The Multiconfiguration Methods in Quantum Chemistry

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Abstract

The multiconfiguration methods are the natural generalization of the well-known Hartree-Fock theory for atoms and molecules. By a variational method, we prove the existence of a minimum of the energy and of infinitely many solutions of the multiconfiguration equations, a finite number of them being interpreted as excited states of the molecule. Our results are valid when the total nuclear charge Z exceeds $N-1$ (N is the number of electrons) and cover most of the methods used by chemists. The saddle points are obtained with a min-max principle; we use a Palais-Smale condition with Morse-type information and a new and simple form of the Euler-Lagrange equations.

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Contents

1 Introduction

We want to prove here some results concerning the multiconfiguration methods (abbreviated in MC) in molecular quantum chemistry. Some of them have been announced in [19].

Under the *Born-Oppenheimer* approximation, the non-relativistic quantum energy of N electrons interacting with M static nuclei is given by

$$\begin{aligned}\mathcal{E}_N(\Psi) = \langle \Psi, \mathcal{H}\Psi\rangle \;\; &= \;\; \sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} \left(\frac{1}{2}|\nabla_{x_i}\Psi(x)|^2 + V(x_i)|\Psi(x)|^2\right) dx \\ &\quad + \sum_{1\leqslant i<j\leqslant N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(x)|^2}{|x_i - x_j|}\, dx \qquad (1)\end{aligned}$$

where $x = (x_1, ..., x_N) \in (\mathbb{R}^3)^N$, and V is the purely Coulombic potential

$$V(u) = -\sum_{m=1}^{M} \frac{z_m}{|u - \bar{x}_m|},$$

$z_m > 0$ and $\bar{x}_m \in \mathbb{R}^3$ being the charge and position of each of the M nuclei.

In the formula (1), $\Psi \in H_a^1(\mathbb{R}^{3N}, \mathbb{R})$ is such that $\|\Psi\|_{L^2} = 1$. The subscript a on H_a^1 indicates that we consider functions Ψ which are antisymmetric under interchanges of variables (expression of the Pauli exclusion principle):

$$\forall \sigma \in S_N,\;\; \Psi(x_1...x_N) = \epsilon(\sigma)\Psi(x_{\sigma(1)}...x_{\sigma(N)})\;\; a.e.$$

$\mathcal{H}$ is the purely Coulombic N-body Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_{x_i} + V(x_i) \right) + \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|x_i - x_j|}.$$

For the sake of simplicity, we restrict ourselves to real-valued functions and do not take the spin into account. In the sequel, we denote by $Z = \sum_{m=1}^{M} z_m$ the total nuclear charge. We refer the reader to [4, 20] for a description of this model and a detailed explanation of the Born-Oppenheimer approximation.

The form of the spectrum of $\mathcal{H}$ is known (see for instance the review [13]): it is bounded from below, $\sigma_{ess}(\mathcal{H}) = [\Sigma; +\infty)$ where $\Sigma \leqslant 0$, and each potential eigenvalue lies in $(-\infty; 0]$. The *N-body ground state energy* is the minimum of $\sigma(\mathcal{H})$ also defined by

$$E_N = \inf\{\mathcal{E}_N(\Psi),\ \Psi \in H^1_a(\mathbb{R}^{3N}),\ \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1\}. \tag{2}$$

The condition $E_N < \Sigma$ translates the physical property that the nuclei are able to bind the N electrons in their vicinity. In agreement with intuition, this is false when Z is not sufficiently large. Zhislin showed in [32] (see also [8]) that when $Z > N - 1$,

$$\sigma(\mathcal{H}) = \{E_N = \lambda_1 \leqslant \lambda_2 \leqslant \cdots \leqslant \lambda_n \leqslant \cdots\} \cup [\Sigma; +\infty)$$

where $(\lambda_i)_{i \geqslant 1}$ are eigenvalues strictly below Σ and whose eigenfunctions are called *excited states*. In the sequel, we shall always assume that $Z > N - 1$.

From the practical point of view, the determination of a minimum for (2) is the main goal to achieve in order to understand the molecular structure, but the computation of excited states is also important: they occur when the molecule gets an excess of energy, that could then be lost in a number of ways. Chemical reactions also often ensue after an initial electronic transition. Since the model contains no empirical parameter (this is an *"ab initio"* theory), one may think that very accurate results could be obtained.

Unfortunately, the numerical computation of a minimum (and *a fortiori* excited states) is extremely difficult, due to the excessive dimension of the space $\mathbb{R}^{3N}$ on which the wavefunctions are defined. This is why chemists have introduced some simplification of (2). One of them is based on a reduction of the space $H = H^1_a(\mathbb{R}^{3N})$ where the minimization has to be done. The idea is to choose a sequence of subsets $M^1 \subset \cdots \subset M^K \subset \cdots \subset H$ such that, intuitively, $M^K \to H$, and then to replace H by M^K in (2). The main advantage of this approach is that the approximate ground state energy is always greater than the true. Nevertheless, the main difficulty is that the Schrödinger linear problem (2) often becomes strongly nonlinear (when the M^i are not linear subspaces of H) and so the methods used to study it are inefficient. The multiconfiguration methods belong to this type of approximation.

In the *multiconfiguration (MC) method of rank K*, the set of admissible wavefunctions is limited to the Ψ which are a linear combination of Slater determinants built with K functions $\phi_1, ..., \phi_K$ in $H^1(\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$

$$\Psi = \sum_{I=\{i_1<i_2<...<i_N\}\subset\{1...K\}} c_I \cdot |\phi_{i_1}...\phi_{i_N}\rangle \tag{3}$$

where

$$|\phi_{i_1}...\phi_{i_N}\rangle(x_1...x_N) = \frac{1}{\sqrt{N!}} \det(\phi_{i_k}(x_l))_{k,l}$$

and

$$\sum_I {c_I}^2 = 1.$$

When there is no possible confusion, we shall use the notation $\Phi_I = |\phi_{i_1}...\phi_{i_N}\rangle$ for $I = \{i_1, ..., i_N\}$ and write

$$\Psi = \sum_I c_I \Phi_I.$$

The set of the functions Ψ that can be written on the form (3) is characterized in terms of the rank of the *one-body density operator* Γ_Ψ: this is the operator acting on $L^2(\mathbb{R}^3)$ with kernel

$$\gamma_\Psi(x, y) = N \int_{\mathbb{R}^{3(N-1)}} \Psi(x, x_2...x_N)\Psi(y, x_2...x_N) dx_2...dx_N,$$

that is to say

$$\Gamma_\Psi(\phi)(x) = \int_{\mathbb{R}^3} \gamma_\Psi(x, y)\phi(y)\, dy.$$

One can easily prove (see [23, 8] and Lemma 1) that Ψ is of the form (3) if and only if $rank(\Gamma_\Psi) \leqslant K$ and $Range(\Gamma_\Psi) \subset span(\phi_i)$. The *total electronic charge density* is defined on $\mathbb{R}^3$ by $\rho_\Psi(x) = \gamma_\Psi(x, x)$ and we have $Tr(\Gamma_\Psi) = \int_{\mathbb{R}^3} \rho(x)\, dx = N$.

If we introduce $rank(\Psi) := rank(\Gamma_\Psi)$, the *$N$-body ground state energy of rank K* is thus defined by

$$E_N^K = \inf\{\mathcal{E}_N(\Psi),\ \Psi \in H^1_a(\mathbb{R}^{3N}),\ \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1,\ rank(\Psi) \leqslant K\}. \tag{4}$$

Since every wave function Ψ can be expressed as a (infinite) linear combination of Slater determinants (see Lemma 1), we have

$$\lim_{K\to+\infty} E_N^K = E_N.$$

When $K = N$, we obtain the well-known *Hartree-Fock* (HF) model [20, 21, 22, 10]: Ψ is a unique Slater determinant and Γ_Ψ a projector of rank N. The existence of a minimum for E_N^N has been proved for the first time by E.H. Lieb and B. Simon in [21]. In [22], P.-L. Lions proved the existence of infinitely many solutions of the Hartree-Fock equations, often interpreted as excited states in the literature (this point is discussed further on). The difference $E_N^N - E_N \geqslant 0$

between the Hartree-Fock and the "exact" energy is called the *electron correlation energy* [16, 17, 18, 24]. It can change quite significantly in many elementary chemical processes: typical examples are transition states in chemical reactions, bond breaking and excited states (see for instance [2, 11, 31]). In such situations, the HF method fails and chemists have to use the more accurate MC.

In practice, chemists rarely work with an expansion of wave functions containing all Slater determinants built with $\phi_1, ..., \phi_K$ like in formula (3). They often select some determinants (*configurations*), chosen for instance thanks to the known symmetry of the molecule or some chemical intuition, and optimize the energy with this form fixed. In the sequel, we shall call this approach *"partial multiconfiguration"*. From the mathematical point of view, these methods are more difficult to deal with since the form may change when another basis of $Range(\Gamma_\Psi)$ is used.

