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A mathematical perspective on density functional perturbation theory

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Abstract

This article is concerned with the mathematical analysis of the perturbation method for extended Kohn-Sham models, in which fractional occupation numbers are allowed. All our results are established in the framework of the reduced Hartree-Fock (rHF) model, but our approach can be used to study other kinds of extended Kohn-Sham models, under some assumptions on the mathematical structure of the exchange-correlation functional. The classical results of Density Functional Perturbation Theory in the non-degenerate case (that is when the Fermi level is not a degenerate eigenvalue of the mean-field Hamiltonian) are formalized, and a proof of Wigner's $(2n+1)$ rule is provided. We then focus on the situation when the Fermi level is a degenerate eigenvalue of the rHF Hamiltonian, which had not been considered so far.

1 Introduction

Eigenvalue perturbation theory has a long history. Introduced by Rayleigh [23] in the 1870's, it was used for the first time in quantum mechanics in an article by Schrödinger [28] published in 1926. The mathematical study of the perturbation theory of self-adjoint operators was initiated by Rellich [26] in 1937, and has been since then the matter of a large number of contributions in the mathematical literature (see [19, 27, 30] and references therein).

Perturbation theory plays a key role in quantum chemistry, where it is used in particular to compute the response properties of molecular systems to external electromagnetic fields (polarizability, hyperpolarizability, magnetic susceptibility, NMR shielding tensor, optical rotation, ...). Unless the number N of electrons in the molecular system under study is very small, it is not possible to solve numerically the $3N$-dimensional electronic Schrödinger equation. In the commonly used Hartree-Fock and Kohn-Sham models, the *linear* $3N$-*dimensional* electronic Schrödinger equation is approximated by a coupled system of N *nonlinear* 3-*dimensional* Schrödinger equations. The adaptation of the standard linear perturbation theory to the nonlinear setting of the Hartree-Fock model is called Coupled-Perturbed Hartree-Fock theory (CPHF) in the chemistry literature [21] (see also [9] for a mathematical analysis). Its adaptation to the Kohn-Sham model is usually referred to as the Density Functional Perturbation Theory (DFPT) [4, 16]. The term Coupled-Perturbed Kohn-Sham theory is also sometimes used.

The purpose of this article is to study, within the reduced Hartree-Fock (rHF) framework, the perturbations of the ground state energy, the ground state density matrix, and the ground state density of a molecular system, when a "small" external potential is turned on.

In the case when the Fermi level $\epsilon_{\rm F}^0$ is not a degenerate eigenvalue of the mean-field Hamiltonian (see Section 2 for a precise definition of these objects), the formalism of DFPT is well-known (see e.g. [13]). It has been used a huge number of publications in chemistry and physics, as well as in a few mathematical publications, e.g. [10, 14]. On the other hand, the degenerate case has not been considered yet, to the best of our knowledge. An interesting feature of DFPT in the degenerate case is that, in contrast with the usual situation in linear perturbation theory, the perturbation does not, in general, split the degenerate eigenvalue; it shifts the Fermi level and modifies the natural occupation numbers at the Fermi level.

The article is organized as follows. In Section 2, we recall the basic properties of rHF ground states and establish some new results on the uniqueness of the ground state density matrix for a few special cases. The classical results of DFPT in the non-degenerate case are recalled in Section 3, and a simple proof of Wigner's $(2n+1)$ rule is provided. This very important rule for applications allows one to compute the perturbation of the energy at the $(2n+1)^{\rm st}$ order from the perturbation of the density matrix at the $n^{\rm th}$ order only. In particular, the atomic forces (first-order perturbations of the energy) can be computed from the unperturbed density matrix (Wigner's rule for $n=0$), while hyperpolarizabilities of molecules (second and third-order perturbations of the energy) can be computed from the first-order perturbation of the density matrix (Wigner's rule for $n=1$). In Section 4, we investigate the situation when the Fermi level is a degenerate eigenvalue of the rHF Hamiltonian. We establish all our results in the rHF framework in the whole space $\mathbb{R}^3$, for a local potential W with finite Coulomb energy. Extensions to other frameworks (Hartree-Fock and Kohn-Sham models, supercell with periodic boundary conditions, non-local potentials, Stark external potentials, ...) are discussed in Section 5. The proofs of the technical results are postponed until Section 6.

2 Some properties of the rHF model

Throughout this article, we consider a reference (unperturbed) system of N electrons subjected to an external potential V. For a molecular system containing M nuclei, V is given by

$$\forall x \in \mathbb{R}^3, \quad V(x) = -\sum_{k=1}^{M} z_k v(x - R_k),$$

where $z_k \in \mathbb{N}^*$ is the charge (in atomic units) and $R_k \in \mathbb{R}^3$ the position of the $k^{\rm th}$ nucleus. For point nuclei $v = |\cdot|^{-1}$, while for smeared nuclei $v = \mu \star |\cdot|^{-1}$, where $\mu \in C_{\rm c}^\infty(\mathbb{R}^3)$ is a non-negative radial function such that $\int_{\mathbb{R}^3} \mu = 1$.

In the framework of the (extended) Kohn-Sham model [13], the ground state energy of this reference system is obtained by minimizing an energy functional of the form

$$E^{\rm KS}(\gamma) := {\rm Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V + \frac{1}{2} D(\rho_\gamma, \rho_\gamma) + E^{\rm xc}(\rho_\gamma) \tag{1}$$

over the set

$$\mathcal{K}_N := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \le \gamma \le 1,\ {\rm Tr}\,(\gamma) = N,\ {\rm Tr}\,(-\Delta\gamma) < \infty\right\}$$

of the admissible one-body density matrices. To simplify the notation, we omit the spin variable. In the above definition, $\mathcal{S}(L^2(\mathbb{R}^3))$ denotes the space of the bounded self-adjoint operators on $L^2(\mathbb{R}^3)$, $0 \le \gamma \le 1$ means that the spectrum of γ is included in the range $[0,1]$, and ${\rm Tr}\,(-\Delta\gamma)$ is the usual notation for ${\rm Tr}\,(|\nabla|\gamma|\nabla|)$, where $|\nabla| := (-\Delta)^{1/2}$ is the square

root of the positive self-adjoint operator $-\Delta$ on $L^2(\mathbb{R}^3)$. The function $\rho_\gamma : \mathbb{R}^3 \to \mathbb{R}_+$ is the electronic density associated with the density matrix γ. Loosely speaking, $\rho_\gamma(x) = \gamma(x,x)$, where $\gamma(x,y)$ is the kernel of the operator γ. It holds

$$\rho_\gamma \geq 0, \quad \int_{\mathbb{R}^3} \rho_\gamma = N, \quad \int_{\mathbb{R}^3} |\nabla \sqrt{\rho_\gamma}|^2 \leq \mathrm{Tr}\,(-\Delta\gamma)$$

(Hoffmann-Ostenhof inequality [18]) so that, in particular, $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. The first term in the right-hand side of (1) is the Kohn-Sham kinetic energy functional, the second one models the interaction of the electrons with the external potential V, $D(\cdot,\cdot)$ is the Coulomb energy functional defined on $L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$ by

$$D(f,g) := \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{f(x)\,g(y)}{|x-y|}\,dx\,dy,$$

and E^{xc} is the exchange-correlation functional. In the reduced Hartree-Fock (rHF) model (also sometimes called the Hartree model), the latter functional is taken identically equal to zero. In the Local Density Approximation (LDA), it is chosen equal to

$$E^{\mathrm{xc}}_{\mathrm{LDA}}(\rho) := \int_{\mathbb{R}^3} e_{\mathrm{xc}}(\rho(x))\,dx, \tag{2}$$

where the function $e_{\mathrm{xc}} : \mathbb{R}_+ \mapsto \mathbb{R}_-$ is such that for all $\overline{\rho} \in \mathbb{R}_+$, the non-positive number $e_{\mathrm{xc}}(\overline{\rho})$ is (an approximation of) the exchange-correlation energy density of the homogeneous electron gas with constant density $\overline{\rho}$. It is known that for neutral or positively charged molecular systems, that is when $Z = \sum_{k=1}^M z_k \geq N$, the minimization problem

$$E_0 := \inf\left\{E^{\mathrm{KS}}(\gamma),\ \gamma \in \mathcal{K}_N\right\}, \tag{3}$$

has a ground state γ_0, for the rHF model [31] ($E^{\mathrm{xc}} = 0$), as well as for the Kohn-Sham LDA model [1] ($E^{\mathrm{xc}} = E^{\mathrm{xc}}_{\mathrm{LDA}}$).

This contribution aims at studying, in the rHF setting, the perturbations of the ground state energy E_0, of the ground state density matrix γ_0, and of the ground state density $\rho_0 = \rho_{\gamma_0}$ induced by an external potential W. In order to deal with both the unperturbed and the perturbed problem using the same formalism, we introduce the functional

$$E^{\mathrm{rHF}}(\gamma, W) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V + \frac{1}{2}D(\rho_\gamma,\rho_\gamma) + \int_{\mathbb{R}^3} \rho_\gamma W,$$

and the minimization problem

$$\mathcal{E}^{\mathrm{rHF}}(W) := \inf\left\{E^{\mathrm{rHF}}(\gamma, W),\ \gamma \in \mathcal{K}_N\right\}. \tag{4}$$

We restrict ourselves to a potential W belonging to the space

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

which can be identified with the dual of the Coulomb space

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

of the charge distributions with finite Coulomb energy. Here, $\mathcal{S}'(\mathbb{R}^3)$ is the space of tempered distributions on $\mathbb{R}^3$ and $\widehat{\rho}$ is the Fourier transform of ρ (we use the normalization

condition for which the Fourier transform is an isometry of $L^2(\mathbb{R}^3)$). When $W \in \mathcal{C}'$, the last term of the energy functional should be interpreted as

$$\int_{\mathbb{R}^3} \rho_\gamma W = \int_{\mathbb{R}^3} \overline{\widehat{\rho_\gamma}(k)}\, \widehat{W}(k)\, dk.$$

The right-hand side of the above equation is well-defined as the functions $k \mapsto |k|^{-1}\widehat{\rho}_\gamma(k)$ and $k \mapsto |k|\widehat{W}(k)$ are both in $L^2(\mathbb{R}^3)$, since $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \subset L^{6/5}(\mathbb{R}^3) \subset \mathcal{C}$.

The reference, unperturbed, ground state is obtained by solving (4) with $W = 0$.

Theorem 1 (unperturbed ground state for the rHF model [31])**.** *If*

$$Z = \sum_{k=1}^{M} z_k \geq N \qquad \textit{(neutral or positively charged molecular system)}, \tag{5}$$

then (4) has a ground state for $W = 0$, and all the ground states share the same density ρ_0. The mean-field Hamiltonian

$$H_0 := -\frac{1}{2}\Delta + V + \rho_0 \star |\cdot|^{-1},$$

is a self-adjoint operator on $L^2(\mathbb{R}^3)$ and any ground state γ_0 is of the form

$$\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0) + \delta_0, \tag{6}$$

with $\epsilon_{\rm F}^0 \leq 0$, $0 \leq \delta_0 \leq 1$, $\mathrm{Ran}(\delta_0) \subset \mathrm{Ker}(H_0 - \epsilon_{\rm F}^0)$.

The real number $\epsilon_{\rm F}^0$, called the Fermi level, can be interpreted as the Lagrange multiplier of the constraint $\mathrm{Tr}\,(\gamma) = N$. The Hamiltonian H_0 is a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and form domain $H^1(\mathbb{R}^3)$. Its essential spectrum is the range $[0, +\infty)$ and it possesses at least N non-positive eigenvalues, counting multiplicities. For each $j \in \mathbb{N}^*$, we set

$$\epsilon_j := \inf_{X_j \subset \mathcal{X}_j} \sup_{v \in X_j,\, \|v\|_{L^2}=1} \langle v|H_0|v\rangle,$$

where $\mathcal{X}_j$ is the set of the vector subspaces of $H^1(\mathbb{R}^3)$ of dimension j, and $v \mapsto \langle v|H_0|v\rangle$ the quadratic form associated with H_0. Recall (see e.g. [25, Section XIII.1]) that $(\epsilon_j)_{j\in\mathbb{N}^*}$ is a non-decreasing sequence of real numbers converging to zero, and that, if ϵ_j is negative, then H_0 possesses at least j negative eigenvalues (counting multiplicities) and ϵ_j is the $j^{\rm th}$ eigenvalue of H_0. We denote by $\phi_1^0, \phi_2^0, \cdots$ an orthonormal family of eigenvectors associated with the non-positive eigenvalues $\epsilon_1 \leq \epsilon_2 \leq \cdots$ of H_0. Three situations can *a priori* be encountered:

- **Case 1 (non-degenerate case):**

$$H_0 \text{ has at least } N \text{ negative eigenvalues and } \epsilon_N < \epsilon_{N+1} \leq 0. \tag{7}$$

  In this case, the Fermi level $\epsilon_{\rm F}^0$ can be chosen equal to any real number in the range $(\epsilon_N, \epsilon_{N+1})$ and the ground state γ_0 is unique:

$$\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_{\rho_0}) = \sum_{i=1}^{N} |\phi_i^0\rangle\langle\phi_i^0|;$$

- **Case 2 (degenerate case):**

$$H_0 \text{ has at least } N+1 \text{ negative eigenvalues and } \epsilon_{N+1} = \epsilon_N. \tag{8}$$

  In this case, $\epsilon_{\rm F}^0 = \epsilon_N = \epsilon_{N+1} < 0$;

- **Case 3 (singular case):** $\epsilon_{\rm F}^0 = \epsilon_N = 0$.

In the non-degenerate case, problem (4), for $W \in \mathcal{C}'$ small enough, falls into the scope of the usual perturbation theory of nonlinear mean-field models dealt with in Section 3. The main purpose of this article is to extend the perturbation theory to the degenerate case. We will leave aside the singular case $\epsilon_N = 0$. It should be emphasized that the terminology *degenerate vs non-degenerate* used throughout this article refers to the possible degeneracy of the Fermi level, that is of a specific eigenvalue of the unperturbed mean-field Hamiltonian H_{ρ_0}, not to the possible degeneracy of the Hessian of the unperturbed energy functional at γ_0. The perturbation method heavily relies on the uniqueness of the ground state density matrix γ_0 and on the invertibility of the Hessian (or more precisely of a reduced Hessian taking the constraints into account). In the non-degenerate case (Case 1), the minimizer γ_0 is unique and the reduced Hessian is always invertible. We will see that the same holds true in the degenerate case (Case 2) under assumption (9) below. We denote by

$$N_{\rm f} := \mathrm{Rank}\left(\mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0)\right)$$

the number of (fully occupied) eigenvalues lower than $\epsilon_{\rm F}^0$, and by

$$N_{\rm p} := \mathrm{Rank}\left(\mathbb{1}_{\{\epsilon_{\rm F}^0\}}(H_0)\right)$$

the number of (partially occupied) bound states of H_0 with energy $\epsilon_{\rm F}^0$. We also denote by $\mathbb{R}_{\rm S}^{N_{\rm p}\times N_{\rm p}}$ the space of real symmetric matrices of size $N_{\rm p} \times N_{\rm p}$.

Lemma 2. *Assume that (5) and (8) are satisfied. If for any $M \in \mathbb{R}_{\rm S}^{N_{\rm p}\times N_{\rm p}}$,*

$$\left(\forall x \in \mathbb{R}^3,\ \sum_{i,j=1}^{N_{\rm p}} M_{ij}\phi_{N_{\rm f}+i}^0(x)\phi_{N_{\rm f}+j}^0(x) = 0\right) \ \Rightarrow\ M = 0, \tag{9}$$

then the ground state γ_0 of (4) for $W = 0$ is unique

The sufficient condition (9) is satisfied in the following cases.

Proposition 3. *Assume that (5) and (8) are satisfied. If at least one of the two conditions below is fulfilled:*

1. *$N_{\rm p} \le 3$,*
2. *the external potential V is radial and the degeneracy of $\epsilon_{\rm F}^0$ is essential,*

then (9) holds true, and the ground state γ_0 of (4) for $W = 0$ is therefore unique.

Let us clarify the meaning of the second condition in Proposition 3. When V is radial, the ground state density is radial, so that H_0 is a Schrödinger operator with radial potential:

$$H_0 = -\frac{1}{2}\Delta + v(|x|).$$

It is well-known (see e.g. [25, Section XIII.3.B]) that all the eigenvalues of H_0 can be obtained by computing the eigenvalues of the one-dimensional Hamiltonians $h_{0,l}$, $l \in \mathbb{N}$, where $h_{0,l}$ is the self-adjoint operator on $L^2(0,+\infty)$ with domain $H^2(0,+\infty) \cap H^1_0(0,+\infty)$ defined by

$$h_{0,l} := -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v(r).$$

If ϵ_{F}^0 is an eigenvalue of $h_{0,l}$, then its multiplicity, as an eigenvalue of H_0, is at least $2l+1$. It is therefore degenerate as soon as $l \geq 1$. If ϵ_{F}^0 is an eigenvalue of no other $h_{0,l'}$, $l' \neq l$, then its multiplicity is exactly $2l+1$, and the degeneracy is called essential. Otherwise, the degeneracy is called accidental. It is well-known that for the very special case when $v(r) = -Zr^{-1}$ (hydrogen-like atom), accidental degeneracy occurs at every eigenvalue but the lowest one, which is non-degenerate. On the other hand, this phenomenon is really exceptional, and numerical simulations seem to show that, as expected, there is no accidental degeneracy at the Fermi level when v is equal to the rHF mean-field potential of an atom (see [22]).

3 Density functional perturbation theory (non-degenerate case)

We denote by $\mathcal{B}(X,Y)$ the space of bounded linear operators from the Banach space X to the Banach space Y (with, as usual, $\mathcal{B}(X) := \mathcal{B}(X,X)$), by $\mathcal{S}(X)$ the space of self-adjoint operators on the Hilbert space X, by $\mathfrak{S}_1$ the space of trace class operators on $L^2(\mathbb{R}^3)$, and by $\mathfrak{S}_2$ the space of Hilbert-Schmidt operators on $L^2(\mathbb{R}^3)$ (all these spaces being endowed with their usual norms [24, 29]). We also introduce the Banach space

$$\mathfrak{S}_{1,1} := \{T \in \mathfrak{S}_1 \mid |\nabla|T|\nabla| \in \mathfrak{S}_1\},$$

with norm

$$\|T\|_{\mathfrak{S}_{1,1}} := \|T\|_{\mathfrak{S}_1} + \||\nabla\,|T|\nabla|\,\|_{\mathfrak{S}_1}.$$

We denote by $B_\eta(\mathcal{H})$ the open ball with center 0 and radius $\eta > 0$ of the Hilbert space $\mathcal{H}$.

Let us recall that in the non-degenerate case,

$$\gamma_0 \in \mathcal{P}_N := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid \gamma^2 = \gamma,\ \mathrm{Tr}\,(\gamma) = N,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty\right\},$$

that is γ_0 is a rank-N orthogonal projector on $L^2(\mathbb{R}^3)$ with range in $H^1(\mathbb{R}^3)$, and

$$\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}^0]}(H_0) = \frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_0)^{-1}\,dz,$$

where $\mathscr{C}$ is (for instance) the circle of the complex plane symmetric with respect to the real axis and intersecting it at points $\epsilon_1 - 1$ and ϵ_{F}^0.

3.1 Density matrix formulation

The linear and multilinear maps introduced in the following lemma will be useful to write down the Rayleigh-Schrödinger expansions in compact forms.

Lemma 4. *Assume that (5) and (7) are satisfied.*

1. *For each $k \in \mathbb{N}^*$, the k-linear map*

$$\begin{array}{rccl} Q^{(k)}: & (\mathcal{C}')^k & \to & \mathfrak{S}_{1,1} \\ & (v_1,\cdots,v_k) & \mapsto & \dfrac{1}{2i\pi}\displaystyle\oint_{\mathscr{C}} (z-H_0)^{-1}v_1(z-H_0)^{-1}v_2\cdots(z-H_0)^{-1}v_k(z-H_0)^{-1}\,dz \end{array}$$

is well-defined and continuous.

