}(H_z^{\rm PP}))$, $\mathcal{H}_{\rm p} = {\rm Ran}(\mathbb{1}_{\{\epsilon^0_{z,{\rm F}}\}}(H_z^{\rm PP}))$ and $\mathcal{H}_{\rm u} = {\rm Ran}(\mathbb{1}_{(\epsilon^0_{z,{\rm F}},+\infty)}(H_z^{\rm PP}))$, and where $P_{\rm f}$, $P_{\rm p}$ and $P_{\rm u}$ are the orthogonal projectors from $L^2(\mathbb{R}^3)$ to $\mathcal{H}_{\rm f}$, $\mathcal{H}_{\rm p}$, and $\mathcal{H}_{\rm u}$, respectively. We then introduce

- the spaces

$$\mathcal{A}_{\rm ux} := \left\{ A_{\rm ux} \in \mathcal{B}(\mathcal{H}_{\rm x}, \mathcal{H}_{\rm u}) \,|\, (P_{\rm u}(H_z^{\rm PP} - \epsilon^0_{\rm F})P_{\rm u})^{1/2} A_{\rm ux} \in \mathcal{B}(\mathcal{H}_{\rm x}, \mathcal{H}_{\rm u}) \right\},$$

  for ${\rm x} \in \{{\rm f}, {\rm p}\}$, endowed with the inner product

$$(A_{\rm ux}, B_{\rm ux})_{\mathcal{A}_{\rm ux}} := {\rm Tr}\,(A_{\rm ux}^* P_{\rm u}(H_z^{\rm PP} - \epsilon^0_{\rm F})P_{\rm u} B_{\rm ux});$$

- the finite dimensional spaces

$$\mathcal{A}_{\rm pf} := \mathcal{B}(\mathcal{H}_{\rm f}, \mathcal{H}_{\rm p}) \quad \text{and} \quad \mathcal{A}_{\rm pp} := \{ A_{\rm pp} \in \mathcal{S}(\mathcal{H}_{\rm p}) \,|\, {\rm Tr}\,(A_{\rm pp}) = 0 \};$$

- the product space

$$\mathcal{A} := \mathcal{A}_{\rm uf} \times \mathcal{A}_{\rm up} \times \mathcal{A}_{\rm pf} \times \mathcal{A}_{\rm pp},$$

  which we endow with the inner product

$$(A, B)_{\mathcal{A}} = \sum_{{\rm x} \in \{{\rm f},{\rm p}\}} (A_{\rm ux}, B_{\rm ux})_{\mathcal{A}_{\rm ux}} + \sum_{{\rm x} \in \{{\rm f},{\rm p}\}} {\rm Tr}\left(A_{\rm px} B_{\rm px}^*\right).$$

Note that the decomposition (5.26), as well as the space $\mathcal{A}$, depend on $V_z^{\rm PP}$. Following [5, Equation (43)], let us first show that the continuous linear map

$$\begin{aligned} \zeta : \mathcal{C}' &\to \mathcal{A}' \\ W &\mapsto -(P_{\rm u} W P_{\rm f}, P_{\rm u} W P_{\rm p} \Lambda, (2-\Lambda) P_{\rm p} W P_{\rm f}, P_{\rm p} W P_{\rm p}), \end{aligned}$$

where Λ is the diagonal matrix containing the partial occupation numbers at the Fermi level, can be extended in a unique way to a continuous linear map from $\mathcal{C}' + L^2_{\rm w}$ to $\mathcal{A}'$. We first observe that for all $W \in C^\infty_{\rm c}(\mathbb{R}^3)$ (where $C^\infty_{\rm c}(\mathbb{R}^3)$ is the space of the C^∞ functions on $\mathbb{R}^3$ with compact support), and all $A \in \mathcal{A}$,

$$\begin{aligned} |{\rm Tr}\,((P_{\rm u} W P_{\rm f})^* A_{uf})| &= |{\rm Tr}\,(P_{\rm f} W P_{\rm u} A_{\rm uf})| \\ &= \left| {\rm Tr}\left(P_{\rm f} W (H_z^{\rm PP} - \epsilon^0_{\rm F})\big|_{\mathcal{H}_{\rm u}}^{-1/2} (P_{\rm u}(H_z^{\rm PP} - \epsilon^0_{\rm F})P_{\rm u})^{1/2} A_{\rm uf} \right) \right|, \end{aligned}$$