For algebraic reasons (see [1, 5, 23, 8] and Appendix), there does not exist N-body wave functions of rank $K = N + 1$ and when $N = 2$, all the Ψ have an even rank. A partial multiconfiguration method of rank $K = N + 2$ was studied by C. Le Bris [16] who considered the minimization over doubly excited configurations

$$\Psi = \alpha|\phi_1...\phi_N\rangle + \beta|\phi_1...\phi_{N-2}\phi_{N+1}\phi_{N+2}\rangle. \tag{5}$$

He proved the existence of a minimum when $Z > N - 1$ and obtained the inequality $E_N^{N+2} < E_N^N$ (see [9] for the generalization $E_N^{K+2} < E_N^K$, $K \geqslant N$).

The existence of a minimum for E_N^K provided $K \geqslant N$ and $Z > N - 1$ was recently proved by G. Friesecke in [8]. He used a very interesting proof based on geometric localization methods, P.-L. Lions' concentration-compactness ideas and the inequality $E_{N+1}^{K+1} < E_N^K$. The latter inequality allowed the author to notice an interesting connection between Lions' method and the celebrated HVZ Theorem. Unfortunately, we think that his method cannot easily be generalized to obtain saddle points. We do not know if it can be adapted to treat the case of partial MC.

To our knowledge, the problem of existence of excited states for multiconfiguration methods and their relation with the eigenvalues of $\mathcal{H}$ have never been tackled from the mathematical point of view, although this is one of the main uses of MC in today's molecular quantum chemistry. Our approach, based on ideas of [22], allows to prove the existence of a minimum and of saddle points for some partial MC, including the "full" MC studied by G. Friesecke, the doubly excited configurations of C. Le Bris, and the other main methods used by chemists. More precisely, for the "full" method,

1. for each $K \geqslant N$, we prove that there exists a sequence of distinct critical points of rank K, whose energy converges to 0;

2. for each $K \geqslant N$, we construct explicitly $\binom{K}{N}$ critical points of rank K with a nonlinear min-max method that is related to the algorithm used by chemists. Their energy converges when $K \to +\infty$ to the "true" critical values of $\mathcal{E}_N$ (the eigenvalues $(\lambda_i)_{i \geqslant 1}$ of the Hamiltonian $\mathcal{H}$).

The solutions of the multiconfiguration equations constructed in the first part are the analogue of P.-L. Lions' result for HF [22]. Our impression is that they cannot really be interpreted as excited states of the molecule (for instance, their energy tends to 0 while $\lambda_i \to \Sigma$ as $i \to +\infty$). The solutions constructed in the second part are better candidates in view of their behaviour when $K \to +\infty$. For each $K \geqslant N$, there is a finite number of such points and only one type (the minima) for the HF case $K = N$. This corresponds to chemists' experience, which suggests that many determinants have to be included in the model to obtain accuracy for a fixed excited state of the molecule.

As for HF in [21, 22], we study the energy in the "one-body space" (as a function of c_I and ϕ_i), in opposition to G. Friesecke's approach in the "N-body space" $H^1_a(\mathbb{R}^{3N})$. Our method is based on a Palais-Smale condition with Morse-type information, and on the Euler-Lagrange equations which were often neglected in the previous studies because of their apparent complexity. We express them in a very simple and useful way (9) that clarifies the connection with the HF model and could also become relevant for numeric simulations.

In the next section, we introduce some notations and definitions in order to state properly the main results of this paper; they can be found in section 3, with some comment on the proofs and on the relation with the algorithms. Section 4 is devoted to the proof of our results.

2 General setting of the model

2.1 Expression of the energy in one-body space

We need some notations. Let Ψ be a wave function of rank K

$$\Psi = \sum_{I=\{i_1<i_2<\ldots<i_N\}\subset\{1\ldots K\}} c_I \cdot |\phi_{i_1}\ldots\phi_{i_N}\rangle.$$

If we use the convention

$$\begin{aligned} \alpha_{i_1\ldots i_N} &= 0 \quad \text{if } \#\{i_1\ldots i_N\} < N \\ &= \frac{\varepsilon(\sigma)}{\sqrt{N!}} c_{\{i_{\sigma(1)}<\ldots<i_{\sigma(N)}\}} \text{ otherwise,} \end{aligned}$$

we get

$$\Psi = \sum_{i_1\ldots i_N} \alpha_{i_1,\ldots,i_N} \phi_{i_1} \otimes \cdots \otimes \phi_{i_N}.$$

We are now able to express the energy as a function of the c_I and ϕ_i:

$$\begin{aligned} \mathcal{E}_N(\Psi) = N \sum_{1\leqslant k_2,\ldots,k_N\leqslant K} \int_{\mathbb{R}^3} \left(\frac{1}{2} \left| \sum_{i=1}^K \alpha_{i,k_2\ldots k_N} \nabla\phi_i \right|^2 + V \left(\sum_{i=1}^K \alpha_{i,k_2\ldots k_N} \phi_i \right)^2 \right) \\ + \frac{N(N-1)}{2} \sum_{1\leqslant k_3,\ldots,k_N\leqslant K} \iint_{\mathbb{R}^6} \frac{\left(\sum_{1\leqslant i,j\leqslant K} \alpha_{i,j,k_3\ldots,k_N} \phi_i(x)\phi_j(y)\right)^2}{|x-y|} dx\,dy. \quad (6) \end{aligned}$$

This can be written on the compact form

$$\mathcal{E}_N(\Psi) = \left\langle \left(\left(-\frac{\Delta}{2} + V \right) \Gamma + W_\Phi \right) \cdot \Phi \, , \, \Phi \right\rangle_{(L^2(\mathbb{R}^3))^K} \tag{7}$$

where $\Phi = (\phi_1, ..., \phi_K)^T \in (H^1(\mathbb{R}^3))^K$ and the $K \times K$ matrices Γ and W_Φ are defined by

$$\Gamma_{i,j} = N \sum_{k_2 \ldots k_N} \alpha_{i,k_2,\ldots k_N} \alpha_{j,k_2,\ldots k_N}$$

$$(W_\Phi)_{i,j}(x) = \frac{N(N-1)}{2} \sum_{k_3 \ldots k_N} \sum_{k,l} \alpha_{i,k,k_3 \ldots k_N} \alpha_{j,l,k_3 \ldots k_N} \left((\phi_k \phi_l) * \frac{1}{|r|} \right)(x).$$

In (7), we have used the notation $\langle \Phi, \Phi' \rangle_{(L^2(\mathbb{R}^3))^K} = \sum_{i=1}^K \int_{\mathbb{R}^3} \phi_i \phi'_i$.

With $c = (c_I) \in \mathbb{R}^{\binom{K}{N}}$ (lexicographical order), we introduce

$$\mathcal{M}_N^K = \left\{ (c, \Phi) \in \mathbb{R}^{\binom{K}{N}} \times (H^1(\mathbb{R}^3))^K, \ \sum_I {c_I}^2 = 1, \ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

and $\mathcal{E}_N^K$, which is defined on $\mathcal{M}_N^K$ by the formula

$$\mathcal{E}_N^K(c, \Phi) = \left\langle \left(\left(-\frac{\Delta}{2} + V \right) \Gamma + W_\Phi \right) \cdot \Phi \, , \, \Phi \right\rangle_{(L^2(\mathbb{R}^3))^K} . \tag{8}$$

We shall denote by $d\mathcal{E}_N^K$ its first derivative, and $d^2_\Phi \mathcal{E}_N^K$ its second derivative with respect to Φ, on the Riemannian manifold $\mathcal{M}_N^K$. Let us notice that we now have

$$E_N^K = \inf_{\mathcal{M}_N^K} \mathcal{E}_N^K.$$

The problem is to prove the existence of a minimum and saddle points for $\mathcal{E}_N^K$ on $\mathcal{M}_N^K$. Such a point (c, Φ) will be a solution of the *multiconfiguration equations* which take the form

$$\left\{ \begin{aligned} \left(\left(-\frac{\Delta}{2} + V \right) \Gamma + 2W_\Phi \right) \cdot \Phi + \Lambda \cdot \Phi = 0 \qquad (9) \\ H_\Phi \cdot c = \beta \cdot c. \qquad (10) \end{aligned} \right.$$

The first equation (9) is a system of K nonlinear PDE's – the Euler-Lagrange equations for the ϕ_i, Λ being the Lagrange multipliers matrix associated to the constraints $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$. The second equation (10) is an eigenvalue problem – the Euler-Lagrange equations for the c_I, with multiplier $\beta = \mathcal{E}_N^K(c, \Phi)$. $H_\Phi = (\langle \Phi_I, \mathcal{H} \Phi_J \rangle)_{I,J}$ is the $\binom{K}{N} \times \binom{K}{N}$ matrix of the Hamiltonian $\mathcal{H}$ on $span(\Phi_I)$.

We shall see that the compact form of equation (9) will largely simplify the study. A formalism to treat the case of partial MC will be introduced later.

We shall compare some critical values of $\mathcal{E}_N^K$ on $\mathcal{M}_N^K$ to the eigenvalues of the Hamiltonian $\mathcal{H}$:

$$\lambda_d = \min_{dim(V)=d} \ \max_{\substack{\Psi \in V, \\ \|\Psi\|_{L^2} = 1}} \langle \mathcal{H}\Psi, \Psi \rangle. \tag{11}$$

2.2 About the orthogonal invariance

Let us now give a precise statement for some facts mentioned in the Introduction, concerning the role of Slater determinants in $H^1_a(\mathbb{R}^{3N})$ and the basic properties of rank K wave functions. We recall that Γ_Ψ is the one-body density operator defined previously.

