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ERIC CANCÈS, GABRIEL STOLTZ, GUSTAVO E. SCUSERIA,
VIKTOR N. STAROVEROV & ERNEST R. DAVIDSON

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Volume 2 (2009), p. 1-42.

<http://msia.cedram.org/item?id=MSIA_2009__2_1_1_0>

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Local Exchange Potentials for Electronic Structure Calculations

ERIC CANCÈS *
GABRIEL STOLTZ **
GUSTAVO E. SCUSERIA ***
VIKTOR N. STAROVEROV †
ERNEST R. DAVIDSON ‡

* Université Paris Est, CERMICS, Project-team Micmac, INRIA-Ecole des Ponts, 6 & 8 Av. Pascal, 77455 Marne-la-Vallée Cedex 2, France

E-mail address: cances@cermics.enpc.fr

** Université Paris Est, CERMICS, Project-team Micmac, INRIA-Ecole des Ponts, 6 & 8 Av. Pascal, 77455 Marne-la-Vallée Cedex 2, France

E-mail address: stoltz@cermics.enpc.fr

*** Department of Chemistry, Rice University, Houston, Texas 77005, United States of America

E-mail address: guscus@rice.edu

† Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada

E-mail address: vstarove@uwo.ca

‡ Department of Chemistry, University of Washington, Seattle, Washington 98195, United States of America

E-mail address: erdavid@u.washington.edu.

Abstract

The Hartree-Fock exchange operator is an integral operator arising in the Hartree-Fock model as well as in some instances of the density functional theory. In a number of applications, it is convenient to approximate this integral operator by a multiplication operator, i.e. by a local potential. This article presents a detailed analysis of the mathematical properties of various local approximations to the nonlocal Hartree-Fock exchange operator including the Slater potential, the optimized effective potential (OEP), the Krieger-Li-Iafrate (KLI) approximation and the common-energy denominator approximation (CEDA) to the OEP, and the effective local potential (ELP). In particular, we show that the Slater, KLI, CEDA and ELP potentials all can be defined as solutions of certain variational problems, and we provide a rigorous derivation of the OEP integral equation. We also establish an existence result for a coupled system of nonlinear partial differential equations introduced by Slater to approximate the Hartree-Fock equations.

1. Introduction

The Hartree-Fock exchange operator associated with an electronic first-order density matrix $\gamma \in H^1(\mathbb{R}^3 \times \mathbb{R}^3)$ is the Hilbert-Schmidt operator on $L^2(\mathbb{R}^3)$ defined by

$$\forall \phi \in L^2(\mathbb{R}^3), \quad (K\phi)(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}' \quad (1.1)$$

(see e.g. [6, 33, 35, 43] for mathematically oriented introductions to the Hartree-Fock model). This nonlocal (integral) operator is the most computationally demanding term in the Hartree-Fock equations, especially for periodic systems. Back in the early days of quantum chemistry,

The work at Rice University was supported by the US National Science Foundation CHE-0457030 and the Welch Foundation.

Keywords: Hartree-Fock model, Density Functional theory, nonlinear eigenvalue problem.

Math. classification: 35P30, 81Q05, 35J60 .

Slater proposed to approximate the Hartree-Fock exchange operator by a more tractable local potential, i.e. by a multiplicative operator [42]. Nowadays, the nonlocality of Hartree-Fock exchange is rarely seen as an obstacle for numerical calculations, at least in Gaussian basis sets. However, there has been a recent revival of interest in representing the exchange interaction with a local potential (see e.g. [11, 14, 17, 20, 27, 15, 13, 16, 22, 26] and references therein), spurred in particular by the emergence of orbital-dependent functionals in Kohn-Sham density functional theory. Local exchange potentials can also be used as input in other techniques, particularly in time-dependent and linear response methods for computing excitation energies and other properties [21, 29, 36, 46].

In his 1951 paper [42], Slater proposed two local approximations to the Hartree-Fock exchange operator. The first one is

$$v_{x,S}(\mathbf{r}) = -\frac{1}{\rho(\mathbf{r})} \int_{\mathbb{R}^3} \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (1.2)$$

where $\rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$ the electronic density. The second one is

$$v_{x,X\alpha}(\mathbf{r}) = -C_x \rho(\mathbf{r})^{1/3}, \quad (1.3)$$

where C_x is a positive constant.

Motivated by Slater's work, Sharp and Horton [41] introduced a variational method for obtaining local potentials that approximate the Hartree-Fock exchange operator. Considering a local potential W and the associated one-electron Schrödinger operator $H_W = -\frac{1}{2}\Delta + W$, they define the energy functional $E(W)$ as the Hartree-Fock energy of the Slater determinant constructed with the lowest N eigenfunctions of H_W . An optimized effective potential (OEP) is a local potential W^{OEP} which minimizes $E(W)$. The exchange part $v_{x,\text{OEP}}$ of W^{OEP} obtained by subtracting from W^{OEP} the nuclear and electronic Coulomb potentials can then be used as an approximation to the Hartree-Fock exchange operator. This track was further explored by Talman and Shadwick [45]. Unfortunately, it is difficult to give a proper mathematical formulation of the (infinite dimensional) OEP optimization problem, and also to build consistent finite dimensional approximations of the OEP problem (of course, the two issues are closely related). On the other hand, it is much easier to solve approximations of the Euler-Lagrange equation of the OEP minimization problem, the so-called OEP integral equation. Two approximations of the OEP integral equation have been proposed in the literature: the KLI [23] (after Krieger, Li and Iafrate) and the CEDA [12] (common energy denominator) approximations, leading to the local exchange potentials $v_{x,\text{KLI}}$ and $v_{x,\text{CEDA}}$.

More recently, several other approaches for generating local exchange potentials have been proposed [18, 44]. These methods associate with a density matrix γ an effective local potential (ELP) that can be considered as a variational approximation to the corresponding nonlocal Hartree-Fock exchange operator. Let us emphasize that it is natural to associate a Slater potential and an ELP with *any* electronic state (described by a density matrix γ). On the other hand, OEP, KLI and CEDA potentials are, by construction, obtained by solving a self-consistent system of equations in which the density matrix is an unknown. It has been pointed out [18, 44] that the CEDA potential coincides with the potential obtained by iterating the ELP procedure until the orbitals and the ELP are consistent with each other. The CEDA potential and the self-consistent ELP also coincide with the localized Hartree-Fock (LHF) potential introduced in Ref. [40]

The purpose of this article is to study the mathematical properties of the local exchange potentials described above. We would like to state it at the outset that the mathematical problems under examination are not trivial and that only partial results have been rigorously established so far. Although several articles on this topic containing mathematical statements have been published, many of them are not based on rigorous arguments and some are even flawed. Most of these flaws originate from *implicit* assumptions (existence and uniqueness of the solution of

an optimization problem or an equation, differentiability of a functional, existence of a limit, convergence of an asymptotic expansion, ...) that cannot be, or at least are not, verified. Our present results may seem weaker than others already published, but at least they are rigorous.

The article is organized as follows. In Section 2, the main mathematical properties of the Hartree-Fock model are briefly reviewed. The Slater potential (1.2) is dealt with in Section 3. We first assume that γ is given and study the asymptotic behavior of the Slater potential at infinity. We also provide a variational characterization of it. We then focus on the self-consistent equations obtained by replacing the Hartree-Fock exchange operator with the Slater potential (1.2) in the Hartree-Fock equations. These self-consistent equations, first written by Slater [42], do not seem to be the Euler-Lagrange equation of some optimization problem. We therefore use a fixed-point method to prove that, in the radial case (one nucleus at the origin and spherically symmetric orbitals), they actually have a solution. Note that the situation is completely different if one uses (1.3) instead of (1.2). Indeed, the corresponding self-consistent equations do have a variational interpretation: they are the Kohn-Sham equations obtained with the exchange functional

$$E_{x,X\alpha}(\rho) = -\frac{3C_x}{4} \int_{\mathbb{R}^3} \rho^{4/3}(\mathbf{r}) \, d\mathbf{r},$$

and have been extensively studied from a mathematical viewpoint in [3].

In Section 4, we focus on the OEP. We summarize the known mathematical results on the OEP minimization problem and provide a rigorous derivation of the OEP integral equation. We also study the KLI and CEDA approximations. We prove in Section 5 that the self-consistent ELP coincides with the CEDA potential. We do not provide a complete mathematical study of the self-consistent KLI, CEDA and ELP equations, but only study the analytical properties of the corresponding exchange potentials. We prove that, given a set of molecular orbitals and under some technical assumptions (always satisfied in practice), the KLI potential and the ELP (hence the CEDA potential) are uniquely defined up to an additive constant.

Section 7 presents some numerical results obtained with the methods mathematically studied in this paper, comparing the results to the reference Hartree-Fock results.

In order to keep the notation as simple as possible, we focus in Sections 2-5 on fully spin-polarized models, i.e. we consider systems with spin-up electrons only. With the notable exceptions of one-electron systems and two-electron systems in the triplet state, very few systems of practical interest are fully spin-polarized. However, the mathematical results stated in Sections 2-5 are generic, in the sense that they can be easily adapted to closed-shell and spin-polarized models. Details are given in Section 6.

All the proofs are postponed until Section 8. Basic concepts of functional analysis that are necessary to understand our arguments are summarized in the Appendix for the non-mathematical readership.

2. Hartree-Fock exchange operator

Let us first recall the mathematical formulation of the Hartree-Fock model. As we deal here with fully spin-polarized systems, the spin variable can be omitted and there is no limitation in working with real-valued functions. In the Hartree-Fock setting, the electronic state of a system of N electrons is described by a collection $\Phi = (\phi_i)_{1 \leq i \leq N}$ of N L^2 -orthonormal orbitals:

$$\int_{\mathbb{R}^3} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}, \tag{2.1}$$

or, equivalently, by the density matrix

$$\gamma_{\Phi}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r}) \phi_i(\mathbf{r}'),$$

the electronic density being given by

$$\rho_{\Phi}(\mathbf{r}) = \gamma_{\Phi}(\mathbf{r}, \mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2. \quad (2.2)$$

Denoting by

$$V_{\text{nuc}}(\mathbf{r}) = - \sum_{k=1}^K \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|} \quad (2.3)$$

the potential generated by the nuclei (z_k is the charge of the k -th nucleus, \mathbf{R}_k its position), the Hartree-Fock functional reads

$$\begin{aligned} E^{\text{HF}}(\Phi) &= \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r} + \int_{\mathbb{R}^3} V_{\text{nuc}}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &\quad - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \end{aligned}$$

Each term of the Hartree-Fock energy functional is well-defined provided $\Phi \in (H^1(\mathbb{R}^3))^N$, that is, provided $\nabla \phi_i \in (L^2(\mathbb{R}^3))^3$ for all $1 \leq i \leq N$, or in other words, provided the kinetic energy of Φ is finite. This property results from the inequalities [8]

$$\left| \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} \right| \leq N^{1/2} \left(\sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r} \right)^{1/2}, \quad (2.4)$$

and

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \leq \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \leq N^{3/2} \left(\sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r} \right)^{1/2}. \quad (2.5)$$

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

$$I^{\text{HF}} = \inf \left\{ E^{\text{HF}}(\Phi), \Phi \in \mathcal{X}_N \right\} \quad (2.6)$$

where

$$\mathcal{X}_N = \left\{ \Phi = (\phi_i)_{1 \leq i \leq N} \in (H^1(\mathbb{R}^3))^N \mid \int_{\mathbb{R}^3} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij} \right\}.$$

The inequalities (2.4) and (2.5) imply that the Hartree-Fock functional is always bounded from below on \mathcal{X}_N . The Hartree-Fock ground state energy is therefore well-defined for any molecular system of arbitrary charge. The existence of a Hartree-Fock ground state, that is, of some $\Phi^{\text{GS}} \in \mathcal{X}_N$ satisfying

$$E^{\text{HF}}(\Phi^{\text{GS}}) = \inf \left\{ E^{\text{HF}}(\Phi), \Phi \in \mathcal{X}_N \right\}$$

has been proved by Lieb and Simon [33] for neutral systems and positive ions. It is also known that ‘‘very negative’’ atomic ions are not stable: Denoting by Z the charge of the nucleus,

- (2.6) has no minimizer when $N > 2Z + 1$ [32];
- there exists a universal constant $Q \geq 0$ (whose optimal value is not known) such that for $N \geq Z + Q$, (2.6) has no minimizer [43].

From a physical point of view, the instability of very negative ions results from the fact that the excess electrons escape to infinity. Mathematically, it is due to a loss of compactness at infinity. The two viewpoints can be linked by the concentration-compactness theory due to Lions [34]. The existence of a Hartree-Fock ground state for ‘‘moderately’’ negative ions is still an open problem (only the stability of H^- has been mathematically established).

LOCAL EXCHANGE POTENTIALS

The Euler-Lagrange equations associated with the minimization problem (2.6) read

$$\mathcal{F}_\Phi \phi_i = \sum_{j=1}^N \lambda_{ij} \phi_j, \quad (2.7)$$

where $\Lambda = (\lambda_{ij})$ is a symmetric $N \times N$ matrix (it is the Lagrange multiplier of the matrix constraint (2.1)), and where \mathcal{F}_Φ is the Fock operator

$$\mathcal{F}_\Phi = -\frac{1}{2}\Delta + V_{\text{nuc}} + \rho_\Phi \star \frac{1}{|\mathbf{r}|} + K_\Phi.$$

In the above expression, \star denotes the convolution product:

$$(f \star g)(\mathbf{r}) := \int_{\mathbb{R}^3} f(\mathbf{r}') g(\mathbf{r} - \mathbf{r}') d\mathbf{r}',$$

and K_Φ is the so-called exact-exchange (or Hartree-Fock exchange) operator. It is the integral (nonlocal) operator defined by

$$(K_\Phi \phi)(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{\gamma_\Phi(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}'. \quad (2.8)$$

It is easy to see that K_Φ is a self-adjoint Hilbert-Schmidt operator on $L^2(\mathbb{R}^3)$. Indeed, the kernel $\frac{\gamma_\Phi(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$ is a square integrable function on $\mathbb{R}^3 \times \mathbb{R}^3$ [33].

For neutral systems and positive ions, \mathcal{F}_Φ (for any $\Phi \in \mathcal{X}_N$) is a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$, and is bounded from below. Its essential spectrum is $\sigma_{\text{ess}}(\mathcal{F}_\Phi) = [0, +\infty)$. For positive ions, the discrete spectrum of \mathcal{F}_Φ consists of an infinite non-decreasing sequence of negative eigenvalues of finite multiplicities, which converges to zero [35].

Any minimizer of (2.6) satisfies the Euler-Lagrange equations (2.7). Using the invariance of the Hartree-Fock problem with respect to orbital rotation [38], it is possible to diagonalize the matrix $\Lambda = [\lambda_{ij}]$ appearing in (2.7). More precisely, if U is an orthogonal $N \times N$ matrix (i.e. such that $U^T U = U U^T = I_N$) and if $\Phi \in \mathcal{X}_N$, then $\Phi U = (\sum_{j=1}^N U_{ji} \phi_j)_{1 \leq i \leq N} \in \mathcal{X}_N$ and $E^{\text{HF}}(\Phi U) = E^{\text{HF}}(\Phi)$ (in fact $\gamma_{\Phi U} = \gamma_\Phi$, so that one also has $\mathcal{F}_{\Phi U} = \mathcal{F}_\Phi$). Let Φ be a solution of (2.7) and U an orthogonal $N \times N$ matrix which diagonalizes the matrix Λ , i.e. such that $U^T \Lambda U = \text{Diag}(\eta_1, \dots, \eta_N)$. Then $\Psi = (\psi_i)_{1 \leq i \leq N} = \Phi U$ is a critical point of (2.7), with the same energy as Φ , such that for all i ,

$$\mathcal{F}_\Phi \psi_i = \mathcal{F}_\Psi \psi_i = \eta_i \psi_i.$$

This means that Ψ is a collection of N orthonormal eigenvectors of the Fock operator. Besides, it can be proved that if Φ is a Hartree-Fock ground state, then

- *Aufbau* principle [33]: the η_i 's are the lowest N eigenvalues of \mathcal{F}_Φ (including multiplicities), i.e. $\eta_i = \epsilon_i$ (up to renumbering of the orbitals);
- No-unfilled-shell property [1]: $\epsilon_N < \epsilon_{N+1}$, i.e. there is always a gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Consequently, solving the system

$$\begin{cases} \mathcal{F}_\Phi \phi_i = \epsilon_i \phi_i, \\ \Phi = (\phi_i)_{1 \leq i \leq N} \in \mathcal{X}_N, \\ \epsilon_1 \leq \epsilon_2 \leq \dots \leq \epsilon_N \text{ are the lowest } N \text{ eigenvalues of } \mathcal{F}_\Phi, \end{cases} \quad (2.9)$$

and applying orbital rotations to the so-obtained solutions provides all the global minimizers of (2.6), as well as, possibly, local minimizers and other kinds of critical points.

Let us finally mention that it is possible to reformulate the Hartree-Fock problem in terms of density operators. Recall that the density operator Υ associated with the density matrix γ is the self-adjoint operator defined by

$$(\Upsilon\phi)(\mathbf{r}) = \int_{\mathbb{R}^3} \gamma(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') d\mathbf{r}'.$$

In other words, the density matrix γ is the kernel of the integral operator Υ . If $\Phi \in \mathcal{X}_N$, the density operator Υ_Φ associated with the density matrix γ_Φ is the rank- N orthogonal projector

$$\Upsilon_\Phi = \sum_{i=1}^N |\phi_i\rangle \langle \phi_i|.$$

The Hartree-Fock energy functional can be written as a functional of the density operator:

$$\mathcal{E}^{\text{HF}}(\Upsilon) = \text{Tr} \left(-\frac{1}{2} \Delta \Upsilon \right) + \int_{\mathbb{R}^3} V_{\text{nuc}}(\mathbf{r}) \rho_\Upsilon(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\Upsilon(\mathbf{r}) \rho_\Upsilon(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

where γ is the kernel of Υ and $\rho_\Upsilon(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$. If γ is regular enough,

$$\text{Tr} \left(-\frac{1}{2} \Delta \Upsilon \right) = -\frac{1}{2} \int_{\mathbb{R}^3} \Delta_{\mathbf{r}} \gamma(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} d\mathbf{r}.$$

The above definition of $\text{Tr} \left(-\frac{1}{2} \Delta \Upsilon \right)$ can be extended to any non-negative self-adjoint operator Υ by noting that

$$\text{Tr} \left(-\frac{1}{2} \Delta \Upsilon \right) = \frac{1}{2} \text{Tr} (|\nabla| \Upsilon |\nabla|)$$

when γ is regular, and since the operator $|\nabla| \Upsilon |\nabla|$ is self-adjoint and non-negative, the right-hand side can always be given a sense in $\mathbb{R}_+ \cup \{+\infty\}$ (it equals the trace of $|\nabla| \Upsilon |\nabla|$ if this operator is trace-class, and takes the value $+\infty$ otherwise).

The Hartree-Fock ground state energy and density matrices can be obtained by solving

$$\inf \left\{ \mathcal{E}^{\text{HF}}(\Upsilon), \Upsilon \in \mathcal{P}_N \right\} \quad (2.10)$$

with

$$\mathcal{P}_N = \left\{ \Upsilon \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid \Upsilon^2 = \Upsilon, \text{Tr}(-\Delta \Upsilon) < \infty, \text{Tr}(\Upsilon) = N \right\}.$$

A remarkable property of the Hartree-Fock functional [30] is that the minimizers of (2.10) coincide with those of

$$\inf \left\{ \mathcal{E}^{\text{HF}}(\Upsilon), \Upsilon \in \tilde{\mathcal{P}}_N \right\} \quad (2.11)$$

where

$$\tilde{\mathcal{P}}_N = \text{Convex hull of } \mathcal{P}_N = \left\{ \Upsilon \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \Upsilon \leq 1, \text{Tr}(-\Delta \Upsilon) < \infty, \text{Tr}(\Upsilon) = N \right\}.$$

Recall that the notation $0 \leq \Upsilon \leq 1$ means

$$\forall \phi \in L^2(\mathbb{R}^3), \quad 0 \leq \langle \phi | \Upsilon | \phi \rangle \leq \|\phi\|_{L^2}^2.$$

Note that a generic element of $\tilde{\mathcal{P}}_N$ is of the form

$$\Upsilon = \sum_{i=1}^{+\infty} n_i |\psi_i\rangle \langle \psi_i|,$$

where (ψ_i) is a Hilbert basis of $L^2(\mathbb{R}^3)$ with $\psi_i \in H^1(\mathbb{R}^3)$, $0 \leq n_i \leq 1$, and $\sum_{i=1}^{+\infty} n_i = N$. This property is the theoretical foundation of efficient algorithms for solving the Hartree-Fock problem [5, 4, 6, 24].