where $(H_z^{\rm PP} - \epsilon^0_{\rm F})\big|_{\mathcal{H}_{\rm u}}^{-1/2}$ denotes the bounded operator on $L^2(\mathbb{R}^3)$ block-diagonal in the decomposition (5.26) identically equal to zero on $\mathcal{H}_{\rm f} \oplus \mathcal{H}_{\rm p}$ and equal to the inverse square root of the invertible positive operator $(H_z^{\rm PP} - \epsilon^0_{\rm F})\big|_{\mathcal{H}_{\rm u}}$ on $\mathcal{H}_{\rm u}$. As the space $\mathcal{A}_{\rm uf}$ consists of finite-rank operators with rank lower or equal to $N_{\rm f}$, the operator and trace norms are equivalent on this space, and we therefore obtain

$$\begin{aligned} \forall A \in \mathcal{A}, \quad |{\rm Tr}\,((P_{\rm u} W P_{\rm f})^* A_{uf})| &\le (E_+ - \epsilon^0_{z,{\rm F}})^{-1/2} \|P_f W\| \, \|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}} \\ &\le (E_+ - \epsilon^0_{z,{\rm F}})^{-1/2} \max_{1 \le n \le N_{\rm f}} \|W \phi_n\|_{L^2} \, \|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}}, \end{aligned}$$

where $(\phi_n)_{1 \le n \le N_{\rm f}}$ is an orthonormal basis of $\mathcal{H}_{\rm f}$. Similar arguments applied to the other components of $\zeta(W)$ lead to

$$\forall W \in C^\infty_{\rm c}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \le C_M \max_{0 \le l \le l_z, -l \le m \le l} \|W \widetilde{\phi}^m_{z,l}\|_{L^2}.$$

Using (5.25), we deduce from the above inequality that

$$\forall W \in C^\infty_{\rm c}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \leq C_M \|W\|_{L^2_{\rm w}}.$$

As ζ is continuous from $\mathcal{C}'$ to $\mathcal{A}'$ (see [5]), we also have

$$\forall W \in C^\infty_{\rm c}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \leq C_M \|W\|_{\mathcal{C}'+L^2_{\rm w}}. \tag{5.27}$$

The space $C^\infty_{\rm c}(\mathbb{R}^3)$ being dense in $\mathcal{C}'+L^2_{\rm w}$, we obtain that the linear map ζ can be extended in a unique way to a continuous linear map from $\mathcal{C}'+L^2_{\rm w}$ to $\mathcal{A}'$.

Let us now consider a sequence $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ which weakly converges to some $V^{\rm PP}_z$ in $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$. As $V_{z,{\rm loc},k}$ coincides with $-\frac{z}{|\cdot|}+\rho^0_{z,{\rm c}}\star|\cdot|^{-1}$ outside $B_{r_{\rm c}}$, we obtain that $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ converges to $V^{\rm PP}_z$ strongly in $\mathcal{M}_{z,\Delta E,r_{\rm c},s/2}$. To prove the compactness of the mapping $\mathcal{M}_{z,\Delta E,r_{\rm c},s} \ni V^{\rm PP}_z \mapsto \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_z) \in \mathfrak{S}_{1,1}$, it is therefore sufficient to show that the mapping $V^{\rm PP}_z \mapsto \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP})$ is strongly continuous from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathfrak{S}_{1,1}$ for any $s>0$. Let us therefore consider a sequence $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ which strongly converges to some $V^{\rm PP}_z$ in $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ and $M\in\mathbb{R}_+$ such that

$$\sup_{k\in\mathbb{N}} \|V^{\rm PP}_{z,k} - V_{\rm ref}\|_{X_{z,\Delta E,r_{\rm c},s}} \leq M.$$

Using [5, equations (42)–(43)], (5.27), the bound

$$\|H^{\rm PP}_{z,k}(1-\Delta)^{-1}\| \leq C_M,$$

and the fact that there exists $0<c_M\leq C_M<+\infty$ such that

$$\forall (A,A')\in\mathcal{A}\times\mathcal{A}, \quad \langle \Theta(A), A\rangle \geq c_M\|A\|^2_{\mathcal{A}} \quad \text{and} \quad \langle \Theta(A), A'\rangle \leq C_M\|A\|_{\mathcal{A}}\|A'\|_{\mathcal{A}},$$

where the bilinear form Θ is defined in [5, equation (59)], we obtain that

$$\sup_{k\in\mathbb{N}} \|\widetilde{\gamma}^{(1)}_W(V^{\rm PP}_{z,k})\|_{\mathfrak{S}_{1,1}} \leq C_M\|W\|_{\mathcal{C}'+L^2_{\rm w}}. \tag{5.28}$$