Lemma 1 (Basic properties of rank K wave functions [23]).

1. *Let $(\phi_i)_{i\in\mathbb{N}}$ be an orthonormal basis of $L^2(\mathbb{R}^3)$ (resp. $H^1(\mathbb{R}^3)$). Then $(|\phi_{i_1}...\phi_{i_N}\rangle)_{i_1<...<i_N}$ is an orthonormal basis of $L^2_a(\mathbb{R}^{3N})$ (resp. $H^1_a(\mathbb{R}^{3N})$).*
2. *Let Ψ be a wave function of rank K (i.e. $rank(\Gamma_\Psi) = K$), and $(\phi_i)_{i=1}^K$ be an orthonormal basis of $Range(\Gamma_\Psi)$. Then Ψ can be expanded as a linear combination of Slater determinants built with $(\phi_i)_{i=1}^K$. Conversely, every wave function which is a linear combination of Slater determinants is of finite rank.*

Assertion *2.* of this lemma corresponds to the *Löwdin Expansion Theorem* [23], while assertion *1.* is just the expression of the classical

$$L^2_a(\mathbb{R}^{3N}) \simeq \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3).$$

When $(\phi_i)_{i=1}^K$ is an orthonormal basis of $Range(\Gamma_\Psi)$, each ϕ_i is, by definition, an *orbital of* Ψ. If moreover they are eigenfunctions of Γ_Ψ, they are called the *natural orbitals of* Ψ. The associated eigenvalues are then the *occupation numbers*. By Löwdin's Theorem, each Ψ of finite rank can be expanded as a linear combination of Slater determinants involving its natural orbitals.

If we now take a wave function of rank K

$$\Psi = \sum_I c_I \Phi_I = \sum_{k_1,...,k_N=1}^{K} \alpha_{k_1,...k_N}\ \phi_{k_1}\otimes\cdots\otimes\phi_{k_N},$$

let us see how $c = (c_I)$ changes when one uses another basis (ϕ'_i) of $Range(\Gamma_\Psi)$. Assuming that $\phi'_i = \sum_{j=1}^K u_{i,j}\phi_j$ with $U = (u_{i,j}) \in \mathcal{O}_K(\mathbb{R})$, we obtain:

$$\begin{aligned} \alpha'_{i_1,...i_N} &= \langle \Psi, \phi'_{i_1}\otimes\cdots\otimes\phi'_{i_N}\rangle_{L^2(\mathbb{R}^{3N})} \\ &= \sum_{j_1,...,j_N=1}^{K} u_{i_1,j_1}\cdots u_{i_N,j_N}\cdot\langle\Psi,\phi_{j_1}\otimes\cdots\otimes\phi_{j_N}\rangle_{L^2(\mathbb{R}^{3N})} \\ &= \sum_{j_1,...,j_N=1}^{K} u_{i_1,j_1}\cdots u_{i_N,j_N}\cdot\alpha_{j_1...j_N}. \end{aligned} \tag{12}$$

This defines a group action of $\mathcal{O}_K(\mathbb{R})$ on $\mathcal{M}_N^K$:

$$U\cdot(c,\Phi) = (c', U\cdot\Phi).$$

We have the following

Lemma 2. *We assume that* $(c', \Phi') = U \cdot (c, \Phi)$*. With obvious notations, we then have :*

$$\Gamma' = U\Gamma U^T \quad \text{and} \quad W'_{\Phi'} = UW_\Phi U^T.$$

In particular $\mathcal{E}_N^K$ *is invariant under the action of* $\mathcal{O}_K(\mathbb{R})$ *on* $\mathcal{M}_N^K$*.*

Proof. – It is easy to see that Γ is the matrix of Γ_Ψ in the basis $(\phi_i)_{i=1}^K$. Its transformation law is thus obvious. For W_Φ, the computation is very easy but tedious. □

It is easy to see that the action of $\mathcal{O}_K(\mathbb{R})$ on $\mathcal{M}_N^K$ is not free when $K > N$. Therefore we believe that the quotient $\mathcal{M}_N^K/\mathcal{O}_K(\mathbb{R})$ is not smooth (that is to say, it is not a manifold) and that is why we shall not really use it here. Nevertheless, this action of $\mathcal{O}_K(\mathbb{R})$ will play an important role in the proof of Theorem 1 since we shall use it to diagonalize matrices.

2.3 Formalism for partial multiconfiguration methods

We introduce

$$\mathcal{A}_N^K = \{I \subset \{1, ..., K\},\ |I| = N\}.$$

In a partial MC method of rank K, a set $\mathcal{I} \subset \mathcal{A}_N^K$ is chosen and the energy $\mathcal{E}_N^K$ is restricted to the submanifold

$$\mathcal{M}_N^{K,\mathcal{I}} = \{(c, \Phi) \in \mathcal{M}_N^K,\ \forall I \notin \mathcal{I},\ c_I = 0\} \subset \mathcal{M}_N^K.$$

The ground state energy associated to the method is then defined by

$$E_N^{K,\mathcal{I}} = \inf_{\mathcal{M}_N^{K,\mathcal{I}}} \mathcal{E}_N^K.$$

Critical points of $\mathcal{E}_N^K$ on $\mathcal{M}_N^{K,\mathcal{I}}$ are now solutions of the following *partial multiconfiguration equations*

$$\begin{cases} \left(\left(-\frac{\Delta}{2} + V\right)\Gamma + 2W_\Phi\right) \cdot \Phi + \Lambda \cdot \Phi = 0 & (13) \\ H_\Phi^{\mathcal{I}} \cdot c_{\mathcal{I}} = \beta \cdot c_{\mathcal{I}}. & (14) \end{cases}$$

where $c_{\mathcal{I}} = (c_I)_{I\in\mathcal{I}}$ and $H_\Phi^{\mathcal{I}} = (\langle\Phi_I, \mathcal{H}\Phi_J\rangle)_{I,J\in\mathcal{I}}$ is the $|\mathcal{I}| \times |\mathcal{I}|$ matrix of the Hamiltonian $\mathcal{H}$ on $span(\Phi_I, I \in \mathcal{I})$.

Compared to the "full" MC, the new difficulty is that one cannot choose any basis $(\phi_i)_{i=1}^K$ of $Range(\Gamma_\Psi)$ for one needs to preserve the form of the wave-function. We introduce

$$\mathcal{O}_{\mathcal{I}} = \left\{U \in \mathcal{O}_K(\mathbb{R}),\ U \cdot \mathcal{M}_N^{K,\mathcal{I}} \subset \mathcal{M}_N^{K,\mathcal{I}}\right\}.$$

In the sequel, we shall restrict ourselves to the following methods:

Definition 1. *We say that* $\mathcal{I} \subset \mathcal{A}_N^K$ *defines a* natural multiconfiguration method of rank K *if*

1. *there exists* $(c,\Phi) \in \mathcal{M}_N^{K,\mathcal{I}}$ *which is of rank* K

2. *for all* $(c,\Phi) \in \mathcal{M}_N^{K,\mathcal{I}}$ *there exists a* $U \in \mathcal{O}_{\mathcal{I}}$ *such that* Γ'*, associated to* $(c',\Phi') = U\cdot(c,\Phi)$*, is a diagonal matrix. In other words, every wavefunction of the method can be expressed in terms of its natural orbitals.*

Let us notice that most of the methods used by chemists are "natural methods" (the natural orbitals have an important physical meaning). Here are some examples:

• (M_1) **Full MC.** It is clear that the general multiconfiguration method explained before is a natural method with $\mathcal{I} = \mathcal{A}_N^K$.

• (M_2) **Two nonvanishing determinants have at least two distinct orbitals.** Suppose that $\mathcal{I}$ satisfies

$$\#(I \cap J) = 1 \Longrightarrow I \notin \mathcal{I} \text{ or } J \notin \mathcal{I}.$$

Then one easily sees that Γ_Ψ is always diagonal and this method is thus natural. As an example, we can quote the method studied by C. Le Bris in [16]

$$\Psi = \alpha|\phi_1 ... \phi_N\rangle + \beta|\phi_1 ... \phi_{N-2}\phi_{N+1}\phi_{N+2}\rangle.$$

See the Appendix for a study of the role of those methods in the cases $N = 2$ and $K = N + 2$.