In what follows, we will denote respectively by K_γ and \mathcal{F}_γ the Hartree-Fock exchange operator and the Fock operator associated with the density matrix γ :

$$(K_\gamma\phi)(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}', \quad \mathcal{F}_\gamma = -\frac{1}{2}\Delta + V_{\text{nuc}} + \rho_\gamma \star \frac{1}{|\mathbf{r}|} + K_\gamma.$$

3. Slater exchange potential

The Slater exchange potential associated with some $\Phi \in \mathcal{X}_N$ has the following expression [42]:

$$v_{x,S}^\Phi(\mathbf{r}) = -\frac{1}{\rho_\Phi(\mathbf{r})} \int_{\mathbb{R}^3} \frac{|\gamma_\Phi(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (3.1)$$

Obviously, the above definition does not make sense if $\rho_\Phi(\mathbf{r}) = 0$. This is not a problem if $\rho_\Phi > 0$ almost everywhere, since, in view of Proposition 3.1 below, (3.1) defines an essentially bounded function on \mathbb{R}^3 . If ρ_Φ vanishes on a set Ω of positive measure, the Slater potential will be set to zero on Ω . There is some arbitrariness here, but as the density of physical systems is positive almost everywhere, this is not an issue.

Note that in the case $N = 1$ and $\rho_\Phi > 0$ almost everywhere, the Slater potential is given by

$$v_{x,S}^\Phi(\mathbf{r}) = -\frac{1}{|\phi_1(\mathbf{r})|^2} \int_{\mathbb{R}^3} \frac{|\phi_1(\mathbf{r})\phi_1(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = - \int_{\mathbb{R}^3} \frac{|\phi_1(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}',$$

and therefore cancels out the Coulomb potential (this is a case of exact self-interaction correction).

The following Proposition collects the main mathematical properties of the Slater potential associated with a given $\Phi \in \mathcal{X}_N$.

Proposition 3.1. *Let $\Phi = (\phi_i)_{1 \leq i \leq N} \in \mathcal{X}_N$.*

(1) *The Slater potential $v_{x,S}^\Phi$ is an essentially bounded function which satisfies almost everywhere*

$$- \int_{\mathbb{R}^3} \frac{\rho_\Phi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \leq v_{x,S}^\Phi(\mathbf{r}) \leq 0.$$

In particular, $v_{x,S}^\Phi$ vanishes at infinity.

Besides, if $\rho_\Phi > 0$ almost everywhere and if one of the conditions below is satisfied:

- *the orbitals ϕ_i are radial (i.e. spherically symmetric);*
- *there exists $1 \leq p < 3/2 < q \leq 2$ such that $|\mathbf{r}|\rho_\Phi \in L^p(\mathbb{R}^3) \cap L^q(\mathbb{R}^3)$,*

the asymptotic behavior of the Slater potential is given by

$$v_{x,S}^\Phi(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} + o\left(\frac{1}{|\mathbf{r}|}\right); \quad (3.2)$$

(2) *If $\rho_\Phi > 0$ almost everywhere, the Slater potential $v_{x,S}^\Phi$ is the unique minimizer of the variational problems*

$$\inf \left\{ I_\Phi^S(v), v \in L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \right\} \quad \text{and} \quad \inf \left\{ J_\Phi^S(v), v \in L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \right\}, \quad (3.3)$$

where

$$I_\Phi^S(v) = \frac{1}{2} \|(v - K_\Phi)\Upsilon_\Phi\|_{\mathfrak{S}_2}^2, \quad J_\Phi^S(v) = \frac{1}{2} \|v\Upsilon_\Phi - K_\Phi\|_{\mathfrak{S}_2}^2.$$

Here and below, \mathfrak{S}_2 denotes the vector space of the Hilbert-Schmidt operators on $L^2(\mathbb{R}^3)$ and $\|\cdot\|_{\mathfrak{S}_2}$ the Hilbert-Schmidt norm (see Appendix). In particular

$$\begin{aligned} I_{\Phi}^{\mathfrak{S}}(v) &= \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left| v(\mathbf{r})\gamma_{\Phi}(\mathbf{r}, \mathbf{r}') + \int_{\mathbb{R}^3} \frac{\gamma_{\Phi}(\mathbf{r}, \mathbf{r}'')\gamma_{\Phi}(\mathbf{r}'', \mathbf{r}')}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' \right|^2 d\mathbf{r} d\mathbf{r}', \\ J_{\Phi}^{\mathfrak{S}}(v) &= \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left| v(\mathbf{r})\gamma_{\Phi}(\mathbf{r}, \mathbf{r}') + \frac{\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right|^2 d\mathbf{r} d\mathbf{r}'. \end{aligned}$$

The condition that there exists $1 \leq p < 3/2 < q \leq 2$ such that $|\mathbf{r}|\rho_{\Phi} \in L^p(\mathbb{R}^3) \cap L^q(\mathbb{R}^3)$ obviously holds true when ρ_{Φ} decays exponentially fast, which is the case, in particular, when Φ is a Hartree-Fock [33] or a Kohn-Sham LDA ground state, or a solution of the self-consistent Slater equation (3.4) (this is a straightforward application of the maximum principle since Kohn-Sham LDA and Slater potentials vanish at infinity).

In general, $v_{x,S}^{\Phi}$ is not a continuous function. This can be seen writing $v_{x,S}^{\Phi}(\mathbf{r})$ as

$$v_{x,S}^{\Phi}(\mathbf{r}) = - \sum_{i,j=1}^N \frac{\phi_i(\mathbf{r})\phi_j(\mathbf{r})}{\rho_{\Phi}(\mathbf{r})} \int_{\mathbb{R}^3} \frac{\phi_i(\mathbf{r}')\phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

The functions

$$\mathbf{r} \mapsto \int_{\mathbb{R}^3} \frac{\phi_i(\mathbf{r}')\phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

are continuous, while the functions $\frac{\phi_i(\mathbf{r})\phi_j(\mathbf{r})}{\rho_{\Phi}(\mathbf{r})}$ can be discontinuous at a given point, either because one of the ϕ_i is discontinuous, or because ρ_{Φ} vanishes. It is worth mentioning two special cases. When $\Phi = (\phi_i)$ is a Hartree-Fock ground state, it can be proved by elliptic regularity arguments (see [33] for instance) that for all $i = 1, \dots, N$,

$$\phi_i \in C^{\infty}(\mathbb{R}^3 \setminus \{\mathbf{R}_k\}) \cap C^{0,1}(\mathbb{R}^3).$$

It then follows that $v_{x,S}^{\Phi}$ is globally Lipschitz in any compact set of $\mathbb{R}^3 \setminus \rho_{\Phi}^{-1}(0)$ and C^{∞} in $\mathbb{R}^3 \setminus (\rho_{\Phi}^{-1}(0) \cup \{\mathbf{R}_k\})$. Stronger regularity can be obtained if $\Phi = (\phi_i)$ is a Kohn-Sham LDA ground state, or a solution of the self-consistent Slater equation (3.4). In this case indeed ρ_{Φ} is positive in \mathbb{R}^3 (the ground state of the corresponding mean-field Hamiltonian is positive and non-degenerate), so that $v_{x,S}^{\Phi}$ is globally Lipschitz in \mathbb{R}^3 and C^{∞} away from the nuclei.

We have not been able to recognize in the self-consistent Slater equations

$$\left\{ \begin{array}{l} \left(-\frac{1}{2}\Delta + V_{\text{nuc}} + \rho_{\Phi} \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Phi} \right) \phi_i = \epsilon_i \phi_i, \\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}, \\ \epsilon_1 \leq \dots \leq \epsilon_N \text{ are the lowest } N \text{ eigenvalues of } \left(-\frac{1}{2}\Delta + V_{\text{nuc}} + \rho_{\Phi} \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Phi} \right), \end{array} \right. \quad (3.4)$$

the Euler-Lagrange equations of some minimization problem. It is however possible to prove by a fixed point method that (3.4) has at least one solution for neutral atoms and positively charged atomic ions, provided only radial orbitals are considered. Recall that a function ϕ is said to be radial if there exists a function φ such that $\phi(\mathbf{r}) = \varphi(|\mathbf{r}|)$. We will denote by $L_r^2(\mathbb{R}^3)$ (resp. $H_r^1(\mathbb{R}^3)$) the set of radial $L^2(\mathbb{R}^3)$ (resp. radial $H^1(\mathbb{R}^3)$) functions, and set

$$\mathcal{X}_N^r = \left\{ \Phi = (\phi_i)_{1 \leq i \leq N} \in (H_r^1(\mathbb{R}^3))^N \mid \int_{\mathbb{R}^3} \phi_i(\mathbf{r})\phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij} \right\}.$$

Theorem 3.2. *In the case of a single nucleus of charge $Z \geq N$, (3.4) has a solution¹ $\Phi = (\phi_i) \in \mathcal{X}_N^r$ with $\epsilon_N > 0$ and the corresponding exchange potential $v_{x,S}^\Phi$ is globally Lipschitz in \mathbb{R}^3 , C^∞ away from the nucleus, and satisfies, for all $\eta > 0$,*

$$v_{x,S}^\Phi(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} + o\left(e^{-(2\sqrt{-2\epsilon_N}-\eta)|\mathbf{r}|}\right).$$

Besides, the minimum of the Hartree-Fock energy over the set of the radial solutions of (3.4) is attained.

In summary, one can associate with any $\Phi \in \mathcal{X}_N$ a Slater potential $v_{x,S}^\Phi$. Among all the local potentials that can be constructed in this way, we can select a few of them which might be more physically relevant than the others:

- (i) the potential $v_{x,S}^{\Phi^{\text{HF}}}$, where Φ^{HF} is a Hartree-Fock ground state of the system;
- (ii) the potential $v_{x,S}^{\Phi^{\text{KS}}}$, where Φ^{KS} is a Kohn-Sham ground state of the system;
- (iii) the potential $v_{x,S}^{\Phi^{\text{SCF}}}$, where Φ^{SCF} is a solution of the self-consistent equations (3.4) which minimizes the Hartree-Fock energy (over the set of the solutions of (3.4)). The existence of such Φ^{SCF} is granted in the radial case for neutral atoms and positive atomic ions by the last assertion of Theorem 3.2.

4. Optimized Effective Potential (OEP)

4.1. Original formulation of the OEP problem

As already mentioned in the introduction, the OEP approach consists in minimizing the energy of the Slater determinant constructed with the lowest N eigenfunctions of some one-electron Schrödinger operator $H_W = -\frac{1}{2}\Delta + W$, W being a “local potential”. Note that in most articles dealing with OEP, the set of admissible local potentials is not defined. Leaving temporarily this issue aside, we denote by \mathcal{Y} a given set of local potentials (\mathcal{Y} can be for instance the vector space $\mathcal{Y} = L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ arising in the mathematical formulation of the density functional theory [31]). We introduce the set of admissible local potentials

$$\mathcal{W} = \left\{ W \in \mathcal{Y} \mid H_W = -\frac{1}{2}\Delta + W \text{ is a self-adjoint operator on } L^2(\mathbb{R}^3), \text{ bounded from below, with at least } N \text{ eigenvalues below its essential spectrum} \right\},$$

and the OEP minimization set

$$\mathcal{X}_N^{\text{OEP}} = \left\{ \Phi = \{\phi_i\}_{1 \leq i \leq N} \mid \phi_i \in H^1(\mathbb{R}^3), (4.2) \text{ and } (4.3) \text{ hold for some } W \in \mathcal{W} \right\}, \quad (4.1)$$

where conditions (4.2) and (4.3) are defined as

$$\begin{cases} H_W \phi_i = \epsilon_i \phi_i, \\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}, \end{cases} \quad (4.2)$$

and

$$\epsilon_1 \leq \dots \leq \epsilon_N \text{ are the lowest } N \text{ eigenvalues of } H_W. \quad (4.3)$$

¹In the *Aufbau* condition “ $\epsilon_1 \leq \dots \leq \epsilon_N$ are the lowest N eigenvalues of $\left(-\frac{1}{2}\Delta + V_{\text{nuc}} + \rho_\Phi \star \frac{1}{|\mathbf{r}|} + v_{x,S}^\Phi\right)$ ”, the mean-field Hamiltonian is here considered as an operator on $L_r^2(\mathbb{R}^3)$.

The optimized effective potential problem then reads

$$I^{\text{OEP}} = \inf \left\{ E^{\text{HF}}(\Phi), \Phi \in \mathcal{X}_N^{\text{OEP}} \right\}. \quad (4.4)$$

Denoting by Φ^{OEP} a minimizer to (4.4), an optimal effective potential is a local potential $W^{\text{OEP}} \in \mathcal{W}$ which allows one to generate Φ^{OEP} through (4.2)-(4.3).

In order to emphasize the mathematical issues arising from the above formulation of the OEP problem, it is worth recalling the general method for proving the existence of solutions of a minimization problem such as (4.4). The first step consists in considering a minimizing sequence, that is, a sequence $(\Phi^n)_{n \in \mathbb{N}}$ of elements of $\mathcal{X}_N^{\text{OEP}}$ such that

$$\lim_{n \rightarrow \infty} E^{\text{HF}}(\Phi^n) = \inf \left\{ E^{\text{HF}}(\Phi), \Phi \in \mathcal{X}_N^{\text{OEP}} \right\}.$$

It is easy to check that the sequence $(\Phi^n)_{n \in \mathbb{N}}$ is bounded in $(H^1(\mathbb{R}^3))^N$, hence weakly converges, up to extraction, toward some $\Phi^\infty \in (H^1(\mathbb{R}^3))^N$. It is then standard to prove (see [33] for instance) that

$$E^{\text{HF}}(\Phi^\infty) \leq \inf \left\{ E^{\text{HF}}(\Phi), \Phi \in \mathcal{X}_N^{\text{OEP}} \right\}. \quad (4.5)$$

The difficult step of the proof is to show that $\Phi^\infty \in \mathcal{X}_N^{\text{OEP}}$ (if $\Phi^\infty \in \mathcal{X}_N^{\text{OEP}}$, we can immediately conclude, using (4.5), that Φ^∞ is a solution of (4.4)). For this purpose, we need to introduce a sequence $(W_n)_{n \in \mathbb{N}}$ of admissible local potentials ($W_n \in \mathcal{W}$) such that Φ^n can be generated by W_n via (4.2)-(4.3). If the set of local potentials \mathcal{Y} is *e.g.* a reflexive Banach space and if $(W_n)_{n \in \mathbb{N}}$ is bounded in \mathcal{Y} , then $(W_n)_{n \in \mathbb{N}}$ converges (up to extraction and in some weak sense) to some potential $W_\infty \in \mathcal{Y}$. We could then try to pass to the limit in the system

$$\begin{cases} H_{W_n} \phi_i^n = \epsilon_i^n \phi_i^n, \\ \int_{\mathbb{R}^3} \phi_i^n(\mathbf{r}) \phi_j^n(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}, \\ \epsilon_1^n \leq \dots \leq \epsilon_N^n \text{ are the lowest } N \text{ eigenvalues of } H_{W_n}, \end{cases}$$

using more or less sophisticated functional analysis arguments, in order to prove that Φ^∞ satisfies

$$\begin{cases} H_{W_\infty} \phi_i^\infty = \epsilon_i^\infty \phi_i^\infty, \\ \int_{\mathbb{R}^3} \phi_i^\infty(\mathbf{r}) \phi_j^\infty(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}, \\ \epsilon_1^\infty \leq \dots \leq \epsilon_N^\infty \text{ are the lowest } N \text{ eigenvalues of } H_{W_\infty}, \end{cases}$$

hence belongs to $\mathcal{X}_N^{\text{OEP}}$.

To make this strategy of proof work, we therefore need to find a functional space \mathcal{Y} for which the sequences of local potentials generating the minimizing sequences of (4.4) are bounded. Unfortunately, we have not been able to find any non trivial² functional space \mathcal{Y} satisfying the above condition. This mathematical difficulty has numerical consequences: It is easy to construct dramatic modifications of the (computed) optimized effective potential that are “almost solutions” of the OEP problem (make the potential oscillate and/or go to infinity at infinity), see *e.g.* [44].

4.2. A well-posed reformulation of the OEP problem

A way to circumvent the issues raised in the previous Section is to replace (4.2)-(4.3) with formally equivalent conditions that do not explicitly refer to a local potential W [2].

²It is of course possible to construct finite dimensional functional spaces \mathcal{Y} for which (4.4), with $\mathcal{X}_N^{\text{OEP}}$ defined by (4.1), has a solution. Reducing artificially the class of admissible potentials is however not a very satisfactory way to tackle the OEP problem.

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Let us first deal with (4.2). For an operator W being considered as a local potential, it needs to be such that

$$(W\phi)\psi = (W\psi)\phi$$

for any regular functions ϕ and ψ . This requirement is in fact, at least formally, a characterization of multiplication operators. Applied to H_W , this characterization reads

$$(H_W\phi)\psi - (H_W\psi)\phi = \frac{1}{2}(\phi\Delta\psi - \psi\Delta\phi) = \frac{1}{2}\operatorname{div}(\phi\nabla\psi - \psi\nabla\phi). \quad (4.6)$$

It is then clear that if $\Phi = (\phi_i) \in (H^1(\mathbb{R}^3))^N$ satisfies (4.2) with an operator H_W for which (4.6) holds true, we also have

$$\begin{cases} \operatorname{div}(\phi_i\nabla\phi_1 - \phi_1\nabla\phi_i) = c_i\phi_1\phi_i, \\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r})\phi_j(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}, \end{cases} \quad (4.7)$$

with $c_i = 2(\epsilon_i - \epsilon_1)$. Conversely, if $\Phi = \{\phi_i\} \in (H^1(\mathbb{R}^3))^N$ satisfies (4.7), then, *at least formally*, Φ satisfies (4.2) with for instance

$$W = \frac{\sum_{i=1}^N \phi_i\Delta\phi_i + \sum_{i=2}^N c_i\phi_i^2}{2\rho_\Phi}, \quad (4.8)$$

$\epsilon_1 = 0$, and $\epsilon_i = c_i/2$ for $2 \leq i \leq N$.

The idea then is to replace condition (4.2) with the formally equivalent condition (4.7), which does not explicitly refer to any local potential.

In order to account for condition (4.3) in the same way, we remark that for any $\Phi \in \mathcal{X}_N$ and all $1 \leq i \leq N$,

$$\forall \psi \in C_0^\infty(\mathbb{R}^3), \quad \frac{1}{2} \int_{\mathbb{R}^3} \phi_i(\mathbf{r})^2 |\nabla\psi(\mathbf{r})|^2 \, d\mathbf{r} = \langle \psi\phi_i | (H_W - \epsilon_i) | \psi\phi_i \rangle,$$

where $C_0^\infty(\mathbb{R}^3)$ is the set of compactly supported $C^\infty(\mathbb{R}^3)$ functions. It follows from the above equality (see [2] for details) that conditions (4.2)-(4.3) are equivalent to

$$\begin{cases} H_W\phi_i = \epsilon_i\phi_i, \\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r})\phi_j(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}, \\ \forall \psi \in C_0^\infty(\mathbb{R}^3), \forall 1 \leq i \leq N-1, \\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r})^2 |\nabla\psi(\mathbf{r})|^2 \geq 2 \sum_{j=1}^i (\epsilon_j - \epsilon_1) \left(\int_{\mathbb{R}^3} \psi(\mathbf{r})\phi_i(\mathbf{r})\phi_j(\mathbf{r}) \, d\mathbf{r} \right)^2, \\ \quad + 2(\epsilon_{i+1} - \epsilon_1) \left(\int_{\mathbb{R}^3} \psi(\mathbf{r})^2 \phi_i(\mathbf{r})^2 \, d\mathbf{r} - \sum_{j=1}^i \left(\int_{\mathbb{R}^3} \psi(\mathbf{r})\phi_i(\mathbf{r})\phi_j(\mathbf{r}) \, d\mathbf{r} \right)^2 \right). \end{cases}$$

Combining the above result with the formal equivalence between (4.2) and (4.7) with $c_i = 2(\epsilon_i - \epsilon_1)$, it is natural to introduce the optimization problem

$$\tilde{I}^{\text{OEP}} = \inf \left\{ E^{\text{HF}}(\Phi), \Phi \in \tilde{\mathcal{X}}_N^{\text{OEP}} \right\}. \quad (4.9)$$

where

$$\begin{aligned} \tilde{\mathcal{X}}_N^{\text{OEP}} = & \left\{ \Phi = \{\phi_i\}_{1 \leq i \leq N} \mid \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}, \exists 0 = c_1 \leq c_2 \leq \dots \leq c_N < \infty, \right. \\ & \forall 2 \leq i \leq N, \operatorname{div}(\phi_i\nabla\phi_1 - \phi_1\nabla\phi_i) = c_i\phi_1\phi_i, \forall 1 \leq i \leq N-1, \forall \psi \in C_0^\infty(\mathbb{R}^3), \\ & \left. \int_{\mathbb{R}^3} \phi_i^2 |\nabla\psi|^2 \geq \sum_{j=2}^i c_j \left(\int_{\mathbb{R}^3} \psi\phi_i\phi_j \right)^2 + c_{i+1} \left(\int_{\mathbb{R}^3} \psi^2 \phi_i^2 - \sum_{j=1}^i \left(\int_{\mathbb{R}^3} \psi\phi_i\phi_j \right)^2 \right) \right\}. \end{aligned}$$

We thus have eliminated any explicit reference to a local potential. Note that for any reasonable definition of \mathcal{Y} , it holds

$$\mathcal{X}^{\text{OEP}} \subset \tilde{\mathcal{X}}_N^{\text{OEP}} \subset \mathcal{X}_N, \quad (4.10)$$

The connection between the original OEP problem (4.4) and its reformulation (4.9) can therefore be stated as follows: If $\tilde{\Phi}^{\text{OEP}} = (\tilde{\phi}_i^{\text{OEP}})_{1 \leq i \leq N}$ is a solution of (4.9), and if the reconstructed potential

$$W^{\text{OEP}} = \frac{\sum_{i=1}^N \tilde{\phi}_i^{\text{OEP}} \Delta \tilde{\phi}_i^{\text{OEP}} + \sum_{i=2}^N c_i |\tilde{\phi}_i^{\text{OEP}}|^2}{2 \rho_{\tilde{\Phi}^{\text{OEP}}}} \quad (4.11)$$

defines an element of \mathcal{W} , then $\tilde{\Phi}^{\text{OEP}}$ is a solution of (4.4) and W^{OEP} is an optimized effective potential.