Let $\varepsilon>0$ and $W\in C^\infty_{\rm c}(\mathbb{R}^3)$ be such that $\|W-W^{\rm Stark}\|_{\mathcal{C}'+L^2_{\rm w}}\leq \varepsilon/(3C_M)$, where C_M is the constant in (5.28). By the triangular inequality,

$$\begin{aligned}\|\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_{z,k}) - \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_z)\|_{\mathfrak{S}_{1,1}} &\leq \frac{2\varepsilon}{3} + \|\widetilde{\gamma}^{(1)}_W(V^{\rm PP}_{z,k}) - \widetilde{\gamma}^{(1)}_W(V^{\rm PP}_z)\|_{\mathfrak{S}_{1,1}} \\ &\leq \frac{2\varepsilon}{3} + \left\| \lim_{\beta\to 0} \beta^{-1}\left(\widetilde{\gamma}_{V^{\rm PP}_{z,k}-V^{\rm PP}_z,\beta W}(V^{\rm PP}_z) - \widetilde{\gamma}_{0,\beta W}(V^{\rm PP}_z)\right)\right\|_{\mathfrak{S}_{1,1}}.\end{aligned}$$

We then infer from the analyticity properties of the mapping $(v,W)\mapsto\widetilde{\gamma}_{v,W}(V^{\rm PP})$ (cf. Proposition 3.10) that for k large enough, the second term of the right-hand side is lower than $\varepsilon/3$. Therefore, the mapping $V^{\rm PP}_z \mapsto \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_z)$ is strongly continuous from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathfrak{S}_{1,1}$.

5.8. Proof of Theorem 3.12. Let $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ be a minimizing sequence for (3.33). As $\alpha>0$ and $J_{\rm t}$ is bounded below, the sequence $(W^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ is bounded for the norm $\|\cdot\|_{H^s}$ defined in (3.32). As $W^{\rm PP}_{z,k}$ coincides with $W^{\rm AA}_z$ outside $B_{r_{\rm c}}$, we can assume, without loss of generality, that $(W^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ converges to some $W^{\rm PP}_z = W^{\rm PP}_{z,{\rm loc}} +$

$\sum_{l=0}^{l_z} P_l V_{z,l} P_l$, weakly for the norm $\|\cdot\|_{H^s}$, and strongly for the norm $\|\cdot\|_{H^{s-\eta}}$ for any $\eta>0$. We then have

$$\frac{1}{2}\|W_z^{\mathrm{PP}}\|_{H^s}^2 \le \liminf_{k\to\infty} J_{\mathrm{s}}(V_{z,k}^{\mathrm{PP}}). \tag{5.29}$$

Reasoning as in the proof of Theorem 3.8, we obtain that the ground state density $\widetilde{\rho}_k$ of

$$\inf\left\{\mathrm{Tr}\left(\left(-\frac{1}{2}\Delta+V_{z,k}^{\mathrm{PP}}\right)\widetilde{\gamma}\right)+\frac{1}{2}D(\rho_{\widetilde{\gamma}},\rho_{\widetilde{\gamma}}),\,\widetilde{\gamma}\in\mathcal{K}_{N_{z,\mathrm{v}}}\right\}$$

converges, when k goes to infinity, to some $\widetilde{\rho}$ in $H^s(\mathbb{R}^3)$, which is in fact the ground state density associated with the self-consistent pseudopotential W_z^{PP}. This implies that $V_{z,\mathrm{loc},k}^{\mathrm{PP}} = W_{z,\mathrm{loc},k}^{\mathrm{PP}} - \widetilde{\rho}_k\star|\cdot|^{-1}$ weakly converges to $V_{z,\mathrm{loc}}^{\mathrm{PP}} := W_{z,\mathrm{loc}}^{\mathrm{PP}} - \widetilde{\rho}\star|\cdot|^{-1}$ in $H^s_{\mathrm{loc}}(\mathbb{R}^3)$. Therefore, $(V_{z,k}^{\mathrm{PP}})_{k\in\mathbb{N}}$ weakly converges in $X_{z,\Delta E,r_{\mathrm{c}},s}$ to $V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}}^{\mathrm{PP}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l$, which belongs to $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ by virtue of Theorem 3.8, and W_z^{PP} is the self-consistent pseudopotential associated with V_z^{PP}. Using (5.29) and the weak lower-semicontinuity property of J_{t}, we finally obtain that