• (M_3) **Complete Active Space method.** The most common method used by chemists is probably the Complete Active Space method [28, 29]. In this method, the electrons are divided into two groups : the *inactive* (or *core*) electrons that are supposed to be correctly described by a Hartree-Fock type model, and the *active* (or *valence*) electrons that are supposed to be the most important to estimate the correlation energy. They are thus described by a "Full" MC. Hence, an integer $N_v \in [0; N]$ is chosen and one takes

$$\mathcal{I}_{CAS} = \{I,\ \{1, ..., N - N_v\} \subset I\}.$$

In other words, the considered wavefunctions have the form

$$\begin{aligned}\Psi &= |\phi_1 ... \phi_{N-N_v}\rangle \wedge \left(\sum_{\substack{I=\{i_1<...<i_{N_v}\}\subset\{N-N_v+1,...,K\},\\ |I|=N_v}} c_I|\phi_{i_1}, ... \phi_{i_{N_v}}\rangle \right)\\ &:= \sum_{\substack{I\subset\{N-N_v+1,...,K\},\\ |I|=N_v}} c_I|\phi_1, ..., \phi_{N-N_v}, \phi_{i_1}, ..., \phi_{i_{N_v}}\rangle\end{aligned}$$

$N_v = N$ corresponds to the "full" MC method of rank K, while $N_v = 0$ is the Hartree-Fock model. Typically, $N_v \in [2; 10]$ in the common chemical programs.

It is easy to see that Γ has the form

$$\Gamma = \begin{pmatrix} I_{N-N_v} & 0 \\ 0 & \Gamma_v \end{pmatrix}$$

so with an appropriate

$$U = \begin{pmatrix} I_{N-N_v} & 0 \\ 0 & U_v \end{pmatrix}$$

that does not change the form of the wavefunction, one can diagonalize Γ. This is thus a natural MC method.

3 Main results and comments

3.1 Our results

We can now state our main results.

The first is a rather technical result which is simply the compactness of Palais-Smale sequences, but with the additional difficulty that the sequence may lose rank:

Theorem 1 (Palais-Smale Condition with Morse-type information). *We assume $Z > N-1$, $K \geqslant N$ and suppose that $\mathcal{I}$ defines a natural MC method of rank K. Let $(c^n, \Phi^n)_{n\in\mathbb{N}}$ be a sequence of $\mathcal{M}_N^{K,\mathcal{I}}$, with associated wavefunctions $(\Psi^n)_{n\in\mathbb{N}}$, such that*

1. $(\mathcal{E}_N^K(c^n, \Phi^n))_{n\in\mathbb{N}}$ *is bounded*
2. $d_\Phi \mathcal{E}_N^K(c^n, \Phi^n) \to 0$ *and* $\frac{\partial \mathcal{E}_N^K}{\partial c_I}(c^n, \Phi^n) \to 0$ *for all* $I \in \mathcal{I}$.
3. *there exists* $j \in \mathbb{N}$ *and a sequence of positive real numbers* $(\delta^n)_{n\in\mathbb{N}}$ *with* $\delta^n \to 0$, *such that for every* n, $d^2_\Phi(\mathcal{E}_N^K)(c^n, \Phi^n)$ *has at most* j *eigenvalues below* $-\delta^n$.

Then, there exists a $K' \in [N; K]$ such that, up to subsequences and after a rotation $U_n \in \mathcal{O}_K(\mathbb{R})$ on each (c^n, Φ^n):

1. $\forall n \in \mathbb{N}$, $\Gamma^n = diag(\gamma_1^n, ..., \gamma_K^n)$.
2. $\forall i = 1, ..., K'$, $\gamma_i^n \to \gamma_i > 0$ *and* $\phi_i^n \to \phi_i$ *strongly in* $H^1(\mathbb{R}^3)$.
3. $\forall i = K'+1, ..., K$, $\gamma_i^n \to 0$ *and* $\sqrt{\gamma_i^n}\phi_i^n \to 0$ *strongly in* $H^1(\mathbb{R}^3)$.
4. *We define* $\mathcal{I}' = \mathcal{I} \cap \mathcal{A}_N^{K'}$, $c' = (c_I)_{I \in \mathcal{A}_N^{K'}}$ *and* $\Phi' = (\phi_1, ..., \phi_{K'})$. *Then* (c', Φ') *is a critical point of* $\mathcal{E}_N^{K'}$ *on* $\mathcal{M}_N^{K',\mathcal{I}'}$ *and is a solution of the partial multiconfiguration equations (13,14) with a* $\Lambda > 0$.
5. $\Psi^n \to \Psi$ *strongly in* $H^1_a(\mathbb{R}^{3N})$, *where* Ψ *is the wavefunction associated to* (c', Φ').
6. *If* $\mathcal{I} = \mathcal{A}_N^K$ *(Full MC), then* $K' \in \{K-1, K\}$.

Remark. – The last assertion $K' \in \{K-1, K\}$ is also true for some partial MC methods, including example (M_3) quoted in section 2.3. See the proof in [9, 16]. In general, this depends on the method.

The existence of a minimum for multiconfiguration methods is then a consequence of the following result:

Corollary 2 (Ground State for Multiconfiguration Methods).
Let $Z > N-1$. For all $K \geqslant N$ and any $\mathcal{I}$ that defines a natural method of rank K, there exists a minimum for $E_N^{K,\mathcal{I}}$.

We now state our result concerning excited states:

Theorem 3 (Excited States for Multiconfiguration Methods).
We assume $Z > N-1$.

(i) For all $K \geqslant N$ and any $\mathcal{I}$ that defines a natural method of rank K, there exists a sequence $(\tilde{c}^i, \tilde{\Phi}^i)_{i\in\mathbb{N}^*}$ of distinct points of $\mathcal{M}_N^{K,\mathcal{I}}$, which are solutions of equation (9) with some $\tilde{\Lambda}_i \geqslant 0$. In addition, if $(\tilde{\Psi}^i)_{i\in\mathbb{N}^*}$ is the associated sequence of wavefunctions, as i goes to infinity,

$$\mathcal{E}_N(\tilde{\Psi}^i) < 0, \quad \mathcal{E}_N(\tilde{\Psi}^i) \to 0, \quad \tilde{\Lambda}_i \to 0,$$

$$\sqrt{\tilde{\Gamma}^i} \cdot (\nabla \tilde{\Phi}^i) \to 0 \ \ in\ (L^2(\mathbb{R}^3))^K, \quad and \quad \nabla \tilde{\Psi}^i \to 0 \ \ in\ L^2_a(\mathbb{R}^{3N}).$$

(ii) For all $K \geqslant N$ and any $\mathcal{I}$ that defines a natural method of rank K, there exists $|\mathcal{I}|$ points $(c_d^K, \Phi_d^K)_{1\leqslant d\leqslant|\mathcal{I}|}$ of $\mathcal{M}_N^{K,\mathcal{I}}$, which are solutions of equation (9) with some $\Lambda_d^K \geqslant 0$, and such that, if $(\Psi_d^K)_{1\leqslant d\leqslant|\mathcal{I}|}$ is the associated sequence of wave functions, we have for all $d \geqslant 1$

$$\mathcal{E}(\Psi_d^K) \geqslant \lambda_d.$$

If moreover $\mathcal{I} = \mathcal{A}_N^K$ (Full MC), then we have (with d fixed)

$$\mathcal{E}(\Psi_d^K) \to \lambda_d \ as\ K \to +\infty.$$

We recall that λ_d is the d^{th} eigenvalue of $\mathcal{H}$ defined in (11). The two parts of Theorem 3 may be interpreted as follows. For a fixed method (i.e. fixed K and $\mathcal{I}$), there are many solutions to the multiconfiguration equations: in the first part (i), we show how an infinity can be exhibited. But, just a finite number of them, defined in part (ii), is related to the true eigenfunctions of the Hamiltonian in the N-body space. Hence, to obtain accuracy for the d^{th} excited state of the molecule, one needs to work with a lot of Slater determinants so that $d \leqslant |\mathcal{I}|$.

Remark. – When $\mathcal{I} = \mathcal{A}_N^K$, we believe that the sequence $(\Psi_d^K)_{K\geqslant N}$ in Theorem 3-ii) is precompact in $H^1_a(\mathbb{R}^{3N})$ and converges, up to a subsequence, to an eigenfunction Ψ_d of $\mathcal{H}$ associated to the eigenvalue λ_d, but we were unable to prove it. This is true in the case of minimizing sequences ($d = 1$), see [8]. We hope to come back to this point in the future.

Finally, let us specify the properties of the orbitals, when they are solutions of the multiconfiguration equations:

Proposition 4. *Let* $(c,\Phi)\in\mathcal{M}_N^K$ *be such that* $\Gamma>0$ *and* Φ *is a solution of*

$$\left(\left(-\frac{\Delta}{2}+V\right)\Gamma+2W_\Phi\right)\cdot\Phi+\Lambda\cdot\Phi=0. \tag{15}$$

Then each ϕ_i *is in* $\bigcap_{2\leqslant p<3}W^{2,p}(\mathbb{R}^3)$ *and is real-analytic on* $\Omega:=\mathbb{R}^3\backslash\{\bar{x}_1...\bar{x}_M\}$. *If moreover* $\Lambda>0$, *then it also has an exponential fall-off.*

Hence, the wavefunctions constructed by our method are real-analytic on Ω^N and have an exponential fall-off. This regularity of the multiconfiguration optimal wavefunctions could be the main reason for the rather slow convergence of these methods when $K\to+\infty$, since the true eigenfunctions (Ψ_i) of $\mathcal{H}$ are known to have a cusp at electrons coalescence points, i.e. $(x_1,...,x_N)\in\Omega^N$ with $\prod_{i\neq j}(x_i-x_j)=0$ [15, 12].