It is proved in [2] that for a neutral or positively charged two-electron system, problem (4.9) has at least one global minimizer $\tilde{\Phi}^{\text{OEP}}$. Unfortunately, we have not been able to establish whether or not the reconstructed potential (4.11) is a well-defined function.

Let us conclude this section by remarking that (4.10) yields

$$I^{\text{HF}} \leq \tilde{I}^{\text{OEP}} \leq I^{\text{OEP}}.$$

A natural question is whether these inequalities are strict or large. We are only aware of two partial answers to this question:

- it is proved in [2] that in the case of a single nucleus of charge $Z \geq 2$ and $N = 2$ electrons occupying radial orbitals,

$$I^{\text{HF}} < \tilde{I}^{\text{OEP}};$$

- a formal perturbation argument is used in [19] to show that $I^{\text{HF}} = I^{\text{OEP}}$ for non-interacting electrons and that $I^{\text{HF}} < I^{\text{OEP}}$ in the presence of an infinitesimal Coulomb repulsion term.

4.3. The OEP integral equation and its approximations

The functional $W \mapsto E^{\text{HF}}(\phi_1^W, \dots, \phi_N^W)$, where $(\phi_1^W, \dots, \phi_N^W)$ satisfy

$$\begin{cases} H_W \phi_i^W = \epsilon_i^W \phi_i^W, \\ \int_{\mathbb{R}^3} \phi_i^W(\mathbf{r}) \phi_j^W(\mathbf{r}) \, d\mathbf{r} = \delta_{ij}, \\ \epsilon_1^W \leq \dots \leq \epsilon_N^W \text{ are the lowest } N \text{ eigenvalues of } H_W, \end{cases} \quad (4.12)$$

is not well-defined for two reasons: First, the set of admissible local potentials has not been properly characterized, and second, (4.12) may have several solutions. It is therefore *a fortiori* not possible to define the derivative of this functional. One can however give a rigorous meaning to the functional and its derivative for local potentials W satisfying the following assumption.

Assumption 4.1. *The potential W belongs to $L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, and the hamiltonian H_W , defined on the domain $D(H_W) = H^2(\mathbb{R}^3)$, is a self-adjoint operator on $L^2(\mathbb{R}^3)$, bounded from below, with at least N eigenvalues (including multiplicities) below its essential spectrum, and there is a gap*

$$\eta = \epsilon_{N+1}^W - \epsilon_N^W > 0 \quad (4.13)$$

between ϵ_N^W (the N -th eigenvalue of H_W) and ϵ_{N+1}^W (the $(N+1)$ -st eigenvalue of H_W , or the bottom of the essential spectrum if H_W has only N eigenvalues below its essential spectrum).

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Under Assumption 4.1, the ground state density operator of H_W is uniquely defined:

$$\Upsilon_W = \sum_{i=1}^N |\phi_i^W\rangle \langle \phi_i^W| = \chi_{(-\infty, \epsilon_F]}(H_W),$$

where $\chi_{(-\infty, \epsilon_F]}$ is the characteristic function of the range $(-\infty, \epsilon_F]$ and

$$\epsilon_F = \frac{\epsilon_N^W + \epsilon_{N+1}^W}{2}. \quad (4.14)$$

It is also easy to check (using the same method as in [6, page 90]) that

$$\Upsilon_W = \operatorname{arginf} \{ \operatorname{Tr}(H_W \Upsilon), \Upsilon \in \mathcal{P}_N \}.$$

In addition, if $w \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$ is such that $\|w\|_{L^\infty} < \eta/2$, then $W+w$ still is a local potential for which Assumption 4.1 holds true (this follows from the Courant-Fischer formula [37]). In this case,

$$\begin{aligned} \Upsilon_{W+w} &= \operatorname{arginf} \{ \operatorname{Tr}(H_{W+w} \Upsilon), \Upsilon \in \mathcal{P}_N \} \\ &= \chi_{(-\infty, \epsilon_F]}(H_{W+w}), \end{aligned}$$

with ϵ_F given by (4.14). It is therefore possible to define the functional

$$w \mapsto \mathcal{E}^{\text{HF}}(\Upsilon_{W+w})$$

on the ball

$$\mathcal{B}_{\eta/2} = \left\{ w \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3), \|w\|_{L^1 \cap L^\infty} < \eta/2 \right\}.$$

For W satisfying Assumption 1, one can also define the exchange part of the potential W as

$$v_x^W = W - V_{\text{nuc}} - \rho_{\gamma_W} \star \frac{1}{|\mathbf{r}|} \quad (4.15)$$

where γ_W is the kernel of Υ_W . It is easy to see that $v_x^W \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. We are now in position to state the main result of this section.

Theorem 4.1. *Let W be a local potential such that Assumption 4.1 holds true. Then, there exists a unique function $\varrho^W \in L^1(\mathbb{R}^3) \cap H^2(\mathbb{R}^3)$ such that*

$$\mathcal{E}^{\text{HF}}(\Upsilon_{W+w}) = \mathcal{E}^{\text{HF}}(\Upsilon_W) + \int_{\mathbb{R}^3} \varrho^W(\mathbf{r}) w(\mathbf{r}) d\mathbf{r} + \mathcal{O}(\|w\|_{L^1 \cap L^\infty}^2). \quad (4.16)$$

In particular, the function $w \mapsto \mathcal{E}^{\text{HF}}(\Upsilon_{W+w})$ is Fréchet differentiable at $w = 0$. Denoting by $R^0(z) = (z - H_W)^{-1}$ the resolvent of H_W , by \mathcal{C} a regular closed contour enclosing the lowest N eigenvalues of H_W (see Figure 1), and by $t_W(\mathbf{r}, \mathbf{r}')$ the kernel of the finite rank operator

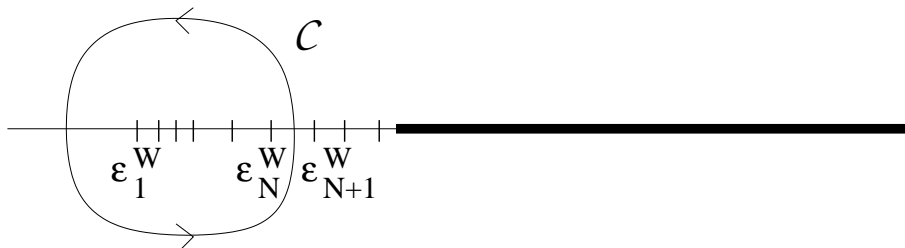
$$T_W = \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) (K_{\gamma_W} - v_x^W) R^0(z) dz, \quad (4.17)$$

it holds $\varrho^W(\mathbf{r}) = t_W(\mathbf{r}, \mathbf{r})$. Let $(\phi_i^W)_{1 \leq i \leq N}$ be a set of N orthonormal eigenvectors of H_W associated with the lowest N eigenvalues $\epsilon_1^W \leq \dots \leq \epsilon_N^W$ of H_W . Then

$$\varrho^W(\mathbf{r}) = 2 \sum_{i=1}^N \phi_i^W(\mathbf{r}) \left[(1 - \Upsilon_W) [\epsilon_i^W - (1 - \Upsilon_W) H_W (1 - \Upsilon_W)]^{-1} (1 - \Upsilon_W) (K_{\gamma_W} - v_x^W) \phi_i^W \right](\mathbf{r}).$$

Let us come back to the formulation (4.4) of the OEP problem. If no artificial restriction on the set of admissible local potentials is enforced, \mathcal{Y} must be such that for all $W \in \mathcal{Y}$, and all $w \in C_0^\infty(\mathbb{R}^3)$, one also has $W + w \in \mathcal{Y}$. Let us now consider a local potential $W \in \mathcal{Y}$ satisfying Assumption 4.1. Then $W \in \mathcal{W}$ and it follows from (4.16) that if W is an optimized effective potential, then

$$\varrho^W = 0. \quad (4.18)$$

FIGURE 1. Integration contour \mathcal{C} in the complex plane

Although not obvious at first sight, (4.18) is a rigorous formulation of the OEP integral equation introduced in [41, 45]. To clarify this point, we now assume that the spectrum of H_W is purely discrete (this assumption is implicitly made in [41, 45], but is obviously violated for isolated molecular systems, since for such systems, W is expected to have a constant, finite value at infinity). In this case, there exists a Hilbert basis $(\phi_n^W)_{n \in \mathbb{N}}$ of $L^2(\mathbb{R}^3)$ consisting of eigenvectors of H_W associated with the eigenvalues $\epsilon_1^W \leq \epsilon_2^W \leq \dots \leq \epsilon_N^W < \epsilon_{N+1}^W \leq \dots$, and the resolvent can be rewritten as

$$R^0(z) = \sum_{n=1}^{+\infty} \frac{|\phi_n^W\rangle \langle \phi_n^W|}{z - \epsilon_n^W}.$$

Then,

$$\begin{aligned} & \left[(1 - \Upsilon_W) [\epsilon_i^W - (1 - \Upsilon_W) H_W (1 - \Upsilon_W)]^{-1} (1 - \Upsilon_W) (K_{\gamma_W} - v_x^W) \phi_i^W \right] (\mathbf{r}) \\ &= \sum_{a=N+1}^{+\infty} \frac{\langle \phi_a^W | K_{\Phi^W} - v_x^W | \phi_i^W \rangle}{\epsilon_i^W - \epsilon_a^W} \phi_a^W (\mathbf{r}), \end{aligned}$$

so that condition (4.18) also reads

$$\sum_{i=1}^N \sum_{a=N+1}^{+\infty} \frac{\langle \phi_a^W | K_{\Phi^W} - v_x^W | \phi_i^W \rangle}{\epsilon_i^W - \epsilon_a^W} \phi_i^W (\mathbf{r}) \phi_a^W (\mathbf{r}) = 0. \quad (4.19)$$

We have found no mathematical result on the existence and uniqueness of the solutions of the self-consistent OEP integral equation in the literature.

The exact OEP integral equation is of little interest in itself, but can be useful to build approximations of optimized effective potentials. It has indeed been proposed [41, 45], instead of approximating the optimization problem (4.4), to approximate the first order optimality condition (4.19). This is the foundation of the KLI (Krieger-Li-Iafate) and CEDA (common energy denominator) approximations.

Starting from the idea of Sharp and Horton [41], Krieger, Li and Iafate proposed the following approximation of the OEP integral equation:

$$\sum_{i=1}^N \sum_{j \in \mathbb{N}^*, j \neq i} \langle \phi_j^W | K_{\Phi^W} - v_{x,\text{KLI}}^{\Phi^W} | \phi_i^W \rangle \phi_i^W (\mathbf{r}) \phi_j^W (\mathbf{r}) = 0. \quad (4.20)$$

We refer to [23] for details on the derivation of equation (4.20). Note that the inner sum runs over all (occupied and virtual) states different from i , which implies in particular that equation (4.20) is not invariant with respect to orbital rotations. In order to cover the general case when H_W has a non-empty continuous spectrum, it is preferable to rewrite equation (4.20) as

$$\rho_{\Phi^W} (\mathbf{r}) v_{x,\text{KLI}}^{\Phi^W} (\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi^W} (\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i=1}^N \langle \phi_i^W | v_{x,\text{KLI}}^{\Phi^W} - K_{\Phi^W} | \phi_i^W \rangle |\phi_i^W (\mathbf{r})|^2. \quad (4.21)$$

The KLI exchange potential $v_{x,\text{KLI}}^{\Phi^W}$ can then be obtained by solving the self-consistent equations

$$\left\{ \begin{array}{l} H_W \phi_i^W = \epsilon_i^W \phi_i^W, \\ \int_{\mathbb{R}^3} \phi_i^W (\mathbf{r}) \phi_j^W (\mathbf{r}) d\mathbf{r} = \delta_{ij}, \\ \epsilon_1^W \leq \dots \leq \epsilon_N^W \text{ are the lowest } N \text{ eigenvalues of } H_W, \\ W = V_{\text{nuc}} + \rho_{\Phi^W} \star \frac{1}{|\mathbf{r}|} + v_{x,\text{KLI}}^{\Phi^W}, \\ \rho_{\Phi^W} (\mathbf{r}) v_{x,\text{KLI}}^{\Phi^W} (\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi^W} (\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i=1}^N \langle \phi_i^W | v_{x,\text{KLI}}^{\Phi^W} - K_{\Phi^W} | \phi_i^W \rangle |\phi_i^W (\mathbf{r})|^2 \quad \text{a.e.} \end{array} \right. \quad (4.22)$$

Note that if $(\Phi^W, v_{x,\text{KLI}}^{\Phi^W})$ is a solution of the above system, so is $(\Phi^W, v_{x,\text{KLI}}^{\Phi^W} + \lambda)$ for any real constant λ . We have not been able to prove an existence result for (4.22). Assuming that (4.22) has a solution $(\Phi^W, v_{x,\text{KLI}}^{\Phi^W})$ with $\Phi^W \in \mathcal{X}_N$, it is however possible to prove the following:

Proposition 4.2. *Let $(\Phi^W, v_{x,\text{KLI}}^{\Phi^W})$ be a solution of (4.22) such that $\Phi^W \in \mathcal{X}_N$ and $\epsilon_1^W < \min \sigma_{\text{ess}}(H_W)$. Then ρ_{Φ^W} is a continuous, positive function on \mathbb{R}^3 , and $v_{x,\text{KLI}}^{\Phi^W}$ is a continuous, bounded function on \mathbb{R}^3 . Besides,*

(1) the potential $v_{x,\text{KLI}}^{\Phi^W}$ is a unique solution, up to an additive constant, to the minimization problem

$$\inf \left\{ J_{\Phi^W}^{\text{KLI}}(v), v \in L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \right\} \quad (4.23)$$

where

$$J_{\Phi^W}^{\text{KLI}}(v) = \frac{1}{2} \left(\|(v - K_{\Phi})\Upsilon_{\Phi}\|_{\mathfrak{S}_2}^2 - \sum_{i=1}^N |\langle \phi_i | (v - K_{\Phi}) | \phi_i \rangle|^2 \right).$$

In particular, Φ^W being given, the KLI potential is uniquely defined up to an additive constant;

(2) it holds

$$v_{x,\text{KLI}}^{\Phi^W}(\mathbf{r}) = v_{x,S}^{\Phi^W}(\mathbf{r}) + \sum_{i=1}^N \left(\alpha_i^{\Phi^W} - \langle \phi_i^W | K_{\Phi^W} | \phi_i^W \rangle \right) \frac{|\phi_i^W(\mathbf{r})|^2}{\rho_{\Phi^W}(\mathbf{r})}, \quad (4.24)$$

where $v_{x,S}^{\Phi^W}$ is the Slater potential associated with Φ^W and where $\alpha^{\Phi^W} = (\alpha_i^{\Phi^W}) \in \mathbb{R}^N$ satisfies

$$(I_N - S^{\Phi^W})\alpha^{\Phi^W} = \beta^{\Phi^W}, \quad (4.25)$$

with

$$S_{ij}^{\Phi^W} = \int_{\mathbb{R}^3} \frac{|\phi_i^W(\mathbf{r})|^2 |\phi_j^W(\mathbf{r})|^2}{\rho_{\Phi^W}(\mathbf{r})} d\mathbf{r}, \quad \beta_i^{\Phi^W} = \int_{\mathbb{R}^3} v_{x,S}^{\Phi^W}(\mathbf{r}) |\phi_i^W(\mathbf{r})|^2 d\mathbf{r} - \sum_{j=1}^N S_{ij}^{\Phi^W} \langle \phi_j^W | K_{\Phi^W} | \phi_j^W \rangle;$$

(3) the solutions of the linear system (4.25) form a one-dimensional affine space of the form

$$\alpha^{\Phi^W} + \mathbb{R}(1, \dots, 1)^T.$$

Replacing α^{Φ^W} with $\alpha^{\Phi^W} + \lambda(1, \dots, 1)^T$ in (4.24), amounts to replacing $v_{x,\text{KLI}}^{\Phi^W}$ with $v_{x,\text{KLI}}^{\Phi^W} + \lambda$.

Note that contrarily to the situation encountered with the Slater potential (see problem (3.3)), the quadratic functional $J_{\Phi^W}^{\text{KLI}}$ is convex (it is non-negative), but not strictly convex. A consequence of that is the non-uniqueness of v_x^{KLI} , which is only defined up to an additive constant.

Let us now turn to the CEDA potential introduced by Gritsenko and Baerends [12]. This approximation consists in replacing in (4.19) the denominators $\epsilon_i^W - \epsilon_a^W$ with a constant, yielding

$$\sum_{i=1}^N \sum_{a=N+1}^{+\infty} \langle \phi_i^W | K_{\Phi^W} - v_{x,\text{CEDA}}^{\Phi^W} | \phi_a^W \rangle \phi_i^W(\mathbf{r}) \phi_a^W(\mathbf{r}) = 0.$$

Here also, it is possible to provide a more explicit formulation of this equation, still valid when H_W has a non-empty continuous spectrum:

$$\rho_{\Phi^W}(\mathbf{r}) v_{x,\text{CEDA}}^{\Phi^W}(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi^W}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i,j=1}^N \langle \phi_i^W | v_{x,\text{CEDA}}^{\Phi^W} - K_{\Phi^W} | \phi_j^W \rangle \phi_i^W(\mathbf{r}) \phi_j^W(\mathbf{r}). \quad (4.26)$$

Let us incidentally mention that the common denominator approximation amounts to replacing in (4.17) the resolvent $R^0(z) = (z - H_W)^{-1}$ with the resolvent $R_{\text{CEDA}}^0(z) = (z - H_W^{\text{CEDA}})^{-1}$ of the operator

$$H_W^{\text{CEDA}} = \underline{\epsilon} \Upsilon_{\Phi^W} + \bar{\epsilon} (1 - \Upsilon_{\Phi^W}),$$

where $\underline{\epsilon}$ and $\bar{\epsilon}$ lay respectively inside and outside \mathcal{C} .

The potential v_x^{CEDA} solves the self-consistent equations

$$\left\{ \begin{array}{l} H_W \phi_i^W = \epsilon_i^W \phi_i^W, \\ \int_{\mathbb{R}^3} \phi_i^W(\mathbf{r}) \phi_j^W(\mathbf{r}) d\mathbf{r} = \delta_{ij}, \\ \epsilon_1^W \leq \dots \leq \epsilon_N^W \text{ are the lowest } N \text{ eigenvalues of } H_W, \\ W = V_{\text{nuc}} + \rho_{\Phi^W} \star \frac{1}{|\mathbf{r}|} + v_{x,\text{CEDA}}^{\Phi^W}, \\ \rho_{\Phi^W}(\mathbf{r}) v_{x,\text{CEDA}}^{\Phi^W}(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi^W}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i,j=1}^N \langle \phi_i^W | v_{x,\text{CEDA}}^{\Phi^W} - K_{\Phi^W} | \phi_j^W \rangle \phi_i^W(\mathbf{r}) \phi_j^W(\mathbf{r}) \quad \text{a.e.} \end{array} \right.$$

To our knowledge, the question of existence and uniqueness of the solution of the above system is still open.

It turns out that $v_{x,\text{CEDA}}^{\Phi^W}$ coincides with the so-called local Hartree-Fock (LHF) exchange potential v_x^{LHF} , obtained by Della Salla and Görling on the basis of completely different arguments (see [40] for details). We will see in the next section that it also equals the self-consistent effective local potential $v_{x,\text{ELP}}^{\Phi^W}$ [20].