$\mathrm{Rank}(Q^{(k)}(v_1,\cdots,v_k)) \leq N$ *and* $\mathrm{Tr}\,(Q^{(k)}(v_1,\cdots,v_k)) = 0$, *for all* $(v_1,\cdots,v_k) \in (\mathcal{C}')^k$, *and there exists* $0 < \alpha, C < \infty$ *such that for all* $k \in \mathbb{N}^*$ *and all* $(v_1,\cdots,v_k) \in (\mathcal{C}')^k$,

$$\|Q^{(k)}(v_1,\cdots,v_k)\|_{\mathfrak{S}_{1,1}} \leq C\alpha^k \|v_1\|_{\mathcal{C}'} \cdots \|v_k\|_{\mathcal{C}'}. \tag{10}$$

2. *The linear map*

$$\begin{aligned} \mathcal{L} : \mathcal{C} &\to \mathcal{C} \\ \rho &\mapsto -\rho_{Q^{(1)}(\rho\star|\cdot|^{-1})}, \end{aligned}$$

associating to a charge density $\rho \in \mathcal{C}$, *minus the density* $\rho_{Q^{(1)}(\rho\star|\cdot|^{-1})}$ *of the trace-class operator* $Q^{(1)}(\rho\star|\cdot|^{-1})$, *is a bounded positive self-adjoint operator on* $\mathcal{C}$. *As a consequence,* $(1+\mathcal{L})$ *is an invertible bounded positive self-adjoint operator on* $\mathcal{C}$.

The main results of non-degenerate rHF perturbation theory for finite systems are gathered in the following theorem.

Theorem 5 (rHF perturbation theory in the non-degenerate case)**.** *Assume that (5) and (7) are satisfied. Then, there exists* $\eta > 0$ *such that*

1. *for all* $W \in B_\eta(\mathcal{C}')$, *(4) has a unique minimizer* γ_W. *In addition,* $\gamma_W \in \mathcal{P}_N$ *and*

$$\gamma_W = \mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}^0]}(H_W) = \frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_W)^{-1}\,dz, \tag{11}$$

where

$$H_W = -\frac{1}{2}\Delta + V + \rho_W \star |\cdot|^{-1} + W,$$

ρ_W *being the density of* γ_W*;*

2. *the mappings* $W \mapsto \gamma_W$, $W \mapsto \rho_W$ *and* $W \mapsto \mathcal{E}^{\mathrm{rHF}}(W)$ *are real analytic from* $B_\eta(\mathcal{C}')$ *into* $\mathfrak{S}_{1,1}$, $\mathcal{C}$ *and* $\mathbb{R}$ *respectively;*

3. *for all* $W \in \mathcal{C}'$ *and all* $-\eta\|W\|_{\mathcal{C}'}^{-1} < \beta < \eta\|W\|_{\mathcal{C}'}^{-1}$,

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)}, \quad \rho_{\beta W} = \rho_0 + \sum_{k=1}^{+\infty} \beta^k \rho_W^{(k)}, \quad \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{E}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)},$$

the series being normally convergent in $\mathfrak{S}_{1,1}$, $\mathcal{C}$ *and* $\mathbb{R}$ *respectively;*

4. *denoting by* $W^{(1)} = W + \rho_W^{(1)} \star |\cdot|^{-1}$ *and* $W^{(k)} = \rho_W^{(k)} \star |\cdot|^{-1}$ *for* $k \geq 2$, *the coefficients* $\rho_W^{(k)}$ *of the expansion of* $\rho_{\beta W}$ *can be obtained by the recursion relation*

$$(1+\mathcal{L})\rho_W^{(k)} = \widetilde{\rho}_W^{(k)}, \tag{12}$$

where $\widetilde{\rho}_W^{(k)}$ *is the density of the operator* $\widetilde{Q}_W^{(k)}$ *defined by*

$$\begin{aligned} &\widetilde{Q}_W^{(1)} = Q^{(1)}(W), \\ &\forall k \geq 2, \quad \widetilde{Q}_W^{(k)} = \sum_{l=2}^{k} \sum_{\substack{1 \leq j_1,\cdots,j_l \leq k-1, \\ \sum_{i=1}^{l} j_i = k}} Q^{(l)}(W^{(j_1)},\cdots,W^{(j_l)}); \end{aligned} \tag{13}$$

5. the coefficients $\gamma_W^{(k)}$ and $\mathcal{E}_W^{(k)}$ are then given by

$$\gamma_W^{(k)} = \frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_0)^{-1} W^{(k)} (z - H_0)^{-1} \, dz + \widetilde{Q}_W^{(k)}, \tag{14}$$

and

$$\mathcal{E}_W^{(k)} = \mathrm{Tr}\left(H_0 \gamma_W^{(k)}\right) + \frac{1}{2} \sum_{l=1}^{k-1} D\left(\rho_W^{(l)}, \rho_W^{(k-l)}\right) + \int_{\mathbb{R}^3} \rho_W^{(k-1)} \, W. \tag{15}$$

3.2 Molecular orbital formulation

When $\epsilon_1 < \epsilon_2 < \cdots < \epsilon_N < \epsilon_{\mathrm{F}}^0$, that is when the lowest N eigenvalues of H_0 are all non-degenerate, it can be seen, following the same lines as in [9], that, for all $W \in \mathcal{C}'$, there exist real analytic functions $\beta \mapsto \epsilon_{W,i}(\beta) \in \mathbb{R}$ and $\beta \mapsto \phi_{W,i}(\beta) \in H^2(\mathbb{R}^3)$ defined in the neighborhood of 0 such that $\epsilon_{W,i}(0) = \epsilon_i$, $\phi_{W,i}(0) = \phi_i^0$, and

$$\begin{cases} H_{\beta W} \phi_{W,i}(\beta) = \epsilon_{W,i}(\beta) \phi_{W,i}(\beta), \\ (\phi_{W,i}(\beta), \phi_{W,j}(\beta))_{L^2} = \delta_{ij}, \\ \epsilon_{W,1}(\beta) < \epsilon_{W,2}(\beta) < \cdots < \epsilon_{W,N}(\beta) \text{ are the lowest eigenvalues of } H_{\beta W} \text{ (counting multiplicities).} \end{cases}$$

The coefficients of the Rayleigh-Schrödinger expansions

$$\epsilon_{W,i}(\beta) = \sum_{k=0}^{+\infty} \beta^k \epsilon_{W,i}^{(k)}, \qquad \phi_{W,i}(\beta) = \sum_{k=0}^{+\infty} \beta^k \phi_{W,i}^{(k)},$$

where $\epsilon_{W,i}^0 = \epsilon_i$ and $\phi_{W,i}^0 = \phi_i^0$, are obtained by solving the system

$$\forall k \in \mathbb{N}^*, \quad \forall 1 \le i \le N, \qquad \begin{cases} (H_0 - \epsilon_i) \, \phi_{W,i}^{(k)} + \displaystyle\sum_{j=1}^{N} K_{ij}^0 \phi_{W,j}^{(k)} = f_{W,i}^{(k)} + \epsilon_{W,i}^{(k)} \phi_i^0, \\ \displaystyle\int_{\mathbb{R}^3} \phi_{W,i}^{(k)} \phi_i^0 = \alpha_{W,i}^{(k)}, \end{cases} \tag{16}$$

where

$$\forall \phi \in L^2(\mathbb{R}^3), \quad K_{ij}^0 \phi = 2 \left(\phi_j^0 \phi \star |\cdot|^{-1}\right) \phi_i^0,$$

and where the right-hand sides

$$f_{W,i}^{(k)} = -W \phi_{W,i}^{(k-1)} - \sum_{j=1}^{N} \sum_{\substack{1 \le l_1, l_2, l_3 \le k-1, \\ l_1 + l_2 + l_3 = k}} \left(\phi_{W,j}^{(l_1)} \phi_{W,j}^{(l_2)} \star |\cdot|^{-1}\right) \phi_{W,i}^{(l_3)} + \sum_{l=1}^{k-1} \epsilon_{W,i}^{(l)} \phi_{W,i}^{(k-l)},$$

and

$$\alpha_{W,i}^{(k)} = -\frac{1}{2} \sum_{l=1}^{k-1} \int_{\mathbb{R}^3} \phi_{W,i}^{(l)} \phi_{W,i}^{(k-l)}.$$

at order k only depend on the coefficients $\phi_{W,j}^{(l)}$ and $\epsilon_{W,j}^{(l)}$ at order $l \le k-1$. System (16) can therefore be considered as an infinite triangular system with respect to k.

The fact that all the terms of the Rayleigh-Schrödinger series are defined unambiguously by (16) is guaranteed by the following lemma and the fact that for all ϕ and ψ in $H^1(\mathbb{R}^3)$, $W\phi \in H^{-1}(\mathbb{R}^3)$ and $\phi\psi \star |\cdot|^{-1} \in L^\infty(\mathbb{R}^3)$.

Lemma 6. *Assume that (5) and (7) are satisfied and that $\epsilon_1 < \epsilon_2 < \cdots < \epsilon_N < \epsilon_{\rm F}^0$. For all $f = (f_1, \cdots, f_N) \in (H^{-1}(\mathbb{R}^3))^N$ and all $\alpha = (\alpha_1, \cdots, \alpha_N) \in \mathbb{R}^N$, the linear problem*

$$\forall 1 \leq i \leq N, \qquad \left\{ \begin{array}{l} (H_0 - \epsilon_i)\, \psi_i + \displaystyle\sum_{j=1}^N K_{ij}^0 \psi_j = f_i + \eta_i \phi_i^0, \\ \displaystyle\int_{\mathbb{R}^3} \psi_i \phi_i^0 = \alpha_i, \end{array} \right. \tag{17}$$

has a unique solution $(\Psi, \eta) = ((\psi_1, \cdots, \psi_N), (\eta_1, \cdots, \eta_N))$ in $(H^1(\mathbb{R}^3))^N \times \mathbb{R}^N$. Moreover, if $f \in (L^2(\mathbb{R}^3))^N$, then $\Psi \in (H^2(\mathbb{R}^3))^N$.

Let us notice that, although the constraints $\int_{\mathbb{R}^3} \phi_{W,i}(\beta)\phi_{W,j}(\beta) = 0$ for $i \neq j$ are not explicitly taken into account in the formal derivation of (16), the unique solution to (16) is compatible with these constraints since it automatically satisfies

$$\forall k \in \mathbb{N}^*, \quad \forall 1 \leq i, j \leq N, \qquad \int_{\mathbb{R}^3} \sum_{l=0}^k \phi_{W,i}^{(l)} \phi_{W,j}^{(k-l)} = 0. \tag{18}$$

A proof of the above result is provided in Section 6.6, together with the proof of Lemma 6.

Let us finally mention that the Rayleigh-Schrödinger expansions of the density matrix $\gamma_{\beta W}$ and of the molecular orbitals $\phi_{W,i}(\beta)$ are related by

$$\gamma_W^{(k)} = \sum_{i=1}^N \sum_{l=0}^k |\phi_{W,i}^{(l)}\rangle\langle\phi_{W,i}^{(k-l)}|,$$

where we have used Dirac's bra-ket notation.

3.3 Wigner's $(2n+1)$-rule

According to (15), the first n coefficients of the Rayleigh-Schrödinger expansion of the density matrix allows one to compute the first n coefficients of the perturbation expansion of the energy. Wigner's $(2n+1)$-rule ensures that, in fact, they provide an approximation of the energy up to order $(2n+1)$. This property, which is very classical in linear perturbation theory, has been extended only recently to the nonlinear DFT framework [2]. In the present section, we complement the results established in [2] by providing a different, more general and compact proof, which also works in the infinite dimensional setting.

In the density matrix formulation, the Wigner's $(2n+1)$-rule can be formulated as follows. We introduce the nonlinear projector Π on $\mathcal{S}(L^2(\mathbb{R}^3))$ defined by

$$\forall T \in \mathcal{S}(L^2(\mathbb{R}^3)), \quad \Pi(T) = \mathbb{1}_{[1/2,+\infty)}(T),$$

and, for $W \in \mathcal{C}'$ and $\beta \in \mathbb{R}$, we denote by

$$\widetilde{\gamma}_W^{(n)}(\beta) := \Pi\left(\gamma_0 + \sum_{k=1}^n \beta^k \gamma_W^{(k)}\right).$$

For $T \in \mathcal{B}(L^2(\mathbb{R}^3))$, resp. $T \in \mathfrak{S}_2$, we denote by

$$\mathrm{dist}(T, \mathcal{P}_N) := \inf\left\{\|T - \gamma\|,\ \gamma \in \mathcal{P}_N\right\},$$

resp.

$$\mathrm{dist}_{\mathfrak{S}_2}(T, \mathcal{P}_N) := \inf\left\{\|T - \gamma\|_{\mathfrak{S}_2},\ \gamma \in \mathcal{P}_N\right\},$$

the distance from T to $\mathcal{P}_N$ for the operator, resp. Hilbert-Schmidt, norm. The projector Π enjoys the following properties.

Lemma 7. *For each* $T \in \Omega := \left\{T \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid \mathrm{dist}(T, \mathcal{P}_N) < 1/2,\ \mathrm{Ran}(T) \subset H^1(\mathbb{R}^3)\right\}$, $\Pi(T) \in \mathcal{P}_N$. *Besides, for each* $T \in \Omega \cap \mathfrak{S}_2$, $\Pi(T)$ *is the unique solution to the variational problem*

$$\|T - \Pi(T)\|_{\mathfrak{S}_2} = \min_{\gamma \in \mathcal{P}_N} \|T - \gamma\|_{\mathfrak{S}_2} = \mathrm{dist}_{\mathfrak{S}_2}(T, \mathcal{P}_N). \tag{19}$$

It follows from Lemma 7 that, for all $W \in \mathcal{C}'$ and $|\beta|$ small enough, $\widetilde{\gamma}_W^{(n)}(\beta)$ is the projection on $\mathcal{P}_N$ (in the sense of (19)) of the Rayleigh-Schrödinger expansion of the density matrix up to order n.

Theorem 8 (Wigner's $(2n+1)$-rule in the non-degenerate case)**.** *Assume that (5) and (7) are satisfied. For each* $n \in \mathbb{N}$ *and all* $W \in \mathcal{C}'$, *it holds*

$$0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{O}(|\beta|^{2n+2}). \tag{20}$$

Note that as $\gamma_0 + \sum_{k=1}^n \beta^k \gamma_W^{(k)}$ has finite-rank N_n, it can be diagonalized in an orthonormal basis of $L^2(\mathbb{R}^3)$ as

$$\gamma_0 + \sum_{k=1}^n \beta^k \gamma_W^{(k)} = \sum_{i=1}^{N_n} g_{W,i}(\beta) |\widetilde{\phi}_{W,i}(\beta)\rangle\langle\widetilde{\phi}_{W,i}(\beta)|, \tag{21}$$

with $(\widetilde{\phi}_{W,i}(\beta), \widetilde{\phi}_{W,j}(\beta))_{L^2} = \delta_{ij}$, $g_{W,i}(\beta) \in \mathbb{R}$, and $|g_{W,i}(\beta)| \geq |g_{W,j}(\beta)|$ for all $i \leq j$. We also have

$$\sum_{i=1}^{N_n} g_{W,i}(\beta) = \mathrm{Tr}\left(\gamma_0 + \sum_{k=1}^n \beta^k \gamma_W^{(k)}\right) = N,$$

since, in view of (13), (14) and Lemma 4, $\mathrm{Tr}\,(\gamma_W^{(k)}) = 0$ for all $k \geq 1$. For $|\beta|$ small enough, the above operator is in Ω, and therefore, $g_{W,1}(\beta) \geq g_{W,2}(\beta) \geq \cdots \geq g_{W,N}(\beta) > 1/2$ and $|g_{W,j}(\beta)| < 1/2$ for all $j \geq N+1$. We then have

$$\widetilde{\gamma}_W^{(n)}(\beta) = \sum_{i=1}^{N} |\widetilde{\phi}_{W,i}(\beta)\rangle\langle\widetilde{\phi}_{W,i}(\beta)|. \tag{22}$$

4 Perturbations of the rHF model in the degenerate case

We consider in this section the degenerate case. We assume that (9) is satisfied, yielding that the ground state γ_0 of the unperturbed problem (4) with $W = 0$ is unique. We also make the following assumption:

$$\epsilon_{\mathrm{F}}^0 < 0, \quad \mathrm{Rank}(\delta_0) = N_{\mathrm{p}}, \quad \mathrm{Ker}(1 - \delta_0) = \{0\}, \tag{23}$$

where δ_0 is the operator in (6). Assumption (23) means that the natural occupation numbers at the Fermi level (or in other words the N_{p} eigenvalues of $\delta_0|_{\mathrm{Ker}(\mathrm{H}_0 - \epsilon_{\mathrm{F}}^0)}$) are strictly comprised between 0 and 1. As a consequence, γ_0 belongs to the subset

$$\mathcal{K}_{N_{\mathrm{f}}, N_{\mathrm{p}}} := \{\gamma \in \mathcal{K}_N \mid \mathrm{Rank}(\gamma) = N_{\mathrm{f}} + N_{\mathrm{p}},\ \mathrm{Rank}(1 - \gamma) = N_{\mathrm{f}}\}$$

of $\mathcal{K}_N$.

We are going to prove that, under assumptions (9) and (23), the rHF problem (4) has a unique minimizer for $\|W\|_{\mathcal{C}'}$ small enough, which belongs to $\mathcal{K}_{N_{\mathrm{f}}, N_{\mathrm{p}}}$ and whose dependence in W is real analytic. To establish those results and compute the perturbation expansion in W of the minimizer, we proceed as follow:

1. we first construct a real analytic local chart of $\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}$ in the vicinity of γ_0 (Section 4.1);

2. we use this local chart to prove that, for $\|W\|_{\mathcal{C}'}$ small enough, the minimization problem
$$\widetilde{\mathcal{E}}^{\mathrm{rHF}}(W) := \inf\left\{E^{\mathrm{rHF}}(\gamma, W),\ \gamma \in \mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}\right\} \tag{24}$$
has a unique local minimizer γ_W in the vicinity of γ_0, and that the mappings $W \mapsto \gamma_W \in \mathfrak{S}_{1,1}$ and $W \mapsto \widetilde{\mathcal{E}}^{\mathrm{rHF}}(W)$ are real analytic; we then prove that γ_W is actually the unique global minimizer of (4) (Section 4.2), hence that $\widetilde{\mathcal{E}}^{\mathrm{rHF}}(W) = \mathcal{E}^{\mathrm{rHF}}(W)$;

3. we finally derive the coefficients of the Rayleigh-Schrödinger expansions of γ_W and $\mathcal{E}^{\mathrm{rHF}}(W)$, and prove that Wigner's $(2n+1)$-rule also holds true in the degenerate case (Section 4.3).

4.1 Parametrization of $\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}$ in the vicinity of γ_0

We first introduce the Hilbert spaces $\mathcal{H}_\mathrm{f} = \mathrm{Ran}(\mathbb{1}_{(-\infty,\epsilon_\mathrm{F}^0)}(H_0))$, $\mathcal{H}_\mathrm{p} = \mathrm{Ran}(\mathbb{1}_{\{\epsilon_\mathrm{F}^0\}}(H_0))$ and $\mathcal{H}_\mathrm{u} = \mathrm{Ran}(\mathbb{1}_{(\epsilon_\mathrm{F}^0,+\infty)}(H_0))$, corresponding respectively to the fully occupied, partially occupied, and unoccupied spaces of the unperturbed ground state density matrix γ_0. For later purpose, we also set $\mathcal{H}_\mathrm{o} = \mathcal{H}_\mathrm{f} \oplus \mathcal{H}_\mathrm{p}$. As
$$L^2(\mathbb{R}^3) = \mathcal{H}_\mathrm{f} \oplus \mathcal{H}_\mathrm{p} \oplus \mathcal{H}_\mathrm{u},$$
any linear operator T on $L^2(\mathbb{R}^3)$ can be written as a 3×3 block operator
$$T = \begin{bmatrix} T_\mathrm{ff} & T_\mathrm{fp} & T_\mathrm{fu} \\ T_\mathrm{pf} & T_\mathrm{pp} & T_\mathrm{pu} \\ T_\mathrm{uf} & T_\mathrm{up} & T_\mathrm{uu} \end{bmatrix},$$
where T_xy is a linear operator from $\mathcal{H}_\mathrm{y}$ to $\mathcal{H}_\mathrm{x}$. In particular, γ_0 and H_0 are block diagonal in this representation, and it holds
$$\gamma_0 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \Lambda & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad H_0 = \begin{bmatrix} H_0^{--} & 0 & 0 \\ 0 & \epsilon_\mathrm{F}^0 & 0 \\ 0 & 0 & H_0^{++} \end{bmatrix}$$
with $0 \le \Lambda = \delta_0|_{\mathcal{H}_p} \le 1$, $H_0^{--} - \epsilon_\mathrm{F}^0 \le -g_- := \epsilon_{N_\mathrm{f}} - \epsilon_\mathrm{F}^0$ and $H_0^{++} - \epsilon_\mathrm{F}^0 \ge g_+ := \epsilon_{N_\mathrm{f}+N_\mathrm{p}+1} - \epsilon_\mathrm{F}^0$.