3.2 Strategy of proof

In this subsection, we make a few comments on the proof of the above results. For the sake of simplicity, we suppose here $\mathcal{I}=\mathcal{A}_N^K$ (full method).

In [22], P.L. Lions uses second order information on the almost critical sequences in order to prove the convergence of minimizing or min-maxing sequences in the Hartree-Fock case. Such sequences can be obtained by using for instance the Borwein-Preiss minimization principle (which is an improvement of Ekeland's variational principle since the perturbations are quadratic) in the case of a minimum, and the later work of Fang-Ghoussoub [7, 10] that deals with suitable min-max. Theorem 1 is thus the first step towards the existence of minima (Corollary 2) and saddle points (Theorem 3).

Therefore, our proof of Theorem 1 is largely inspired of the study of the Hartree-Fock functional in [22]. There are two main new difficulties.

The first is that we have lost the "crucial orthogonal invariance of the energy" (see [16]). It is linked to the fact that, in the Hartree-Fock theory, one has $\Gamma=I_N$ and so one may suppose that Γ and Λ are both diagonal, which simplifies the arguments since the problem splits into N less coupled scalar equations. For the general MC theory, we have seen (Lemma 2) that if $\Phi'=U\cdot\Phi$ where $U\in\mathcal{O}_K(\mathbb{R})$, then $\Gamma'=U\Gamma U^T$, $W'_{\Phi'}=UW_\Phi U^T$. This implies $\Lambda'=U\Lambda U^T$ in (9). Hence, we may suppose either Γ or Λ diagonal, according to what we need, but we cannot assume that they are simultaneous diagonal.

The second difficulty is that the occupation numbers (the eigenvalues $(\gamma_i^n)_{i=1}^K$ of Γ^n), which were all equal to 1 in HF, may go to 0 in a MC method; this corresponds to a lost of rank. Since we just know that the $\sqrt{\gamma_i^n}\phi_i^n$ are bounded in $H^1(\mathbb{R}^3)$ (see Lemma 3), this could obstruct the convergence of the (ϕ_i^n) when $\gamma_i^n\to 0$.

The scheme of our proof is the following:

Step 1 : We first show *3.*, thanks to the information on the first derivative with regard to c of the Palais-Smale sequence, and define K'. This allows us to work in $\mathcal{M}_N^{K'}$ and assume $\Gamma^n\geqslant\gamma I$ where $\gamma>0$. In this step, we diagonalize Γ^n.

Step 2 : We use the information on the first and second derivatives of the sequence to prove that the Lagrange multipliers cannot tend to 0. More precisely, we show that there exists a $\lambda > 0$ such that $\Lambda^n \geqslant \lambda I$. In this step, we diagonalize Λ^n.

Step 3 : We use the Euler-Lagrange equation and the nondegeneracy information of step 2 on the sequence of multipliers (Λ^n) to prove that the sequence is relatively compact.

Using Theorem 1, it is then easy to prove the existence of a minimum, as it is stated in Corollary 2

Let us now give a sketch of the proof of Theorem 3.

As in [22, 10], we use the fact that $\mathcal{E}_N^K$ is even in c and Φ in order to define appropriate min-max methods to obtain critical points. If a group G acts on two topological spaces X and Y, we recall that a function $\phi : X \to Y$ is G-*equivariant* if $\phi(g \cdot x) = g \cdot \phi(x)$ for all $g \in G$ and $x \in X$. We denote by $\mathcal{C}_G(X, Y)$ the set of all continuous G-equivariant functions. In our case, we shall consider, as in [22, 10, 26], min-maxing methods of the form:

$$\min_{f \in \mathcal{C}_G(S^{d-1}, \mathcal{M}_N^K)} \max_{(c,\Phi) \in f(S^{d-1})} \mathcal{E}_N^K(c, \Phi) \tag{16}$$

where $G = \mathbb{Z}_2 \simeq \{\pm 1\}$ acts obviously on the Euclidian sphere S^{d-1} of $\mathbb{R}^d$. It remains to find an appropriate action of $\mathbb{Z}_2$ on $\mathcal{M}_N^K$. Actually, we shall define two distinct actions and prove (i) and (ii) separately.

Suppose that we want to approximate the "true" eigenvalues of the Hamiltonian λ_d defined in (11). Let us denote by

$$\begin{array}{rccc} \Pi_N^K : & \mathcal{M}_N^K & \longrightarrow & H_a^1(\mathbb{R}^{3N}, \mathbb{R}) \\ & (c, \Phi) & \longmapsto & \Psi = \sum_I c_I \Phi_I \end{array}$$

the natural projection from the one-body space into the N-body space. One can prove that

$$\lambda_d = \min_{g \in \Theta_d} \max_{\Psi \in g(S^{d-1})} \langle \mathcal{H}\Psi, \Psi \rangle$$

where Θ_d is the collection of all odd continuous map from S^{d-1} into the sphere of $H_a^1(\mathbb{R}^{3N})$. To be able to compare our min-max with λ_d, we shall choose an action of $\mathbb{Z}_2 \simeq \{\pm 1\}$ on $\mathcal{M}_N^K$ such that $g = \Pi_N^K \circ f \in \Theta_d$ for all $\mathbb{Z}_2$-equivariant function $f : S^{d-1} \to \mathcal{M}_N^K$, that is to say $\Pi_N^K \circ f$ is odd. In standard theories, compact symmetric sets are often used and one chooses $(-) \cdot (c, \Phi) = (-c, -\Phi)$, a group action that does not have this property when N is odd.

The following group action has the requested property

$$(-) \cdot_c (c, \Phi) = (-c, \Phi).$$

Nevertheless, it allows to construct only a finite number of critical points. To see this point, let us introduce the projection

$$\begin{array}{rccc} P : & \mathcal{M}_N^K & \longrightarrow & S^{\binom{K}{N}-1} \\ & (c, \Phi) & \longmapsto & c \end{array}$$

By the Borsuk-Ulam Theorem, one obtains $\mathcal{C}_G(S^{d-1},\mathcal{M}_N^K)=\varnothing$ when $d>\binom{K}{N}$ and so only $\binom{K}{N}$ min-max will be really defined by a formula like (16).

This point being explained, we consider the following two group actions of $\mathbb{Z}_2$ on $\mathcal{M}_N^K$:

$$\begin{aligned}(-)\cdot_c(c,\Phi) &= (-c,\Phi) &(17)\\ (-)\cdot_\Phi(c,\Phi) &= (c,-\Phi). &(18)\end{aligned}$$

A function $f:S^{d-1}\longrightarrow\mathcal{M}_N^K$ is said to be $(\mathbb{Z}_2)_c$-equivariant when

$$f(x)=(c,\Phi)\implies f(-x)=(-c,\Phi)$$

and $(\mathbb{Z}_2)_\Phi$-equivariant when

$$f(x)=(c,\Phi)\implies f(-x)=(c,-\Phi).$$

We remark that $\mathcal{E}_N^K$ is both $(\mathbb{Z}_2)_c$ and $(\mathbb{Z}_2)_\Phi$-invariant on $\mathcal{M}_N^K$, that is to say

$$\mathcal{E}_N^K(c,\Phi)=\mathcal{E}_N^K(-c,\Phi)=\mathcal{E}_N^K(c,-\Phi).$$

We can now define:

$$\lambda_d^K=\min_{f\in\mathcal{C}_{(\mathbb{Z}_2)_c}(S^{d-1},\mathcal{M}_N^K)}\ \max_{(c,\Phi)\in f(S^{d-1})}\mathcal{E}_N^K(c,\Phi) \tag{19}$$

for $1\leqslant d\leqslant\binom{K}{N}$, and

$$\mu_d^K=\min_{f\in\mathcal{C}_{(\mathbb{Z}_2)_\Phi}(S^{d-1},\mathcal{M}_N^K)}\ \max_{(c,\Phi)\in f(S^{d-1})}\mathcal{E}_N^K(c,\Phi) \tag{20}$$

for all $d\geqslant 1$.

This discussion can be easily adapted to the case of partial multiconfiguration methods. Since for all $\mathcal{I}\subset\mathcal{A}_N^K$, $\mathcal{M}_N^{K,\mathcal{I}}$ is globally invariant under the two group actions, we may thus define similarly

$$\lambda_d^{K,\mathcal{I}}=\min_{f\in\mathcal{C}_{(\mathbb{Z}_2)_c}(S^{d-1},\mathcal{M}_N^{K,\mathcal{I}})}\ \max_{(c,\Phi)\in f(S^{d-1})}\mathcal{E}_N^K(c,\Phi) \tag{21}$$

for $1\leqslant d\leqslant|\mathcal{I}|$, and

$$\mu_d^{K,\mathcal{I}}=\min_{f\in\mathcal{C}_{(\mathbb{Z}_2)_\Phi}(S^{d-1},\mathcal{M}_N^{K,\mathcal{I}})}\ \max_{(c,\Phi)\in f(S^{d-1})}\mathcal{E}_N^K(c,\Phi) \tag{22}$$

for all $d\geqslant 1$.