5. Effective Local Potential (ELP)

The effective local potential associated with a given $\Phi \in \mathcal{X}_N$ was originally defined as the local potential minimizing the function [20]

$$v \mapsto S_{\Phi}(v) = \sum_{i=1}^N \sum_{a=N+1}^{+\infty} |\langle \phi_i | (v - K_{\Phi}) | \phi_a \rangle|^2,$$

$(\phi_a)_{a \geq N+1}$ being a Hilbert basis of the orthogonal of the vector space generated by $(\phi_i)_{1 \leq i \leq N}$. A simple calculation shows that $S_{\Phi}(v) = J_{\Phi}^{\text{ELP}}(v)$ where

$$J_{\Phi}^{\text{ELP}}(v) = \frac{1}{2} \| [v - K_{\Phi}, \Upsilon_{\Phi}] \|_{\mathfrak{S}_2}^2,$$

$[A, B] = AB - BA$ denoting the commutator of the operators A and B . An intrinsic formulation of the ELP problem therefore reads

$$\inf \{ J_{\Phi}^{\text{ELP}}(v), v \in L^3(\mathbb{R}^3) + L^{\infty}(\mathbb{R}^3) \}. \quad (5.1)$$

The similarities between the ELP and the OEP are investigated in [10].

Proposition 5.1. *Let $\Phi = (\phi_i)_{1 \leq i \leq N} \in \mathcal{X}_N$. Any solution $v_{x,\text{ELP}}^{\Phi}$ of (5.1) satisfies*

$$\rho_{\Phi}(\mathbf{r}) v_{x,\text{ELP}}^{\Phi}(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i,j=1}^N \left(\langle \phi_i | v_{x,\text{ELP}}^{\Phi} | \phi_j \rangle - \langle \phi_i | K_{\Phi} | \phi_j \rangle \right) \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \quad (5.2)$$

and the symmetric matrix $M^{\Phi} = [\langle \phi_i | v_{x,\text{ELP}}^{\Phi} | \phi_j \rangle]$ is a solution of the linear system

$$(I - A^{\Phi}) M^{\Phi} = G^{\Phi}, \quad (5.3)$$

with

$$A_{kl,ij}^{\Phi} = \int_{\mathbb{R}^3} \frac{\phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi_k(\mathbf{r}) \phi_l(\mathbf{r})}{\rho_{\Phi}(\mathbf{r})} d\mathbf{r}, \quad G_{kl}^{\Phi} = \int_{\mathbb{R}^3} v_{x,S}^{\Phi}(\mathbf{r}) \phi_k(\mathbf{r}) \phi_l(\mathbf{r}) d\mathbf{r} - \sum_{i,j=1}^N A_{kl,ij}^{\Phi} \langle \phi_i | K_{\Phi} | \phi_j \rangle.$$

Besides, if the orbitals ϕ_i are continuous and if the open set $\mathbb{R}^3 \setminus \rho_{\Phi}^{-1}(0)$ is connected, then the solutions of (5.3) form a one-dimensional affine set of the form

$$M^{\Phi} + \mathbb{R}I_N,$$

so that $v_{x,\text{ELP}}^\Phi$ is uniquely defined, up to an additive constant, on the set where $\rho_\Phi > 0$, and can be given arbitrary values on the set where $\rho_\Phi = 0$.

Comparing (5.2) and (4.26), one immediately recognizes that the self-consistent CEDA potential and the self-consistent ELP potential defined by

$$\left\{ \begin{array}{l} H_W \phi_i^W = \epsilon_i^W \phi_i^W, \\ \int_{\mathbb{R}^3} \phi_i^W(\mathbf{r}) \phi_j^W(\mathbf{r}) d\mathbf{r} = \delta_{ij}, \\ \epsilon_1^W \leq \dots \leq \epsilon_N^W \text{ are the lowest } N \text{ eigenvalues of } H_W, \\ W = V_{\text{nuc}} + \rho_{\Phi^W} \star \frac{1}{|\mathbf{r}|} + v_{x,\text{ELP}}^{\Phi^W}, \\ \rho_{\Phi^W}(\mathbf{r}) v_{x,\text{ELP}}^{\Phi^W}(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi^W}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i,j=1}^N \langle \phi_i^W | v_{x,\text{ELP}}^{\Phi^W} - K_{\Phi^W} | \phi_j^W \rangle \phi_i^W(\mathbf{r}) \phi_j^W(\mathbf{r}) \quad \text{a.e.} \end{array} \right. \quad (5.4)$$

coincide. As already mentioned, we are not aware of a proof of existence of the solution of this system. We can however use Proposition 5.1 to show that if (5.4) has a solution $(\Phi^W, v_{x,\text{ELP}}^{\Phi^W})$ with $\Phi^W \in \mathcal{X}_N$ and if $\epsilon_1 < \min \sigma_{\text{ess}}(H_W)$, then $v_{x,\text{ELP}}^{\Phi^W}$ can be obtained from Φ^W by solving an optimization problem, which has a unique solution, up to an additive constant (the proof follows the same lines as the proof of Proposition 4.2: ϕ_1^W then is a continuous, positive function on \mathbb{R}^3 , which implies that ρ_{Φ^W} is positive and that the above connectivity condition is satisfied).

6. Extensions to the Generalized, Unrestricted and Restricted Hartree-Fock models

In the generalized Hartree-Fock (GHF) model, each molecular spin-orbital ϕ_i is a complex-valued function³ with spin-up and spin-down components, i.e. $\phi_i \in L^2(\mathbb{R}^3, \mathbb{C}^2)$. The orthonormality constraint (2.1) is replaced with

$$\int_{\mathbb{R}^3} \phi_i(\mathbf{r}) \cdot \phi_j(\mathbf{r})^* d\mathbf{r} = \delta_{ij},$$

where

$$\phi_i(\mathbf{r}) = \begin{pmatrix} \phi_i(\mathbf{r}, \uparrow) \\ \phi_i(\mathbf{r}, \downarrow) \end{pmatrix} \quad \text{and} \quad \phi_i(\mathbf{r}) \cdot \phi_j(\mathbf{r})^* = \sum_{\sigma \in \{\uparrow, \downarrow\}} \phi_i(\mathbf{r}, \sigma) \phi_j(\mathbf{r}, \sigma)^*.$$

The density-matrix can then be represented by a 2×2 hermitian matrix

$$\gamma_\Phi(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \gamma_\Phi^{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}') & \gamma_\Phi^{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') \\ \gamma_\Phi^{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}') & \gamma_\Phi^{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') \end{pmatrix}$$

with

$$\gamma_\Phi^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r}, \sigma) \phi_i(\mathbf{r}', \sigma')^*,$$

and the electronic density ρ_Φ is the sum of its spin-up and spin-down components:

$$\rho_\Phi(\mathbf{r}) = \rho_\Phi^\uparrow(\mathbf{r}) + \rho_\Phi^\downarrow(\mathbf{r}), \quad \rho_\Phi^\uparrow(\mathbf{r}) = \gamma_\Phi^{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}), \quad \rho_\Phi^\downarrow(\mathbf{r}) = \gamma_\Phi^{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}).$$

The Hartree-Fock exchange operator associated with γ_Φ is the integral operator on $L^2(\mathbb{R}^3, \mathbb{C}^2)$ defined by

$$\forall \phi \in L^2(\mathbb{R}^3, \mathbb{C}^2), \quad (K_\gamma \phi)(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \gamma(\mathbf{r}, \mathbf{r}') \cdot \phi(\mathbf{r}') d\mathbf{r}',$$

³GHF models are of particular interest for systems subjected to magnetic fields; for such systems, complex-valued wavefunctions are needed.

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where \cdot denotes the usual matrix-vector product, and local exchange potentials are 2×2 hermitian matrices of the form

$$v(\mathbf{r}) = \begin{pmatrix} v^{\uparrow\uparrow}(\mathbf{r}) & v^{\uparrow\downarrow}(\mathbf{r}) \\ v^{\downarrow\uparrow}(\mathbf{r}) & v^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}.$$

The variational definition of the Slater potential given in Section 3 provides a natural way to define a Slater potential for the GHF framework: It is the local potential v which minimizes the Hilbert-Schmidt norm of the operator $(v - K_\Phi)\Upsilon_\Phi$. A simple calculation leads to

$$\begin{aligned} v_{x,S}^\Phi(\mathbf{r}) &= -R_\Phi(\mathbf{r})^{-1}\Xi_\Phi(\mathbf{r}) - \frac{1}{\rho_\Phi(\mathbf{r})} \left[\Xi_\Phi(\mathbf{r}) - R_\Phi(\mathbf{r})^{-1}\Xi_\Phi(\mathbf{r})R_\Phi(\mathbf{r}) \right] \\ &= -\Xi_\Phi(\mathbf{r})R_\Phi(\mathbf{r})^{-1} - \frac{1}{\rho_\Phi(\mathbf{r})} \left[\Xi_\Phi(\mathbf{r}) - R_\Phi(\mathbf{r})\Xi_\Phi(\mathbf{r})R_\Phi(\mathbf{r})^{-1} \right] \end{aligned} \quad (6.1)$$

where

$$R_\Phi(\mathbf{r}) = \gamma_\Phi(\mathbf{r}, \mathbf{r}) \quad \text{and} \quad \Xi_\Phi(\mathbf{r}) = \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \gamma_\Phi(\mathbf{r}, \mathbf{r}') \cdot \gamma(\mathbf{r}, \mathbf{r}')^* d\mathbf{r}'.$$

Within the unrestricted Hartree-Fock (UHF) model, each molecular spin-orbital is (generally) chosen real-valued and either spin-up, i.e. $\phi_i(\mathbf{r}) = \begin{pmatrix} \phi_i^\uparrow(\mathbf{r}) \\ 0 \end{pmatrix}$, or spin-down, i.e. $\phi_i(\mathbf{r}) = \begin{pmatrix} 0 \\ \phi_i^\downarrow(\mathbf{r}) \end{pmatrix}$. Denoting by N_α (resp. N_β) the number of spin-up (resp. spin-down) orbitals, and ordering the spin-orbitals in such a way that the first N_α of them are spin-up, the UHF density matrix reads

$$\gamma_\Phi(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \gamma_\Phi^{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}') & 0 \\ 0 & \gamma_\Phi^{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') \end{pmatrix}$$

with

$$\gamma_\Phi^{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_\alpha} \phi_i^\uparrow(\mathbf{r})\phi_i^\uparrow(\mathbf{r}'), \quad \gamma_\Phi^{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_\beta} \phi_{N_\alpha+i}^\downarrow(\mathbf{r})\phi_{N_\alpha+i}^\downarrow(\mathbf{r}').$$

Likewise, the UHF exchange operator is diagonal:

$$K_\gamma = \begin{pmatrix} K_\gamma^{\uparrow\uparrow} & 0 \\ 0 & K_\gamma^{\downarrow\downarrow} \end{pmatrix} \quad \text{with} \quad \forall \phi \in L^2(\mathbb{R}^3), \quad (K_\gamma^{\sigma\sigma}\phi)(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma^{\sigma,\sigma}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}'.$$

It is then easy to check that in the UHF setting, the generalized formula (6.1) reduces to

$$v_{x,S}^\Phi(\mathbf{r}) = \begin{pmatrix} v_{x,S}^{\Phi,\uparrow\uparrow}(\mathbf{r}) & 0 \\ 0 & v_{x,S}^{\Phi,\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

with

$$v_{x,S}^{\Phi,\sigma\sigma}(\mathbf{r}) = -\frac{1}{\rho_\Phi^\sigma(\mathbf{r})} \int_{\mathbb{R}^3} \frac{|\gamma_\Phi^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad \rho_\Phi^\sigma(\mathbf{r}) = \gamma_\Phi^{\sigma\sigma}(\mathbf{r}, \mathbf{r}).$$

One recovers in this way the spin-up and spin-down local potentials originally introduced by Slater in [42].

In closed-shell models, each molecular orbital $\phi_i \in L^2(\mathbb{R}^3)$ is occupied by one spin-up and one spin-down electrons. Denoting by $N_p = N/2$ the number of electron pairs, it holds

$$\gamma_\Phi^{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}') = \gamma_\Phi^{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_p} \phi_i(\mathbf{r})\phi_i(\mathbf{r}'), \quad \rho_\Phi^\uparrow(\mathbf{r}) = \rho_\Phi^\downarrow(\mathbf{r}), \quad v_{x,S}^{\Phi,\uparrow\uparrow}(\mathbf{r}) = v_{x,S}^{\Phi,\downarrow\downarrow}(\mathbf{r}),$$

$$\gamma_\Phi^{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') = \gamma_\Phi^{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}') = 0, \quad v_{x,S}^{\Phi,\uparrow\downarrow}(\mathbf{r}) = v_{x,S}^{\Phi,\downarrow\uparrow}(\mathbf{r}) = 0.$$

Proposition 3.1, Theorem 4.1, Proposition 4.2, and Proposition 5.1 apply *mutatis mutandis* to the RHF setting, as well as to the spin-up and spin-down components of the UHF exchange

operator and local potentials. As outlined above from the Slater potential, the variational characterizations (4.23) and (5.1) of the KLI and ELP potentials can be used to define KLI and ELP potentials in the GHF setting.

7. Numerical results

We present here some numerical results for the models introduced in the previous sections. Other numerical simulations have been published elsewhere [20]. All the models under consideration in this section, namely the Hartree-Fock equations (2.9), the self-consistent Slater equations (3.4), and the self-consistent ELP equations (5.4), can be formulated as nonlinear eigenvalue problems of the form: find $\Phi = (\phi_1, \dots, \phi_N) \in \mathcal{X}_N$ such that

$$\begin{cases} \mathcal{G}^{\gamma_\Phi} \phi_i = \epsilon_i \phi_i, \\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}, \\ \epsilon_1 \leq \dots \leq \epsilon_N \text{ are the lowest } N \text{ eigenvalues of } \mathcal{G}^{\gamma_\Phi}, \end{cases} \quad (7.1)$$

for some self-adjoint operator $\mathcal{G}^{\gamma_\Phi}$ depending self-consistently on its lowest energy eigenvectors $\Phi = (\phi_1, \dots, \phi_N)$ through the density matrix

$$\gamma_\Phi(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r}) \phi_i(\mathbf{r}').$$

Problem (7.1) can be discretized in a finite basis set $\chi = \{\chi_1, \dots, \chi_M\}$, using the Galerkin approximation. Denoting by $C = (C_1 | \dots | C_N) \in \mathbb{R}^{M \times N}$ the matrix gathering the components of the orbitals (ϕ_1, \dots, ϕ_N) in the basis $\chi = (\chi_1, \dots, \chi_M)$, i.e.

$$\phi_i(\mathbf{r}) = \sum_{m=1}^M C_{m,i} \chi_m(\mathbf{r}), \quad (7.2)$$

the Galerkin approximation of (7.1) can be written as a nonlinear generalized matrix eigenvalue problem

$$\begin{cases} G(CC^T)C_i = \epsilon_i^C SC_i, \\ C^*SC = \text{Id}_N, \\ \epsilon_1^C \leq \dots \leq \epsilon_N^C \text{ are the lowest } N \text{ eigenvalues of } G(CC^T). \end{cases} \quad (7.3)$$

The entries of the overlap matrix S and of the mean-field Hamiltonian matrix G are respectively given by

$$S_{k,l} = \int_{\mathbb{R}^3} \chi_k(\mathbf{r}) \chi_l(\mathbf{r}) d\mathbf{r},$$

and

$$G(CC^T)_{k,l} = \int_{\mathbb{R}^3} \chi_k(\mathbf{r}) \left(\mathfrak{G}^{CC^T} \chi_l \right) (\mathbf{r}) d\mathbf{r},$$

where \mathfrak{G}^{CC^T} is the operator $\mathcal{G}^{\gamma_\Phi}$ for Φ obtained from C through (7.2). Note that $D = CC^T$ is the matrix of γ_Φ in the basis $(\chi_m \otimes \chi_{m'})$:

$$\gamma_\Phi(\mathbf{r}, \mathbf{r}') = \sum_{m,m'=1}^M D_{mm'} \chi_m(\mathbf{r}) \chi_{m'}(\mathbf{r}').$$

It is easy to check that the matrices S and $G(C)$ are both symmetric.

The nonlinear generalized eigenvalue problem (7.3) is solved using a fixed-point algorithm. This algorithm is a modification of the natural fixed-point method, called the Roothaan algorithm in the Chemistry literature. In the Roothaan algorithm, the iterations are performed as follows:

(1) set $D^n = C^n C^{nT}$ and assemble the matrix $G(D^n)$ associated with the trial density matrix D^n ;

(2) solve the *linear* generalized eigenvalue problem

$$\begin{cases} G(C^n C^{nT}) C_i^{n+1} = \epsilon_i^{n+1} S C_i^{n+1}, \\ C^{n+1T} S C^{n+1} = \text{Id}_N, \\ \epsilon_1^{n+1} \leq \epsilon_2^{n+1} \leq \epsilon_3^{n+1} \leq \dots \end{cases}$$

(3) set

$$C^{n+1} = (C_1^{n+1} | \dots | C_N^{n+1}).$$

In the Hartree-Fock setting, the Roothaan algorithm has been analyzed from a mathematical viewpoint in [7]. It was proved that the Roothaan algorithm has the following behavior: it either converges toward a local minimum of the Hartree-Fock energy functional, or it oscillates between two states, none of them being solutions of the Hartree-Fock equations. Still in the Hartree-Fock setting, it was shown in [5, 4] that convergence could be enforced by using a damping strategy on the density matrix ensuring that the energy decreases at each step. The resulting algorithm reads as follows

(1) set

$$D^n = \alpha_n C^n C^{nT} + (1 - \alpha_n) D^{n-1}, \quad (7.4)$$

where $\alpha_n \in [0, 1]$ is chosen in such a way that D^n is the minimizer of the Hartree-Fock energy on the segment line $[D^{n-1}, C^n C^{nT}]$, and assemble the matrix $G(D^n)$ associated with the new trial density matrix D^n ;

(2) solve the *linear* generalized eigenvalue problem

$$\begin{cases} G(C^n C^{nT}) C_i^{n+1} = \epsilon_i^{n+1} S C_i^{n+1}, \\ C^{n+1T} S C^{n+1} = \text{Id}_N, \\ \epsilon_1^{n+1} \leq \epsilon_2^{n+1} \leq \epsilon_3^{n+1} \leq \dots \end{cases}$$

(3) set

$$C^{n+1} = (C_1^{n+1} | \dots | C_N^{n+1}).$$

The algorithm proposed in [5, 4] was then improved in [25]. We refer to [6, 24] and references therein for more details on the numerical algorithms commonly used to solve the Hartree-Fock problem.

The numerical analysis of the fixed point methods in the case when (7.3) originates from the Galerkin approximation of the self-consistent Slater equations (3.4), or of the self-consistent ELP equations (5.4), have not been carried out so far. We have observed that the Roothaan algorithm sometimes oscillates between two states which are not solutions of the self-consistent equations, and that the basic fixed step mixing strategy which consists in replacing (7.4) with $D^n = \alpha C^n C^{nT} + (1 - \alpha) D^{n-1}$, $\alpha > 0$ denoting a small, fixed parameter, is enough to provide convergence, at least for simple molecular systems.

Table 1 gathers the energies of three different Slater determinants, for a selection of closed-shell atoms. The energy of the Hartree-Fock ground state (E_{HF}) is reported in the second column. The third column contains the difference $E_{\text{ELP//HF}} - E_{\text{HF}}$. The energy $E_{\text{ELP//HF}}$ is the energy of the Slater determinant formed by the solution of the system

$$\begin{cases} \mathcal{F}_{\Phi}^{\text{ELP//HF}} \phi_i = \epsilon_i \phi_i, \\ \int_{\mathbb{R}^3} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}, \\ \Phi = (\phi_i)_{1 \leq i \leq N} \in \mathcal{X}_N, \\ \epsilon_1 \leq \epsilon_2 \leq \dots \leq \epsilon_N \text{ are the lowest } N \text{ eigenvalues of } \mathcal{F}_{\Phi}^{\text{ELP//HF}}, \end{cases} \quad (7.5)$$

Atom	E_{HF}	$E_{\text{ELP//HF}} - E_{\text{HF}}$	$E_{\text{SCELP}} - E_{\text{HF}}$
He	-2.861680	0.000000	0.000000
Be	-14.573023	0.000742	0.000742
Ne	-128.54708	0.00224	0.00229
Mg	-199.61462	0.00392	0.00397
Ar	-526.81749	0.00710	0.00717
Ca	-676.75815	0.00820	0.00830
Zn	-1777.8481	0.0168	0.0174
Kr	-2752.0549	0.0153	0.0155
Sr	-3131.5454	0.0159	0.0161
Cd	-5465.1328	0.0240	0.0246
Xe	-7232.1378	0.0230	0.0232
Ba	-7883.5432	0.0231	0.0233

TABLE 1. Energies of selected closed-shell atoms computed using the universal Gaussian basis set (UGBS). All values are in hartrees (1 hartree = 27.2114 eV = 2625.5 kJ/mol).

with

$$\mathcal{F}_{\Phi}^{\text{ELP//HF}} = -\frac{1}{2}\Delta + V_{\text{nuc}} + \rho_{\Phi} \star \frac{1}{|\mathbf{r}|} + v_{x,\text{ELP}}^{\Phi,\text{HF}},$$

the local potential $v_{x,\text{ELP}}^{\Phi,\text{HF}}$ satisfying (5.2). The fourth column contains the difference $E_{\text{SCELP}} - E_{\text{HF}}$ between the energy of the Slater determinant formed by the solution of the self-consistent ELP problem (Eq. (5.4)) and the energy of the Hartree-Fock ground state.