We then introduce

- the spaces of finite-rank operators
$$\mathcal{A}_\mathrm{ux} := \left\{A_\mathrm{ux} \in \mathcal{B}(\mathcal{H}_\mathrm{x}, \mathcal{H}_\mathrm{u}) \mid (H_0^{++} - \epsilon_\mathrm{F}^0)^{1/2} A_\mathrm{ux} \in \mathcal{B}(\mathcal{H}_\mathrm{x}, \mathcal{H}_\mathrm{u})\right\},$$
for $\mathrm{x} \in \{\mathrm{f}, \mathrm{p}\}$, endowed with the inner product
$$(A_\mathrm{ux}, B_\mathrm{ux})_{\mathcal{A}_\mathrm{ux}} := \mathrm{Tr}\,(A_\mathrm{ux}^*(H_0^{++} - \epsilon_\mathrm{F}^0)B_\mathrm{ux});$$

- the finite dimensional spaces
$$\mathcal{A}_{\rm pf} := \mathcal{B}(\mathcal{H}_{\rm f}, \mathcal{H}_{\rm p})$$
and
$$\mathcal{A}_{\rm pp} := \{A_{\rm pp} \in \mathcal{S}(\mathcal{H}_{\rm p}) \mid {\rm Tr}\,(A_{\rm pp}) = 0\};$$
- the product space
$$\mathcal{A} := \mathcal{A}_{\rm uf} \times \mathcal{A}_{\rm up} \times \mathcal{A}_{\rm pf} \times \mathcal{A}_{\rm pp},$$
which we endow with the inner product
$$(A, B)_{\mathcal{A}} = \sum_{\rm x\in\{f,p\}} (A_{\rm ux}, B_{\rm ux})_{\mathcal{A}_{\rm ux}} + \sum_{\rm x\in\{f,p\}} {\rm Tr}\,\left(A_{\rm px} B_{\rm px}^*\right).$$

To any $A = (A_{\rm uf}, A_{\rm up}, A_{\rm pf}, A_{\rm pp}) \in \mathcal{A}$, we associate the bounded linear operator $\Gamma(A)$ on $L^2(\mathbb{R}^3)$ defined as

$$\Gamma(A) := \exp\left(L_{\rm uo}(A)\right)\, \exp\left(L_{\rm pf}(A)\right)\, \left(\gamma_0 + L_{\rm pp}(A)\right)\, \exp\left(-L_{\rm pf}(A)\right)\, \exp\left(-L_{\rm uo}(A)\right), \quad (25)$$

where

$$L_{\rm uo}(A) := \begin{bmatrix} 0 & 0 & -A_{\rm uf}^* \\ 0 & 0 & -A_{\rm up}^* \\ A_{\rm uf} & A_{\rm up} & 0 \end{bmatrix}, \quad L_{\rm pf}(A) := \begin{bmatrix} 0 & -A_{\rm pf}^* & 0 \\ A_{\rm pf} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad L_{\rm pp}(A) := \begin{bmatrix} 0 & 0 & 0 \\ 0 & A_{\rm pp} & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Note that Γ is real analytic from $\mathcal{A}$ to $\mathfrak{S}_{1,1}$, $\Gamma(0) = \gamma_0$, and $\Gamma(A) \in \mathcal{K}_N$ for all $A_{\rm pp}$ such that $0 \le \Lambda + A_{\rm pp} \le 1$. In addition, it follows from Assumption (23) that $\Gamma(A) \in \mathcal{K}_{N_{\rm f},N_{\rm p}}$ for all $A \in \mathcal{A}$ small enough. The following lemma provides the parametrization of $\mathcal{K}_{N_{\rm f},N_{\rm p}}$ near γ_0 our analysis is based upon.

Lemma 9. *Assume that (5), (8), (9) and (23) are satisfied. Then there exists an open neighborhood $\mathcal{O}$ of 0 in $\mathcal{A}$ and an open neighborhood $\mathcal{O}'$ of γ_0 in $\mathfrak{S}_{1,1}$ such that the real analytic mapping*
$$\begin{array}{rcl} \mathcal{O} & \to & \mathcal{K}_{N_{\rm f},N_{\rm p}} \cap \mathcal{O}' \\ A & \mapsto & \Gamma(A) \end{array} \quad (26)$$
is bijective.

In other words, the inverse of the above mapping is a local chart of $\mathcal{K}_{N_{\rm f},N_{\rm p}}$ in the vicinity of γ_0. Note that a similar, though not identical, parametrization of the finite-dimensional counterpart of $\mathcal{K}_{N_{\rm f},N_{\rm p}}$ obtained by discretization in atomic orbital basis sets, was used in [8] to design quadratically convergent self-consistent algorithms for the extended Kohn-Sham model.

4.2 Existence and uniqueness of the minimizer of (4) for W small enough

We now define the energy functional
$$E(A, W) := E^{\rm rHF}(\Gamma(A), W), \quad (27)$$
for all $A \in \mathcal{O}$ and all $W \in \mathcal{C}'$, which, in view of Lemma 9 allows us to study the existence and uniqueness of local minimizers of (24) in the vicinity of γ_0 when $\|W\|_{\mathcal{C}'}$ is small enough. The functional E is clearly real analytic; we denote by
$$F(A, W) := \nabla_A E(A, W), \quad (28)$$

the gradient of E with respect to A, evaluated at point (A, W). As γ_0 is the unique minimizer of the functional $\gamma \mapsto E^{\mathrm{rHF}}(\gamma, 0)$ on $\mathcal{K}_N$, hence on $\mathcal{K}_{N_{\mathrm{f}},N_{\mathrm{p}}}$, 0 is the unique minimizer of the functional $A \mapsto E(A, 0)$ on $\mathcal{O}$, so that

$$F(0,0) = 0.$$

Lemma 10. *Assume that (5), (8), (9) and (23) are satisfied. Let*

$$\Theta := \frac{1}{2} F'_A(0,0)|_{\mathcal{A}\times\{0\}},$$

where $F'_A(0,0)|_{\mathcal{A}\times\{0\}}$ is the restriction to the subspace $\mathcal{A} \times \{0\} \equiv \mathcal{A}$ of $\mathcal{A} \times \mathcal{C}'$ of the derivative of F with respect to A at $(0,0)$. The linear map Θ is a bicontinuous coercive isomorphism from $\mathcal{A}$ to its dual $\mathcal{A}'$.

We infer from Lemma 10 and the real analytic version of the implicit function theorem that for $W \in \mathcal{C}'$ small enough, the equation $F(A, W) = 0$ has a unique solution $\widetilde{A}(W)$ in $\mathcal{O}$, and that the function $W \mapsto \widetilde{A}(W)$ is real analytic in the neighborhood of 0. It readily follows from (28) and Lemma 9 that for $W \in \mathcal{C}'$ small enough,

$$\gamma_W := \Gamma(\widetilde{A}(W)) \tag{29}$$

is the unique critical point of (24) in the vicinity of γ_0. This critical point is in fact a local minimizer since Θ, which is in fact the second derivative of the energy functional $A \mapsto E(A, 0)$, is coercive. We have actually the following much stronger result.

Lemma 11. *Assume that (5), (8), (9) and (23) are satisfied. Then, for $\|W\|_{\mathcal{C}'}$ small enough, the density matrix γ_W defined by (29) is the unique global minimizer of (4).*

We conclude this section by providing the explicit form of Θ, which is useful to prove Lemma 10, but also to compute the Rayleigh-Schrödinger expansion of γ_W:

$$\begin{aligned}
[\Theta(A)]_{\mathrm{uf}} &= -A_{\mathrm{uf}}(H_0^{--} - \epsilon_{\mathrm{F}}^0) + (H_0^{++} - \epsilon_{\mathrm{F}}^0)A_{\mathrm{uf}} + \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{uf}}, \\
[\Theta(A)]_{\mathrm{up}} &= (H_0^{++} - \epsilon_{\mathrm{F}}^0)A_{\mathrm{up}}\Lambda + \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{up}}, \\
[\Theta(A)]_{\mathrm{pf}} &= -(1-\Lambda)A_{\mathrm{pf}}\left(H_0^{--} - \epsilon_{\mathrm{F}}^0\right) + \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{pf}}, \\
[\Theta(A)]_{\mathrm{pp}} &= \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{pp}},
\end{aligned}$$

$\mathcal{J}$ denoting the linear operator from $\mathcal{A}$ to $\mathcal{A}'$ defined by

$$\forall (A, A') \in \mathcal{A} \times \mathcal{A}, \quad \langle \mathcal{J}(A), A' \rangle = D(\rho_{\gamma_1(A)}, \rho_{\gamma_1(A')}),$$

where

$$\gamma_1(A) = \langle \Gamma'(0), A \rangle = [L_{\mathrm{uo}}(A) + L_{\mathrm{pf}}(A), \gamma_0] + L_{\mathrm{pp}}(A). \tag{30}$$

A key observation for the sequel is that

$$\forall A \in \mathcal{A}, \quad \mathrm{Tr}\,(H_0\gamma_1(A)) = 0. \tag{31}$$

4.3 Rayleigh-Schrödinger expansions

It immediately follows from the previous two sections that, for any $W \in \mathcal{C}'$, the functions $\beta \mapsto A_W(\beta) := \widetilde{A}(\beta W)$ and $\beta \mapsto \gamma_{\beta W} := \Gamma(\widetilde{A}(\beta W))$ are well-defined and real analytic in the vicinity of 0. The purpose of this section is to provide a method to compute the coefficients $A_W^{(k)}$, $\gamma_W^{(k)}$ and $\mathcal{E}_W^{(k)}$ of the expansions

$$A_W(\beta) = \sum_{k=1}^{+\infty} \beta^k A_W^{(k)}, \quad \gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)} \quad \text{and} \quad \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{E}^{\mathrm{rHF}}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)}.$$

We can already notice that the coefficients $\gamma_W^{(k)}$ and $\mathcal{E}_W^{(k)}$ are easily deduced from the coefficients $A_W^{(k)}$. Using the following version of the Baker-Campbell-Hausdorff formula

$$e^X Y e^{-X} = Y + [X,Y] + \frac{1}{2!}[X,[X,Y]] + \frac{1}{3!}[X,[X,[X,Y]]] + ...,$$

we indeed obtain

$$\gamma_W^{(k)} = \sum_{1 \le l \le k} \sum_{\alpha \in (\mathbb{N}^*)^l \,|\, |\alpha|_1 = k} \gamma_{W,l}^{\alpha} \qquad \text{with} \qquad \gamma_{W,l}^{\alpha} = \gamma_l(A_W^{(\alpha_1)}, \cdots, A_W^{(\alpha_l)}), \tag{32}$$

where for all $\alpha = (\alpha_1, \cdots, \alpha_l) \in (\mathbb{N}^*)^l$, $|\alpha|_1 = \alpha_1 + \cdots + \alpha_l$, $|\alpha|_\infty = \max(\alpha_i)$, and

$$\begin{aligned} \gamma_l(A_1, \cdots, A_l) \;=\; & \sum_{i+j=l} \frac{1}{i!j!}[L_{\mathrm{uo}}(A_1), \cdots, [L_{\mathrm{uo}}(A_i), [L_{\mathrm{pf}}(A_{i+1}), \cdots, [L_{\mathrm{pf}}(A_l), \gamma_0] \cdots] \\ + & \sum_{i+j=l-1} \frac{1}{i!j!}[L_{\mathrm{uo}}(A_1), ..., [L_{\mathrm{uo}}(A_i), [L_{\mathrm{pf}}(A_{i+1}), \cdots, [L_{\mathrm{pf}}(A_{l-1}), L_{\mathrm{pp}}(A_l)] \cdots], \end{aligned}$$

for all $(A_1, \cdots, A_l) \in \mathcal{A}^l$. Note that for $l = 1$, the above definition agrees with (30), and that, more generally,

$$\forall A \in \mathcal{A}, \quad \Gamma(A) = \gamma_0 + \sum_{l=1}^{+\infty} \gamma_l(A, \cdots, A). \tag{33}$$

It follows from (31) and (32) that

$$\mathcal{E}_W^{(1)} = \int_{\mathbb{R}^3} \rho_{\gamma_0} W, \tag{34}$$

and that for all $k \ge 2$,

$$\mathcal{E}_W^{(k)} = \mathrm{Tr}\left(-\frac{1}{2}\Delta \gamma_W^{(k)}\right) + \int_{\mathbb{R}^3} \rho_{\gamma_W^{(k)}} V + \frac{1}{2}\sum_{l=0}^{k} D\left(\rho_{\gamma_W^{(l)}}, \rho_{\gamma_W^{(k-l)}}\right) + \int_{\mathbb{R}^3} \rho_{\gamma_W^{(k-1)}} W \tag{35}$$

We will see however that the above formula is far from being optimal, in the sense that $\mathcal{E}_W^{(k)}$ can be computed using the coefficients $A_W^{(j)}$ for $1 \le j \le k/2$ only (see formulation (39) of Wigner's $(2n+1)$-rule), whereas the direct evaluation of $\mathcal{E}_W^{(k)}$ based on (32) and (35) requires the knowledge of the $A_W^{(j)}$'s up to $j = k$.

4.4 Main results for the degenerate case

The following theorem collects the results obtained so far, and provides a systematic way to construct the $A_W^{(k)}$'s, as well as an extension to Wigner's $(2n+1)$-rule to the degenerate case.

Theorem 12. *Assume that (5), (8), (9) and (23) are satisfied. Then there exists $\eta > 0$, such that*

1. existence and uniqueness of the ground state: *for all $W \in B_\eta(\mathcal{C}')$, the rHF model (4) has a unique ground state γ_W;*

2. no energy level splitting at the Fermi level: *the mean-field Hamiltonian*

$$H_W = -\frac{1}{2}\Delta + V + \rho_W \star |\cdot|^{-1} + W$$

(where ρ_W is the density of γ_W) has at least $N_\mathrm{o} = N_\mathrm{f} + N_\mathrm{p}$ negative eigenvalues (counting multiplicities), the degeneracy of the $(N_\mathrm{f}+1)^{\mathrm{st}}$ eigenvalue, which is also the Fermi level ϵ_F^W of the system, being equal to N_p, and it holds

$$\gamma_W = \mathbb{1}_{(-\infty,\epsilon_\mathrm{F}^W)}(H_W) + \delta_W,$$

where $0 \le \delta_W \le 1$ is an operator such that $\mathrm{Ran}(\delta_W) \subset \mathrm{Ker}(H_W - \epsilon_\mathrm{F}^W)$ with maximal rank N_p;

3. analyticity of the ground state: *the functions $W \mapsto \gamma_W$ and $W \mapsto \mathcal{E}^{\mathrm{rHF}}(W)$ are real analytic from $B_\eta(\mathcal{C}')$ to $\mathfrak{S}_{1,1}$ and $\mathbb{R}$ respectively. For all $W \in \mathcal{C}'$ and all $-\eta\|W\|_{\mathcal{C}'}^{-1} < \beta < \eta\|W\|_{\mathcal{C}'}^{-1}$,*

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)}, \quad \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{E}^{\mathrm{rHF}}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)},$$

the series being normally convergent in $\mathfrak{S}_{1,1}$ and $\mathbb{R}$ respectively;

4. Rayleigh-Schrödinger expansions: *the coefficients $\gamma_W^{(k)}$ are given by (32), where the $A_W^{(k)}$'s are obtained recursively by solving the well-posed linear problem in $\mathcal{A}$*

$$\Theta(A_W^{(k)}) = -\frac{1}{2} B_W^{(k)}, \tag{36}$$

where the $B_W^{(k)}$'s are defined by

$$\forall A \in \mathcal{A}, \quad \langle B_W^{(1)}, A\rangle = \int_{\mathbb{R}^3} \rho_{\gamma_1(A)} W, \tag{37}$$

and for all $k \ge 2$ and all $A \in \mathcal{A}$,

$$\begin{aligned}\langle B_W^{(k)}, A\rangle = &\sum_{l=3}^{k+1} \sum_{\substack{\alpha\in(\mathbb{N}^*)^{l-1} \\ |\alpha|_1=k,\, |\alpha|_\infty\le k-1}} \sum_{i=1}^{l} \mathrm{Tr}\left(H_0 \gamma_l(\tau_{(i,l)}(A_W^{(\alpha_1)}, \cdots, A_W^{(\alpha_{l-1})}, A))\right) \\ &+ \sum_{\substack{3\le l+l'\le k+1 \\ l\ge1,\, l'\ge1}} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'-1} \\ |\alpha|_1+|\alpha'|_1=k,\, \max(|\alpha|_\infty,|\alpha'|_\infty)\le k-1}} \sum_{i=1}^{l'} D\left(\rho_{\gamma_{W,l}^\alpha}, \rho_{\gamma_{l'}(\tau_{(i,l')}(A_W^{(\alpha'_1)},\cdots,A_W^{(\alpha'_{l'-1})},A))}\right) \\ &+ \sum_{l=2}^{k} \sum_{\substack{\alpha\in(\mathbb{N}^*)^{l-1} \\ |\alpha|_1=k-1,\, |\alpha|_\infty\le k-2}} \sum_{i=1}^{l} \int_{\mathbb{R}^3} \rho_{\gamma_l(\tau_{(i,l)}(A_W^{(\alpha_1)},\cdots,A_W^{(\alpha_{l-1})},A))} W;\end{aligned} \tag{38}$$

where $\tau_{(i,j)}$ is the transposition swapping the ith and j^{th} terms (by convention $\tau_{(i,i)}$ is the identity);

5. *first formulation of Wigner's $(2n+1)$-rule: for all $n \in \mathbb{N}$, and all $\epsilon \in \{0,1\}$,*

$$\begin{aligned}\mathcal{E}_W^{(2n+\epsilon)} &= \sum_{2\leq l\leq 2n+\epsilon} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon,\, |\alpha|_\infty\leq n} \mathrm{Tr}\,(H_0\gamma_{W,l}^\alpha) \\ &+ \frac{1}{2}\sum_{\substack{2\leq l+l'\leq 2n+\epsilon \\ l,l'\geq 1}} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'} \,|\, |\alpha|_1+|\alpha'|_1=2n+\epsilon \\ \max(|\alpha|_\infty,\, |\alpha'|_\infty)\leq n}} D\left(\rho_{\gamma_{W,l}^\alpha}, \rho_{\gamma_{W,l'}^{\alpha'}}\right) \\ &+ \sum_{1\leq l\leq 2n+\epsilon-1} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon-1,\, |\alpha|_\infty\leq n} \int_{\mathbb{R}^3} \rho_{\gamma_{W,l}^\alpha} W; \end{aligned} \tag{39}$$

6. *second formulation of Wigner's $(2n+1)$-rule: it holds*

$$0 \leq E^{\mathrm{rHF}}\left(\Gamma\left(\sum_{k=1}^n \beta^k A_W^{(k)}\right), W\right) - \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{O}(|\beta|^{2n+2}). \tag{40}$$

Note that both formulations of Wigner's $(2n+1)$-rule state that an approximation of the energy $\mathcal{E}^{\mathrm{rHF}}(\beta W)$ up to order $(2n+1)$ in β, can be obtained from the $A_W^{(k)}$ for $1 \leq k \leq n$. They are yet different since the first formulation consists in computing all the coefficients $\mathcal{E}_W^{(k)}$ up to order $(2n+1)$, while the second formulation is based on the computation of the density matrix $\Gamma\left(\sum_{k=1}^n \beta^k A_W^{(k)}\right)$.