In section 4, we show that $(\lambda_d^{K,\mathcal{I}})_{1\leqslant d\leqslant|\mathcal{I}|}$ and $(\mu_d^{K,\mathcal{I}})_{d\geqslant 1}$ yield solutions to the multiconfiguration equations, and that they allow to prove respectively (ii) and (i) of Theorem 3.

Remarks. – (i) The sequence $(\mu_d^{K,\mathcal{I}})_{d\geqslant 1}$ is the natural generalization of the one that was used in the proof for $K = N$ (HF) in [22, 10] (see also [6] for the relativistic case), and its study will use exactly the same ideas.

(ii) We suppose here $\mathcal{I} = \mathcal{A}_N^K$. A basis $\mathcal{B} = (\phi_i)_{i\in\mathbb{N}^*}$ of $H^1(\mathbb{R}^3)$ being fixed, it is also natural to introduce, for all $K \geqslant N$ and $d \geqslant 1$ such that $\binom{K}{N} \geqslant d$

$$\lambda_{\mathcal{B},d}^K = \min_{V\subset V_{\mathcal{B}}^K,\ dim(V)=d} \max_{\substack{\Psi\in V,\\ \|\Psi\|_{L^2}=1}} \langle \mathcal{H}\Psi, \Psi\rangle$$

where $V_{\mathcal{B}}^K = span(|\phi_{i_1}, ..., \phi_{i_N}\rangle,\ 1 \leqslant i_k \leqslant K)$. This method is called by chemists *Full Configuration-Interaction.* We shall prove in section 4.4 that

$$\lambda_d \leqslant \lambda_d^K \leqslant \lambda_{\mathcal{B},d}^K$$

and that $\lim_{K\to+\infty} \lambda_{\mathcal{B},d}^K = \lambda_d$.

3.3 About the algorithms

We now make some comments on the connection between our min-max defining $\lambda_d^{K,\mathcal{I}}$ and the algorithms used by chemists. Although there is a lot of different approaches, the general form of the numerical algorithms used to calculate the $(d-1)^{th}$ excited state with a fixed geometry can be summarized as follows (see for instance [30, 31, 29]):

1. Start with $(c_{\mathcal{I}}, \Phi)$ obtained from a previous Hartree-Fock or Configuration-Interaction calculation.
2. Compute the matrix $H_\Phi^{\mathcal{I}}$ of the quadratic form $\mathcal{E}_N$ associated to $\mathcal{H}$ on the subspace $Span(\Phi_I,\ I \in \mathcal{I})$ where $\Phi_I = |\phi_{i_1}, ..., \phi_{i_N}\rangle$ if $I = \{i_1, ..., i_N\}$.
3. Find $c'_{\mathcal{I}}$ as the d^{th} eigenvector of this matrix.
4. This $c'_{\mathcal{I}}$ being fixed, minimize the energy with regard to Φ to obtain a new Φ'.
5. Replace $(c_{\mathcal{I}}, \Phi)$ by $(c'_{\mathcal{I}}, \Phi')$ and return to step 2.

According to chemists, the aim of such an algorithm is to solve a problem of the form

$$\begin{aligned}\tilde{\lambda}_d^{K,\mathcal{I}} &= \min_{\substack{\Phi=(\phi_i)_{i=1}^K,\\ \int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij}}} \min_{\substack{V\subset V^{K,\mathcal{I}}(\Phi),\\ dim(V)=d}} \max_{\substack{\Psi\in V,\\ \|\Psi\|_{L^2}=1}} \langle \mathcal{H}\Psi, \Psi\rangle && (23)\\ &= \min_{\substack{\Phi=(\phi_i)_{i=1}^K,\\ \int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij}}} \lambda_d(\Phi) && (24)\end{aligned}$$

where $V^{K,\mathcal{I}}(\Phi) = Span(\Phi_I,\ I \in \mathcal{I})$ and $\lambda_d(\Phi)$ is the d^{th} eigenvalue of the matrix $H_\Phi^{\mathcal{I}} = (\langle \Phi_I, \mathcal{H}\Phi_J\rangle)_{I,J\in\mathcal{I}}$. In other words, *"the MCSCF energy results from minimizing the appropriate eigenvalue of the Hamiltonian matrix with respect to orbital variations"* [29].

All the sets in the "min" part of (23) can be written $f(S^{d-1})$ with a $f \in \mathcal{C}_{(\mathbb{Z}_2)_c}(S^{d-1}, \mathcal{M}_N^{K,\mathcal{I}})$ and so one easily obtains

$$\lambda_d \leqslant \lambda_d^{K,\mathcal{I}} \leqslant \tilde{\lambda}_d^{K,\mathcal{I}}.$$

However, it is not obvious that the min-max method (23) yields the existence of critical points. Let us notice that this may be viewed as a special case of the following abstract problem: let X be a Banach space, and $A : X \to \mathcal{S}_N(\mathbb{R})$ that is bounded and smooth ($\mathcal{S}_N(\mathbb{R})$ is the set of all $N \times N$ symmetric real matrices). We denote by $\lambda_d(x)$ the d^{th} eigenvalue of $A(x)$ and consider

$$\begin{aligned} \lambda_d &= \min_{x \in X} \lambda_d(x) \\ &= \min_{x \in X} \min_{dim(V)=d} \max_{\substack{v \in V, \\ \|v\|=1}} \langle A(x)v, v\rangle. \end{aligned}$$

We introduce

$$F(x,v) = \langle A(x)v, v\rangle$$

and want to know if this method gives a critical point of F on $X \times S^{N-1}$.

To see that critical points may not exist when degeneracies of eigenvalues occur, we consider a simple example due to Rellich and adapted by Reed and Simon [27]:

$$A(x) = \begin{pmatrix} \sin(x_1) & \sin(x_2) \\ \sin(x_2) & -\sin(x_1) \end{pmatrix}$$

for $x = (x_1, x_2) \in X = \mathbb{R}^2$. We have

$$\lambda_2(x) = \sqrt{\sin(x_1)^2 + \sin(x_2)^2}$$

and so

$$\lambda_2 = 0 = \lambda_2(0).$$

But $\frac{\partial F}{\partial x_1}(0,v) = \frac{\partial F}{\partial x_2}(0,v) = 0$ if and only if $v = 0$, and this method does not give a critical point of F on $\mathbb{R}^2 \times S^1$.

If $X = \mathbb{R}$ and A is analytic, a simplification appears due to a theorem of Rellich (see [27]), and critical points exist even when the optimal eigenvalue is degenerate. We now show that the algorithm described previously may possibly not converge. Consider for instance

$$A(x) = \sin(x) \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

for $x \in X = \mathbb{R}$. We have

$$\lambda_2(x) = \sqrt{2}|\sin(x)|$$

and so

$$\lambda_2 = 0 = \lambda_2(0).$$

If we denote v_1 and v_2 two eigenvectors of $A'(0) = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$ such that $\langle v_i, v_j\rangle = \delta_{ij}$, it is then easy to see that $(0, v)$ with $v = (v_1 + v_2)/\sqrt{2}$ is a critical point of F on $\mathbb{R} \times S^1$.

But for any initial guess $x_0 \in [\pi/2; \pi/2]$ such that $x_0 \neq 0$, the algorithm does not converge and oscillates between $x = \pi/2$ and $-\pi/2$. This shows that even if critical points exist, degeneracies may obstruct convergence.

In the case of the MC method, oscillations are frequently obtained when using the algorithm described before.

All these difficulties explain why we focused on the more "theorical" min-max $\lambda_d^{K,\mathcal{I}}$ that takes into account the strong nonlinearity of $\mathcal{E}_N^K$.

4 Proofs

This section is devoted to the proof of our results. Some of them are adaptations of the proofs that recently appear in [19], but we shall give here all the details for the reader's convenience.

4.1 Some preliminaries

In this section, we give some basic properties that will be used in the proof of our results.

4.1.1 Properties of $\mathcal{E}_N^K$

Lemma 3. *(i) When it is defined by the formula (8), $\mathcal{E}_N^K$ is continuous on $\mathcal{M}_N^K$, and weakly lower semi-continuous on $\mathbb{R}^{\binom{K}{N}} \times (H^1(\mathbb{R}^3))^K$.*
(ii) If $(c, \Phi) \in \mathcal{M}_N^K$ is such that $\Gamma = diag(\gamma_1, ..., \gamma_K)$, then one has

$$\mathcal{E}_N^K(c, \Phi) \geqslant \sum_{i=1}^{K} \frac{\gamma_i}{2}(\|\nabla\phi_i\|^2_{L^2(\mathbb{R}^3)} - C\|\nabla\phi_i\|_{L^2(\mathbb{R}^3)}). \tag{25}$$

In particular, $\mathcal{E}_N^K$ is bounded from below on $\mathcal{M}_N^K$. If $(c^n, \Phi^n) \in \mathcal{M}_N^K$ is such that $\mathcal{E}_N^K(c^n, \Phi^n)$ is bounded, then $(\sqrt{\Gamma^n} \cdot \Phi^n)$ is bounded in $(H^1(\mathbb{R}^3))^K$.