The orbitals ϕ_i are discretized in the universal Gaussian basis set (UGBS) [9], which effectively consists of products of spherical harmonics and radial gaussians optimized for each nucleus for the purpose of chemistry computations. The ELP//HF and the SCELP potential are also represented as an optimal linear combination of functions belonging to the UGBS basis set.

From Table 1, it is seen that the energies obtained from the self-consistent procedure (SCELP) and the ones obtained by simply solving (7.5) (*i.e.* by fixing the local exchange potential) are very similar. In both cases, these energies are only slightly above the energy of the Hartree-Fock ground state, which means that the local exchange potential is a good local approximation of the nonlocal exchange potential.

Figure 2 compares the local exchange potentials generated by the OEP method, the ELP method and the self-consistent Slater equations, for two noble gas atoms. The optimized effective potential W satisfying (4.18) defines a local exchange potential v_x^W through (4.15). The OEP and ELP//HF were discretized in a carefully chosen even-tempered auxiliary basis of 15 primitive Gaussian s -functions with exponents $\alpha_n = \alpha_{\text{max}}/\beta^{n-1}$ ($n = 1, 2, \dots, 15$), where $\beta = 2$ and $\alpha_{\text{max}} = 1503.7$ for Ar, $\alpha_{\text{max}} = 2871.4$ for Kr. The OEP was obtained by a direct minimization procedure using the method described in [47, 48]. The local exchange potentials obtained using these various procedures are very smooth and physically reasonable. Notice also that the ELP//HF greatly improves the simple Slater exchange potential since it is much closer to the reference OEP.

8. Proofs of the main results

Throughout this section, we denote by B_R the open ball of \mathbb{R}^3 of radius R centered at 0, *i.e.* $B_R = \{\mathbf{r} \in \mathbb{R}^3, |\mathbf{r}| < R\}$ and by $B_R^c = \mathbb{R}^3 \setminus B_R$.

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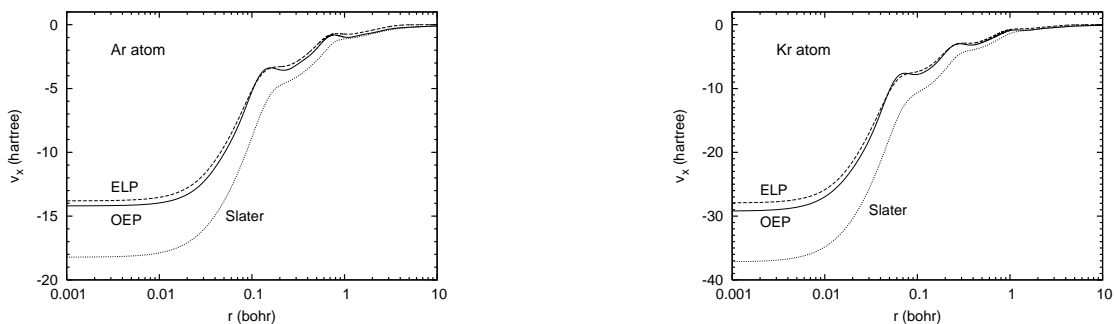


FIGURE 2. The optimized effective potential (OEP), the effective local potential based on the Hartree-Fock orbitals (ELP//HF) and the self-consistent Slater potential for the Ar atom (left) and the Kr atom (right).

In order to simplify the notation, we adopt here the usual loose notation consisting in denoting an integral operator and its kernel by the same symbol.

8.1. Proof of Proposition 3.1: Properties of the Slater potential

It follows from the Cauchy-Schwarz inequality that

$$|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2 = \left| \sum_{i=1}^N \phi_i(\mathbf{r}) \phi_i(\mathbf{r}') \right|^2 \leq \left(\sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \right) \left(\sum_{i=1}^N |\phi_i(\mathbf{r}')|^2 \right) = \rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}').$$

In the set where $\rho_{\Phi} > 0$, one therefore has

$$-\int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = -\frac{1}{\rho_{\Phi}(\mathbf{r})} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \leq -\frac{1}{\rho_{\Phi}(\mathbf{r})} \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = v_{x,S}^{\Phi}(\mathbf{r}) \leq 0.$$

In order to establish the decay property, we rewrite $v_{x,S}^{\Phi}$ as

$$v_{x,S}^{\Phi}(\mathbf{r}) = - \sum_{i,j=1}^N \frac{\phi_i(\mathbf{r}) \phi_j(\mathbf{r})}{\rho_{\Phi}(\mathbf{r})} \int_{\mathbb{R}^3} \frac{\phi_i(\mathbf{r}') \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}',$$

remark that

$$\left| \frac{\phi_i(\mathbf{r}) \phi_j(\mathbf{r})}{\rho_{\Phi}(\mathbf{r})} \right| \leq 1,$$

and conclude using the following lemma.

Lemma 8.1. *Let $\Phi = (\phi_i)_{1 \leq i \leq N} \in \mathcal{X}_N$ and*

$$V_{ij}(\mathbf{r}) = \int_{\mathbb{R}^3} \frac{\phi_i(\mathbf{r}') \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

Then V_{ij} vanishes at infinity. Besides, if the ϕ_i are radial or if there exists $1 \leq p < 3/2 < q \leq 2$ such that $|\mathbf{r}| |\phi_i \phi_j| \in L^p(\mathbb{R}^3) \cap L^q(\mathbb{R}^3)$, then

$$V_{ij}(\mathbf{r}) = \frac{\delta_{ij}}{|\mathbf{r}|} + o\left(\frac{1}{|\mathbf{r}|}\right).$$

Proof of Lemma 8.1. Let us denote by $\rho_{ij} = \phi_i \phi_j$. By Sobolev embeddings, $\rho_{ij} \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. For all $R > 0$ and all $\mathbf{r} \in \mathbb{R}^3$ such that $|\mathbf{r}| \geq 2R$, one has

$$|V_{ij}(\mathbf{r})| \leq \int_{|\mathbf{r}'| < R} \frac{|\rho_{ij}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int_{|\mathbf{r}'| > R} \frac{|\rho_{ij}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \leq \frac{1}{R} + \left\| |\rho_{ij}| \chi_{B_R^c} \star \frac{1}{|\cdot|} \right\|_{L^\infty}.$$

It then follows from the Young inequality and the Lebesgue-dominated convergence theorem that

$$\begin{aligned} \left\| |\rho_{ij}| \chi_{B_R^c} \star \frac{1}{|\cdot|} \right\|_{L^\infty} &\leq \left\| |\rho_{ij}| \chi_{B_R^c} \star \frac{\chi_{B_1}}{|\cdot|} \right\|_{L^\infty} + \left\| |\rho_{ij}| \chi_{B_R^c} \star \frac{\chi_{B_1^c}}{|\cdot|} \right\|_{L^\infty} \\ &\leq \left\| |\rho_{ij}| \chi_{B_R^c} \right\|_{L^3} \left\| \frac{\chi_{B_1}}{|\cdot|} \right\|_{L^{3/2}} + \left\| |\rho_{ij}| \chi_{B_R^c} \right\|_{L^1} \left\| \frac{\chi_{B_1^c}}{|\cdot|} \right\|_{L^\infty} \xrightarrow{R \rightarrow +\infty} 0. \end{aligned}$$

Therefore, V_{ij} vanishes at infinity.

The case of radial orbitals can be dealt with using the Gauss theorem, which provides the following expression for the potential V_{ij} :

$$V_{ij}(\mathbf{r}) = \int_{\mathbb{R}^3} \frac{\rho_{ij}(\mathbf{r}')}{\max(|\mathbf{r}|, |\mathbf{r}'|)} d\mathbf{r}' \quad (\text{radial orbitals}).$$

Indeed,

$$\begin{aligned} \left| V_{ij}(\mathbf{r}) - \frac{\delta_{ij}}{|\mathbf{r}|} \right| &= \left| \int_{\mathbb{R}^3} \frac{\rho_{ij}(\mathbf{r}')}{\max(|\mathbf{r}|, |\mathbf{r}'|)} d\mathbf{r}' - \frac{\delta_{ij}}{|\mathbf{r}|} \right| = \left| -\frac{1}{|\mathbf{r}|} \int_{|\mathbf{r}'| \geq |\mathbf{r}|} \rho_{ij} + \int_{|\mathbf{r}'| \geq |\mathbf{r}|} \frac{\rho_{ij}(\mathbf{r}')}{|\mathbf{r}'|} d\mathbf{r}' \right| \\ &\leq \frac{2}{|\mathbf{r}|} \int_{|\mathbf{r}'| \geq |\mathbf{r}|} |\rho_{ij}(\mathbf{r}')| d\mathbf{r}'. \end{aligned} \quad (8.1)$$

We conclude using the Lebesgue-dominated convergence theorem.

Let us now prove (3.2) in the general case (non-radial orbitals), under the additional assumption that there exists $1 \leq p < 3/2 < q \leq 2$ such that $|\mathbf{r}| |\rho_{ij}| \in L^p(\mathbb{R}^3) \cap L^q(\mathbb{R}^3)$. For all $\mathbf{r} \in \mathbb{R}^3$,

$$|\mathbf{r}| |V_{ij}(\mathbf{r}) - \delta_{ij}| = \left| \int_{\mathbb{R}^3} \frac{|\mathbf{r}| - |\mathbf{r} - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}'|} \rho_{ij}(\mathbf{r}') d\mathbf{r}' \right| \leq \int_{\mathbb{R}^3} \frac{|\mathbf{r}'| |\rho_{ij}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

It suffices to show that the right-hand side vanishes at infinity. For all $R > 0$ and all $\mathbf{r} \in \mathbb{R}^3$ such that $|\mathbf{r}| \geq R(R+1)$,

$$\begin{aligned} \int_{\mathbb{R}^3} \frac{|\mathbf{r}'| |\rho_{ij}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' &= \int_{|\mathbf{r}'| < R} \frac{|\mathbf{r}'| |\rho_{ij}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int_{|\mathbf{r}'| > R} \frac{|\mathbf{r}'| |\rho_{ij}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &\leq \frac{1}{R} + \left\| |\rho_{ij}| \chi_{B_R^c} \star \frac{1}{|\cdot|} \right\|_{L^\infty}, \end{aligned}$$

where $f_{ij}(\mathbf{r}) = |\mathbf{r}| |\rho_{ij}(\mathbf{r})|$. We then use the same argument as above:

$$\begin{aligned} \left\| f_{ij} \chi_{B_R^c} \star \frac{1}{|\cdot|} \right\|_{L^\infty} &\leq \left\| f_{ij} \chi_{B_R^c} \star \frac{\chi_{B_1}}{|\cdot|} \right\|_{L^\infty} + \left\| f_{ij} \chi_{B_R^c} \star \frac{\chi_{B_1^c}}{|\cdot|} \right\|_{L^\infty} \\ &\leq \|f_{ij} \chi_{B_R^c}\|_{L^q} \left\| \frac{\chi_{B_1}}{|\cdot|} \right\|_{L^{q'}} + \|f_{ij} \chi_{B_R^c}\|_{L^p} \left\| \frac{\chi_{B_1^c}}{|\cdot|} \right\|_{L^{p'}} \xrightarrow{R \rightarrow +\infty} 0, \end{aligned}$$

where $p' = (1 - p^{-1})^{-1} \in (3, +\infty]$ and $q' = (1 - q^{-1})^{-1} \in [2, 3)$. The proof of Lemma 8.1 is complete. \square

Let us now turn to the proof of the second assertion of Proposition 3.1. For all $v \in L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, the operator $v\gamma_\Phi$ is Hilbert-Schmidt. Indeed

$$(v\gamma_\Phi)(\mathbf{r}, \mathbf{r}') = v(\mathbf{r})\gamma_\Phi(\mathbf{r}, \mathbf{r}') \in L^2(\mathbb{R}^3 \times \mathbb{R}^3)$$

since $|\gamma_\Phi(\mathbf{r}, \mathbf{r}')| \leq \rho_\Phi(\mathbf{r})\rho_\Phi(\mathbf{r}')$ with $\rho_\Phi \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. One can thus define on $L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ the functional

$$J_\Phi^S(v) = \frac{1}{2} \|v\gamma_\Phi - K_\Phi\|_{\mathfrak{S}_2}^2 = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left| v(\mathbf{r})\gamma_\Phi(\mathbf{r}, \mathbf{r}') + \frac{\gamma_\Phi(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right|^2 d\mathbf{r} d\mathbf{r}'.$$

For all v and h in $L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$,

$$J_\Phi^S(v+h) = J_\Phi^S(v) + \int_{\mathbb{R}^3} \left(v(\mathbf{r})\rho_\Phi(\mathbf{r}) + \int_{\mathbb{R}^3} \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) h(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \|h\gamma_\Phi\|_{\mathfrak{S}_2}^2.$$

Therefore, all the local minima of J_Φ^S are global, and they are characterized by the equation

$$v(\mathbf{r})\rho_\Phi(\mathbf{r}) + \int_{\mathbb{R}^3} \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = 0.$$

If $\rho_\Phi > 0$ almost everywhere, the Slater potential is a unique solution of the above equation, and therefore the unique global minimizer of J_Φ^S .

The fact that the minimizers of J_Φ^S and I_Φ^S are the same comes from the fact that $\gamma_\Phi^2 = \gamma_\Phi$ implies $\langle K_\Phi \gamma_\Phi, v\gamma_\Phi \rangle_{\mathfrak{S}_2} = \langle K_\Phi, v\gamma_\Phi \rangle_{\mathfrak{S}_2}$. \square

8.2. Proof of Theorem 3.2: Self-consistent Slater equation

The strategy of proof is based on a fixed-point argument. Notice that variational methods cannot be used since (3.4) seems to have no variational interpretation.

For all $\eta \geq 0$, we consider the problem

$$\begin{cases} \left(-\frac{1}{2}\Delta - \frac{Z+\eta}{|\mathbf{r}|} + \rho_{\Phi^\eta} \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Phi^\eta, \eta} \right) \phi_i^\eta = \epsilon_i^\eta \phi_i^\eta, \\ \int_{\mathbb{R}^3} \phi_i^\eta \phi_j^\eta = \delta_{ij}, \\ \epsilon_1^\eta \leq \dots \leq \epsilon_N^\eta \text{ are the lowest } N \text{ eigenvalues of } \left(-\frac{1}{2}\Delta - \frac{Z+\eta}{|\mathbf{r}|} + \rho_{\Phi^\eta} \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Phi^\eta, \eta} \right) \text{ (on } L_r^2(\mathbb{R}^3)) \end{cases} \quad (8.2)$$

where

$$v_{x,S}^{\Phi, \eta}(\mathbf{r}) = -\frac{1}{\rho_\Phi(\mathbf{r}) + \eta} \int_{\mathbb{R}^3} \frac{|\gamma_\Phi(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

The proof of existence of a solution of (8.2) for $\eta = 0$ follows the lines of the proof of Theorem III.3 in [35]. We first construct, for $\eta > 0$, a continuous application T^η whose fixed points are solutions of (8.2) in \mathcal{X}_N^r . We then prove the existence of a fixed point of T^η using the Schauder theorem. The existence of a solution of (8.2) in the case when $\eta = 0$ is finally obtained using some limiting procedure. Note that we have introduced the parameter η both in the nucleus-electron interaction and in the Slater potential. In the former term, η plays the same role as in [35] (i.e.

it enables us to control the decay of the orbitals at infinity). The role of η in the latter term is to ensure the continuity of the nonlinear application T^η for $\eta > 0$.

First step. Construction of the application T^η .

Let $\eta > 0$ and

$$K = \left\{ \Psi = (\psi_i)_{1 \leq i \leq N} \in (H_r^1(\mathbb{R}^3))^N \mid \left[\int_{\mathbb{R}^3} \psi_i \psi_j \right] \leq I_N \right\},$$

I_N denoting the identity matrix of rank N . The semidefinite constraint $[\int_{\mathbb{R}^3} \psi_i \psi_j] \leq I_N$ means

$$\forall \mathbf{x} \in \mathbb{R}^N, \quad \sum_{i,j=1}^N \left(\int_{\mathbb{R}^3} \psi_i \psi_j \right) x_i x_j \leq |\mathbf{x}|^2.$$

It is easy to see that K is a nonempty, closed, bounded, convex subset of the Hilbert space $(H_r^1(\mathbb{R}^3))^N$, containing \mathcal{X}_N^r . For $\Psi \in K$, we denote by $\gamma_\Psi(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \psi_i(\mathbf{r})\psi_i(\mathbf{r}')$, $\rho_\Psi(\mathbf{r}) = \gamma_\Psi(\mathbf{r}, \mathbf{r})$ and

$$\tilde{F}_\Psi^\eta = -\frac{1}{2}\Delta - \frac{Z+\eta}{|\mathbf{r}|} + \rho_\Psi \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Psi,\eta}.$$

As the potential $V_\Psi^\eta = -\frac{Z+\eta}{|\mathbf{r}|} + \rho_\Psi \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Psi,\eta}$ belongs to

$$L^2(\mathbb{R}^3) + L_\epsilon^\infty(\mathbb{R}^3) = \left\{ W \mid \forall \epsilon > 0, \exists (W_2, W_\infty) \in L^2(\mathbb{R}^3) \times L^\infty(\mathbb{R}^3), \|W_\infty\|_{L^\infty} \leq \epsilon, W = W_2 + W_\infty \right\},$$

it is a compact perturbation of the kinetic energy operator. By Weyl's theorem [37], $\sigma_{\text{ess}}(\tilde{F}_\Psi^\eta) = \sigma_{\text{ess}}(-\frac{1}{2}\Delta) = [0, \infty)$. Besides, using Gauss' theorem and the inequalities $-\frac{N}{|\cdot|} \leq -\rho_\Psi \star \frac{1}{|\mathbf{r}|} \leq v_{x,S}^{\Psi,\eta} \leq 0$, one has $-\frac{Z+\eta}{|\mathbf{r}|} \leq V_\Psi^\eta \leq -\frac{\eta}{|\mathbf{r}|}$. Hence,

$$\mathcal{G}^{Z+\eta} := -\frac{1}{2}\Delta - \frac{Z+\eta}{|\mathbf{r}|} \leq \tilde{F}_\Psi^\eta \leq \mathcal{G}^\eta := -\frac{1}{2}\Delta - \frac{\eta}{|\mathbf{r}|}. \quad (8.3)$$

As the hydrogen-like Hamiltonian \mathcal{G}^η , considered as an operator on $L_r^2(\mathbb{R}^3)$, has infinitely many negative eigenvalues, so does \tilde{F}_Ψ^η (this is a straightforward consequence of the Courant-Fischer minimax principle). Besides, the eigenvalues of the radial Schrödinger operator \tilde{F}_Ψ^η being simple, the spectral problem

$$\begin{cases} \tilde{F}_\Psi^\eta \phi_i = \epsilon_i \phi_i, \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \\ \epsilon_1 \leq \dots \leq \epsilon_N \text{ are the lowest } N \text{ eigenvalues of } \tilde{F}_\Psi^\eta \text{ (on } L_r^2(\mathbb{R}^3)), \end{cases}$$

has a unique solution $\Phi = (\phi_i)$ in $\mathcal{X}_N^r \subset K$ up to the signs of the orbitals ϕ_i . We can therefore define a nonlinear application T^η from K to K which associates with any $\Psi \in K$ the unique solution $\Phi = (\phi_i) \in \mathcal{X}_N^r \subset K$ of (8.2), for which $\phi_i \geq 0$ in a neighborhood of $\mathbf{r} = 0$, for all $1 \leq i \leq N$ (by the strong maximum principle, ϕ_i cannot vanish on an open set of \mathbb{R}^3).

Second step. Existence of a solution of (8.2) for $\eta > 0$.