Remark 13. *Although we were not able to rigorously prove that assumptions (5), (8), (9) and (23) were actually satisfied for a specific molecular system, we strongly believe that this is the case for some atoms. Recall that the singlet-spin state rHF model is obtained from the spinless rHF model dealt with here by replacing N by $N/2$ (the number of electron pairs) and ρ_γ by $2\rho_\gamma$ (each state is occupied by one spin-up and one spin-down electron), so that all our results can be applied mutatis mutandis to the singlet-spin state rHF model. We have performed numerical simulations of a carbon atom within the singlet-spin state rHF model [22] and observed that for this system, the lowest two eigenvalues of H_0, corresponding to the 1s and 2s shells, are negative and non-degenerate, while the third lowest eigenvalue, corresponding to the 2p shell, is threefold degenerate. As the carbon atom contains six electrons, that is three electron pairs, the Fermi level coincides with the third lowest eigenvalue. Using the first statement of Proposition 3, we obtain that assumptions (8) is satisfied, hence that the ground state density matrix γ_0 is unique, yielding that, by symmetry, all the occupation numbers at the Fermi level are equal to $1/3$. Numerical simulations therefore suggest that assumptions (8), (9) and (23) are satisfied for the singlet-spin state rHF model of a carbon atom, while (5) is obviously satisfied since this system is electrically neutral.*

Remark 14. *In order to illustrate what may happen when assumption (23) is not satisfied, we consider the toy model*

$$\mathcal{E}^{\mathrm{TM}}(w) = \inf\left\{E^{\mathrm{TM}}(\gamma, w),\ \gamma \in \mathcal{K}_2\right\}, \tag{41}$$

where

$$E^{\mathrm{TM}}(\gamma, w) = \mathrm{Tr}\,(H_0^{\mathrm{TM}}\gamma) + \frac{1}{2}\left(\mathrm{Tr}\,\left((\gamma - \gamma_0^{\mathrm{TM}})^2\right)\right)^2 + \mathrm{Tr}\,(\gamma w),$$

$$H_0^{\mathrm{TM}} = -2|e_1\rangle\langle e_1| - |e_2\rangle\langle e_2| - |e_3\rangle\langle e_3|, \quad \gamma_0^{\mathrm{TM}} = |e_1\rangle\langle e_1| + |e_2\rangle\langle e_2|,$$

e_1, e_2, e_3 being pairwise orthonormal vectors of $L^2(\mathbb{R}^3)$. For $w = 0$, the unique ground state of (41) is γ_0^{TM} and the mean-field Hamiltonian of the unperturbed system is H_0^{TM}. We are therefore in the degenerate case with $\epsilon_{\mathrm{F}}^0 = -1$ and $\delta_0^{\mathrm{TM}} = |e_2\rangle\langle e_2|$, and we have $N_{\mathrm{f}} = 1$, $1 = \mathrm{Rank}(\delta_0^{\mathrm{TM}}) < N_{\mathrm{p}} = 2$, $\mathrm{Ker}(1 - \delta_0^{\mathrm{TM}}) = \mathbb{R}e_2 \neq \{0\}$, so that condition (23) is not fulfilled. A simple calculation shows that for $w = |e_3\rangle\langle e_3|$, it holds

$$\mathcal{E}^{\mathrm{TM}}(\beta w) = \left| \begin{array}{ll} -3 - \frac{3}{8}|\beta|^{4/3} & \textit{for } \beta < 0, \\ -3 & \textit{for } \beta \geq 0. \end{array} \right.$$

Clearly, real-analytic perturbation theory cannot be applied.

Remark 15. *The block representation of $\gamma_W^{(1)}$, the first-order term of the perturbation expansion of the ground state density matrix, is given by*

$$\gamma_W^{(1)} = \begin{bmatrix} 0 & (A_{\mathrm{pf}}^{(1)})^*(1-\Lambda) & (A_{\mathrm{uf}}^{(1)})^* \\ (1-\Lambda)A_{\mathrm{pf}}^{(1)} & A_{\mathrm{pp}}^{(1)} & \Lambda(A_{\mathrm{up}}^{(1)})^* \\ A_{\mathrm{uf}}^{(1)} & A_{\mathrm{up}}^{(1)}\Lambda & 0 \end{bmatrix}, \tag{42}$$

where the above operators solve the following system

$$\Theta(A_{\mathrm{uf}}^{(1)}, A_{\mathrm{up}}^{(1)}, A_{\mathrm{pf}}^{(1)}, A_{\mathrm{pp}}^{(1)}) = -(W_{\mathrm{uf}}, W_{\mathrm{up}}\Lambda, (1-\Lambda)W_{\mathrm{pf}}, \frac{1}{2}W_{\mathrm{pp}}), \tag{43}$$

where W_{xy} is the xy-block of the operator "multiplication by W". We also have

$$\mathcal{E}_W^{(2)} = \mathrm{Tr}\left(H_0\gamma_{W,2}^{(1,1)}\right) + \frac{1}{2}D\left(\rho_{\gamma_{W,1}^{(1)}}, \rho_{\gamma_{W,1}^{(1)}}\right) + \int_{\mathbb{R}^3} \rho_{\gamma_{W,1}^{(1)}} W.$$

The second-order term $\gamma_W^{(2)}$ is also useful to compute nonlinear responses. For brevity, we do not provide here the explicit formula to compute this term and refer the reader to [22].

Remark 16. *In the degenerate case, there is no analogue of (12), that is no explicit closed recursion relation on the coefficients of the Rayleigh-Schrödinger expansion of the density.*

5 Extensions to other settings

Although all the results in the preceding sections are formulated for finite molecular systems in the whole space, in the all-electron rHF framework, some of them can be easily extended to other settings:

- all the results in Sections 3 and 4 can be extended to valence electron calculations with nonlocal pseudopotentials, as well as to regular nonlocal perturbations of the rHF model, that is to any perturbation modeled by an operator W such that $W(1-\Delta)$ is a bounded operator on $L^2(\mathbb{R}^3)$, the term $\int_{\mathbb{R}^3} \rho_\gamma W$ being then replaced with $\mathrm{Tr}\,(\gamma W)$;
- all the results in Section 3 can be extended to the rHF model for locally perturbed insulating or semiconducting crystals (see in particular [10], where the analogues of the operators $\mathcal{L}$ and $Q^{(k)}$ in Lemma 4 are introduced and analyzed); the extension to conducting crystals is a challenging task, see [15] for results on the particular case of the homogeneous electron gas;

- extending our results to the Kohn-Sham LDA model for finite molecular systems in the whole space is difficult as the ground state density decays exponentially to zero at infinity while the LDA exchange-correlation energy density is not twice differentiable at 0 (it behaves as the function $\mathbb{R}_+ \ni \rho \mapsto -\rho^{4/3} \in \mathbb{R}_-$). On the other hand, all the results in Sections 3 and 4 can be extended to the Kohn-Sham LDA model on a supercell with periodic boundary conditions as well as to the periodic Kohn-Sham LDA model for perfect crystals, as in this case, the ground state density is periodic and bounded away from zero (see e.g. [6, 7]). Let us emphasize however that in the LDA setting, it is not known whether the ground state density of the unperturbed problem is unique. We must therefore restrict ourselves to local perturbation theory in the vicinity of a local minimizer and make a coercivity assumption on the Hessian of the energy functional at the unperturbed local minimizer γ_0. In the supercell setting, the operator $\mathcal{L}$ was used in [14] to study the stability of crystals;

- the Hartree-Fock model consists in minimizing the energy functional

$$E^{\mathrm{HF}}(\gamma, W) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma (V+W) + \frac{1}{2} D(\rho_\gamma, \rho_\gamma) - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\gamma(x,y)|^2}{|x-y|}\, dx\, dy$$

over the set $\mathcal{P}_N$ of Slater determinants with finite kinetic energy. It turns out that all the local minimizers of $E^{\mathrm{HF}}(\gamma, W)$ on $\mathcal{K}_N$ are on $\mathcal{P}_N$ (Lieb's variational principle [20]). Consequently, an equivalent formulation of the Hartree-Fock model is

$$\mathcal{E}(W) := \inf\left\{E^{\mathrm{HF}}(\gamma, W),\ \gamma \in \mathcal{K}_N\right\}. \tag{44}$$

Uniqueness for problem (44) is an essentially open question (see however [17] for partial results). In order to apply perturbation theory, we therefore need a coercivity assumption on the Hessian at the minimizer γ_0, just as in the LDA setting. It is known that there are no unfilled shells in the Hartree-Fock theory [3], which implies that we are always in the non-degenerate case. The first three statements and the fifth statement of Theorem 5 can be transposed to the Hartree-Fock setting under the above mentioned coercivity assumption. On the other hand, there is no analogue of (12) for the Hartree-Fock model. A mathematical analysis of the perturbation theory for the molecular orbital formulation of the Hartree-Fock model was published in [9]. It is easily checked that our proof of Wigner's $(2n+1)$-rule also applies to the Hartree-Fock setting;

- the extension to some of our results to Stark potentials $W(x) = -E\cdot x$, where $E \in \mathbb{R}^3$ is a uniform electric field, will be dealt with in a future work [11].

6 Proofs

6.1 Proof of Lemma 2

Let γ_0 and γ_0' be two ground states of (4) for $W = 0$. By Theorem 1, $\gamma_0 - \gamma_0' = \sigma$, with $\sigma \in \mathcal{S}(L^2(\mathbb{R}^3))$, $\mathrm{Ran}(\sigma) \subset \mathrm{Ker}(H_0 - \epsilon_{\mathrm{F}}^0)$, $\mathrm{Tr}\,(\sigma) = 0$. Therefore,

$$\sigma = \sum_{i,j=1}^{N_{\mathrm{p}}} M_{ij} |\phi^0_{N_{\mathrm{f}}+i}\rangle\langle\phi^0_{N_{\mathrm{f}}+j}|$$

for some symmetric matrix $M \in \mathbb{R}_{\mathrm{S}}^{N_{\mathrm{p}} \times N_{\mathrm{p}}}$ such that $\mathrm{Tr}\,(M) = 0$. As, still by Theorem 1, γ_0 and γ_0' share the same density, the density of σ is identically equal to zero, that is

$$\forall x \in \mathbb{R}^3, \quad \sum_{i,j=1}^{N_{\mathrm{p}}} M_{ij} \phi^0_{N_{\mathrm{f}}+i}(x) \phi^0_{N_{\mathrm{f}}+j}(x) = 0.$$

If Assumption (9) is satisfied, then $M = 0$; therefore $\sigma = 0$, and uniqueness is proved.

6.2 Proof of Proposition 3

Let us first notice that as for all $1 \leq i \leq N_{\mathrm{p}}$, $\phi^0_{N_{\mathrm{f}}+i} \in D(H_0) = H^2(\mathbb{R}^3) \hookrightarrow C^0(\mathbb{R}^3)$, condition (9) is mathematically well-defined.

Case 1: Let $M \in \mathbb{R}_{\mathrm{S}}^{N_{\mathrm{p}} \times N_{\mathrm{p}}}$ be such that

$$\forall x \in \mathbb{R}^3, \quad \sum_{i,j=1}^{N_{\mathrm{p}}} M_{ij} \phi^0_{N_{\mathrm{f}}+i}(x) \phi^0_{N_{\mathrm{f}}+j}(x) = 0.$$

The matrix M being symmetric, there exists an orthogonal matrix $U \in O(N_{\mathrm{p}})$ such that $UMU^T = \mathrm{diag}(n_1, \cdots, n_{N_{\mathrm{p}}})$ with $n_1 \leq \cdots \leq n_{N_{\mathrm{p}}}$. Let $\widetilde{\phi}^0_{N_{\mathrm{f}}+i}(x) = \sum_{j=1}^{N_{\mathrm{p}}} U_{ij} \phi^0_{N_{\mathrm{f}}+j}(x)$. The functions $\widetilde{\phi}^0_{N_{\mathrm{f}}+i}$ form an orthonormal basis of $\mathrm{Ker}(H_0 - \epsilon^0_{\mathrm{F}})$ and it holds

$$\forall x \in \mathbb{R}^3, \quad \sum_{i=1}^{N_{\mathrm{p}}} n_i |\widetilde{\phi}^0_{N_{\mathrm{f}}+i}(x)|^2 = 0,$$

from which we deduce that $\sum_{i=1}^{N_{\mathrm{p}}} n_i = 0$. Consider first the case when $N_{\mathrm{p}} = 2$. If $M \neq 0$, then $n_2 = -n_1 = n > 0$, so that

$$\forall x \in \mathbb{R}^3, \quad |\widetilde{\phi}^0_{N_{\mathrm{f}}+1}(x)|^2 = |\widetilde{\phi}^0_{N_{\mathrm{f}}+2}(x)|^2.$$

In particular, the two eigenfunctions $\widetilde{\phi}^0_{N_{\mathrm{f}}+1}$ and $\widetilde{\phi}^0_{N_{\mathrm{f}}+2}$ have the same nodal surfaces (that is $(\widetilde{\phi}^0_{N_{\mathrm{f}}+1})^{-1}(0) = (\widetilde{\phi}^0_{N_{\mathrm{f}}+2})^{-1}(0)$). Consider now the case when $N_{\mathrm{p}} = 3$. If $M \neq 0$, then either $n_2 = 0$ and $\widetilde{\phi}^0_{N_{\mathrm{f}}+1}$ and $\widetilde{\phi}^0_{N_{\mathrm{f}}+3}$ have the same nodes, or $n_2 \neq 0$. Replacing M with $-M$, we can, without loss of generality assume that $n_1 < 0 < n_2 \leq n_3$, which leads to

$$\forall x \in \mathbb{R}^3, \quad |\widetilde{\phi}^0_{N_{\mathrm{f}}+1}(x)|^2 = \frac{|n_2|}{|n_1|} |\widetilde{\phi}^0_{N_{\mathrm{f}}+2}(x)|^2 + \frac{|n_3|}{|n_1|} |\widetilde{\phi}^0_{N_{\mathrm{f}}+3}(x)|^2.$$

We infer from the above equality that the nodal surfaces of $\widetilde{\phi}^0_{N_{\mathrm{f}}+1}(x)$ are included in those of $\widetilde{\phi}^0_{N_{\mathrm{f}}+2}(x)$. Let Ω be a connected component of the open set $\mathbb{R}^3 \setminus (\widetilde{\phi}^0_{N_{\mathrm{f}}+1})^{-1}(0)$, and let H_0^{Ω} be the self-adjoint operator on $L^2(\Omega)$ with domain

$$D(H_0^{\Omega}) = \left\{ u \in H_0^1(\Omega) \mid \Delta u \in L^2(\Omega) \right\}$$

defined by

$$\forall u \in D(H_0^{\Omega}), \quad H_0^{\Omega} u = -\frac{1}{2} \Delta u + V u + (\rho_0 \star |\cdot|^{-1}) u.$$

As both $\psi_1 = \widetilde{\phi}^0_{N_{\mathrm{f}}+1}|_{\Omega}$ and $\psi_2 = \widetilde{\phi}^0_{N_{\mathrm{f}}+2}|_{\Omega}$ are in $D(H_0^{\Omega})$ and satisfy $H_0^{\Omega}\psi_1 = \epsilon^0_{\mathrm{F}}\psi_1$, $H_0^{\Omega}\psi_2 = \epsilon^0_{\mathrm{F}}\psi_2$, $|\psi_1| > 0$ in Ω, we deduce from [25, Theorem XIII.44] that ϵ^0_{F} is the non-degenerate ground state eigenvalue of H_0^{Ω}, so that there exists a real constant $C \in \mathbb{R}$

such that $\psi_2 = C\psi_1$. It follows from the unique continuation principle (see e.g. [25, Theorem XIII.57]) that $\widetilde{\phi}^0_{N_\mathrm{f}+2} = C\widetilde{\phi}^0_{N_\mathrm{f}+1}$ on $\mathbb{R}^3$, which contradicts the fact that $\widetilde{\phi}^0_{N_\mathrm{f}+1}$ and $\widetilde{\phi}^0_{N_\mathrm{f}+2}$ are orthogonal and non identically equal to zero. Thus, $M = 0$ and the proof of case 1 is complete.

Case 2. The degeneracy being assumed essential, ϵ^0_F is $(2l+1)$-times degenerate for some integer $l \geq 1$, and there exists an orthonormal basis of associated eigenfunctions of the form

$$\forall 1 \leq i \leq N_\mathrm{p} = 2l+1, \quad \phi^0_{N_\mathrm{f}+i}(x) = R_l(r)\, \mathcal{Y}_l^{-l+i-1}(\theta,\varphi),$$

where (r,θ,φ) are the spherical coordinates of the point $x \in \mathbb{R}^3$, and where the functions $\mathcal{Y}_l^m$ are the spherical harmonics. In particular,

$$\sum_{i,j=1}^{2l+1} M_{ij}\phi^0_{N_\mathrm{f}+i}(x)\phi^0_{N_\mathrm{f}+j}(x) = R_l(r)^2 \sum_{i,j=1}^{2l+1} M_{ij}\, \mathcal{Y}_l^{-l+i-1}(\theta,\varphi)\, \mathcal{Y}_l^{-l+j-1}(\theta,\varphi).$$

We therefore have to prove that for any symmetric matrix $M \in \mathbb{R}_\mathrm{S}^{(2l+1)\times(2l+1)}$,

$$\left(\sum_{i,j=1}^{2l+1} M_{ij}\mathcal{Y}_l^{-l+i-1}\mathcal{Y}_l^{-l+j-1} = 0\right) \;\Rightarrow\; M = 0.$$

Let $M \in \mathbb{R}_\mathrm{S}^{(2l+1)\times(2l+1)}$ a symmetric matrix such that

$$\sum_{i,j=1}^{2l+1} M_{ij}\mathcal{Y}_l^{-l+i-1}\mathcal{Y}_l^{-l+j-1} = 0$$

on the unit sphere $\mathbb{S}^2$. Using the relation

$$\mathcal{Y}_l^{m_1}\mathcal{Y}_l^{m_2} = \sum_{L=0}^{2l} \sqrt{\frac{(2l+1)^2(2L+1)}{4\pi}} \begin{pmatrix} l & l & L \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix} \begin{pmatrix} l & l & L \\ 0 & 0 & 0 \end{pmatrix} \mathcal{Y}_L^{m_1+m_2},$$

where the $\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ denote the Wigner 3-j symbols (see [5] for instance), and where, by convention, $\mathcal{Y}_L^m = 0$ whenever $|m| > L$, we obtain

$$\begin{aligned}
0 &= \frac{\sqrt{4\pi}}{2l+1} \sum_{i,j=1}^{2l+1} M_{ij}\mathcal{Y}_l^{-l+i-1}\mathcal{Y}_l^{-l+j-1} \\
&= \sum_{i,j=1}^{2l+1} M_{ij} \sum_{L=0}^{2l} \sqrt{2L+1} \begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & 2l+2-i-j \end{pmatrix} \begin{pmatrix} l & l & L \\ 0 & 0 & 0 \end{pmatrix} \mathcal{Y}_L^{i+j-2l-2} \\
&= \sum_{m=-2l}^{2l} \sum_{L=0}^{2l} \sqrt{2L+1} \begin{pmatrix} l & l & L \\ 0 & 0 & 0 \end{pmatrix} \left[\sum_{\substack{1 \leq i,j \leq 2l+1 \\ i+j-2l-2=m}} \begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} M_{ij} \right] \mathcal{Y}_L^m.
\end{aligned}$$

Using the fact that the Wigner 3-j symbol $\begin{pmatrix} l & l & L \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix}$ is equal to zero unless

$$|m_1| \leq l, \quad |m_2| \leq l, \quad |m_1+m_2| \leq L, \quad 0 \leq L \leq 2l, \quad \text{and} \quad L \in 2\mathbb{N} \text{ if } m_1 = m_2 = 0,$$

we obtain that for all $L \in \{0, 2, \cdots, 2l\}$ and all $-L \leq m \leq L$,

$$\sum_{\substack{1 \leq i,j \leq 2l+1 \\ i+j-2l-2=m}} \begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} M_{ij} = 0. \tag{45}$$

For $m = -2l$ and $L = 2l$, the above expression reduces to

$$\begin{pmatrix} l & l & 2l \\ -l & -l & 2l \end{pmatrix} M_{11} = 0, \qquad \text{where} \qquad \begin{pmatrix} l & l & 2l \\ -l & -l & 2l \end{pmatrix} = \frac{1}{\sqrt{4l+1}}.$$

Hence $M_{11} = 0$. More generally, for each integer value of m in the range $[-2l, 2l]$, equation (45) gives rise to a linear system of $n_{m,l}$ equations (obtained for the various even values of L in the range $[|m|, 2l]$) with $n_{m,l}$ unknowns (the $M_{i,j}$'s satisfying $i \leq j$ - recall that the matrix M is symmetric - and $i+j = 2l+2+m$). Using the symmetry property

$$\begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} = \begin{pmatrix} l & l & L \\ -l+j-1 & -l+i-1 & -m \end{pmatrix}$$

and the orthogonality relation stating that for all $-2l \leq m \leq 2l$, and all $|m| \leq L, L' \leq 2l$,

$$\sum_{\substack{1 \leq i,j \leq 2l+1 \\ i+j-2l-2=m}} \begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} \begin{pmatrix} l & l & L' \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} = \frac{\delta_{LL'}}{(2L+1)},$$

it is easy to see that this linear system is free, and that the corresponding entries of M are therefore equal to 0. Hence, the matrix M is identically equal to zero, which completes the proof.