Proof. – The continuity of $\mathcal{E}_N^K$ on $\mathcal{M}_N^K$ is obvious. To prove its weakly lower semi-continuity, we consider a sequence (c^n, Φ^n) in $\mathbb{R}^{\binom{K}{N}} \times (H^1(\mathbb{R}^3))^K$, such that $c^n \to c$ and $\Phi^n \rightharpoonup \Phi$ weakly in $(H^1(\mathbb{R}^3))^K$. We introduce $L = \liminf_{n\to+\infty} \mathcal{E}_N^K(c^n, \Phi^n)$ and suppose (by extracting a subsequence if necessary) that $\Phi^n \to \Phi$ strongly in $(L^2_{loc}(\mathbb{R}^3))^K$ and a.e., and that $\mathcal{E}_N^K(c^n, \Phi^n) \to L$. Since for all $k_2 ... k_N$,

$$\sum_{i=1}^{K} \alpha^n_{i,k_2...k_N} \phi_i^n \rightharpoonup \sum_{i=1}^{K} \alpha_{i,k_2...k_N} \phi_i$$

weakly in $H^1(\mathbb{R}^3)$ and strongly in $L^2_{loc}(\mathbb{R}^3)$, we have

$$\int_{\mathbb{R}^3} V\left(\sum_{i=1}^{K} \alpha^n_{i,k_2\ldots k_N}\phi^n_i\right)^2 \to \int_{\mathbb{R}^3} V\left(\sum_{i=1}^{K} \alpha_{i,k_2\ldots k_N}\phi_i\right)^2$$

$$\int_{\mathbb{R}^3}\left|\sum_{i=1}^{K} \alpha_{i,k_2\ldots k_N}\nabla\phi_i\right|^2 \leqslant \liminf_{n\to+\infty}\int_{\mathbb{R}^3}\left|\sum_{i=1}^{K} \alpha^n_{i,k_2\ldots k_N}\nabla\phi^n_i\right|^2 .$$

But Fatou's lemma yields

$$\iint_{\mathbb{R}^6} \frac{\left(\sum_{i,j=1}^{K} \alpha_{i,j,k_3\ldots,k_N}\phi_i(x)\phi_j(y)\right)^2}{|x-y|}dxdy$$

$$\leqslant \liminf_{n\to+\infty}\iint_{\mathbb{R}^6} \frac{\left(\sum_{i,j=1}^{K} \alpha^n_{i,j,k_3\ldots,k_N}\phi^n_i(x)\phi^n_j(y)\right)^2}{|x-y|}dxdy$$

which easily concludes the proof of (i).

The proof of (25) is standard: we recall that

$$\int_{\mathbb{R}^3}\frac{\phi(x)^2}{|x-\bar{x}|}dx \leqslant C'\|\phi\|_{L^2(\mathbb{R}^3)}\|\nabla\phi\|_{L^2(\mathbb{R}^3)}$$

for all $\phi\in H^1(\mathbb{R}^3)$ and all $\bar{x}\in\mathbb{R}^3$ (C' is a constant independent of $\bar{x}$ and ϕ). Let $(c,\Phi)\in\mathcal{M}_N^K$ be such that $\Gamma = diag(\gamma_1\ldots\gamma_K)$. We have

$$\begin{aligned}
\mathcal{E}_N^K(c,\Phi) &= \left\langle\left(\left(-\frac{\Delta}{2}+V\right)\Gamma + W_\Phi\right)\cdot\Phi\,,\,\Phi\right\rangle\\
&\geqslant \left\langle\left(-\frac{\Delta}{2}+V\right)\Gamma\cdot\Phi\,,\,\Phi\right\rangle\\
&= \sum_{i=1}^{K}\gamma_i\left(\frac{1}{2}\int_{\mathbb{R}^3}|\nabla\phi_i|^2 + \int_{\mathbb{R}^3}V(\phi_i)^2\right)\\
&\geqslant \sum_{i=1}^{K}\frac{\gamma_i}{2}\left(\|\nabla\phi_i\|^2_{L^2(\mathbb{R}^3)} - 2ZC'\|\nabla\phi_i\|_{L^2(\mathbb{R}^3)}\right)
\end{aligned}$$

which obviously implies that $\mathcal{E}_N^K$ is bounded from below.

Finally, if we take an arbitrary sequence (c^n,Φ^n) in $\mathcal{M}_N^K$ such that $\mathcal{E}_N^K(c^n,\Phi^n)$ is bounded, we can find for each n, a $U_n\in\mathcal{O}_K(\mathbb{R})$ such that $U_n\Gamma^nU_n^T = diag(\gamma_1^n\ldots\gamma_K^n)$. We then use the latter inequality and the fact that $\mathcal{O}_K(\mathbb{R})$ is compact to obtain $(\sqrt{\Gamma^n}\cdot\Phi^n)$ bounded in $(H^1(\mathbb{R}^3))^K$. □

Remark. – As it has been pointed out by G. Friesecke in [8], $\mathcal{E}_N$ is not weakly lower semi-continuous on $H^1_a(\mathbb{R}^{3N})$. This shows the benefit to work in the one-body space $\mathcal{M}_N^K$.

4.1.2 About the inequality $Z > N-1$

As in [21, 22, 10, 8], our results are stated with $Z > N-1$ (i.e. for neutral molecules and positive ions). The reason is that we shall often use the following

Lemma 4. *For all $k \geqslant 1$ and all $0 \leqslant m < Z$, there exists a k-dimensional subspace $V_{k,m}$ of $H^1(\mathbb{R}^3)$ and a $\delta_{k,m} > 0$ such that*

$$\int_{\mathbb{R}^3} \frac{1}{2}|\nabla\phi|^2 + \left(V + \mu * \frac{1}{|r|}\right)\phi^2 \leqslant -\delta_{k,m} < 0$$

for all $\phi \in V_{k,m}$ with $\|\phi\|_{L^2(\mathbb{R}^3)} = 1$, and all bounded non-negative measure μ on $\mathbb{R}^3$ that satisfies $\mu(\mathbb{R}^3) \leqslant m$.

Moreover, $V_{k,m}$ can be chosen such that $V_{k,m} = span(\phi_1, ..., \phi_k)$ where the $(\phi_i)_{i=1}^k$ are radially symmetric functions in $\mathcal{D}(\mathbb{R}^3)$, with disjoint supports.

In particular, the Hamiltonian

$$H_\mu = -\frac{1}{2}\Delta + V + \mu * \frac{1}{|r|}$$

admit at least k eigenvalues strictly below $-\delta_{k,m}$.

Proof. – See the proof of a similar lemma in [22, 10]. $\square$

4.2 Proof of Theorem 1

Our method of proof is in the spirit of [22], with the additional difficulties quoted before.

Let (c^n, Φ^n) be as in the Theorem. Since the method is natural, we may suppose that for all n, $\Gamma^n = diag(\gamma_1^n ... \gamma_K^n)$, with $0 \leqslant \gamma_i^n \leqslant 1$ and $\gamma_1^n \geqslant ... \geqslant \gamma_K^n$ (we recall that $\Gamma^n = I_N$ if $K = N$). We may also assume that $c_I^n \to c_I$ for all $I \in \mathcal{I}$. Thus each γ_i^n converges to some $\gamma_i \geqslant 0$.

By lemma 3, for all $i = 1...K$, $\gamma_i^n \int_{\mathbb{R}^3} |\nabla\phi_i^n|^2$ is bounded, so either $\gamma_i = 0$ or $(\phi_i^n)_{n\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$.

Step 1 : Let us suppose for instance that $\gamma_K^n \to 0$ (this cannot happen when $K = N$ since $\gamma_i^n = 1$ for all $i = 1, ..., N$ and $n \in \mathbb{N}$). Since $(\phi_K^n)_{n\in\mathbb{N}}$ is bounded in $L^2(\mathbb{R}^3)$, we may assume –by extracting subsequences if necessary– that $\sqrt{\gamma_K^n}\phi_K^n \to 0$ in $L^2(\mathbb{R}^3)$ and $\sqrt{\gamma_K^n}\phi_K^n \rightharpoonup 0$ weakly in $H^1(\mathbb{R}^3)$. We now show that this last convergence is strong.