Using standard perturbation arguments, it is not difficult to prove that T^η is continuous (for the H^1 norm topology). Let us prove that T^η is compact. Let (Ψ^n) be a bounded sequence in K , and let $\Phi^n = T^\eta \Psi^n$. There is no restriction in assuming that (Ψ^n) converges to some $\Psi^\eta \in (H^1(\mathbb{R}^3))^N$, weakly in $(H^1(\mathbb{R}^3))^N$, strongly in $(L_{\text{loc}}^2(\mathbb{R}^3))^N$ and almost everywhere. This implies in particular that the sequence $(\rho_{\Psi^n} \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Psi^n,\eta})$ is bounded in L^∞ and converges almost

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everywhere to $\rho_{\Psi^n} \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Psi^n, \eta}$ when n goes to infinity. Using again (8.3) and denoting by ϵ_i^n the i -th eigenvalue of $\tilde{F}_{\Psi^n}^\eta$, one obtains

$$\frac{1}{2} \sum_{i=1}^N (\|\nabla \phi_i^n\|_{L^2}^2 - 2(Z + \eta))^2 - 2(Z + \eta)^2 \leq \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i^n|^2 - \int_{\mathbb{R}^3} \frac{Z + \eta}{|\mathbf{r}|} \rho_{\Phi^n} \leq \sum_{i=1}^N \epsilon_i^n < 0.$$

Thus, for all $1 \leq i \leq N$, the sequence $(\phi_i^n)_{n \in \mathbb{N}^*}$ is uniformly bounded in $H^1(\mathbb{R}^3)$ (independently of (Ψ^n)), and therefore converges, up to extraction, to some $\phi_i^\eta \in H_r^1(\mathbb{R}^3)$, weakly in $H^1(\mathbb{R}^3)$, strongly in $L_{\text{loc}}^2(\mathbb{R}^3)$ and almost everywhere. Besides, using (8.3) and the Courant-Fischer formula, one obtains

$$-\frac{(Z + \eta)^2}{2i^2} \leq \epsilon_i^n \leq -\frac{\eta^2}{2i^2}.$$

Up to extraction, (ϵ_i^n) therefore converges to some $\epsilon_i^\eta \in [-\frac{(Z+\eta)^2}{2i^2}, -\frac{\eta^2}{2i^2}]$. Next, by the Kato inequality [37],

$$\begin{aligned} -\Delta |\phi_i^n| &\leq -\text{sgn}(\phi_i^n) \Delta \phi_i^n = 2(\epsilon_i^n - V_{\Psi^n}^\eta) |\phi_i^n| \\ &\leq 2 \left(\frac{Z + \eta}{|\mathbf{r}|} - \frac{\eta^2}{i^2} \right) |\phi_i^n|. \end{aligned} \quad (8.4)$$

As, moreover, (Ψ^n) and (Φ^n) are bounded for the H^1 norm topology, $(V_{\Psi^n}^\eta \phi_i^n)$ is bounded in $L^2(\mathbb{R}^3)$, so that (ϕ_i^n) is bounded in $H^2(\mathbb{R}^3)$, hence in $L^\infty(\mathbb{R}^3)$. Consequently, it follows from (8.4) and the maximum principle that there exists $\delta > 0$ small enough and $M \geq 0$ independent of i and n , such that

$$|\phi_i^n(\mathbf{r})| \leq M e^{-\left(\frac{\sqrt{2}\eta}{N} - \delta\right)|\mathbf{r}|}.$$

This implies that $(\phi_i^n)_{n \in \mathbb{N}^*}$ converges (up to extraction) to ϕ_i^η strongly in $L^2(\mathbb{R}^3)$. In particular, $\Phi^\eta = (\phi_i^\eta) \in \mathcal{X}_N^r$. It is then possible to check, using the convergence of (Ψ^n) to Ψ^η and the convergence - up to extraction - of (Φ^n) to Φ^η and of (ϵ_i^n) to ϵ_i^η , that

$$-\frac{1}{2} \Delta \phi_i^\eta + V_{\Psi^\eta}^\eta \phi_i^\eta = \epsilon_i^\eta \phi_i^\eta$$

and next, using the positivity of $\rho_{\Psi^n} \star \frac{1}{|\mathbf{r}|} + v_{x,S}^{\Psi^n, \eta}$ and Fatou lemma, that

$$\begin{aligned} \liminf_{n \rightarrow +\infty} - \int_{\mathbb{R}^3} |\nabla \phi_i^n|^2 &= \liminf_{n \rightarrow +\infty} 2 \int_{\mathbb{R}^3} (V_{\Psi^n}^\eta - \epsilon_i^n) |\phi_i^n|^2 \\ &\geq 2 \int_{\mathbb{R}^3} (V_{\Psi^\eta}^\eta - \epsilon_i^\eta) |\phi_i^\eta|^2 = - \int_{\mathbb{R}^3} |\nabla \phi_i^\eta|^2. \end{aligned}$$

As on the other hand,

$$\int_{\mathbb{R}^3} |\nabla \phi_i^\eta|^2 \leq \liminf_{n \rightarrow +\infty} \int_{\mathbb{R}^3} |\nabla \phi_i^n|^2,$$

(Ψ^n) converges to Ψ^η strongly in $(H^1(\mathbb{R}^3))^N$, which proves that T^η is compact. It then follows from the Schauder fixed-point theorem [49] that T^η has a fixed point $\Phi^\eta \in \mathcal{X}_N^r$, which is solution of (8.2).

Third step. Existence of a solution of (8.2) for $\eta = 0$.

Let (η_n) be a sequence of positive real numbers converging to zero. As the sequence of corresponding fixed points (Φ^{η_n}) is uniformly bounded in $(H^1(\mathbb{R}^3))^N$ and as $-\frac{(Z+\eta_n)^2}{2i^2} \leq \epsilon_i^{\eta_n} \leq 0$, there is no restriction in assuming that (Φ^{η_n}) converges to some $\Phi^* \in (H^1(\mathbb{R}^3))^N$, weakly in $(H^1(\mathbb{R}^3))^N$, strongly in $(L_{\text{loc}}^2(\mathbb{R}^3))^N$ and almost everywhere, and that $(\epsilon_i^{\eta_n})$ converges to $\epsilon_i^* \leq 0$. Besides, the sequence (Φ^{η_n}) is bounded in $(H^2(\mathbb{R}^3))^N$, hence in $(L^\infty(\mathbb{R}^3))^N$.

Passing to the limit in the equation $\tilde{F}_{\Phi^{n_m}}^{\eta_n} \phi_i^{\eta_n} = \epsilon_i^{\eta_n} \phi_i^{\eta_n}$ yields

$$-\frac{1}{2}\Delta\phi_i^* - \frac{Z}{|\mathbf{r}|}\phi_i^* + \left(\rho_{\Phi^*} \star \frac{1}{|\mathbf{r}|}\right)\phi_i^* + v_{x,S}^{\Phi^*}\phi_i^* = \epsilon_i^*\phi_i^*.$$

Assume that $\int_{\mathbb{R}^3} \rho_{\Phi^*} < N$. As

$$\tilde{F}_{\Phi^{\eta_n}}^{\eta_n} \leq -\frac{1}{2}\Delta - \frac{Z}{|\mathbf{r}|} + \rho_{\Phi^{\eta_n}} \star \frac{1}{|\mathbf{r}|},$$

one has, using the Courant-Fischer formula, and denoting by $\lambda_i(A)$ the i -th eigenvalue of A ,

$$\begin{aligned} \epsilon_i^* &= \lim_{n \rightarrow +\infty} \epsilon_i^{\eta_n} \\ &= \lim_{n \rightarrow +\infty} \lambda_i\left(\tilde{F}_{\Phi^{\eta_n}}^{\eta_n}\right) \\ &\leq \lim_{n \rightarrow +\infty} \lambda_i\left(-\frac{1}{2}\Delta - \frac{Z}{|\mathbf{r}|} + \rho_{\Phi^{\eta_n}} \star \frac{1}{|\mathbf{r}|}\right) \\ &= \lambda_i\left(-\frac{1}{2}\Delta - \frac{Z}{|\mathbf{r}|} + \rho_{\Phi^*} \star \frac{1}{|\mathbf{r}|}\right) \\ &\leq \lambda_i\left(-\frac{1}{2}\Delta - \frac{N - \int_{\mathbb{R}^3} \rho_{\Phi^*}}{|\mathbf{r}|}\right) \\ &= -\frac{(N - \int_{\mathbb{R}^3} \rho_{\Phi^*})^2}{2i^2} < 0. \end{aligned}$$

It follows that for n large enough, the sequence $(\epsilon_i^{\eta_n})$ is isolated from zero. As (Φ^{η_n}) is bounded in $(L^\infty(\mathbb{R}^3))^N$, we conclude, reasoning as above, that there exists $M \in \mathbb{R}_+$ and $\alpha > 0$ such that for n large enough

$$|\phi_i^{\eta_n}(\mathbf{r})| \leq M e^{-\alpha|\mathbf{r}|}.$$

This implies that (Φ^{η_n}) converges to $\Phi^* \in (H^1(\mathbb{R}^3))^N$ strongly in $(L^2(\mathbb{R}^3))^N$, and consequently that $\int_{\mathbb{R}^3} \rho_{\Phi^*} = N$. We reach a contradiction. This means that $\int_{\mathbb{R}^3} \rho_{\Phi^*} = N$ and therefore that $\Phi^* \in \mathcal{X}_N^r$.

This proves that (ϕ_i^*) are orthonormal eigenvectors of $\tilde{F}_{\Phi^*}^0$. The fact that $\epsilon_1^* < \dots < \epsilon_N^*$ are the lowest eigenvalues of $\tilde{F}_{\Phi^*}^0$ follows from the Courant-Fischer formula.

In view of Proposition 3.1, the Slater potential $v_{x,S}^{\Phi^*}$ is equivalent to $-\frac{1}{|\mathbf{r}|}$ at infinity. This proves that $\epsilon_1^* < \dots < \epsilon_N^* < 0$, from which it follows that the orbitals ϕ_i^* enjoy exponential decay: For all $\eta > 0$, there exists $M \in \mathbb{R}^3$ such that

$$|\phi_i^*(\mathbf{r})| \leq M e^{-(\sqrt{-2\epsilon_N^* - \eta/3})|\mathbf{r}|}.$$

Using (8.1), one obtains

$$v_{x,S}^{\Phi^*}(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} + o\left(e^{-(2\sqrt{-2\epsilon_N^* - \eta})|\mathbf{r}|}\right).$$

Lastly, the same arguments as above can be used to prove that the minimum of the Hartree-Fock energy over the set of solutions of (3.4) is attained. \square

8.3. Proof of Theorem 4.1: OEP Integral equation

Straightforward computations show that

$$\mathcal{E}^{\text{HF}}(\gamma_{W+w}) = \mathcal{E}^{\text{HF}}(\gamma_W) + \text{Tr}(\mathcal{F}_{\gamma_W}(\gamma_{W+w} - \gamma_W)) + \alpha(\gamma_{W+w} - \gamma_W, \gamma_{W+w} - \gamma_W), \quad (8.5)$$

where

$$\alpha(\gamma_1, \gamma_2) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\gamma_1(\mathbf{r}, \mathbf{r}) \gamma_2(\mathbf{r}', \mathbf{r}') - \gamma_1(\mathbf{r}, \mathbf{r}') \gamma_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'.$$

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The second term of the right-side of (8.5) is well-defined since both γ_{W+w} and γ_W are finite-rank operators with range in $H^2(\mathbb{R}^3) = D(\mathcal{F}_{\gamma_W}) = D(\mathcal{F}_{\gamma_{W+w}})$. Let

$$\delta = \left(\max_{z \in \mathcal{C}} \|R^0(z)\| \right)^{-1}.$$

Denoting by $R^w(z) = (z - H_{W+w})^{-1}$, one has for all $w \in \mathcal{B}_{\eta/2} = \{w \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3), \|w\|_{L^1 \cap L^\infty} < \eta/2\}$ such that $\|w\|_{L^\infty} < \delta$,

$$R^w(z) = (z - H_{W+w})^{-1} = (z - H_W - w)^{-1} = ((z - H_W)(1 - R^0(z)w))^{-1} = (1 - R^0(z)w)^{-1}R^0(z)$$

and

$$(1 - R^0(z)w)^{-1} - 1 = (1 - R^0(z)w)^{-1}R^0(z)w = R^0(z)w(1 - R^0(z)w)^{-1}.$$

Using the complex-plane integral representation

$$\gamma_{W+w} = \frac{1}{2\pi i} \oint_{\mathcal{C}} R^w(z) dz,$$

one is led to

$$\begin{aligned} \gamma_{W+w} - \gamma_W &= \frac{1}{2\pi i} \oint_{\mathcal{C}} (R^w(z) - R^0(z)) dz = \frac{1}{2\pi i} \oint_{\mathcal{C}} (1 - R^0(z)w)^{-1} R^0(z)w R^0(z) dz \\ &= \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z)w R^0(z) dz + \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z)w(1 - R^0(z)w)^{-1} R^0(z)w R^0(z) dz. \end{aligned}$$

Hence,

$$\begin{aligned} \mathcal{F}_{\gamma_W}(\gamma_{W+w} - \gamma_W) &= \frac{1}{2\pi i} \oint_{\mathcal{C}} \mathcal{F}_{\gamma_W} R^0(z)w R^0(z) dz + \frac{1}{2\pi i} \oint_{\mathcal{C}} \mathcal{F}_{\gamma_W} R^0(z)w(1 - R^0(z)w)^{-1} R^0(z)w R^0(z) dz \\ &= \frac{1}{2\pi i} \oint_{\mathcal{C}} H_W R^0(z)w R^0(z) dz + \frac{1}{2\pi i} \oint_{\mathcal{C}} (K_{\gamma_W} - v_x^W) R^0(z)w R^0(z) dz \\ &\quad + \frac{1}{2\pi i} \oint_{\mathcal{C}} \mathcal{F}_{\gamma_W} R^0(z)w(1 - R^0(z)w)^{-1} R^0(z)w R^0(z) dz \\ &= \frac{1}{2\pi i} \oint_{\mathcal{C}} (-1 + zR^0(z))w R^0(z) dz + \frac{1}{2\pi i} \oint_{\mathcal{C}} (K_{\gamma_W} - v_x^W) R^0(z)w R^0(z) dz \\ &\quad + \frac{1}{2\pi i} \oint_{\mathcal{C}} \mathcal{F}_{\gamma_W} R^0(z)w(1 - R^0(z)w)^{-1} R^0(z)w R^0(z) dz \\ &= -w\gamma_W + \frac{1}{2\pi i} \oint_{\mathcal{C}} zR^0(z)w R^0(z) dz + \frac{1}{2\pi i} \oint_{\mathcal{C}} (K_{\gamma_W} - v_x^W) R^0(z)w R^0(z) dz \\ &\quad + \frac{1}{2\pi i} \oint_{\mathcal{C}} \mathcal{F}_{\gamma_W} R^0(z)w(1 - R^0(z)w)^{-1} R^0(z)w R^0(z) dz. \end{aligned}$$

To proceed further, we make use of the following technical lemmas whose proofs are postponed until the end of the present section.

Lemma 8.2. *For all $z \in \rho(H_W)$, $(1 - \Delta)R^0(z)$ and $R^0(z)(1 - \Delta)$ are bounded operators on $L^2(\mathbb{R}^3)$ and $(1 - \Delta)R^0(z)$ is the adjoint of $R^0(z)(1 - \Delta)$. Besides the functions*

$$z \mapsto R^0(z)(1 - \Delta) \quad \text{and} \quad z \mapsto (1 - \Delta)R^0(z)$$

are analytic from $\rho(H_W)$ into $\mathcal{L}(L^2(\mathbb{R}^3))$.

Lemma 8.3.

(1) *For all $v \in L^1(\mathbb{R}^3)$, the operator $(1 - \Delta)^{-1}v(1 - \Delta)^{-1}$ is trace-class and*

$$\|(1 - \Delta)^{-1}v(1 - \Delta)^{-1}\|_{\mathfrak{S}_1} \leq \frac{1}{8\pi} \|v\|_{L^1}.$$

(2) For all $v \in L^2(\mathbb{R}^3)$, the operator $v(1 - \Delta)^{-1}$ and its adjoint $(1 - \Delta)^{-1}v$ are Hilbert-Schmidt and

$$\|v(1 - \Delta)^{-1}\|_{\mathfrak{S}_2} = \|(1 - \Delta)^{-1}v\|_{\mathfrak{S}_2} = \frac{\|v\|_{L^2}}{(8\pi)^{1/2}}.$$

Using the above two lemmas, it follows

$$\begin{aligned} \operatorname{Tr} \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} z R^0(z) w R^0(z) dz \right) &= \frac{1}{2\pi i} \oint_{\mathcal{C}} z \operatorname{Tr} \left(R^0(z) w R^0(z) \right) dz \\ &= \frac{1}{2\pi i} \oint_{\mathcal{C}} z \operatorname{Tr} \left(R^0(z) (1 - \Delta) (1 - \Delta)^{-1} w (1 - \Delta)^{-1} (1 - \Delta) R^0(z) \right) dz \\ &= \frac{1}{2\pi i} \oint_{\mathcal{C}} z \operatorname{Tr} \left((1 - \Delta) R^0(z)^2 (1 - \Delta) (1 - \Delta)^{-1} w (1 - \Delta)^{-1} \right) dz \\ &= \operatorname{Tr} \left((1 - \Delta) \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} z R^0(z)^2 dz \right) (1 - \Delta) (1 - \Delta)^{-1} w (1 - \Delta)^{-1} \right). \end{aligned}$$

Denoting by

$$H_W = \int_{-\infty}^{+\infty} \lambda dP_\lambda$$

the spectral decomposition of H_W , it holds

$$\begin{aligned} \frac{1}{2\pi i} \oint_{\mathcal{C}} z R^0(z)^2 dz &= \frac{1}{2\pi i} \oint_{\mathcal{C}} \left(\int_{-\infty}^{+\infty} \frac{z}{(z - \lambda)^2} dP_\lambda \right) dz \\ &= \int_{-\infty}^{+\infty} \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{z}{(z - \lambda)^2} dz \right) dP_\lambda \\ &= \int_{-\infty}^{\epsilon_F} dP_\lambda = \gamma_W. \end{aligned}$$

Hence,

$$\operatorname{Tr} \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} z R^0(z) w R^0(z) dz \right) = \operatorname{Tr} \left((1 - \Delta) \gamma_W (1 - \Delta) (1 - \Delta)^{-1} w (1 - \Delta)^{-1} \right) = \operatorname{Tr} (\gamma_W w).$$

We thus obtain

$$\begin{aligned} \mathcal{E}^{\text{HF}}(\gamma_{W+w}) &= \mathcal{E}^{\text{HF}}(\gamma_W) + \operatorname{Tr} \left((K_{\gamma_W} - v_x^W) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) \\ &\quad + \operatorname{Tr} \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} \mathcal{F}_{\gamma_W} R^0(z) w (1 - R^0(z) w)^{-1} R^0(z) w R^0(z) dz \right) \quad (8.6) \\ &\quad + \alpha(\gamma_{W+w} - \gamma_W, \gamma_{W+w} - \gamma_W). \end{aligned}$$

Let us denote by

$$\beta = \max_{z \in \mathcal{C}} \|(1 - \Delta) R^0(z)\|.$$

As $W \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, one also has $v_x^W \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$. Let $v_2 \in L^2(\mathbb{R}^3)$ and $v_\infty \in L^\infty(\mathbb{R}^3)$ such that $v_x^W = v_2 + v_\infty$. Then,

$$\begin{aligned} \left| \operatorname{Tr} \left((K_{\gamma_W} - v_x^W) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) \right| &\leq \left| \operatorname{Tr} \left((K_{\gamma_W} - v_\infty) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) \right| \\ &\quad + \left| \operatorname{Tr} \left(v_2 \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) \right|, \end{aligned}$$

with

$$\begin{aligned} \left| \operatorname{Tr} \left((K_{\gamma_W} - v_\infty) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) \right| &\leq \frac{|\mathcal{C}| \beta^2}{2\pi} (\|K_{\gamma_W}\| + \|v_\infty\|_{L^\infty}) \|(1 - \Delta)^{-1} w (1 - \Delta)^{-1}\|_{\mathfrak{S}_1} \\ &\leq C \|w\|_{L^1} \leq C \|w\|_{L^1 \cap L^\infty}, \end{aligned} \quad (8.7)$$

and

$$\begin{aligned}
 \left| \operatorname{Tr} \left(v_2 \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) \right| &= \left| \operatorname{Tr} \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} v_2 (1 - \Delta)^{-1} (1 - \Delta) R^0(z) w (1 - \Delta)^{-1} (1 - \Delta) R^0(z) dz \right) \right| \\
 &\leq \frac{|\mathcal{C}| \beta^2}{2\pi} \|v_2 (1 - \Delta)^{-1}\|_{\mathfrak{S}_2} \|w (1 - \Delta)^{-1}\|_{\mathfrak{S}_2} \\
 &\leq C \|w\|_{L^2} \leq C \|w\|_{L^1 \cap L^\infty}.
 \end{aligned} \tag{8.8}$$

The linear form

$$w \mapsto \operatorname{Tr} \left((K_{\gamma_W} - v_x^W) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right)$$

therefore is continuous on $L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$. It remains to prove that the last two terms of the right-hand side of (8.6) are $O(\|w\|_{L^1 \cap L^\infty}^2)$. The first one is easy to deal with. Indeed,

$$\begin{aligned}
 &\left| \operatorname{Tr} \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} \mathcal{F}_{\gamma_W} R^0(z) w (1 - R^0(z) w)^{-1} R^0(z) w R^0(z) dz \right) \right| \\
 &\leq \frac{|\mathcal{C}| \beta^3 \|\mathcal{F}_{\gamma_W} (1 - \Delta)^{-1}\|}{2\pi \left(1 - \frac{\|w\|_{L^\infty}}{\delta}\right)} \|w\|_{L^\infty} \|(1 - \Delta)^{-1} w (1 - \Delta)^{-1}\|_{\mathfrak{S}_1} \leq \frac{|\mathcal{C}| \beta^3 \|\mathcal{F}_{\gamma_W} (1 - \Delta)^{-1}\|}{16\pi^2 \left(1 - \frac{\|w\|_{L^\infty}}{\delta}\right)} \|w\|_{L^1 \cap L^\infty}^2.
 \end{aligned}$$