6.3 Proof of Lemma 4

As $\mathscr{C}$ is a compact subset of the resolvent set of H_0 and as the domain of H_0 is $H^2(\mathbb{R}^3)$, there exists $C_0 \in \mathbb{R}_+$ such that

$$\max_{z \in \mathscr{C}} (\|(z-H_0)^{-1}\|, \|(1-\Delta)(z-H_0)^{-1}\|, \|(z-H_0)(1-\Delta)^{-1}\|) \leq C_0.$$

It follows from the Kato-Seiler-Simon inequality [29] that for all $v \in \mathcal{C}'$,

$$\|v(z-H_0)^{-1}\| \leq C_0 \|v(1-\Delta)^{-1}\| \leq C_0 \|v(1-\Delta)^{-1}\|_{\mathfrak{S}_6} \leq C\|v\|_{L^6} \leq \alpha \|v\|_{\mathcal{C}'},$$

for constants $\alpha, C \in \mathbb{R}_+$ independent of v. The k-linear map $Q^{(k)}$ is therefore well-defined and continuous from $(\mathcal{C}')^k$ to the space of bounded operators on $L^2(\mathbb{R}^3)$. Denoting by $\gamma_0^\perp = 1 - \gamma_0$, we have

$$Q^{(k)}(v_1, \cdots, v_k) = \sum_{(P_j)_{0 \leq j \leq k} \in \left\{\gamma_0, \gamma_0^\perp\right\}^{k+1}} \frac{1}{2i\pi} \oint_{\mathscr{C}} (z-H_0)^{-1} P_0 \prod_{j=1}^{k} \left(v_j (z-H_0)^{-1} P_j\right) dz.$$

In the above sum, the term with all the P_j's equal to $\gamma_0^\perp$ is equal to zero as a consequence of Cauchy's residue formula. In all the remaining terms, one of the P_j's is equal to the rank-N operator γ_0. The operators $(z-H_0)^{-1}$ and $v_j(z-H_0)^{-1}$ being bounded, $Q^{(k)}(v_1,\cdots,v_k)$ is finite-rank, hence trace-class, and it holds

$$\|Q^{(k)}(v_1,\cdots,v_k)\|_{\mathfrak{S}_1} \leq \frac{|\mathscr{C}|}{2\pi} N C_0 \alpha^k \|v_1\|_{\mathcal{C}'} \cdots \|v_k\|_{\mathcal{C}'}.$$

Likewise, the operator

$$\begin{aligned}
&|\nabla| Q^{(k)}(v_1,\cdots,v_k)|\nabla| \\
&= \sum_{(P_j)\in\left\{\gamma_0,\gamma_0^\perp\right\}^{k+1}} \frac{1}{2i\pi}\oint_{\mathscr{C}} |\nabla|(z-H_0)^{-1/2}P_0 \prod_{j=1}^{k}\left((z-H_0)^{-1/2}v_j(z-H_0)^{-1/2}P_j\right)(z-H_0)^{-1/2}|\nabla|\,dz
\end{aligned}$$

is finite rank and

$$\|\,|\nabla| Q^{(k)}(v_1,\cdots,v_k)|\nabla|\,\|_{\mathfrak{S}_1} \leq C\alpha^k \|v_1\|_{\mathcal{C}'}\cdots\|v_k\|_{\mathcal{C}'},$$

for some constant C independent of $v_1,\cdots,v_k$. Therefore $Q^{(k)}$ is a continuous linear map from $(\mathcal{C}')^k$ to $\mathfrak{S}_{1,1}$ and the bound (10) holds true. It then follows from Cauchy's residue formula and the cyclicity of the trace that, for $k\geq 1$,

$$\begin{aligned}
\mathrm{Tr}\,(Q^{(k)}(v_1,\cdots,v_k)) &= \mathrm{Tr}\left(\frac{1}{2i\pi}\oint_{\mathscr{C}}(z-H_0)^{-1}\prod_{j=1}^{k}\left(v_j(z-H_0)^{-1}\right)\,dz\right) \\
&= \sum_{(P_j)\in\left\{\gamma_0,\gamma_0^\perp\right\}^{k+1}} \mathrm{Tr}\left(\frac{1}{2i\pi}\oint_{\mathscr{C}}(z-H_0)^{-1}P_0\prod_{j=1}^{k}\left(v_j(z-H_0)^{-1}P_j\right)\,dz\right) \\
&= \sum_{j=1}^{k}\sum_{(P_l)\in\left\{\gamma_0,\gamma_0^\perp\right\}^{k}} \mathrm{Tr}\left(\frac{1}{2i\pi}\oint_{\mathscr{C}}\prod_{l=1}^{k-1}\left(v_{l+j \bmod(k)}(z-H_0)^{-1}P_l\right)v_j(z-H_0)^{-2}\gamma_0\,dz\right) = 0.
\end{aligned}$$

Let $\rho\in\mathcal{C}$ and $Q := Q^{(1)}(\rho\star|\cdot|^{-1})$. Proceeding as above, we obtain that for all $\phi\in C_{\mathrm{c}}^\infty(\mathbb{R}^3)$,

$$\begin{aligned}
\left|\int_{\mathbb{R}^3}\rho_Q\phi\right| &= |\mathrm{Tr}\,(Q\phi)| = \left|\mathrm{Tr}\left(\frac{1}{2i\pi}\oint_{\mathscr{C}}(z-H_0)^{-1}(\rho\star|\cdot|^{-1})(z-H_0)^{-1}\phi\,dz\right)\right| \\
&\leq C\|\rho\|_{\mathcal{C}}\|\phi\|_{\mathcal{C}'},
\end{aligned}$$

for a constant $C\in\mathbb{R}_+$ independent of ρ and ϕ. Therefore, ρ_Q is in $\mathcal{C}$ and $\|\rho_Q\|_{\mathcal{C}}\leq C\|\rho\|_{\mathcal{C}}$. This proves that $\mathcal{L}$ is a bounded operator on $\mathcal{C}$. In addition, for all ρ_1,ρ_2 in $\mathcal{C}$,

$$(\mathcal{L}\rho_1,\rho_2)_{\mathcal{C}} = -\mathrm{Tr}\left(\frac{1}{2i\pi}\oint_{\mathscr{C}}(z-H_0)^{-1}(\rho_1\star|\cdot|^{-1})(z-H_0)^{-1}(\rho_2\star|\cdot|^{-1})\,dz\right) = (\rho_1,\mathcal{L}\rho_2)_{\mathcal{C}},$$

where we have used again the cyclicity of the trace. Thus, $\mathcal{L}$ is self-adjoint. Lastly, for all $\rho\in\mathcal{C}$,

$$(\mathcal{L}\rho,\rho)_{\mathcal{C}} = \sum_{i=1}^{N}\langle\gamma_0^\perp((\rho\star|\cdot|^{-1})\phi_i^0)|(H_0^\perp-\epsilon_i)^{-1}|\gamma_0^\perp((\rho\star|\cdot|^{-1})\phi_i^0)\rangle \geq 0,$$

where $H_0^\perp$ is the self-adjoint operator on $\mathrm{Ran}(\gamma_0^\perp)=\mathrm{Ker}(\gamma_0)$ defined by $\forall v\in\mathrm{Ran}(\gamma_0^\perp)$, $H_0^\perp v = H_0 v$.

6.4 Stability of the spectrum of the mean-field Hamiltonian

We assume here that we are

- either in the non-degenerate case ($\epsilon_N < 0$ and $\epsilon_N < \epsilon_{N+1}$), in which case we set $\epsilon_{\rm F}^0 = \frac{\epsilon_N + \epsilon_{N+1}}{2}$;
- or in the degenerate case ($\epsilon_N = \epsilon_{N+1} = \epsilon_{\rm F}^0 < 0$).

We recall that $N_{\rm f} = {\rm Rank}(\mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0))$, $N_{\rm p} = {\rm Rank}(\mathbb{1}_{\{\epsilon_{\rm F}^0\}}(H_0))$ and $N_{\rm o} = N_{\rm f} + N_{\rm p}$. We also have $g_- = \epsilon_{\rm F}^0 - \epsilon_{N_{\rm f}}$ and $g_+ = \epsilon_{N_{\rm f}+N_{\rm p}+1} - \epsilon_{\rm F}^0$. By definition $g_- > 0$ and $g_+ > 0$ since $\epsilon_{\rm F}^0 < 0$.

Lemma 17. *Let*

$$\alpha_1 = \epsilon_1 - 1,\ \alpha_2 = \epsilon_{\rm F}^0 - \frac{3g_-}{4},\ \alpha_3 = \epsilon_{\rm F}^0 - \frac{g_-}{4},\ \alpha_4 = \epsilon_{\rm F}^0 + \frac{g_+}{4},\ \alpha_5 = \epsilon_{\rm F}^0 + \frac{3g_+}{4}.$$

There exists $\eta > 0$ such that for all $v \in B_\eta(\mathcal{C}')$,

$$\begin{aligned}&{\rm Rank}(\mathbb{1}_{(-\infty,\alpha_1]}(H_0+v)) = 0,\ {\rm Rank}(\mathbb{1}_{(\alpha_1,\alpha_2)}(H_0+v)) = N_{\rm f},\ {\rm Rank}(\mathbb{1}_{[\alpha_2,\alpha_3]}(H_0+v)) = 0,\\ &{\rm Rank}(\mathbb{1}_{(\alpha_3,\alpha_4]}(H_0+v)) = N_{\rm p},\ {\rm Rank}(\mathbb{1}_{(\alpha_4,\alpha_5]}(H_0+v)) = 0.\end{aligned}$$

Proof. Let $z \in \{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5\}$. As $z \notin \sigma(H_0)$, we have

$$z - (H_0 + v) = \left(1 + v(1-\Delta)^{-1}(1-\Delta)(z - H_0)^{-1}\right)\ (z - H_0).$$

Besides, as $D(H_0) = H^2(\mathbb{R}^3)$, there exists a constant $C \in \mathbb{R}_+$ independent of the choice of $z \in \{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5\}$, such that

$$\|(1-\Delta)(z - H_0)^{-1}\| \leq C.$$

In addition, there exists a constant $C' \in \mathbb{R}_+$ such that for all $v \in \mathcal{C}'$,

$$\|v(1-\Delta)^{-1}\| \leq \|v(1-\Delta)^{-1}\|_{\mathfrak{S}_6} \leq C'\|v\|_{\mathcal{C}'}.$$

Let $\eta = (CC')^{-1}$. We obtain that for all $v \in B_\eta(\mathcal{C}')$,

$$\|v(1-\Delta)^{-1}(1-\Delta)(z - H_0)^{-1}\| < 1,$$

so that $z - (H_0 + v)$ is invertible. Therefore, for all $v \in B_\eta(\mathcal{C}')$, none of the real numbers $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5$ are in $\sigma(H_0 + v)$. It also follows from the above arguments that for all $v \in \mathcal{C}'$, the multiplication by v is a H_0-bounded operator on $L^2(\mathbb{R}^3)$. Using Kato's perturbation theory, we deduce from a simple continuity argument that the ranks of the spectral projectors

$$\mathbb{1}_{(-\infty,\alpha_1]}(H_0+v),\ \mathbb{1}_{(\alpha_1,\alpha_2)}(H_0+v),\ \mathbb{1}_{[\alpha_2,\alpha_3]}(H_0+v),\ \mathbb{1}_{(\alpha_3,\alpha_4]}(H_0+v),\ \text{and}\ \mathbb{1}_{(\alpha_4,\alpha_5]}(H_0+v)$$

are constant for $v \in B_\eta(\mathcal{C}')$, and therefore equal to their values for $v = 0$, namely 0, $N_{\rm f}$, 0, $N_{\rm p}$ and 0 respectively. $\square$

6.5 Proof of Theorem 5

Step 1: proof of statement 1.

Let us introduce the relaxed constrained problem

$$\mathcal{E}^{\mathrm{rHF}}_{\leq N}(W) = \inf\left\{E^{\mathrm{rHF}}(\gamma, W),\ \gamma \in \mathcal{K}_{\leq N}\right\}, \tag{46}$$

where

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

As $\epsilon^0_{\mathrm{F}} < 0$, γ_0 is the unique minimizer of (46) for $W = 0$, and as $\mathcal{K}_{\leq N}$ is convex, the corresponding optimality condition reads

$$\forall \gamma \in \mathcal{K}_{\leq N}, \quad \mathrm{Tr}\,(H_0(\gamma - \gamma_0)) \geq 0. \tag{47}$$

Let $W \in \mathcal{C}'$, and $(\gamma'_k)_{k\in\mathbb{N}^*}$ a minimizing sequence for (46) for which

$$\forall k \geq 1, \quad E^{\mathrm{rHF}}(\gamma'_k, W) \leq \mathcal{E}^{\mathrm{rHF}}_{\leq N}(W) + \frac{1}{k}. \tag{48}$$

Set $\rho'_k = \rho_{\gamma'_k}$. We obtain on the one hand, using (47),

$$\begin{aligned}
\mathcal{E}^{\mathrm{rHF}}_{\leq N}(W) &\geq E^{\mathrm{rHF}}(\gamma'_k, W) - \frac{1}{k} \\
&= E^{\mathrm{rHF}}(\gamma'_k, 0) + \int_{\mathbb{R}^3} \rho'_k W - \frac{1}{k} \\
&= \mathcal{E}^{\mathrm{rHF}}_{\leq N}(0) + \mathrm{Tr}\,(H_0(\gamma'_k - \gamma_0)) + \frac{1}{2}D(\rho'_k - \rho_0, \rho'_k - \rho_0) + \int_{\mathbb{R}^3} \rho'_k W - \frac{1}{k} \\
&\geq \mathcal{E}^{\mathrm{rHF}}_{\leq N}(0) + \frac{1}{2}D(\rho'_k - \rho_0, \rho'_k - \rho_0) + \int_{\mathbb{R}^3} \rho'_k W - \frac{1}{k},
\end{aligned}$$

and on the other hand

$$\mathcal{E}^{\mathrm{rHF}}_{\leq N}(W) \leq E^{\mathrm{rHF}}(\gamma_0, W) = \mathcal{E}^{\mathrm{rHF}}_{\leq N}(0) + \int_{\mathbb{R}^3} \rho_0 W.$$

Therefore,

$$\frac{1}{2}D(\rho'_k - \rho_0, \rho'_k - \rho_0) \leq \int_{\mathbb{R}^3} (\rho_0 - \rho'_k) W + \frac{1}{k},$$

from which we get

$$\frac{1}{2}\|\rho'_k - \rho_0\|^2_{\mathcal{C}} \leq \|W\|_{\mathcal{C}'}\|\rho'_k - \rho_0\|_{\mathcal{C}} + \frac{1}{k},$$

and finally

$$\|\rho'_k - \rho_0\|_{\mathcal{C}} \leq 2\|W\|_{\mathcal{C}'} + \left(2k^{-1}\right)^{1/2}. \tag{49}$$

Then, using Cauchy-Schwarz, Hardy and Hoffmann-Ostenhof [18] inequalities, we obtain

$$\begin{aligned}
\mathcal{E}^{\mathrm{rHF}}_{\leq N}(0) &= \mathcal{E}^{\mathrm{rHF}}(0) = E^{\mathrm{rHF}}(\gamma_0, 0) = E^{\mathrm{rHF}}(\gamma_0, W) - \int_{\mathbb{R}^3} \rho_0 W \\
&\geq \mathcal{E}^{\mathrm{rHF}}_{\leq N}(W) - \int_{\mathbb{R}^3} \rho_0 W \geq E^{\mathrm{rHF}}(\gamma'_k, W) - \int_{\mathbb{R}^3} \rho_0 W - \frac{1}{k} \\
&= \frac{1}{2}\mathrm{Tr}\,(-\Delta\gamma'_k) + \int_{\mathbb{R}^3} V\rho'_k + \frac{1}{2}D(\rho'_k, \rho'_k) + \int_{\mathbb{R}^3} \rho'_k W - \int_{\mathbb{R}^3} \rho_0 W - \frac{1}{k} \\
&\geq \frac{1}{2}\mathrm{Tr}\,(-\Delta\gamma'_k) - 2ZN^{\frac{1}{2}}(\mathrm{Tr}\,(-\Delta\gamma'_k))^{1/2} + \frac{1}{2}\|\rho'_k\|^2_{\mathcal{C}} - \|\rho'_k\|_{\mathcal{C}}\|W\|_{\mathcal{C}'} - \|\rho_0\|_{\mathcal{C}}\|W\|_{\mathcal{C}'} - \frac{1}{k} \\
&\geq \frac{1}{2}((\mathrm{Tr}\,(-\Delta\gamma'_k))^{1/2} - 2ZN^{\frac{1}{2}})^2 + \frac{1}{2}(\|\rho'_k\|_{\mathcal{C}} - \|W\|_{\mathcal{C}'})^2 - 2Z^2N - \frac{1}{2}\|\rho_0\|^2_{\mathcal{C}} - \|W\|^2_{\mathcal{C}'} - \frac{1}{k} \\
&\geq \frac{1}{2}((\mathrm{Tr}\,(-\Delta\gamma'_k))^{1/2} - 2ZN^{\frac{1}{2}})^2 - 2Z^2N - \frac{1}{2}\|\rho_0\|^2_{\mathcal{C}} - \|W\|^2_{\mathcal{C}'} - \frac{1}{k},
\end{aligned}$$

from which we infer that

$$\mathrm{Tr}\,(-\Delta\gamma_k') \leq C_0(1+\|W\|_{\mathcal{C}'}^2),$$

for some constant $C_0 \in \mathbb{R}_+$ independent of W and k. This estimate, together with (49) and the fact that $\|\gamma_k'\|_{\mathfrak{S}_1} = \mathrm{Tr}\,(\gamma_k') \leq N$, shows that the sequences $(\gamma_k')_{k\in\mathbb{N}^*}$ and $(\rho_k')_{k\in\mathbb{N}^*}$ are bounded in $\mathfrak{S}_{1,1}$ and $\mathcal{C}$ respectively. We can therefore extract from $(\gamma_k')_{k\in\mathbb{N}^*}$ a subsequence $(\gamma_{k_j}')_{j\in\mathbb{N}^*}$ such that $(\gamma_{k_j}')_{j\in\mathbb{N}}$ converges to γ_W for the weak-$*$ topology of $\mathfrak{S}_{1,1}$, and $(\rho_{k_j}')_{j\in\mathbb{N}}$ converges to $\rho_W := \rho_{\gamma_W}$ weakly in $\mathcal{C}$ and strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for all $1 \leq p < 3$. This implies that

$$\gamma_W \in \mathcal{K}_{\leq N} \quad \text{and} \quad E^{\mathrm{rHF}}(\gamma_W, W) \leq \liminf_{j\to\infty} E^{\mathrm{rHF}}(\gamma_{k_j}', W) = \mathcal{E}^{\mathrm{rHF}}_{\leq N}(W).$$

Thus γ_W is a minimizer of (46). In addition, as the rHF model is strictly convex in the density, all the minimizers of (46) have the same density ρ_W, and, passing in the limit in (49), we obtain that ρ_W satisfies

$$\|\rho_W - \rho_0\|_{\mathcal{C}} \leq 2\|W\|_{\mathcal{C}'}.$$

Denoting by

$$v_W = W + (\rho_W - \rho_0) \star |\cdot|^{-1}, \tag{50}$$

we have

$$H_W = -\frac{1}{2}\Delta + V + W + \rho_W \star |\cdot|^{-1} = H_0 + v_W, \tag{51}$$

with

$$\|v_W\|_{\mathcal{C}'} \leq \|W\|_{\mathcal{C}'} + \|(\rho_W - \rho_0) \star |\cdot|^{-1}\|_{\mathcal{C}'} \leq 3\|W\|_{\mathcal{C}'}. \tag{52}$$

By Lemma 17, for all $W \in B_{\eta/3}(\mathcal{C}')$, we have

$$\mathrm{Rank}(\mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}^0 - g_-/2]}(H_W)) = N \quad \text{and} \quad \mathrm{Rank}(\mathbb{1}_{(\epsilon_{\mathrm{F}}^0 - g_-/2, \epsilon_{\mathrm{F}}^0 + g_-/2]}(H_W)) = 0.$$

In particular, H_W has a least N negative eigenvalues, from which we infer that $\mathrm{Tr}\,(\gamma_W) = N$. Therefore, γ_W is a minimizer of (4). In addition, $\gamma_W = \mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}^0]}(H_W)$ and it holds

$$\gamma_W = \frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_W)^{-1}\, dz. \tag{53}$$

Step 2: proof of statement 2.