$$J(V_z^{\mathrm{PP}}) \le \liminf_{k\to\infty} J(V_{z,k}^{\mathrm{PP}}),$$

which implies that V_z^{PP} is a minimizer to (3.33).

5.9. Proof of Lemma 3.13. Let $(V_{z,k}^{\mathrm{PP}})_{k\in\mathbb{N}}$ be a sequence of elements of $\mathcal{M}_{z,\Delta E,\mathrm{c},s}$ weakly converging to V_z^{PP} in $\mathcal{X}_{z,\Delta E,\mathrm{c},s}$. By Theorem 3.8, $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ and by Theorem 3.11, the sequence $(\widetilde{\gamma}^{(1)}_{W^{\mathrm{Stark}}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ strongly converges to $\widetilde{\gamma}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}})$ in $\mathfrak{S}_{1,1}$. Consequently, $(\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ converges to $\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}})$ strongly in $L^{6/5}(\mathbb{R}^3)$, which implies that $(\mathbb{1}_{\mathbb{R}^3\setminus B_{r_{\mathrm{c}}}}\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ converges to $\mathbb{1}_{\mathbb{R}^3\setminus B_{r_{\mathrm{c}}}}\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}})$ in $L^{6/5}(\mathbb{R}^3)$ and, hence, converges in $\mathcal{C}$, which implies that the sequence of non-negative real-numbers $(J_{\mathrm{t}}^{\mathrm{Stark}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ converges to $J_{\mathrm{t}}^{\mathrm{Stark}}(V_z^{\mathrm{PP}})$.

Appendix A. List of the main symbols used throughout the article.

z: atomic number of the atom (atom z: atom with atomic number z);
$\mathcal{K}_N$: set of admissible (one-body) density matrices with N electrons.

Functional setting:

$\mathcal{H}_l = \mathrm{Ker}(\mathbf{L}^2 - l(l+1))$: eigenspace of $\mathbf{L}^2$ (square of the angular momentum operator);
P_l: orthogonal projector on $\mathcal{H}_l$ (in $L^2(\mathbb{R}^3)$ or any Sobolev space $H^s(\mathbb{R}^3)$);
$(\mathcal{Y}_l^m)_{l\in\mathbb{N},\,-l\le m\le l}$: real spherical harmonics;
$B_\eta(\mathcal{H})$: open ball of the Hilbert space $\mathcal{H}$ with center 0 and radius η;
$\mathcal{B}(\mathcal{H})$: space of bounded linear operators on the Hilbert space $\mathcal{H}$;
$\mathcal{S}(\mathcal{H})$: space of bounded self-adjoint operators on the Hilbert space $\mathcal{H}$;
$\mathfrak{S}_p(\mathcal{H})$: Schatten class of order p on the Hilbert space $\mathcal{H}$;
$\mathfrak{S}_{1,1} := \left\{T\in\mathfrak{S}_1(L^2(\mathbb{R}^3))\cap\mathcal{S}(L^2(\mathbb{R}^3))\,|\,|\nabla|T|\nabla|\in\mathfrak{S}_1(L^2(\mathbb{R}^3))\right\}$;
$L^p_{\mathrm{r}}(\mathbb{R}^3)$, $H^s_{\mathrm{r}}(\mathbb{R}^3)$, $H^s_{\mathrm{loc,r}}(\mathbb{R}^3)$: spaces of *radial* L^p, H^s, H^s_{loc} functions on $\mathbb{R}^3$;
$L^2_{\mathrm{o}}(\mathbb{R})$, $H^s_{\mathrm{o}}(\mathbb{R})$: spaces of *odd* L^2, H^s functions on $\mathbb{R}$;
$\mathcal{R}$: unitary mapping between $H^s_{\mathrm{r}}(\mathbb{R}^3)$ and $H^s_{\mathrm{o}}(\mathbb{R})$ (for any $s\ge 0$);
$\mathcal{C}$: Coulomb space, $D(\cdot,\cdot)$: Coulomb bilinear form (inner product of $\mathcal{C}$); $\mathcal{C}'$: dual of $\mathcal{C}$.