The second term can be split as

$$\alpha(\gamma_{W+w} - \gamma_W, \gamma_{W+w} - \gamma_W) = \frac{1}{2} D(\rho_{\gamma_{W+w}} - \rho_{\gamma_W}, \rho_{\gamma_{W+w}} - \rho_{\gamma_W}) - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{(\gamma_{W+w} - \gamma_W)(\mathbf{r}, \mathbf{r}')^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

where $D(\cdot, \cdot)$ denotes, as usual, the Coulomb energy

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

for which [37]

$$\exists C \in \mathbb{R}_+ \text{ s.t. } \forall f \in L^{6/5}(\mathbb{R}^3), \quad 0 \leq D(f, f) \leq C \|f\|_{L^{6/5}}^2.$$

As both $\rho_{\gamma_{W+w}}$ and ρ_{γ_W} belong to $L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$,

$$\begin{aligned}
 D(\rho_{\gamma_{W+w}} - \rho_{\gamma_W}, \rho_{\gamma_{W+w}} - \rho_{\gamma_W}) &\leq C \|\rho_{\gamma_{W+w}} - \rho_{\gamma_W}\|_{L^{6/5}}^2 \\
 &\leq C \|\rho_{\gamma_{W+w}} - \rho_{\gamma_W}\|_{L^1}^{4/3} \|\rho_{\gamma_{W+w}} - \rho_{\gamma_W}\|_{L^2}^{2/3}.
 \end{aligned}$$

We now make use of the following characterization of the L^p norm [28], which is valid for all $1 \leq p \leq +\infty$:

$$\|f\|_{L^p} = \sup_{g \in L^{p'}(\mathbb{R}^3), \|g\|_{L^{p'}}=1} \int_{\mathbb{R}^3} f g,$$

where $\frac{1}{p} + \frac{1}{p'} = 1$. In our case, one obtains

$$\begin{aligned}
 \|\rho_{\gamma_{W+w}} - \rho_{\gamma_W}\|_{L^1} &= \sup_{g \in L^\infty, \|g\|_{L^\infty}=1} \int_{\mathbb{R}^3} (\rho_{\gamma_{W+w}} - \rho_{\gamma_W}) g \\
 &= \sup_{g \in L^\infty, \|g\|_{L^\infty}=1} \operatorname{Tr}((\gamma_{W+w} - \gamma_W) g) \\
 &\leq \sup_{g \in L^\infty, \|g\|_{L^\infty}=1} \|(\gamma_{W+w} - \gamma_W) g\|_{\mathfrak{S}_1} \\
 &= \sup_{g \in L^\infty, \|g\|_{L^\infty}=1} \left\| \frac{1}{2\pi i} \oint_{\mathcal{C}} (1 - R^0(z) w)^{-1} R^0(z) w R^0(z) g dz \right\|_{\mathfrak{S}_1} \\
 &\leq \frac{|\mathcal{C}| \beta^2}{16\pi^2 \left(1 - \frac{\|w\|_{L^\infty}}{\delta}\right)} \|w\|_{L^1},
 \end{aligned}$$

and

$$\begin{aligned}
 \|\rho_{\gamma_{W+w}} - \rho_{\gamma_W}\|_{L^2} &= \sup_{g \in L^2, \|g\|_{L^2}=1} \int_{\mathbb{R}^3} (\rho_{\gamma_{W+w}} - \rho_{\gamma_W})g \\
 &= \sup_{g \in L^2, \|g\|_{L^2}=1} \text{Tr}((\gamma_{W+w} - \gamma_W)g) \\
 &\leq \sup_{g \in L^2, \|g\|_{L^2}=1} \|(\gamma_{W+w} - \gamma_W)g\|_{\mathfrak{S}_1} \\
 &= \sup_{g \in L^2, \|g\|_{L^2}=1} \left\| \frac{1}{2\pi i} \oint_{\mathcal{C}} (1 - R^0(z)w)^{-1} R^0(z)w R^0(z)g dz \right\|_{\mathfrak{S}_1} \\
 &= \sup_{g \in L^2, \|g\|_{L^2}=1} \frac{|\mathcal{C}| \beta^2}{2\pi(1 - \frac{\|w\|_{L^\infty}}{\delta})} \|(1 - \Delta)^{-1}w\|_{\mathfrak{S}_2} \|(1 - \Delta)^{-1}g\|_{\mathfrak{S}_2} \\
 &\leq \frac{|\mathcal{C}| \beta^2}{16\pi^2 \left(1 - \frac{\|w\|_{L^\infty}}{\delta}\right)} \|w\|_{L^2}.
 \end{aligned}$$

Hence,

$$0 \leq D(\rho_{\gamma_{W+w}} - \rho_{\gamma_W}, \rho_{\gamma_{W+w}} - \rho_{\gamma_W}) \leq \frac{C}{1 - \frac{\|w\|_{L^\infty}}{\delta}} \|w\|_{L^1 \cap L^\infty}^2.$$

Lastly, one obtains, using again the Cauchy-Schwarz and Hardy inequalities,

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|(\gamma_{W+w} - \gamma_W)(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \leq 2 \|\gamma_{W+w} - \gamma_W\|_{\mathfrak{S}_2} \|\nabla \gamma_{W+w} - \nabla \gamma_W\|_{\mathfrak{S}_2}.$$

As

$$\|\gamma_{W+w} - \gamma_W\|_{\mathfrak{S}_2} \leq \|\gamma_{W+w} - \gamma_W\|_{\mathfrak{S}_1} \leq \frac{|\mathcal{C}| \beta^2}{16\pi^2 \left(1 - \frac{\|w\|_{L^\infty}}{\delta}\right)} \|w\|_{L^1},$$

and

$$\begin{aligned}
 \|\nabla \gamma_{W+w} - \nabla \gamma_W\|_{\mathfrak{S}_2} &\leq \left\| \nabla \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z)w R^0(z) dz \right\|_{\mathfrak{S}_2} \\
 &\quad + \left\| \nabla \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z)w(1 - R^0(z)w)^{-1} R^0(z)w R^0(z) dz \right\|_{\mathfrak{S}_2} \\
 &= \left\| \frac{1}{2\pi i} \oint_{\mathcal{C}} \nabla(1 - \Delta)^{-1}(1 - \Delta)R^0(z)w(1 - \Delta)^{-1}(1 - \Delta)R^0(z) dz \right\|_{\mathfrak{S}_2} \\
 &\quad + \left\| \frac{1}{2\pi i} \oint_{\mathcal{C}} \nabla(1 - \Delta)^{-1}(1 - \Delta)R^0(z)w(1 - R^0(z)w)^{-1} R^0(z)w(1 - \Delta)^{-1}(1 - \Delta)R^0(z) dz \right\|_{\mathfrak{S}_2} \\
 &\leq C \left(\|w\|_{L^2} + \frac{\|w\|_{L^2} \|w\|_{L^\infty}}{1 - \frac{\|w\|_{L^\infty}}{\delta}} \right),
 \end{aligned}$$

we conclude that

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|(\gamma_{W+w} - \gamma_W)(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = O(\|w\|_{L^1 \cap L^\infty}^2).$$

We have therefore established that the Fréchet derivative of the function $w \mapsto \mathcal{E}^{\text{HF}}(\gamma_{W+w})$ is the linear form

$$w \mapsto \text{Tr} \left((K_{\gamma_W} - v_x^W) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z)w R^0(z) dz \right).$$

It follows from (8.7)-(8.8) that this linear form is in fact continuous on $L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$. Therefore, there exists $\varrho^W \in (L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3))' = L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, such that for all $w \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$,

$$\mathrm{Tr} \left((K_{\gamma_W} - v_x^W) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) = \int_{\mathbb{R}^3} \varrho^W w.$$

Using $[R^0(z), \gamma_W] = 0$, the analyticity of the function $z \mapsto (1 - \gamma_W)R^0(z)(1 - \gamma_W)$ in the interior domain defined by \mathcal{C} , and Cauchy's formula [39], it is easy to show that

$$\begin{aligned} \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz &= \frac{1}{2\pi i} \oint_{\mathcal{C}} \gamma_W R^0(z) \gamma_W w (1 - \gamma_W) R^0(z) (1 - \gamma_W) dz \\ &\quad + \frac{1}{2\pi i} \oint_{\mathcal{C}} (1 - \gamma_W) R^0(z) (1 - \gamma_W) w \gamma_W R^0(z) \gamma_W dz. \end{aligned}$$

The left-hand side of the above equation therefore defines a finite-rank operator. Let $(\phi_i^W)_{1 \leq i \leq N}$ be a set of N orthonormal eigenvectors of H_W associated with the lowest N eigenvalues $\epsilon_1^W \leq \dots \leq \epsilon_N^W$ of H_W . It holds

$$\begin{aligned} \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz &= \sum_{i=1}^N (|\phi_i^W\rangle \langle \phi_i^W|) w \frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{1}{z - \epsilon_i^W} (1 - \gamma_W) R^0(z) (1 - \gamma_W) dz \\ &\quad + \sum_{i=1}^N \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{1}{z - \epsilon_i^W} (1 - \gamma_W) R^0(z) (1 - \gamma_W) dz \right) w (|\phi_i^W\rangle \langle \phi_i^W|). \end{aligned}$$

Using again the analyticity of the function $z \mapsto (1 - \gamma_W)R^0(z)(1 - \gamma_W)$ in the interior domain defined by \mathcal{C} , and Cauchy's formula, we then obtain

$$\frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{1}{z - \epsilon_i^W} (1 - \gamma_W) R^0(z) (1 - \gamma_W) dz = (1 - \gamma_W) [\epsilon_i^W - (1 - \gamma_W) H_W (1 - \gamma_W)]^{-1} (1 - \gamma_W).$$

Multiplying the above equality by $(K_{\gamma_W} - v_x^W)$ on the left-hand side and taking the trace, we are led to

$$\mathrm{Tr} \left((K_{\gamma_W} - v_x^W) \frac{1}{2\pi i} \oint_{\mathcal{C}} R^0(z) w R^0(z) dz \right) = \int_{\mathbb{R}^3} \varrho^W w$$

with

$$\varrho^W(\mathbf{r}) = 2 \sum_{i=1}^N \phi_i^W(\mathbf{r}) \left[(1 - \gamma_W) [\epsilon_i^W - (1 - \gamma_W) H_W (1 - \gamma_W)]^{-1} (1 - \gamma_W) (K_{\gamma_W} - v_x^W) \phi_i^W \right](\mathbf{r}).$$

As the ϕ_i^W 's are in $H^2(\mathbb{R}^3)$ and as the range of the operator $[\epsilon_i^W - (1 - \gamma_W) H_W (1 - \gamma_W)]^{-1}$ is contained in $H^2(\mathbb{R}^3)$, the function ρ_W belongs to $L^1(\mathbb{R}^3) \cap H^2(\mathbb{R}^3)$. Using similar arguments, one can easily show that the operator T_W defined by (4.17) is finite-rank and that $\rho_W(\mathbf{r}) = t_W(\mathbf{r}, \mathbf{r})$.

It remains to prove lemmas 8.2 and 8.3.

Proof of Lemma 8.2. Let z be in the resolvent set $\rho(H_W)$ of H_W . By Assumption 4.1, $D(H_W) = H^2(\mathbb{R}^3)$. Hence, $(z - H_W)$, considered as an operator from $H^2(\mathbb{R}^3)$ to $L^2(\mathbb{R}^3)$, is invertible. As $W \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, it is also continuous, hence bicontinuous in view of the inverse mapping theorem [37]. As so is $(1 - \Delta)$, $(1 - \Delta)R^0(z)$ is a bounded operator on $L^2(\mathbb{R}^3)$.

On the other hand, it holds, for all $c > 0$ such that $(z - c) \in \rho(H_W)$,

$$R^0(z)(1 - \Delta) = R^0(z)((z - c) - H_W)R^0(z - c)(c - \Delta/2)(c - \Delta/2)^{-1}(1 - \Delta).$$

The operators $R^0(z)((z - c) - H_W) = 1 - cR^0(z)$ and $(c - \Delta/2)^{-1}(1 - \Delta)$ are bounded operators on $L^2(\mathbb{R}^3)$. Besides,

$$(c - \Delta/2)^{-1}(z - c - H_W) = - \left(1 - (c - \Delta/2)^{-1}(z - W) \right).$$

As $W \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, one can write W as $W = W_2 + W_\infty$ with $W_2 \in L^2(\mathbb{R}^3)$ and $W_\infty \in L^\infty(\mathbb{R}^3)$. The operator $(c - \Delta/2)^{-1}(z - W_\infty)$ is a bounded operator and its norm vanishes when c approaches $+\infty$. Lastly, the operator $(c - \Delta/2)^{-1}W_2$ is Hilbert-Schmidt, and its Hilbert-Schmidt norm

$$\left\| (c - \Delta/2)^{-1}W_2 \right\|_{\mathfrak{S}_2} = \frac{1}{8\pi} \left(\int_{\mathbb{R}^3} \frac{e^{-\sqrt{2c}|\mathbf{r}|}}{|\mathbf{r}|^2} d\mathbf{r} \right)^{1/2} \|W_2\|_{L^2},$$

hence its norm in $\mathcal{L}(L^2(\mathbb{R}^3))$, go to zero when c goes to infinity. The operator $(c - \Delta/2)^{-1}(z - c - H_W)$ is therefore bounded on $L^2(\mathbb{R}^3)$ and invertible for c large enough. Its inverse, $R^0(z - c)(c - \Delta/2)$ also defines a bounded operator. This proves that $R^0(z)(1 - \Delta)$ is a bounded operator.

The analyticity of the functions $z \mapsto (1 - \Delta)R^0(z)$ and $z \mapsto R^0(z)(1 - \Delta)$ follows from the analyticity of the resolvent on the resolvent set: For $z_0 \in \rho(H_W)$ and $z \in \rho(H_W)$ such that $|z - z_0| < \|R^0(z_0)\|^{-1}$, it holds

$$R^0(z) = \sum_{n=0}^{+\infty} (z - z_0)^n R^0(z_0)^{n+1}.$$

□

Proof of Lemma 8.3. Let us first prove the second assertion. The kernel of the operator $v(1 - \Delta)^{-1}$ is explicit and reads

$$k(\mathbf{r}, \mathbf{r}') = v(\mathbf{r}) \frac{e^{-|\mathbf{r} - \mathbf{r}'|}}{4\pi|\mathbf{r} - \mathbf{r}'|}.$$

As

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} k(\mathbf{r}, \mathbf{r}')^2 d\mathbf{r} d\mathbf{r}' = \left(\int_{\mathbb{R}^3} v^2 \right) \left(\int_{\mathbb{R}^3} \frac{e^{-2|\mathbf{r}|}}{16\pi^2|\mathbf{r}|^2} d\mathbf{r} \right) = \frac{\|v\|_{L^2}^2}{8\pi},$$

$v(1 - \Delta)^{-1}$ is Hilbert-Schmidt and $\|v(1 - \Delta)^{-1}\|_{\mathfrak{S}_2} = \frac{\|v\|_{L^2}}{(8\pi)^{1/2}}$.

In order to prove the second assertion, we write v as $v = v_+ - v_-$ with $v_+ = \max(v, 0)$ and $v_- = \max(-v, 0)$, and introduce the operators $A_\pm = \sqrt{v_\pm}(1 - \Delta)^{-1}$. As $\sqrt{v_\pm} \in L^2(\mathbb{R}^3)$, the operators A_\pm are Hilbert-Schmidt and such that $\|A_\pm\|_{\mathfrak{S}_2} = \|\sqrt{v_\pm}\|_{L^2}/(8\pi)^{1/2}$. Hence, $(1 - \Delta)^{-1}v(1 - \Delta)^{-1} = A_+^*A_+ - A_-^*A_-$ is trace-class and

$$\|(1 - \Delta)^{-1}v(1 - \Delta)^{-1}\| \leq \frac{1}{8\pi} \left(\|\sqrt{v_+}\|_{L^2}^2 + \|\sqrt{v_-}\|_{L^2}^2 \right) = \frac{\|v\|_{L^1}}{8\pi}.$$

□

8.4. Proof of Proposition 4.2: Properties of the KLI potential

As $D(H_W) = H^2(\mathbb{R}^3)$, the eigenfunctions ϕ_i^W are in $H^2(\mathbb{R}^3)$, and are therefore continuous on \mathbb{R}^3 . Under the assumption that $\epsilon_1^W < \min \sigma_{\text{ess}}(H_W)$, the ground state ϕ_1^W is non-degenerate, and positive on \mathbb{R}^3 . Consequently, ρ_Φ is continuous, and positive on \mathbb{R}^3 , so that

$$v_{x, \text{KLI}}^{\Phi^W}(\mathbf{r}) = v_{x, S}^{\Phi^W}(\mathbf{r}) + \sum_{i=1}^N \left(\langle \phi_i^W | v_{x, \text{KLI}}^{\Phi^W} | \phi_i^W \rangle - \langle \phi_i^W | K_{\Phi^W} | \phi_i^W \rangle \right) \frac{|\phi_i^W(\mathbf{r})|^2}{\rho_{\Phi^W}(\mathbf{r})}, \quad (8.9)$$

is a continuous, bounded function on \mathbb{R}^3 .

Proceeding as in Section 8.1, one can show that the functional J_Φ^{KLI} is well-defined on $L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ and that the global minimizers v of (4.23) are exactly the solutions of the KLI equation

$$\rho_{\Phi^W}(\mathbf{r})v(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_{\Phi^W}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i=1}^N \langle \phi_i^W | v - K_{\Phi^W} | \phi_i^W \rangle |\phi_i^W(\mathbf{r})|^2. \quad (8.10)$$

It remains to prove that the set of solutions of the above equation is a one-dimensional affine space. To this end, we note that the potential

$$v(\mathbf{r}) = v_{x,S}^{\Phi^W}(\mathbf{r}) + \sum_{i=1}^N \left(\alpha_i^{\Phi^W} - \langle \phi_i^W | K_{\Phi^W} | \phi_i^W \rangle \right) \frac{|\phi_i^W(\mathbf{r})|^2}{\rho_{\Phi^W}(\mathbf{r})}$$

is a solution of (8.10) if and only if the vector $\alpha^{\Phi^W} = (\alpha_i^{\Phi^W}) \in \mathbb{R}^N$ is a solution of the linear system (4.25). We therefore have to show that $\text{Ker}(I_N - S^{\Phi^W}) = \mathbb{R}(1, \dots, 1)^T$ and that $\beta^{\Phi^W} \in \text{Ran}(I_N - S^{\Phi^W})$.

Let $y \in \mathbb{R}^N$. One has

$$y^T(I_N - S^{\Phi^W})y = \sum_{i=1}^N y_i^2 - \int_{\mathbb{R}^3} \frac{\left(\sum_{i=1}^N y_i (\phi_i^W)^2 \right)^2}{\sum_{i=1}^N (\phi_i^W)^2} \geq \sum_{i=1}^N y_i^2 - \int_{\mathbb{R}^3} \frac{\left(\sum_{i=1}^N y_i^2 (\phi_i^W)^2 \right) \left(\sum_{i=1}^N (\phi_i^W)^2 \right)}{\sum_{i=1}^N (\phi_i^W)^2} = 0,$$

with equality if and only if, for all $\mathbf{r} \in \mathbb{R}^3$, there exists $\lambda(\mathbf{r})$ such that $y_i \phi_i^W(\mathbf{r}) = \lambda(\mathbf{r}) \phi_i^W(\mathbf{r})$ for all $1 \leq i \leq N$. As $\phi_1^W > 0$ on \mathbb{R}^3 , this condition is equivalent to $y = (y_i) \in \mathbb{R}(1, \dots, 1)^T$. Thus, $\text{Ker}(I_N - S^{\Phi^W}) = \mathbb{R}(1, \dots, 1)^T$. Lastly, using the fact that S^{Φ^W} is symmetric, one obtains

$$\text{Ran}(I_N - S^{\Phi^W}) = \text{Ker}(I_N - S^{\Phi^W})^\perp = \left\{ z = (z_i) \in \mathbb{R}^N, \sum_{i=1}^N z_i = 0 \right\}.$$

It is easy to check that $\beta^{\Phi^W} \in \text{Ran}(I_N - S^{\Phi^W})$.