It follows from (50), (51) and (53) that

$$\forall W \in B_{\eta/3}(\mathcal{C}'), \quad \mathcal{X}(v_W) = W,$$

where $\mathcal{X}$ is the mapping from $B_{\eta/3}(\mathcal{C}')$ to $\mathcal{C}'$ defined by

$$\mathcal{X}(v) = v - \rho_{\frac{1}{2i\pi}\oint_{\mathscr{C}}((z-H_0-v)^{-1}-(z-H_0)^{-1})\,dz} \star |\cdot|^{-1}.$$

The mapping $\mathcal{X}$ is real analytic. Besides, denoting by v_{c} the Coulomb operator associating to each density $\rho \in \mathcal{C}$ the electrostatic potential $v_{\mathrm{c}}(\rho) = \rho \star |\cdot|^{-1} \in \mathcal{C}'$, we have

$$\mathcal{X}'(0) = v_{\mathrm{c}}(1+\mathcal{L})v_{\mathrm{c}}^{-1}.$$

It follows from the second statement of Lemma 4 and from the fact that $v_{\mathrm{c}} : \mathcal{C} \to \mathcal{C}'$ is a bijective isometry that $\mathcal{X}'(0)$ is bijective. Applying the real analytic implicit function

theorem, we obtain that the mapping $W \mapsto v_W$ is real analytic from some ball $B_{\eta'}(\mathcal{C}')$ (for some $\eta' > 0$) to $\mathcal{C}'$. By composition of real analytic functions, the functions

$$\gamma_W = \frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_0 - v_W)^{-1}\, dz,\ \rho_W = \rho_0 + v_{\mathrm{c}}^{-1}(v_W - W) \text{ and } \mathcal{E}^{\mathrm{rHF}}(W) = E^{\mathrm{rHF}}(\gamma_W, W)$$

are real analytic from $B_{\eta'}(\mathcal{C}')$ to $\mathfrak{S}_{11}$, $\mathcal{C}$ and $\mathbb{R}$ respectively.

Step 3: proof of statements 3 and 4.

Let $W \in B_{\eta'}(\mathcal{C}')$. It follows from the above result that the functions $\beta \mapsto \gamma_{\beta W}$, $\beta \mapsto \rho_{\beta W}$, and $\beta \mapsto \mathcal{E}^{\mathrm{rHF}}(\beta W)$ are real analytic in the vicinity of 0, so that, for $|\beta|$ small enough,

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)}, \quad \rho_{\beta W} = \rho_0 + \sum_{k=1}^{+\infty} \beta^k \rho_W^{(k)}, \quad \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{E}^{\mathrm{rHF}}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)},$$

the series being normally convergent in $\mathfrak{S}_{11}$, $\mathcal{C}$ and $\mathbb{R}$ respectively. The Dyson expansion of (11) gives

$$\gamma_{\beta W} \quad = \quad \gamma_0 + \sum_{k=1}^{+\infty} Q^{(k)}\left(v_{\beta W}, \cdots, v_{\beta W}\right).$$

As

$$v_{\beta W} = \beta W + \sum_{k=1}^{+\infty} \beta^k (\rho_W^{(k)} \star |\cdot|^{-1}) = \sum_{k=1}^{+\infty} \beta^k W^{(k)},$$

where we recall that $W^{(1)} = W + \rho_W^{(1)} \star |\cdot|^{-1}$ and $W^{(k)} = \rho_W^{(k)} \star |\cdot|^{-1}$, we obtain

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} Q^{(k)}\left(\sum_{j=1}^{+\infty} \beta^j W^{(j)}, \cdots, \sum_{j=1}^{+\infty} \beta^j W^{(j)}\right),$$

from which we deduce (14). Taking the densities of both sides of (14), we get

$$\rho_W^{(k)} = -\mathcal{L}(\rho_W^{(k)}) + \widetilde{\rho}_W^{(k)}.$$

This proves (12).

6.6 Proof of Lemma 6 and of (18)

The proof of Lemma 6 is similar to the proof of Lemma 1 in [9]. We only sketch it here for brevity. We denote by $\mathcal{V} := (H^1(\mathbb{R}^3))^N$, by $\Phi^0 = (\phi_1^0, \cdots, \phi_N^0)^T \in \mathcal{V}$ and by $\mathscr{H}$ the bounded linear operator from $\mathcal{V}$ to $\mathcal{V}' \equiv (H^{-1}(\mathbb{R}^3))^N$ defined by

$$\forall \Psi \in \mathcal{V}, \quad (\mathscr{H}\Psi)_i = (H_0 - \epsilon_i)\psi_i + \sum_{j=1}^{N} K_{ij}^0 \psi_j.$$

We then decompose $\mathcal{V}$ as

$$\mathcal{V} = \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0 + \Phi_\perp^0 = \mathbb{D}\Phi^0 + \mathbb{S}^0\Phi^0 + \mathbb{A}\Phi^0 + \Phi_\perp^0,$$

where $\mathbb{D}$, $\mathbb{A}$, $\mathbb{S}$, and $\mathbb{S}^0$ denote the vector spaces of $N \times N$ real-valued matrices which are respectively diagonal, antisymmetric, symmetric, and symmetric with zero entries on the diagonal, and where

$$\Phi_\perp^0 = \left\{\Phi = (\phi_i)_{1 \le i \le N} \in \mathcal{V} \mid \forall 1 \le i, j \le N,\ (\phi_i, \phi_j^0)_{L^2} = 0\right\}.$$

Likewise, it holds

$$\mathcal{V}' = \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0 + \Phi^0_{\perp\!\!\!\perp} \quad \text{with} \quad \Phi^0_{\perp\!\!\!\perp} = \big\{ g = (g_i)_{1\le i\le N} \in \mathcal{V}' \mid \forall 1 \le i,j \le N,\ \langle g_i, \phi^0_j\rangle = 0 \big\}$$

and it is easily checked that

$$\big\{ g \in \mathcal{V}' \mid \forall \chi \in \Phi^0_\perp,\ \langle g, \chi\rangle = 0 \big\} = \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0. \tag{54}$$

Denoting by $F = (f_1, \cdots, f_N)^T \in \mathcal{V}'$ and by $\alpha \in \mathbb{D}$ the $N \times N$ diagonal matrix with entries $\alpha_1, \cdots, \alpha_N$, we have to show that there exists a unique pair $(\Psi, \eta) \in \mathcal{V} \times \mathbb{D}$ such that

$$\left\{ \begin{array}{l} \mathscr{H}\Psi = F + \eta\Phi^0, \\ \Psi - \alpha\Phi^0 \in \mathbb{S}^0\Phi^0 + \mathbb{A}\Phi^0 + \Phi^0_\perp. \end{array} \right. \tag{55}$$

For this purpose, we first introduce the matrix $S \in \mathbb{S}$ defined by

$$\forall 1 \le i \le N,\ S_{ii} = \alpha_i \quad \text{and} \quad \forall 1 \le i \ne j \le N,\ S_{ij} = \frac{\langle f_j, \phi^0_i\rangle - \langle f_i, \phi^0_j\rangle}{\epsilon_j - \epsilon_i},$$

and observe that $\widetilde{F} := F - \mathscr{H}(S\Phi^0) \in \mathbb{S}\Phi^0 + \Phi^0_{\perp\!\!\!\perp}$. Next, using the fact that $\epsilon_1 < \cdots < \epsilon_N < \epsilon^0_{\mathrm{F}}$ and the positivity of the operator K^0, namely

$$\forall \Psi = (\psi_i)_{1\le i\le N} \in \mathcal{V}, \quad \sum_{i,j=1}^N \langle K^0_{ij}\psi_j, \psi_i\rangle = 2\,D\left(\sum_{i=1}^N \phi^0_i\psi_i, \sum_{i=1}^N \phi^0_i\psi_i\right) \ge 0,$$

we can see that the operator $\mathscr{H}$ is coercive on $\Phi^0_\perp$. Therefore, by Lax-Milgram lemma and (54), there exists a unique $\widetilde{\Psi} \in \Phi^0_\perp$ such that $\mathscr{H}\widetilde{\Psi} - \widetilde{F} \in \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0$. As $\widetilde{F} \in \mathbb{S}\Phi^0 + \Phi^0_{\perp\!\!\!\perp}$ and

$$\forall 1 \le i,k \le N, \quad \forall \Psi = (\psi_j)_{1\le j\le N} \in \mathcal{V}, \quad \sum_{j=1}^N \langle K^0_{ij}\psi_j, \phi^0_k\rangle = \sum_{j=1}^N \langle K^0_{kj}\psi_j, \phi^0_i\rangle,$$

we have in fact $\mathscr{H}\widetilde{\Psi} - \widetilde{F} \in \mathbb{S}\Phi^0$. Setting $\Psi' = \widetilde{\Psi} + S\Phi^0$, we get $\mathscr{H}\Psi' - F \in \mathbb{S}\Phi^0$. We now observe that $\mathscr{H}$ is an isomorphism from $\mathbb{A}\Phi^0$ to $\mathbb{S}^0\Phi^0$. Decomposing $\mathscr{H}\Psi' - F$ as $\mathscr{H}\Psi' - F = -S'\Phi^0 + \eta\Phi^0$ with $S' \in \mathbb{S}^0$ and $\eta \in \mathbb{D}$, and denoting by A the unique element of $\mathbb{A}$ such that $\mathscr{H}(A\Phi^0) = S'\Phi^0$, and by $\Psi = \Psi' + A\Phi^0$, we finally obtain that the pair (Ψ, η) is the unique solution to (55) in $\mathcal{V} \times \mathbb{D}$.

The fact that $\Psi \in (H^2(\mathbb{R}^3))^N$ whenever $f \in (L^2(\mathbb{R}^3))^N$ follows from simple elliptic regularity arguments.

To prove (18), we introduce, for $k \in \mathbb{N}^*$,

$$\chi_{i,k}(\beta) = \sum_{l=0}^k \beta^l \phi^{(l)}_{\beta W,i}, \quad \eta_{i,k}(\beta) = \sum_{l=0}^k \beta^l \epsilon^{(l)}_{\beta W,i},$$

$$H_k(\beta) = -\frac{1}{2}\Delta + V + \left(\sum_{i=1}^N \chi_{i,k}(\beta)^2\right) \star |\cdot|^{-1} + \beta W, \quad f_{i,k}(\beta) = H_k(\beta)\chi_{i,k}(\beta) - \eta_{i,k}(\beta)\chi_{i,k}(\beta).$$

By construction, $|\eta_{i,k}(\beta) - \epsilon_{\beta W,i}| + \|\chi_{i,k}(\beta) - \phi_{\beta W,i}\|_{H^2} + \|f_{i,k}(\beta)\|_{H^{-1}} \in \mathcal{O}(\beta^{k+1})$ when β goes to zero, for all $1 \le i \le N$. As the operator $H_k(\beta)$ is self-adjoint, it holds

$$\langle f_{i,k}, \chi_{j,k}\rangle + \eta_{i,k}\langle \chi_{i,k}, \chi_{j,k}\rangle = \langle H_k\chi_{i,k}, \chi_{j,k}\rangle = \langle H_k\chi_{j,k}, \chi_{i,k}\rangle = \langle f_{j,k}, \chi_{i,k}\rangle + \eta_{j,k}\langle \chi_{j,k}, \chi_{i,k}\rangle$$

(the variable β has been omitted in the above equalities). As by assumption $\epsilon_1 < \epsilon_2 < \cdots < \epsilon_{N+1}$, we obtain

$$\langle \chi_{i,k}(\beta), \chi_{j,k}(\beta)\rangle = \frac{\langle f_{i,k}(\beta), \chi_{j,k}(\beta)\rangle - \langle f_{j,k}(\beta), \chi_{i,k}(\beta)\rangle}{\eta_{j,k}(\beta) - \eta_{i,k}(\beta)} \in \mathcal{O}(\beta^{k+1}),$$

from which we deduce (18).

6.7 Proof of Lemma 7

Let $T \in \Omega$ and $\gamma \in \mathcal{P}_N$ such that $\|T-\gamma\|_{\mathfrak{S}_2} < 1/2$. As $\|T-\gamma\| \leq \|T-\gamma\|_{\mathfrak{S}_2} < 1/2$, $\sigma(\gamma) = \{0,1\}$ and $\mathrm{Rank}(\gamma) = N$, $\mathrm{Rank}(\Pi(T)) = \mathrm{Rank}(\mathbb{1}_{[1/2,+\infty)}(T)) = N$. Therefore $\Pi(T) \in \mathcal{P}_N$. If, in addition, $T \in \mathfrak{S}_2$, then

$$\begin{aligned}
\|T-\Pi(T)\|_{\mathfrak{S}_2}^2 &= \|T-\gamma+\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2 \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + \|\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2 + 2\mathrm{Tr}\,((T-\gamma)(\gamma-\Pi(T))) \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + \|\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2 + 2\mathrm{Tr}\,(T(\gamma-\Pi(T))) - (2N - 2\mathrm{Tr}\,(\gamma\Pi(T))) \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + 2\,\mathrm{Tr}\,(T(\gamma-\Pi(T))) \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + 2\,\mathrm{Tr}\,((T-1/2)(\gamma-\Pi(T)))\,,
\end{aligned}$$

where we have used that both γ and $\Pi(T)$ are in $\mathcal{P}_N$ and that for all $P \in \mathcal{P}_N$, $\|P\|_{\mathfrak{S}_2}^2 = \mathrm{Tr}\,(P^2) = \mathrm{Tr}\,(P) = N$. Let $A = T - 1/2$ and $Q = \gamma - \Pi(T)$. The self-adjoint operator A has exactly N positive eigenvalues (counting multiplicities), and all its other eigenvalues are negative. Remarking that $\Pi(T) = \mathbb{1}_{[0,+\infty)}(A)$, and denoting $A^{++} = \Pi(T)A\Pi(T)$, $A^{--} = (1-\Pi(T))A(1-\Pi(T))$, $Q^{--} = \Pi(T)(\gamma-\Pi(T))\Pi(T)$, $Q^{++} = (1-\Pi(T))(\gamma-\Pi(T))(1-\Pi(T))$, and $g := \mathrm{dist}(0,\sigma(A))$, we obtain, using the fact that $A^{++} \geq g$, $A^{--} \leq -g$, $Q^{++} \geq 0$, $Q^{--} \leq 0$ and $Q^2 = Q^{++} - Q^{--}$,

$$\begin{aligned}
\mathrm{Tr}\,((T-1/2)(\gamma-\Pi(T))) &= \mathrm{Tr}\,(A^{++}Q^{--} + A^{--}Q^{++}) \\
&\leq -g\mathrm{Tr}\,(Q^{++} - Q^{--}) = -g\mathrm{Tr}\,(Q^2) = -g\|\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2.
\end{aligned}$$

Hence, $\Pi(T)$ is the unique minimizer of (19).

6.8 Proof of Theorem 8

Throughout the proof, W is a fixed potential of $\mathcal{C}'$, chosen once and for all, and C denotes a constant depending on W but not on β, which may vary from one line to another. For all $\beta \in \mathbb{R}$, we denote by $Q_W^{(n)}(\beta) := \widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{\beta W}$. When $|\beta|$ is small enough, $\widetilde{\gamma}_W^{(n)}(\beta) \in \mathcal{P}_N$, so that we have

$$\begin{aligned}
E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) &\geq \mathcal{E}^{\mathrm{rHF}}(\beta W) \\
&= E^{\mathrm{rHF}}(\gamma_{\beta W}, \beta W) \\
&= E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta) - Q_W^{(n)}(\beta), \beta W) \\
&= E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathrm{Tr}\,\left(H_{\beta W} Q_W^{(n)}(\beta)\right) - \frac{1}{2} D\left(\rho_{Q_W^{(n)}(\beta)}, \rho_{Q_W^{(n)}(\beta)}\right) \\
&= E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathrm{Tr}\,\left(|H_{\beta W} - \epsilon_{\mathrm{F}}^0|(Q_W^{(n)}(\beta))^2\right) - \frac{1}{2}\|\rho_{Q_W^{(n)}(\beta)}\|_{\mathcal{C}}^2,
\end{aligned}$$

where we have used Lemma 18 below. We thus obtain that for $|\beta|$ small enough,

$$0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathrm{Tr}\,\left(|H_{\beta W} - \epsilon_{\mathrm{F}}^0|(Q_W^{(n)}(\beta))^2\right) + \frac{1}{2}\|\rho_{Q_W^{(n)}(\beta)}\|_{\mathcal{C}}^2.$$

Using (51), (52) and the bound $\|v(1-\Delta)^{-1}\| \leq C\|v\|_{\mathcal{C}'}$ for all $v \in \mathcal{C}'$, we obtain that for all $|\beta|$ small enough,

$$|H_{\beta W} - \epsilon_{\mathrm{F}}^0| \leq C(1-\Delta).$$

Hence, for $|\beta|$ small enough,

$$\begin{aligned}
0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) &\leq C\mathrm{Tr}\,\left((1-\Delta)(Q_W^{(n)}(\beta))^2\right) + \frac{1}{2}\|\rho_{Q_W^{(n)}(\beta)}\|_{\mathcal{C}}^2 \\
&\leq C\|Q_W^{(n)}(\beta)\|_{\mathfrak{S}_{1,1}}^2,
\end{aligned}$$

where we have used the continuity of the linear mapping $\mathfrak{S}_{1,1} \ni \gamma \mapsto \rho_\gamma \in \mathcal{C}$. The latter property is proved as followed: we infer from the Kato-Seiler-Simon inequality and the Sobolev inequality $\|V\|_{L^6(\mathbb{R}^3)} \leq C_6 \|\nabla V\|_{L^2(\mathbb{R}^3)} = C_6 \|V\|_{\mathcal{C}'}$ that there exists a constant $C \in \mathbb{R}_+$ such that for all $\gamma \in \mathfrak{S}_{1,1} \cap \mathcal{S}(L^2(\mathbb{R}^3))$,

$$\begin{aligned} \|\rho_\gamma\|_{\mathcal{C}} &= \sup_{V \in \mathcal{C}' \setminus \{0\}} \frac{\mathrm{Tr}\,(\gamma V)}{\|V\|_{\mathcal{C}'}} = \sup_{V \in \mathcal{C}' \setminus \{0\}} \frac{\mathrm{Tr}\,((1-\Delta)^{1/2}\gamma(1-\Delta)^{1/2}(1-\Delta)^{-1/2}V(1-\Delta)^{-1/2})}{\|V\|_{\mathcal{C}'}} \\ &\leq C\|\gamma\|_{\mathfrak{S}_{1,1}}. \end{aligned} \tag{56}$$

Denoting by

$$\gamma_{W,n}(\beta) := \gamma_0 + \sum_{k=1}^{n} \beta^k \gamma_W^{(k)},$$

we get

$$0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) \leq C \left(\|\widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_{1,1}}^2 + \|\gamma_{W,n}(\beta) - \gamma_{\beta W}\|_{\mathfrak{S}_{1,1}}^2 \right).$$

We infer from the third statement of Theorem 5 that

$$\|\gamma_{W,n}(\beta) - \gamma_{\beta W}\|_{\mathfrak{S}_{1,1}} \leq C\beta^{n+1}.$$

We now observe that as W is fixed, all the functions $\widetilde{\phi}_{W,i}(\beta)$ in (21)-(22) lay in a finite dimensional subspace of $H^1(\mathbb{R}^3)$ independent of β. Using the equivalence of norms in finite dimension, the fact that $\widetilde{\gamma}_W^{(n)}(\beta) = \Pi\left(\gamma_{W,n}(\beta)\right)$ and Lemma 7, we obtain that

$$\|\widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_{1,1}} \leq C\|\widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_2} \leq C\|\gamma_{\beta W} - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_2} \leq C\beta^{n+1},$$

which completes the proof of (20).