All-electron Hartree model:
E_z^{AA}: all-electron energy functional of atom z (Hartree model);
I_z^{AA}, ρ_z^0, γ_z^0: Hartree ground state energy, density and density matrix of atom z;
$H_z^{\mathrm{AA}} = -\frac{1}{2}\Delta + W_z^{\mathrm{AA}}$: all-electron Hartree Hamiltonian of atom z;
$\epsilon_{z,\mathrm{F}}^0$: Fermi level for atom z;
$\varepsilon_{z,j}$: lowest jth negative eigenvalue of H_z^{AA}, counting multiplicities;
$n_{z,l}$: number of distinct negative eigenvalues of $H_{z,l}^{\mathrm{AA}} := H_z^{\mathrm{AA}}|_{\mathcal{H}_l}$;
$\epsilon_{z,1,l} < \epsilon_{z,2,l} < \cdots < \epsilon_{z,n_{z,l},l}$: eigenvalues of $H_{z,l}^{\mathrm{AA}}$;
$(p_{z,n,l})_{1\le n\le n_{z,l}}$: occupation numbers of the states with energies $(\epsilon_{z,n,l})_{1\le n\le n_{z,l}}$;
$(\phi_{z,n,l}^m)_{-m\le l\le m}$: Hartree orbitals associated with $\epsilon_{z,n,l}$;
$R_{z,n,l}$: eigenfunction of the radial Schrödinger equation (3.4) associated with $\epsilon_{z,n,l}$.

Pseudopotential model:
$\Delta E = (E_-, E_+) \subset \mathbb{R}$: energy window partitioning core and valence electrons;
$n_{z,l}^*$: unique integer such that $\epsilon_{z,n_{z,l}^*,l} \in \Delta E$;
$N_{z,\mathrm{c}}$, $N_{z,\mathrm{v}}$: number of core and valence electrons of atom z (for a given ΔE);
$l_z^+ = \min\{l \in \mathbb{N} \,|\, n_{z,l+1} = 0\}$; $l_z^- = \max\{0 \le l \le l_z^+ \,|\, p_{z,1,l} > 0\}$; $l_z^- \le l_z \le l_z^+$;
$V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l$: (generic norm-conserving) pseudopotential for atom z;
$V_{z,\mathrm{loc}}$: local component of the pseudopotential;
$\widetilde{\rho}_z^0$: ground state pseudo-density of atom z (for a given V_z^{PP});
$W_z^{\mathrm{PP}} = V_z^{\mathrm{PP}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1} = W_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l$: self-consistent pseudopotential;
$W_{z,\mathrm{loc}} = V_{z,\mathrm{loc}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1}$: local component of the self-consistent pseudopotential;
$H_z^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_z^{\mathrm{PP}}$: pseudo Hartree Hamiltonian;
$\widetilde{\epsilon}_{z,\mathrm{F}}^0$: pseudo Fermi level (can be chosen equal to $\epsilon_{z,\mathrm{F}}^0$);
$\widetilde{R}_{z,l}$: radial part of the pseudo-orbital associated with $R_{z,n_{z,l}^*,l}$;
$\rho_{z,\mathrm{c}}^0$, $\rho_{z,\mathrm{v}}^0$: core and valence all-electron ground state densities;
$\widetilde{\rho}_{z,\mathrm{c}}^0 = \rho_0^z - \widetilde{\rho}_z^0$: core pseudo-density; $E_{z,\mathrm{c}}$: core energy;
$r_{\mathrm{c},l}$: core radius for shell l; $r_{\mathrm{c}} = \max_{0\le l\le l_z} r_{\mathrm{c},l}$: core radius;
$r_{z,\Delta E,\mathrm{c}}^0$: critical core radius for atom z and energy window ΔE;
$r_{z,\Delta E,\mathrm{c}}^-$, $r_{z,\Delta E,\mathrm{c}}^+$: (computable) lower and upper bounds of $r_{z,\Delta E,\mathrm{c}}^0$;
$\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$: set of admissible pseudopotentials for atom z, energy window ΔE, core radius r_{c} and Sobolev regularity s.

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