8.5. Proof of Proposition 5.1: Properties of the ELP

For all $v \in L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, the operator $B^\Phi v = [v, \gamma_\Phi]$ is Hilbert-Schmidt. One can therefore define on $L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ the functional

$$J_\Phi^{\text{ELP}}(v) = \frac{1}{2} \| [v - K_\Phi, \gamma_\Phi] \|_{\mathfrak{S}_2}^2 = \frac{1}{2} \| B^\Phi v - [K_\Phi, \gamma_\Phi] \|_{\mathfrak{S}_2}^2.$$

For all v and h in $L^3(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$,

$$J_\Phi^{\text{ELP}}(v + h) = J_\Phi^{\text{ELP}}(v) + \langle B^\Phi v - [K_\Phi, \gamma_\Phi], B^\Phi h \rangle_{\mathfrak{S}_2} + \frac{1}{2} \| B^\Phi h \|_{\mathfrak{S}_2}^2,$$

and

$$\begin{aligned} & \langle B^\Phi v - [K_\Phi, \gamma_\Phi], B^\Phi h \rangle_{\mathfrak{S}_2} \\ &= 2 \int_{\mathbb{R}^3} \left(\rho_\Phi(\mathbf{r}) v(\mathbf{r}) + \int_{\mathbb{R}^3} \frac{|\gamma_\Phi(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \sum_{i,j=1}^N \langle \phi_i | v - K_\Phi | \phi_j \rangle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \right) h(\mathbf{r}) d\mathbf{r}. \end{aligned}$$

The global minimizers v of (5.1) are therefore exactly the solutions of the equation

$$\rho_\Phi(\mathbf{r}) v(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_\Phi(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i,j=1}^N \langle \phi_i | v - K_\Phi | \phi_j \rangle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}). \quad (8.11)$$

Multiplying the above equation by $\frac{\phi_i \phi_j}{\rho}$ and integrating over \mathbb{R}^3 , one then observes that the function v satisfying

$$\rho_\Phi(\mathbf{r}) v(\mathbf{r}) = - \int_{\mathbb{R}^3} \frac{|\gamma_\Phi(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_{i,j=1}^N (M_{ij} - \langle \phi_i | K_\Phi | \phi_j \rangle) \phi_i(\mathbf{r}) \phi_j(\mathbf{r})$$

is a solution of (8.11) if and only if the matrix M is a solution of the linear system

$$(I - A^\Phi)M = G^\Phi. \quad (8.12)$$

Let us now prove that, if the orbitals ϕ_i are continuous and if $\mathbb{R}^3 \setminus \rho_\Phi^{-1}(0)$ is connected, then $\text{Ker}(I - A^\Phi) = \mathbb{R}I_N$ and $G^\Phi \in \text{Ran}(I - A^\Phi)$. For this purpose, let us consider a matrix $M \in \mathcal{M}_S(N)$ such that $(I - A^\Phi)M = 0$. As M is symmetric, it can be diagonalized in an orthonormal basis set as

$$M = U^T \text{Diag}(\lambda_1, \dots, \lambda_N) U$$

where U is a unitary matrix. Denoting by $(\psi_1, \dots, \psi_N)^T = U(\phi_1, \dots, \phi_N)^T$, a simple calculation leads to

$$0 = ((I - A^\Phi)M, M)_F = \sum_{i=1}^N \lambda_i^2 - \int_{\mathbb{R}^3} \left| \sum_{i=1}^N \lambda_i \psi_i(\mathbf{r}) \right|^2 \frac{d\mathbf{r}}{\rho_\Phi(\mathbf{r})},$$

where $(\cdot, \cdot)_F$ is the Frobenius inner product on $\mathcal{M}_S(N)$. As U is a unitary transform, the ψ_i are orthonormal for the $L^2(\mathbb{R}^3)$ inner product and $\sum_{i=1}^N \psi_i(\mathbf{r})^2 = \rho_\Phi(\mathbf{r})$. Therefore, using the Cauchy-Schwarz inequality,

$$\left| \sum_{i=1}^N \lambda_i \psi_i(\mathbf{r}) \right|^2 \leq \left(\sum_{i=1}^N \psi_i(\mathbf{r})^2 \right) \left(\sum_{i=1}^N \lambda_i^2 \psi_i(\mathbf{r})^2 \right) = \rho_\Phi(\mathbf{r}) \sum_{i=1}^N \lambda_i^2 \psi_i(\mathbf{r})^2,$$

with equality if and only if there exists $C(\mathbf{r})$ such that $\lambda_i \psi_i(\mathbf{r}) = C(\mathbf{r}) \psi_i(\mathbf{r})$ for all $1 \leq i \leq N$. Hence,

$$\sum_{i=1}^N \lambda_i^2 - \int_{\mathbb{R}^3} \left| \sum_{i=1}^N \lambda_i \psi_i(\mathbf{r}) \right|^2 \frac{d\mathbf{r}}{\rho_\Phi(\mathbf{r})} \geq \sum_{i=1}^N \lambda_i^2 - \int_{\mathbb{R}^3} \sum_{i=1}^N \lambda_i^2 \psi_i^2 = 0,$$

with equality if and only if for almost all $\mathbf{r} \in \mathbb{R}^3$, there exists $C(\mathbf{r})$ such that $\lambda_i \psi_i(\mathbf{r}) = C(\mathbf{r}) \psi_i(\mathbf{r})$ for all $1 \leq i \leq N$.

If the orbitals ϕ_i are continuous, so are the functions ψ_i . Let us consider the open sets $\Omega_i = \mathbb{R}^3 \setminus \psi_i^{-1}(0)$ and $\Omega = \cup_{i=1}^N \Omega_i = \mathbb{R}^3 \setminus \rho_\Phi^{-1}(0)$. On Ω_i , one has $C(\mathbf{r}) = \lambda_i$. This implies that the function $C(\mathbf{r})$ is constant on each connected component of Ω . If Ω is connected, one therefore has $\lambda_1 = \lambda_2 = \dots = \lambda_N$, i.e. M is proportional to the identity matrix.

In summary, under the assumptions that the orbitals ϕ_i are continuous and that $\mathbb{R}^3 \setminus \rho_\Phi^{-1}(0)$ is connected,

- (1) the linear equation (8.12) has a solution if and only if $G^\Phi \in \text{Ran}(I - A^\Phi)$. Note that $\text{Ran}(I - A^\Phi) = \text{Ker}(I - (A^\Phi)^*)^\perp = \text{Ker}(I - A^\Phi)^\perp$, since A^Φ is self-adjoint for the Frobenius inner product. It then follows that $\text{Ran}(I - A^\Phi) = \text{Span}(I_N)^\perp$. Since $(I_N, G^\Phi)_F = \text{Tr}(G^\Phi) = 0$, $G^\Phi \in \text{Ran}(I - A^\Phi)$ and (8.12) has at least one solution M_\star^Φ ;
- (2) if M_\star^Φ is a solution of (8.12), then the set of the solutions of (8.12) is $\{M_\star^\Phi + \lambda I_{\mathbb{R}^N}, \lambda \in \mathbb{R}\}$.

Note that replacing M^Φ with $M^\Phi + \lambda I_{\mathbb{R}^N}$ in (8.12) amounts to replacing $v_{x,\text{ELP}}^\Phi$ with $v_{x,\text{ELP}}^\Phi + \lambda$.

Appendix: Brief review of functional analysis

This Appendix aims at providing to quantum chemists the basis of functional analysis needed to understand the *statements* of the results contained in the present article. The additional concepts and results used in the proofs can be found in [37].

Let us first recall the definition of the functional spaces used throughout this article. In the following, all the considered functions are real-valued Lebesgue measurable functions on \mathbb{R}^3 . As usual, two functions which differ only on a set of measure zero are identified.

For $1 \leq p < \infty$, the L^p space is defined as

$$L^p(\mathbb{R}^3) = \left\{ u \mid \int_{\mathbb{R}^3} |u(\mathbf{r})|^p d\mathbf{r} < \infty \right\}.$$

Endowed with the norm

$$\|u\|_{L^p} = \left(\int_{\mathbb{R}^3} |u(\mathbf{r})|^p d\mathbf{r} \right)^{1/p},$$

$L^p(\mathbb{R}^3)$ is a Banach space. The space $L^2(\mathbb{R}^3)$ is a Hilbert space for the inner product

$$\langle u|v \rangle = \int_{\mathbb{R}^3} u(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}.$$

The space $L^\infty(\mathbb{R}^3)$ is the vector space of essentially bounded functions. A measurable function u is essentially bounded if there exists a constant M such that $|u| \leq M$ almost everywhere (a.e.), i.e. everywhere except, possibly, on a set of measure zero. Endowed with the norm

$$\|u\|_{L^\infty} = \inf \{ M \geq 0 \mid |u| \leq M \text{ a.e.} \},$$

$L^\infty(\mathbb{R}^3)$ is a Banach space. One has for all $u \in L^\infty(\mathbb{R}^3)$,

$$|u(\mathbf{r})| \leq \|u\|_{L^\infty} \text{ a.e.}$$

For all $1 \leq p < q \leq \infty$, the space $L^p(\mathbb{R}^3) \cap L^q(\mathbb{R}^3)$, endowed with the norm $\|\cdot\|_{L^p \cap L^q} = \|\cdot\|_{L^p} + \|\cdot\|_{L^q}$, is a Banach space. Likewise, for all $1 < p < q \leq \infty$ the space

$$L^p(\mathbb{R}^3) + L^q(\mathbb{R}^3) = \left\{ u \mid \exists (u_p, u_q) \in L^p(\mathbb{R}^3) \times L^q(\mathbb{R}^3), u = u_p + u_q \right\},$$

endowed with the norm

$$\|u\|_{L^p + L^q} = \inf \left\{ \|u_p\|_{L^p} + \|u_q\|_{L^q}, (u_p, u_q) \in L^p(\mathbb{R}^3) \times L^q(\mathbb{R}^3), u = u_p + u_q \right\}$$

is a Banach space.

In quantum mechanics, the kinetic energy of a one-particle wavefunction ϕ is $\frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi|^2$. It is therefore natural to introduce the vector space

$$H^1(\mathbb{R}^3) = \left\{ u \in L^2(\mathbb{R}^3) \mid \nabla u \in (L^2(\mathbb{R}^3))^3 \right\}.$$

Endowed with the inner product

$$(u, v)_{H^1} = \int_{\mathbb{R}^3} u(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \int_{\mathbb{R}^3} \nabla u(\mathbf{r}) \cdot \nabla v(\mathbf{r}) d\mathbf{r},$$

$H^1(\mathbb{R}^3)$ is a Hilbert space. We will also use the Hilbert space

$$H^2(\mathbb{R}^3) = \left\{ u \in H^1(\mathbb{R}^3) \mid \forall 1 \leq i, j \leq 3, \frac{\partial^2 u}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \in L^2(\mathbb{R}^3) \right\}$$

whose inner product is

$$(u, v)_{H^2} = \int_{\mathbb{R}^3} u(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \int_{\mathbb{R}^3} \nabla u(\mathbf{r}) \cdot \nabla v(\mathbf{r}) d\mathbf{r} + \sum_{i,j=1}^3 \int_{\mathbb{R}^3} \frac{\partial^2 u}{\partial \mathbf{r}_i \partial \mathbf{r}_j}(\mathbf{r}) \frac{\partial^2 v}{\partial \mathbf{r}_i \partial \mathbf{r}_j}(\mathbf{r}) d\mathbf{r}.$$

The functional spaces $H^1(\mathbb{R}^3)$ and $H^2(\mathbb{R}^3)$ belong to the class of Sobolev spaces.

Lastly, $L^p_{\text{loc}}(\mathbb{R}^3)$ is the vector space of the functions u such that $\int_K |u(\mathbf{r})|^p d\mathbf{r} < \infty$ for all compact sets $K \subset \mathbb{R}^3$.

The second part of this Appendix is devoted to linear operators on $L^2(\mathbb{R}^3)$. The set of the continuous linear operators from $L^2(\mathbb{R}^3)$ to $L^2(\mathbb{R}^3)$, also called bounded operators on $L^2(\mathbb{R}^3)$, is denoted by $\mathcal{L}(L^2(\mathbb{R}^3))$. The adjoint of a continuous linear operator $T \in \mathcal{L}(L^2(\mathbb{R}^3))$ is the unique operator of $\mathcal{L}(L^2(\mathbb{R}^3))$, denoted by T^* , defined by

$$\forall (u, v) \in L^2(\mathbb{R}^3) \times L^2(\mathbb{R}^3), \quad \langle T^*u | v \rangle = \langle u | Tv \rangle.$$

The operator $T \in \mathcal{L}(L^2(\mathbb{R}^3))$ is called self-adjoint if $T^* = T$. The vector space of self-adjoint continuous linear operators on $L^2(\mathbb{R}^3)$ is denoted by $\mathcal{S}(L^2(\mathbb{R}^3))$. If T is a self-adjoint operator, it is usual to write

$$\langle u | Tv \rangle = \langle Tu | v \rangle = \langle u | Tv \rangle.$$

Let $T \in \mathcal{L}(L^2(\mathbb{R}^3))$ and $(e_n)_{n \in \mathbb{N}}$ be a Hilbert basis of $L^2(\mathbb{R}^3)$. The value of the sum

$$\sum_{n \in \mathbb{N}} \|Te_n\|_{L^2}^2$$

is independent of the choice of the Hilbert basis $(e_n)_{n \in \mathbb{N}}$. The operator T is called Hilbert-Schmidt if

$$\|T\|_{\mathfrak{S}_2} := \left(\sum_{n \in \mathbb{N}} \|Te_n\|_{L^2}^2 \right)^2 < \infty.$$

The set of Hilbert-Schmidt operators forms a vector space, denoted by \mathfrak{S}_2 . It is in fact a Hilbert space for the inner product

$$\langle S, T \rangle_{\mathfrak{S}_2} = \sum_{n \in \mathbb{N}} \langle Se_n | Te_n \rangle.$$

The norm associated with $\langle \cdot, \cdot \rangle_{\mathfrak{S}_2}$ is denoted by $\| \cdot \|_{\mathfrak{S}_2}$. It can be proved that $T \in \mathcal{L}(L^2(\mathbb{R}^3))$ is Hilbert-Schmidt if and only if there exists a function of $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$, called the kernel of the operator T and usually denoted by T as well, such that

$$(Tu)(\mathbf{r}) = \int_{\mathbb{R}^3} T(\mathbf{r}, \mathbf{r}') u(\mathbf{r}') d\mathbf{r}'.$$

It holds

$$\|T\|_{\mathfrak{S}_2} = \left(\int_{\mathbb{R}^3 \times \mathbb{R}^3} |T(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}' \right)^{1/2},$$

and T is self-adjoint if and only if $T(\mathbf{r}', \mathbf{r}) = T(\mathbf{r}, \mathbf{r}')$.

Let now $T \in \mathcal{S}(L^2(\mathbb{R}^3))$ be a non-negative self-adjoint operator (i.e. $\langle u | Tu \rangle \geq 0$ for all $u \in L^2(\mathbb{R}^3)$) and $(e_n)_{n \in \mathbb{N}}$ a Hilbert basis of $L^2(\mathbb{R}^3)$. The value of the sum

$$\sum_{n \in \mathbb{N}} \langle e_n | T | e_n \rangle$$

does not depend on the choice of the Hilbert basis $(e_n)_{n \in \mathbb{N}}$. If this sum is finite, T is called trace-class and the trace of T is defined as

$$\text{Tr}(T) = \sum_{n \in \mathbb{N}} \langle e_n | T | e_n \rangle.$$

A (non-necessarily self-adjoint) operator $T \in \mathcal{L}(L^2(\mathbb{R}^3))$ is called trace-class if the non-negative self-adjoint continuous operator $|T| = (T^*T)^{1/2}$ is trace-class (the square root of a non-negative self-adjoint operator is defined below). The set of trace-class operators on $L^2(\mathbb{R}^3)$ forms a vector subspace of \mathfrak{S}_2 , denoted by \mathfrak{S}_1 . Endowed with the norm

$$\|T\|_{\mathfrak{S}_1} = \text{Tr}(|T|),$$

\mathfrak{S}_1 is a Banach space. For all $T \in \mathfrak{S}_1$, the sum $\sum_{n \in \mathbb{N}} \langle e_n | T | e_n \rangle$ is finite and independent of the choice of the Hilbert basis $(e_n)_{n \in \mathbb{N}}$. The trace Tr defines a continuous linear form on \mathfrak{S}_1 .

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Most linear operators arising in quantum mechanics are not continuous linear operators. An example is the one-particle kinetic energy operator $T_K = -\frac{1}{2}\Delta$. As the Laplacian of a function of $L^2(\mathbb{R}^3)$ is not, in general, a function of $L^2(\mathbb{R}^3)$, T_K cannot be defined as a linear application from $L^2(\mathbb{R}^3)$ to itself. The useful definition of linear operators is the following: A linear operator T on $L^2(\mathbb{R}^3)$ is a $L^2(\mathbb{R}^3)$ -valued linear application defined on a subspace $D(T)$ of $L^2(\mathbb{R}^3)$. The set $D(T)$ is called the domain of the linear operator T . For instance T_K is a linear operator on $L^2(\mathbb{R}^3)$ with domain $D(T_K) = H^2(\mathbb{R}^3)$ (for all $u \in H^2(\mathbb{R}^3)$, $\Delta u \in L^2(\mathbb{R}^3)$, and $T_K u$ therefore is a function of $L^2(\mathbb{R}^3)$).

Let T be a linear operator on $L^2(\mathbb{R}^3)$ with dense domain $D(T)$. The adjoint of T is the unique linear operator on $L^2(\mathbb{R}^3)$ defined by

$$D(T^*) = \left\{ u \in L^2(\mathbb{R}^3) \mid \exists v_u \in L^2(\mathbb{R}^3) \text{ such that } \langle v_u | w \rangle = \langle u | T w \rangle \forall w \in D(T) \right\}$$

$$T^* u = v_u \quad (v_u \text{ is uniquely defined since } D(T) \text{ is dense in } L^2(\mathbb{R}^3)).$$

The operator T is called self-adjoint if $T^* = T$ (i.e. if $D(T^*) = D(T)$ and if for all $u \in D(T) = D(T^*)$, $T^* u = T u$).

Let T be a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $D(T)$, and $z \in \mathbb{C}$. In order to simplify the notation, we denote by $z - T$ the operator $z I_{L^2(\mathbb{R}^3)} - T$ where $I_{L^2(\mathbb{R}^3)}$ is the identity operator on $L^2(\mathbb{R}^3)$. If $z - T$ is an invertible operator from $D(T)$ to $L^2(\mathbb{R}^3)$, it can be proved that $R(z) = (z - T)^{-1}$ defines a continuous linear operator on $L^2(\mathbb{R}^3)$ (with range $D(T)$). The set

$$\rho(T) = \{ z \in \mathbb{C} \mid z - T \text{ is an invertible operator from } D(T) \text{ to } L^2(\mathbb{R}^3) \}$$

is called the resolvent set of T , and the family $(R(z))_{z \in \rho(T)}$ the resolvent of T . The spectrum of T is the set $\sigma(T) = \mathbb{C} \setminus \rho(T)$. The set $\rho(T)$ is an open set of \mathbb{C} and $\sigma(T)$ is a closed subset of \mathbb{R} . An eigenvalue of T is a complex number λ for which there exists $u \in L^2(\mathbb{R}^3)$ such that $T u = \lambda u$. The set of all the eigenvalues of T is called the point spectrum of T and is denoted by $\sigma_p(T)$. Obviously, $\sigma_p(T) \subset \sigma(T)$ (in particular, all the eigenvalues of a self-adjoint operator are real). The set $\sigma_c(T) = \sigma(T) \setminus \sigma_p(T)$ is called the continuous spectrum of T . If the continuous spectrum of T is empty (i.e. if $\sigma(T) = \sigma_p(T)$), there exists a Hilbert basis $(e_n)_{n \in \mathbb{N}^*}$ of $L^2(\mathbb{R}^3)$ which diagonalizes T :

$$T = \sum_{n \in \mathbb{N}} \lambda_n \langle e_n | \cdot \rangle e_n \quad \left(= \sum_{n \in \mathbb{N}} \lambda_n |e_n\rangle \langle e_n| \quad \text{in bra-ket notation} \right),$$

with $\lambda_n \in \mathbb{R}$. In this case $\sigma(T) = \{\lambda_n\}$. If $f : \mathbb{R} \rightarrow \mathbb{C}$ is continuous in a neighborhood of $\sigma(T)$, the operator $f(T)$ is defined as

$$D(f(T)) = \left\{ u = \sum_{n \in \mathbb{N}} u_n e_n \in L^2(\mathbb{R}^3) \mid \sum_{n \in \mathbb{N}} (1 + |f(\lambda_n)|^2) |u_n|^2 < \infty \right\}$$

$$f(T) = \sum_{n \in \mathbb{N}} f(\lambda_n) \langle e_n | \cdot \rangle e_n = \sum_{n \in \mathbb{N}} f(\lambda_n) |e_n\rangle \langle e_n|.$$

This definition can be generalized to any self-adjoint operator T by means of the spectral theorem [37]. Note that if T is non-negative, $\sigma(T) \subset \mathbb{R}_+$ and the operator $T^{1/2}$ can therefore be given a sense.

Lastly, the spectrum $\sigma(T)$ of a self-adjoint operator can also be partitioned as follows

$$\sigma(T) = \sigma_d(T) \cup \sigma_{\text{ess}}(T),$$

where $\sigma_d(T)$ is the set of all the isolated eigenvalues of T of finite multiplicity, and where $\sigma_{\text{ess}}(T) = \sigma(T) \setminus \sigma_d(T)$. The sets $\sigma_d(T)$ and $\sigma_{\text{ess}}(T)$ are called respectively the discrete spectrum and the essential spectrum of T .

Acknowledgements

We warmly thank C. Le Bris and M. Lewin for useful discussions and comments.

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