Lemma 18. *Let H be a bounded below self-adjoint operator on a Hilbert space $\mathcal{H}$, $\epsilon_{\mathrm{F}} \in \mathbb{R}$, and $\gamma := \mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}]}(H)$. Assume that $\mathrm{Tr}\,(\gamma) < \infty$. Then, for all orthogonal projector $\gamma' \in \mathcal{S}(\mathcal{H})$ such that $\mathrm{Tr}\,(\gamma') = \mathrm{Tr}\,(\gamma)$, it holds*

$$0 \leq \mathrm{Tr}\,(HQ) = \mathrm{Tr}\,(|H - \epsilon_{\mathrm{F}}|Q^2),$$

where $Q = \gamma' - \gamma$.

Proof. We first observe that

$$\begin{aligned} Q = \gamma' - \gamma = (\gamma')^2 - \gamma^2 &= Q^2 + \gamma\gamma' + \gamma'\gamma - 2\gamma, \\ H - \epsilon_{\mathrm{F}} &= (1-\gamma)(H-\epsilon_{\mathrm{F}})(1-\gamma) + \gamma(H-\epsilon_{\mathrm{F}})\gamma, \\ |H - \epsilon_{\mathrm{F}}| &= (1-\gamma)(H-\epsilon_{\mathrm{F}})(1-\gamma) - \gamma(H-\epsilon_{\mathrm{F}})\gamma, \\ Q^2 &= (1-\gamma)Q(1-\gamma) - \gamma Q \gamma. \end{aligned}$$

As $\mathrm{Tr}\,(Q) = 0$, it follows that

$$\begin{aligned} \mathrm{Tr}\,(HQ) &= \mathrm{Tr}\,((H-\epsilon_{\mathrm{F}})Q) = \mathrm{Tr}\,\left((H-\epsilon_{\mathrm{F}})Q^2\right) + \mathrm{Tr}\,\left((H-\epsilon_{\mathrm{F}})(\gamma\gamma' + \gamma'\gamma - 2\gamma)\right) \\ &= \mathrm{Tr}\,\left((H-\epsilon_{\mathrm{F}})Q^2\right) + 2\,\mathrm{Tr}\,(\gamma(H-\epsilon_{\mathrm{F}})\gamma Q) \\ &= \mathrm{Tr}\,\left((H-\epsilon_{\mathrm{F}})Q^2\right) + 2\,\mathrm{Tr}\,(\gamma(H-\epsilon_{\mathrm{F}})\gamma Q\gamma) \\ &= \mathrm{Tr}\,\left((H-\epsilon_{\mathrm{F}})Q^2\right) - 2\,\mathrm{Tr}\,\left(\gamma(H-\epsilon_{\mathrm{F}})\gamma Q^2\right) \\ &= \mathrm{Tr}\,\left(|H-\epsilon_{\mathrm{F}}|Q^2\right). \end{aligned}$$

Note that all the terms in the above series of equalities containing γ are finite, since $\mathrm{Tr}\,(\gamma) < \infty$ and H is bounded below, while the other terms may be equal to $+\infty$. □

6.9 Proof of Lemma 9

Using the fact that $L^2(\mathbb{R}^3) = \mathcal{H}_{\rm o} \oplus \mathcal{H}_{\rm u}$, any linear operator T on $L^2(\mathbb{R}^3)$ can be represented by a 2×2 block operator

$$T = \begin{pmatrix} T_{\rm oo} & T_{\rm ou} \\ T_{\rm uo} & T_{\rm uu} \end{pmatrix},$$

where $T_{\rm xy}$ is a linear operator from $\mathcal{H}_{\rm y}$ to $\mathcal{H}_{\rm x}$ (with $x, y \in \{{\rm o}, {\rm u}\}$). In particular, the operators $P_0 := \mathbb{1}_{(-\infty, \epsilon_{\rm F}^0]}(H_0)$ (the orthogonal projector on $\mathcal{H}_{\rm o}$), $P_0^\perp := \mathbb{1}_{(\epsilon_{\rm F}^0, +\infty)}(H_0)$ and H_0 are block diagonal in this representation, and we have

$$P_0 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \qquad P_0^\perp = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \qquad H_0 = \begin{pmatrix} H_{\rm oo} & 0 \\ 0 & H_{\rm uu} \end{pmatrix},$$

with $H_{\rm oo} - \epsilon_{\rm F}^0 \leq 0$ and $H_{\rm uu} - \epsilon_{\rm F}^0 = H_0^{++} - \epsilon_{\rm F}^0 \geq g_+ > 0$.

We consider the submanifold

$$\mathcal{P}_{N_{\rm o}} := \left\{ P \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid P^2 = P,\ {\rm Tr}\,(P) = N_{\rm o},\ {\rm Tr}\,(-\Delta P) < \infty \right\}$$

of $\mathcal{S}(L^2(\mathbb{R}^3))$ consisting of the rank-$N_{\rm o}$ orthogonal projectors on $L^2(\mathbb{R}^3)$ with range in $H^1(\mathbb{R}^3)$, and the Hilbert space

$$\mathcal{Z} = \left\{ Z = \begin{pmatrix} 0 & -Z_{\rm uo}^* \\ Z_{\rm uo} & 0 \end{pmatrix} \mid (H_{\rm uu} - \epsilon_{\rm F}^0)^{1/2} Z_{\rm uo} \in \mathcal{B}(\mathcal{H}_{\rm o}, \mathcal{H}_{\rm u}) \right\},$$

endowed with the inner product

$$(Z, Z')_{\mathcal{Z}} = {\rm Tr}\,(Z_{\rm uo}^* (H_{\rm uu} - \epsilon_{\rm F}^0) Z'_{\rm uo}).$$

We are going to use the following lemma, the proof of which is postponed until the end of the section.

Lemma 19. *There exists an open connected neighborhood $\widetilde{\mathcal{O}}$ of P_0 in $\mathcal{P}_{N_{\rm o}}$, and $\eta > 0$ such that the real analytic mapping*

$$\begin{array}{rcl} B_\eta(\mathcal{Z}) & \to & \widetilde{\mathcal{O}} \\ Z & \mapsto & e^Z P_0 e^{-Z} \end{array}$$

is bijective.

By continuity, there exists a neighborhood $\mathcal{O}$ of 0 in $\mathcal{A}$ such that

$$\forall A \in \mathcal{O}, \quad \mathbb{1}_{(0,1]}\left(\Gamma(A)\right) \subset \widetilde{\mathcal{O}}.$$

Let A and A' in $\mathcal{O}$ be such that $\Gamma(A) = \Gamma(A')$. Then

$$e^{L_{\rm uo}(A')} P_0 e^{-L_{\rm uo}(A')} = \mathbb{1}_{(0,1]}\left(\Gamma(A')\right) = \mathbb{1}_{(0,1]}\left(\Gamma(A)\right) = e^{L_{\rm uo}(A)} P_0 e^{-L_{\rm uo}(A)},$$

and we infer from Lemma 19 that $L_{\rm uo}(A') = L_{\rm uo}(A)$. Therefore,

$$e^{L_{\rm pf}(A')}(\gamma_0 + L_{\rm pp}(A')) e^{-L_{\rm pf}(A')} = e^{L_{\rm pf}(A)}(\gamma_0 + L_{\rm pp}(A)) e^{-L_{\rm pf}(A)}. \tag{57}$$

In particular (using again functional calculus),

$$e^{L_{\rm pf}(A')} \gamma_0 e^{-L_{\rm pf}(A')} = e^{L_{\rm pf}(A)} \gamma_0 e^{-L_{\rm pf}(A)}.$$

Using the finite dimensional analogue of Lemma 19 (a standard result on finite dimensional Grassmann manifolds), we obtain that, up to reducing the size of the neighborhood $\mathcal{O}$ if necessary, $L_{\rm pf}(A') = L_{\rm pf}(A)$. Getting back to (57), we see that $L_{\rm pp}(A') = L_{\rm pp}(A)$. Therefore, $A = A'$, which proves the injectivity of the mapping (26).

We now consider a neighborhood $\mathcal{O}'$ of γ_0 in $\mathfrak{S}_{1,1}$ in such that $\Gamma(\mathcal{O}) \subset \mathcal{O}'$ and $\mathbb{1}_{(0,1]}\left(\mathcal{K}_{N_{\rm f},N_{\rm p}} \cap \mathcal{O}'\right) \subset \widetilde{\mathcal{O}}$. Let $\gamma \in \mathcal{K}_{N_{\rm f},N_{\rm p}} \cap \mathcal{O}'$. By Lemma 19, there exists a unique $Z \in B_\eta(\mathcal{Z})$ such that $\mathbb{1}_{(0,1]}(\gamma) = e^Z P_0 e^{-Z}$, and by the classical finite-dimensional version of the latter lemma, there exists a unique $A_{\rm pf} \in \mathcal{A}_{\rm pf}$ in the vicinity of 0 such that $\mathbb{1}_{\{1\}}(\gamma) = e^Z e^{L_{\rm pf}(0,0,A_{\rm pf},0)} \mathbb{1}_{\{1\}}(\gamma_0) e^{-L_{\rm pf}(0,0,A_{\rm pf},0)} e^{-Z}$. It is then easily seen that the operator

$$e^{-Z} e^{-L_{\rm pf}(0,0,A_{\rm pf},0)} \gamma e^{L_{\rm pf}(0,0,A_{\rm pf},0)} e^{Z}$$

is of the form $\gamma_0 + L_{\rm pp}(0,0,0,A_{\rm pp})$ for some $A_{\rm pp} \in \mathcal{A}_{\rm pp}$, which is close to 0 if $\mathcal{O}'$ is small enough. Decomposing $Z_{\rm uo}$ as $(A_{\rm uf}, A_{\rm up})$ and setting $A = (A_{\rm uf}, A_{\rm up}, A_{\rm pf}, A_{\rm pp})$, we obtain that A is the unique element of $\mathcal{A}$ in the vicinity of 0 such that $\gamma = \Gamma(A)$.

Proof of Lemma 19. Let

$$\mathcal{U} := \left\{ U \in \mathrm{GL}(H^1(\mathbb{R}^3)) \mid \|U\phi\|_{L^2} = \|\phi\|_{L^2},\ \forall \phi \in H^1(\mathbb{R}^3) \right\}$$

where $\mathrm{GL}(H^1(\mathbb{R}^3))$ is the group of the inversible bounded operators on $H^1(\mathbb{R}^3)$. In view of [12, Theorem 4.8], the mapping

$$\begin{array}{rcl} \mathcal{U} & \to & \mathcal{P}_{N_{\rm o}} \\ U & \mapsto & U P_0 U^{-1} \end{array}$$

is a real analytic submersion. Besides [12, Lemma 2.5], $\mathcal{U}$ is a Banach-Lie group with Lie algebra

$$\mathscr{U} = \left\{ Z \in \mathcal{B}(L^2(\mathbb{R}^3)) \mid Z^* = -Z,\ Z(H^1(\mathbb{R}^3)) \subset H^1(\mathbb{R}^3) \right\}$$

(with the slight abuse of notation consisting of denoting by Z the restriction to $H^1(\mathbb{R}^3)$ of an operator $Z \in \mathcal{B}(L^2(\mathbb{R}^3))$ such that $Z(H^1(\mathbb{R}^3)) \subset H^1(\mathbb{R}^3)$), and [12, Remark 4.7], the isotropy group of the action of $\mathcal{U}$ on $\mathcal{P}_{N_{\rm o}}$ is the Banach-Lie group with Lie algebra

$$\mathscr{U}_0 = \left\{ Z \in \mathcal{B}(L^2(\mathbb{R}^3)) \mid Z^* = -Z,\ Z(H^1(\mathbb{R}^3)) \subset H^1(\mathbb{R}^3),\ Z_{\rm uo} = 0 \right\}.$$

Hence, denoting by

$$\widetilde{\mathcal{Z}} = \left\{ Z = \begin{pmatrix} 0 & -Z_{\rm uo}^* \\ Z_{\rm uo} & 0 \end{pmatrix} \mid (1-\Delta)^{1/2} Z_{\rm uo} \in \mathcal{B}(\mathcal{H}_{\rm o}, \mathcal{H}_{\rm u}) \right\},$$

there exists an open connected neighborhood $\widetilde{\mathcal{O}}$ of P_0 in $\mathcal{P}_{N_{\rm o}}$, and $\widetilde{\eta} > 0$ such that the real analytic mapping

$$\begin{array}{rcl} B_{\widetilde{\eta}}(\widetilde{\mathcal{Z}}) & \to & \widetilde{\mathcal{O}} \\ Z & \mapsto & e^Z P_0 e^{-Z} \end{array}$$

is bijective. As there exists $0 < c < C < \infty$ such that $c(1-\Delta) \leq (H_{\rm uu} - \epsilon_{\rm F}^0) \leq C(1-\Delta)$ on $\mathcal{H}_{\rm u}$, we have $\widetilde{\mathcal{Z}} = \mathcal{Z}$, which concludes the proof of the lemma. $\square$

6.10 Proof of Lemma 10

In view of (33), the density matrix $\Gamma(A)$ can be expanded as

$$\Gamma(A) = \gamma_0 + \gamma_1(A) + \gamma_2(A,A) + O(\|A\|_{\mathcal{V}}^3), \tag{58}$$

with

$$\begin{aligned}
\gamma_1(A) &= \langle \Gamma'(0), A\rangle = [L_{\rm uo}(A) + L_{\rm pf}(A), \gamma_0] + L_{\rm pp}(A) \\
\gamma_2(A,A) &= \frac{1}{2}[\Gamma''(0)](A,A) \\
&= \frac{1}{2}\left[L_{\rm uo}(A), [L_{\rm uo}(A), \gamma_0]\right] + [L_{\rm uo}(A), [L_{\rm pf}(A), \gamma_0]] + \frac{1}{2}\left[L_{\rm pf}(A), [L_{\rm pf}(A), \gamma_0]\right] \\
&\quad + [L_{\rm uo}(A), L_{\rm pp}(A)] + [L_{\rm pf}(A), L_{\rm pp}(A)] \\
&= \frac{1}{2}\left\{L_{\rm uo}(A)^2 + L_{\rm pf}(A)^2, \gamma_0\right\} + [L_{\rm uo}(A) + L_{\rm pf}(A), L_{\rm pp}(A)] \\
&\quad + L_{\rm uo}(A)L_{\rm pf}(A)\gamma_0 + \gamma_0 L_{\rm pf}(A)L_{\rm uo}(A) - (L_{\rm uo}(A) + L_{\rm pf}(A))\gamma_0(L_{\rm uo}(A) + L_{\rm pf}(A)),
\end{aligned}$$

where $\{X,Y\} = XY + YX$ denotes the anticommutator of X and Y. As in Section 4, we denote by $F(A,0) = \nabla_A E(A,0)$ and $\Theta = \frac{1}{2}F'_A(0,0)|_{\mathcal{A}\times\{0\}}$. It follows from (58) and the analyticity properties of the mapping $A \mapsto E(A,0)$ that for all $(A,A') \in \mathcal{A}\times\mathcal{A}$,

$$E(A,0) = E_0 + {\rm Tr}\,(H_0\gamma_1(A)) + {\rm Tr}\,(H_0\gamma_2(A,A)) + \frac{1}{2}D(\rho_{\gamma_1(A)}, \rho_{\gamma_1(A)}) + O(\|A\|_{\mathcal{A}}^3),$$

and

$$\langle \Theta(A), A\rangle = {\rm Tr}\,(H_0\gamma_2(A,A)) + \frac{1}{2}D(\rho_{\gamma_1(A)}, \rho_{\gamma_1(A)}).$$

Besides, a simple calculation leads to

$$\begin{aligned}
{\rm Tr}\,(H_0\gamma_2(A,A)) &= {\rm Tr}\,\left(A_{\rm uf}^*\left(H_0^{++} - \epsilon_{\rm F}^0\right)A_{\rm uf}\right) - {\rm Tr}\,\left(A_{\rm uf}\left(H_0^{--} - \epsilon_{\rm F}^0\right)A_{\rm uf}^*\right) \\
&\quad + {\rm Tr}\,\left(\left(H_0^{++} - \epsilon_{\rm F}^0\right)A_{\rm up}\Lambda A_{\rm up}^*\right) - {\rm Tr}\,\left(\left(H_0^{--} - \epsilon_{\rm F}^0\right)A_{\rm pf}^*(1-\Lambda)A_{\rm pf}\right).
\end{aligned}$$

Hence,

$$\langle \Theta(A), A'\rangle = a(A,A') + \frac{1}{2}D(\rho_{\gamma_1(A)}, \rho_{\gamma_1(A')}), \tag{59}$$

where

$$\begin{aligned}
a(A,A') &= {\rm Tr}\,\left(A_{\rm uf}^*\left(H_0^{++} - \epsilon_{\rm F}^0\right)A'_{\rm uf}\right) - {\rm Tr}\,\left(A'_{\rm uf}\left(H_0^{--} - \epsilon_{\rm F}^0\right)A_{\rm uf}^*\right) \\
&\quad + {\rm Tr}\,\left(\left(H_0^{++} - \epsilon_{\rm F}^0\right)A'_{\rm up}\Lambda A_{\rm up}^*\right) - {\rm Tr}\,\left(\left(H_0^{--} - \epsilon_{\rm F}^0\right)A_{\rm pf}^*(1-\Lambda)A'_{\rm pf}\right).
\end{aligned}$$

For all A and A' in $\mathcal{A}$, we have

$$|a(A,A')| \leq \left(1 + \frac{\epsilon_{\rm F}^0 - \epsilon_1}{g_+}\right)\|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}}\|A'_{\rm uf}\|_{\mathcal{A}_{\rm uf}} + \|A_{\rm up}\|_{\mathcal{A}_{up}}\|A'_{\rm up}\|_{\mathcal{A}_{\rm up}} + (\epsilon_{\rm F}^0 - \epsilon_1)\|A_{\rm pf}\|_{\mathcal{A}_{\rm pf}}\|A'_{\rm pf}\|_{\mathcal{A}_{\rm pf}}.$$

We thus deduce from (56) that there exists a constant $C' \in \mathbb{R}_+$ such that for all $A \in \mathcal{A}$,

$$\|\rho_{\gamma_1(A)}\|_{\mathcal{C}} \leq C\|\gamma_1(A)\|_{\mathfrak{S}_{1,1}} \leq C'\|A\|_{\mathcal{A}}.$$

The bilinear form in (59) is therefore continuous on the Hilbert space $\mathcal{A}$. It is also positive since for all $A \in \mathcal{A}$,

$$\langle \Theta(A), A\rangle \geq \|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}}^2 + \lambda_-\|A_{\rm up}\|_{\mathcal{A}_{\rm up}}^2 + (1-\lambda_+)g_-\|A_{\rm pf}\|_{\mathcal{A}_{\rm pf}}^2 + \frac{1}{2}\|\rho_{\gamma_1(A)}\|_{\mathcal{C}}^2, \tag{60}$$

where $0 < \lambda_- \leq \lambda_+ < 1$ are the lowest and highest eigenvalues of Λ. To prove that it is in fact coercive, we proceed by contradiction and assume that there exists a normalized sequence $(A_k)_{k\in\mathbb{N}}$ in $\mathcal{A}$ such that $\lim_{k\to\infty}\langle\Theta(A_k), A_k\rangle = 0$. We infer from (60) that $\|(A_k)_{\rm uf}\|_{\mathcal{A}_{\rm uf}}$, $\|(A_k)_{\rm up}\|_{\mathcal{A}_{\rm up}}$, $\|(A_k)_{\rm pf}\|_{\mathcal{A}_{\rm pf}}$ and $\|\rho_{\gamma_1(A_k)}\|_{\mathcal{C}}$ converge to zero when k goes to infinity. Denoting by $(M_k)_{ij} := (\phi^0_{N_{\rm f}+i}, (A_k)_{\rm pp}\phi^0_{N_{\rm f}+j})_{L^2}$, this implies that $\|M_k\|_2 = \|(A_k)_{\rm pp}\|_{\mathcal{A}_{\rm pp}} \to 1$ and

$$\left\| \sum_{i,j=1}^{N_{\rm p}} (M_k)_{ij}\phi^0_{N_{\rm f}+i}\phi^0_{N_{\rm f}+j} \right\|_{\mathcal{C}} \to 0.$$

Extracting from $(M_k)_{k\in\mathbb{N}}$ a subsequence $(M_{k_n})_{n\in\mathbb{N}}$ converging to some $M \in \mathbb{R}^{N_{\rm p}\times N_{\rm p}}_{\rm S}$, and letting n go to infinity, we obtain

$$\|M\|_2 = 1 \qquad \text{and} \qquad \sum_{i,j=1}^{N_{\rm p}} M_{ij}\phi^0_{N_{\rm f}+i}\phi^0_{N_{\rm f}+j} = 0.$$

This contradicts (9). The bilinear form (59) is therefore coercive on $\mathcal{A}$. As it is also continuous, we obtain that the linear map Θ is a bicontinuous coercive isomorphism from $\mathcal{A}$ to $\mathcal{A}'$.

6.11 Proof of Lemma 11

We can prove the existence of a minimizer $\widetilde{\gamma}_W$ to (4) reasoning as in the proof of the first statement of Theorem 5 (non-degenerate case) up to (52). Only the final argument is slightly different. In the degenerate case, we deduce that H_W has at least N negative eigenvalues from the fact that $\mathrm{Rank}(\mathbb{1}_{(-\infty,\alpha_5]}(H_W)) = N_{\rm o} \geq N$.

We now have to prove that $\widetilde{\gamma}_W = \gamma_W$, where γ_W is defined by (29). We know that γ_W is the unique local minimizer of (24) in the neighborhood of γ_0. Decomposing the space $L^2(\mathbb{R}^3)$ as

$$L^2(\mathbb{R}^3) = \mathcal{H}^W_{\rm f} \oplus \mathcal{H}^W_{\rm p} \oplus \mathcal{H}^W_{\rm u}, \tag{61}$$

where $\mathcal{H}^W_{\rm f} = \mathrm{Ran}(\mathbb{1}_{\{1\}}(\gamma_W))$, $\mathcal{H}^W_{\rm p} = \mathrm{Ran}(\mathbb{1}_{(0,1)}(\gamma_W))$, and $\mathcal{H}^W_{\rm u} = \mathrm{Ran}(\mathbb{1}_{\{0\}}(\gamma_W))$, we can parametrize $\mathcal{K}_{N_{\rm f},N_{\rm p}}$ in the neighborhood of γ_W using the local map

$$\Gamma^W(A) := \exp\left(L^W_{\rm uo}(A)\right)\, \exp\left(L^W_{\rm pf}(A)\right)\, \left(\gamma_W + L^W_{\rm pp}(A)\right)\, \exp\left(-L^W_{\rm pf}(A)\right)\, \exp\left(-L^W_{\rm uo}(A)\right),$$

where

$$L^W_{\rm uo}(A) := \begin{bmatrix} 0 & 0 & -A^*_{\rm uf} \\ 0 & 0 & -A^*_{\rm up} \\ A_{\rm uf} & A_{\rm up} & 0 \end{bmatrix}, \quad L^W_{\rm pf}(A) := \begin{bmatrix} 0 & -A^*_{\rm pf} & 0 \\ A_{\rm pf} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad L^W_{\rm pp}(A) := \begin{bmatrix} 0 & 0 & 0 \\ 0 & A_{\rm pp} & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

the block decomposition of the operators $L^W_{\rm xy}(A)$ being done with respect to the decomposition (61) of the space $L^2(\mathbb{R}^3)$. As $A = 0$ is the unique minimizer of the functional $A \mapsto \mathcal{E}^{\rm rHF}(\Gamma^W(A), W)$ in the neighborhood of 0, we obtain that the block decomposition of the operator $\widetilde{H} = -\frac{1}{2}\Delta + V + \rho_{\gamma_W} \star |\cdot|^{-1} + W$ reads

$$\widetilde{H} := \begin{bmatrix} \widetilde{H}_{\rm ff} & 0 & 0 \\ 0 & \widetilde{H}_{\rm pp} & 0 \\ 0 & 0 & \widetilde{H}_{\rm uu} \end{bmatrix}$$

(first-order optimality conditions), and that there exists $\epsilon \in \mathbb{R}$ such that

$$\widetilde{H}_{\rm ff} - \epsilon \leq 0, \quad \widetilde{H}_{\rm pp} - \epsilon = 0, \quad \widetilde{H}_{\rm uu} - \epsilon \geq 0$$

(second-order optimality conditions). These conditions also read

$$\gamma_W = \mathbb{1}_{(-\infty,\epsilon)}(\widetilde{H}) + \delta_W, \tag{62}$$

with $0 \leq \delta_W \leq 1$, $\mathrm{Ran}(\delta_W) \subset \mathrm{Ker}(\widetilde{H} - \epsilon)$, $\mathrm{Tr}\,(\gamma_W) = N$, which are precisely the Euler conditions for problem (4). Thus, γ_W is a minimizer to (4).

It follows that all the minimizers $\widetilde{\gamma}_W$ of (4) have density $\rho_W := \rho_{\gamma_W}$ and are of the form

$$\widetilde{\gamma}_W = \mathbb{1}_{(-\infty,\epsilon)}(\widetilde{H}) + \widetilde{\delta}_W,$$

with $0 \leq \widetilde{\delta}_W \leq 1$, $\mathrm{Ran}(\widetilde{\delta}_W) \subset \mathrm{Ker}(\widetilde{H} - \epsilon)$, $\mathrm{Tr}\,(\widetilde{\gamma}_W) = N$. As the optimization problem (4) is convex, the set of its minimizers is convex. Therefore, for any $t \in [0,1]$

$$(1-t)\gamma_W + t\widetilde{\gamma}_W = \mathbb{1}_{(-\infty,\epsilon)}(\widetilde{H}) + (1-t)\delta_W + t\widetilde{\delta}_W,$$

is a global minimizer of (4), hence of (24) for t small enough. As we know that γ_W is the unique minimizer to (24) in the vicinity of γ_0, we obtain that $\widetilde{\delta}_W = \delta_W$, which proves that γ_W is the unique minimizer of (4).

6.12 Proof of Theorem 12

The first statement of Theorem 12 has been proved in the previous section. The second statement is a consequence of (62) and of the fact that $\gamma_W \in \mathcal{K}_{N_{\rm f},N_{\rm p}}$. The third statement follows from the real analyticity of the mappings $B_\eta(\mathcal{C}') \ni W \mapsto \widetilde{A}(W) \in \mathcal{A}$, $\mathcal{A} \ni A \mapsto \Gamma(A) \in \mathfrak{S}_{1,1}$, and $\mathfrak{S}_{1,1} \times \mathcal{C}' \ni (\gamma, W) \mapsto E^{\rm rHF}(\gamma, W) \in \mathbb{R}$ and the chain rule.

It follows from (33) that for all $A \in \mathcal{O}$ and all $W \in \mathcal{C}'$,

$$\begin{aligned} E(A,W) &= E_0 + \int_{\mathbb{R}^3} \rho_{\gamma_0} W + \langle \Theta(A), A\rangle + \int_{\mathbb{R}^3} \rho_{\gamma_1(A)} W + \sum_{l\geq 3} \mathrm{Tr}\,(H_0 \gamma_l(A,\cdots,A)) \\ &+ \frac{1}{2} \sum_{\substack{l+l'\geq 3 \\ l,l'\geq 1}} D(\rho_{\gamma_l(A,\cdots,A)}, \rho_{\gamma_{l'}(A,\cdots,A)}) + \sum_{l\geq 2} \int_{\mathbb{R}^3} \rho_{\gamma_l(A,\cdots,A)} W. \end{aligned}$$

As a consequence, we obtain that that for any $A' \in \mathcal{O}$,

$$\begin{aligned} (\nabla_A E(A,W), A')_{\mathcal{A}} &= 2\langle \Theta(A), A'\rangle + \int_{\mathbb{R}^3} \rho_{\gamma_1(A')} W + \sum_{l\geq 3} \mathrm{Tr}\,(H_0 \Gamma_l(A,A')) \\ &+ \sum_{\substack{l+l'\geq 3 \\ l\geq 1,\, l'\geq 1}} D(\rho_{\gamma_l(A,\cdots,A)}, \rho_{\Gamma_{l'}(A,A')}) + \sum_{l\geq 2} \int_{\mathbb{R}^3} \rho_{\Gamma_l(A,A')} W, \end{aligned} \tag{63}$$

with where $\Gamma_1(A,A') = \gamma_1(A')$ is in fact independent of A, and where for all $l \geq 2$, $\Gamma_l(A,A') = \sum_{i=1}^{l} \gamma_l(\tau_{(i,l)}(A,\cdots,A,A'))$ (recall that $\tau_{(i,l)}$ denotes the transposition swapping the $i^{\rm th}$ and $l^{\rm th}$ elements, and that, by convention $\tau_{l,l}$ is the identity). By definition of $A_W(\beta)$, we have

$$\forall A' \in \mathcal{A}, \quad (\nabla_A E(A_W(\beta), \beta W), A')_{\mathcal{A}} = 0. \tag{64}$$

Using (63) and observing that

$$\Gamma_l(A_W(\beta), A') = \sum_{k\geq l-1} \beta^k \sum_{\substack{\alpha\in(\mathbb{N}^*)^{l-1}\\ |\alpha|_1=k, |\alpha|_\infty<k}} \sum_{i=1}^{l} \gamma_l(\tau_{(i,l)}(A_W^{(\alpha_1)}, \cdots, A_W^{(\alpha_{l-1})}, A')), \tag{65}$$

we can rewrite (64) by collecting the terms of order β^k as

$$\forall k \in \mathbb{N}^*, \quad \forall A' \in \mathcal{A}, \quad \langle 2\Theta(A_W^{(k)}) + B_W^{(k)}, A'\rangle = 0,$$

where $B_W^{(k)}$ is given by (37) for $k = 1$ and by (38) for the general case $k \geq 2$. Thus (36) is proved.

Using (30) and (32), we can rewrite (35) for $k = 2n + \epsilon$ ($n \in \mathbb{N}$, $\epsilon \in \{0, 1\}$) as

$$\begin{aligned}
\mathcal{E}_W^{(2n+\epsilon)} &= \mathrm{Tr}\,(H_0\gamma_1(A_W^{(2n+\epsilon)})) + \sum_{2\leq l\leq 2n+\epsilon} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon} \mathrm{Tr}\,(H_0\gamma_{W,l}^{\alpha}) \\
&+ \frac{1}{2} \sum_{\substack{2\leq l+l'\leq 2n+\epsilon\\ l,l'\geq 1}} \sum_{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'} \,|\, |\alpha|_1+|\alpha'|_1=2n+\epsilon} D(\rho_{\gamma_{W,l}^{\alpha}}, \rho_{\gamma_{W,l'}^{\alpha'}}) \\
&+ \sum_{2\leq l\leq 2n+\epsilon-1} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon-1} \int_{\mathbb{R}^3} \rho_{\gamma_{W,l}^{\alpha}} W \\
&= \sum_{2\leq l\leq 2n+\epsilon} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon,\, |\alpha|_\infty\leq n} \mathrm{Tr}\,(H_0\gamma_{W,l}^{\alpha}) \\
&+ \frac{1}{2} \sum_{\substack{2\leq l+l'\leq 2n+\epsilon\\ l,l'\geq 1}} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'} \,|\, |\alpha|_1+|\alpha'|_1=2n+\epsilon\\ \max(|\alpha|_\infty,\, |\alpha'|_\infty)\leq n}} D(\rho_{\gamma_{W,l}^{\alpha}}, \rho_{\gamma_{W,l'}^{\alpha'}}) \\
&+ \sum_{2\leq l\leq 2n+\epsilon-1} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon-1,\, |\alpha|_\infty\leq n} \int_{\mathbb{R}^3} \rho_{\gamma_{W,l}^{\alpha}} W + J_{2n+\epsilon}(A_W^{(1)}, ..., A_W^{(2n+\epsilon-1)}),
\end{aligned}$$

where

$$\begin{aligned}
J_{2n+\epsilon}(A_W^{(1)}, ..., A_W^{(2n+\epsilon-1)}) = & \sum_{2\leq l\leq 2n+\epsilon} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon\\ |\alpha|_\infty>n}} \mathrm{Tr}\,(H_0\gamma_l^{(\alpha)}) \\
&+ \frac{1}{2} \sum_{\substack{2\leq l_1+l_2\leq 2n+\epsilon\\ l_1,l_2\geq 1}} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'} \,|\, |\alpha|_1+|\alpha'|_1=2n+\epsilon\\ \max(|\alpha|_\infty,|\alpha'|_\infty)>n}} D(\rho_{\gamma_{l_1}^{(\alpha)}}, \rho_{\gamma_{l_2}^{(\alpha')}}) \\
&+ \sum_{1\leq l\leq 2n+\epsilon-1} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon-1\\ |\alpha|_\infty>n}} \int_{\mathbb{R}^3} \rho_{\gamma_l^{(\alpha)}} W.
\end{aligned}$$

As

$$J_{2n+\epsilon}(A_W^{(1)}, ..., A_W^{(2n+\epsilon-1)}) = \sum_{k=n}^{2n+\epsilon-1} \langle 2\Theta(A_W^{(2n+\epsilon-k)}) + B_W^{(2n+\epsilon-k)}, A_W^{(k)}\rangle = 0,$$

the proof of the fifth statement is complete. Lastly, the sixth statement can be established reasoning as in the proof of Theorem 8.

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References

[1] A. Anantharaman and E. Cancès, *Existence of minimizers for Kohn-Sham models in quantum chemistry.*,Ann. I. H. Poincaré, An. 26 (2009) 2425–2455.

[2] J.G. Ángyán, *Wigner's* $(2n+1)$ *rule for nonlinear Schrödinger equations*, J. Math. Chem. 46 (2009) 1–14.

[3] V. Bach, E. H. Lieb, M. Loss, and J.-P. Solovej, *There are no unfilled shells in unrestricted Hartree-Fock theory*, Phys. Rev. Lett. 72 (1994) 2981–2983.

[4] S. Baroni, P. Giannozzi and A. Testa, *Green's-function approach to linear response in solids*, Phys. Rev. Lett. 58 (1987) 1861.

[5] D. M. Brink and G. R. Satchler, *Angular Momentum*, 3rd edition, Clarendon, Oxford, 1993.

[6] E. Cancès, R. Chakir and Y. Maday, *Numerical analysis of the planewave discretization of orbital-free and Kohn-Sham models*, M2AN 46 (2012) 341-388.

[7] E. Cancès, A. Deleurence and M. Lewin, *Non-perturbative embedding of local defects in crystalline materials*, J. Phys.: Condens. Matter 20 (2008) 294213.

[8] E. Cancès, K. Kudin, G.E. Scuseria and G. Turinici, *Quadratically convergent algorithm for fractional occupation numbers*, J. Chem. Phys. 118 (2003) 5364–5368.

[9] E. Cancès and C. Le Bris, *On the perturbation method for some nonlinear Quantum Chemistry models*, Math. Mod. and Meth. in App. Sci. 8 (1998) 55–94.

[10] E. Cancès and M. Lewin. *The dielectric permittivity of crystals in the reduced Hartree-Fock approximation*, Arch. Ration. Mech. Anal. 197 (2010) 139–177.

[11] E. Cancès and N. Mourad, in preparation.

[12] E. Chiumiento and M. Melgaard, *Stiefel and Grassmann manifolds in quantum chemistry*, J. Geom. Phys. 62 (8) (2012) 1866–188.

[13] R. Dreizler and E.K.U Gross. *Density functional theory.* Springer Verlag, 1990.

[14] W. E and L. Lu, *The Kohn-Sham equation for deformed crystals*, Memoirs of the American Mathematical Society, American Mathematical Society, 2013.

[15] R. Frank, M. Lewin, E.H. Lieb, and R. Seiringer, *A positive density analogue of the Lieb-Thirring inequality*, Duke Math. Journal 162 (2012) 435–495.

[16] X. Gonze, *Perturbation expansion of variational principles at arbitrary order*, Phys. Rev. A 52 (1995) 1086; X. Gonze, *Adiabatic density-functional perturbation theory*, Phys. Rev. A 52 (1995) 1096.

[17] M. Griesemer and F. Hantsch, *Unique solutions to Hartree-Fock equations for closed shell atoms*, Arch. Ration. Mech. Anal. 203 (2012) 883–900.

[18] M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, *"Schrödinger inequalities" and asymptotic behavior of the electron density of atoms and molecules*, Phys. Rev. A 16 (1977) 1782–1785.

[19] T. Kato. *Perturbation theory for linear operators, 2nd. ed.*. Springer-Verlag, Berlin, Heidelberg, New York 1980.

[20] E.H. Lieb, *Variational principle for many-fermion systems*, Phys. Rev. Lett. 46 (1981) 457–459.

[21] R. McWeeny, *Methods of Molecular Quantum Mechanics, Second Edition*, Academic Press, London, 1992.

[22] N. Mourad, PhD thesis, University Paris-Est, in preparation.

[23] J.W.S. Rayleigh. *The theory of sound. Vol. I.* London : Macmillan, 1877.

[24] M. Reed and B. Simon. *Methods of Modern Mathematical Physics, Vol I, Functional Analysis. Second Ed.* Academic Press, New York, 1980.

[25] M. Reed and B. Simon. *Methods of Modern Mathematical Physics, Vol IV, Analysis of Operators.* Academic Press, New York, 1978.

[26] F. Rellich. *Störungstheorie der Spektralzerlegung. I-V.* Math. Ann. 113 (1937) 600–619; 113 (1937) 677-685; 116 (1939) 555–570; 117 (1940) 356-382; 118 (1942) 462–484.

[27] F. Rellich. *Perturbation theory of eigenvalue problems.* Gordon & Breach, New York, 1969.

[28] E. Schrödinger, *Quantisierung als Eigenwertproblem. III.* Ann. der Physik 80 (1926) 457–490.

[29] B. Simon. *Trace ideals and their applications.* London Mathematical Society Lecture Note Series, vol. 35. Cambridge University Press, 1979.

[30] B. Simon. *Fifty years of eigenvalue perturbation theory.* Bull. Amer. Math. Soc. 24 (1991) 303–319.

[31] J.P. Solovej. *Proof of the ionization conjecture in a reduced Hartree-Fock model.* Invent. Math. 104 (1991), 291–311.