Let $I \in \mathcal{I}$ be such that $K \in I$. Since $\mathcal{E}$ is quadratic with regard to the (c_I), we have

$$\mathcal{E}_N^K(c^n, \Phi^n) = \left(\sum_{i\in I}\int_{\mathbb{R}^3} |\nabla\phi_i^n|^2\right)(c_I^n)^2 + A_n(c_I^n)^2 + B_n c_I^n + C_n$$

where $A_n(c_I^n)^2$ and $B_n c_I^n \to 0$: for instance one of the terms appearing in $A_n(c_I^n)^2$ is

$$(c_I^n)^2 \int_{\mathbb{R}^3} \frac{\phi_K^n(x)^2}{|x|} dx \leqslant \int_{\mathbb{R}^3} \frac{(\sqrt{\gamma_K^n}\phi_K^n(x))^2}{|x|} dx \to 0.$$

The second assumption of Theorem 1 now yields the existence of a bounded sequence of Lagrange multipliers $(\beta^n)_{n\in\mathbb{N}}$ such that

$$\frac{\partial \mathcal{E}_N^K}{\partial c_I}(c^n,\Phi^n) = 2\left(\sum_{i\in I}\int_{\mathbb{R}^3}|\nabla\phi_i^n|^2\right)(c_I^n) + 2A_n c_I^n + B_n + \beta^n c_I^n \to 0.$$

Multiplying by c_I^n, we obtain

$$\left(\sum_{i\in I}\int_{\mathbb{R}^3}|\nabla\phi_i|^2\right)(c_I^n)^2 \to 0.$$

as $n\to+\infty$. Since we have

$$\gamma_K^n = \sum_{I,\ K\in I}(c_I^n)^2 = \sum_{I\in\mathcal{I},\ K\in I}(c_I^n)^2,$$

this shows that $\sqrt{\gamma_K^n}\phi_K^n \to 0$ strongly in $H^1(\mathbb{R}^3)$.

Let $K'\geqslant N$ be such that $\gamma_{K'+1}=0$ and $\gamma_{K'}\neq 0$. By the same argument, one has $\sqrt{\gamma_i^n}\phi_i^n\to 0$ strongly in $H^1(\mathbb{R}^3)$ for $i=K'+1,...,K$.

We now introduce $\mathcal{I}'=\mathcal{I}\cap\mathcal{A}_N^{K'}$,

$$\tilde{c}_I^n = \frac{c_I^n}{\sqrt{\sum_{J\subset\{1...K'\}}(c_J^n)^2}} \quad \text{for all}\quad I\in\mathcal{A}_N^{K'},$$

$$\text{and}\quad \tilde{\Phi}^n = (\phi_1^n...\phi_{K'}^n)^T$$

so that $(\tilde{c}^n,\tilde{\Phi}^n)\in\mathcal{M}_N^{K',\mathcal{I}'}$. If $(\tilde{\Psi}^n)$ is the corresponding sequence of wave functions, the previous arguments imply that we have $\Psi^n=\tilde{\Psi}^n+r^n$ where $r^n\to 0$ in $H_a^1(\mathbb{R}^{3N})$. The convergence of $(\phi_i^n)_{i=1}^{K'}$ will imply those of $\tilde{\Psi}^n$ and then Ψ^n. The new sequence $(\tilde{c}^n,\tilde{\Phi}^n)_{n\in\mathbb{N}}$ satisfies the assumptions 1), 2), 3) of Theorem 1 on $\mathcal{M}_N^{K',\mathcal{I}'}$ and also $\tilde{\Gamma}^n\geqslant\gamma I_{K'}$ with $\gamma=\gamma_{K'}>0$. We now work with this new Palais-Smale sequence and omit the $\sim$ for simplicity.

Step 2 : The first order condition also yields the existence of a $K'\times K'$ symmetric matrix Λ^n such that

$$\frac{\partial\mathcal{E}_N^K}{\partial\Phi}(c^n,\Phi^n) = \left(\left(-\frac{\Delta}{2}+V\right)\Gamma^n + 2W_{\Phi^n}\right)\cdot\Phi^n + \Lambda^n\cdot\Phi^n \to 0. \tag{26}$$

We now prove that there exists a $\lambda>0$ such that $\Lambda^n\geqslant\lambda I_{K'}$. Let U_n be an orthogonal matrix such that $\check{\Lambda}^n := U_n\Lambda U_n^T = diag(\lambda_1^n...\lambda_{K'}^n)$. We work in this step with $(\check{c}_n,\check{\Phi}_n)=U_n\cdot(c_n,\Phi_n)$. The second order condition of Theorem 1 implies, for all $i=1,...,K'$ and all ϕ in a closed subspace F_n of $H^1(\mathbb{R}^3)$ of codimension at most $K+j$

$$\check{\gamma}_{ii}^n\int_{\mathbb{R}^3}|\nabla\phi|^2 + \int_{\mathbb{R}^3}\left(\check{\gamma}_{ii}^n V + \check{\gamma}_{ii}^n\rho_i^n * \frac{1}{|r|} + \lambda_i^n + \check{\gamma}_{ii}^n\varepsilon_i^n\right)\phi^2 - N(N-1)D_i^n \geqslant 0$$

where $\varepsilon_i^n \to 0$ and

$$\rho_i^n = \frac{N(N-1)}{\check{\gamma}_{ii}^n} \sum_{k_3 \dots k_N} \left(\sum_k \check{\alpha}_{i,k,k_3 \dots,k_N}^n \check{\phi}_k^n \right)^2$$

$$D_i^n = \sum_{k_3 \dots k_N} \iint_{\mathbb{R}^6} \frac{\left(\phi(x) \sum_k \check{\alpha}_{i,k,k_3 \dots,k_N}^n \check{\phi}_k^n(x)\right) \left(\phi(y) \sum_k \check{\alpha}_{i,k,k_3 \dots,k_N}^n \check{\phi}_k^n(y)\right)}{|x-y|} dxdy.$$

Hence we obtain (it is easy to see that $D_i^n \geqslant 0$)

$$\int_{\mathbb{R}^3} |\nabla \phi|^2 + \int_{\mathbb{R}^3} \left(V + \rho_i^n * \frac{1}{|r|} + \frac{\lambda_i^n}{\check{\gamma}_{ii}^n} + \varepsilon_i^n \right) \phi^2 \ \geqslant \ 0$$

for all $\phi \in F_n$.

Since we have

$$\int_{\mathbb{R}^3} \rho_i^n = \frac{N(N-1)}{\check{\gamma}_{ii}^n} \sum_{k,k_3 \dots k_N} (\check{\alpha}_{i,k,k_3 \dots,k_N}^n)^2 = N-1 < Z,$$

we can use Lemma 4 and the method of [22] to obtain a $\delta > 0$ such that

$$\forall n, \ \frac{\lambda_i^n}{\check{\gamma}_{ii}^n} + \varepsilon_i^n \geqslant \delta$$

and thus we obtain from $\check{\Gamma}^n = U_n \Gamma^n U_n^T \ \geqslant \ \gamma I_{K'}$ (and for n large enough)

$$\lambda_i^n \geqslant \check{\gamma}_{ii}^n(\delta/2) \geqslant \gamma(\delta/2) = \lambda > 0.$$

This shows that $\check{\Lambda}^n \ \geqslant \ \lambda I_{K'}$ and so $\Lambda^n \ \geqslant \ \lambda I_{K'}$. But (26) yields

$$\mathcal{E}_N^K(c^n, \Phi^n) + \langle W_{\Phi^n} \cdot \Phi^n, \Phi^n \rangle + Tr(\Lambda^n) \to 0$$

and so (Λ^n) is bounded. We finally obtain (up to subsequences) $\Lambda^n \to \Lambda > 0$.

Step 3 : Since $\gamma_i^n \geqslant \gamma > 0$, the $(\phi_i^n)_{n \in \mathbb{N}}$ are bounded in $H^1(\mathbb{R}^3)$ and thus we may assume that ϕ_i^n converges weakly in $H^1(\mathbb{R}^3)$ (and a.e. in $\mathbb{R}^3$) to some ϕ_i. We now prove that this convergence is strong.

Passing to the limit in (26), we get

$$\left(\left(-\frac{\Delta}{2} + V \right) \Gamma + 2W_\Phi \right) \cdot \Phi + \Lambda \cdot \Phi = 0.$$

This implies

$$\begin{aligned} \limsup_{n \to +\infty} \langle \Lambda^n \cdot \Phi^n, \Phi^n \rangle \ &= \ - \liminf_{n \to +\infty} \left\langle \left(\left(-\frac{\Delta}{2} + V \right) \Gamma^n + 2W_{\Phi^n} \right) \cdot \Phi^n, \Phi^n \right\rangle \\ &\leqslant \ - \left\langle \left(\left(-\frac{\Delta}{2} + V \right) \Gamma + 2W_\Phi \right) \cdot \Phi, \Phi \right\rangle = \langle \Lambda \cdot \Phi, \Phi \rangle, \end{aligned}$$

by using the same arguments as the one used to show that $\mathcal{E}_N^K$ is weakly lower semi-continuous on $\mathbb{R}^{\binom{K}{N}} \times (H^1(\mathbb{R}^3))^K$. So $\Phi^n \to \Phi$ in $(L^2(\mathbb{R}^3))^{K'}$, and then in $(H^1(\mathbb{R}^3))^{K'}$. The convergence of (Ψ^n) follows.

Step 4 : It remains to show that, when $\mathcal{I} = \mathcal{A}_N^K$, $K' = K$ or $K-1$. This is obtained by the same proof as in [16, 9] to show the inequality $E_N^{K+2} < E_N^K$ and we refer the reader to these papers. Let us notice that this uses the analyticity of the orbitals, independently proved in Proposition 4. This ends the proof of Theorem 1. □

4.3 Proof of Corollary 2

Let (c^n, Φ^n) be a minimizing sequence of $E_N^{K,\mathcal{I}}$. We use the minimization principle of Borwein and Preiss (see [3, 10]) to obtain a new minimizing sequence $(\tilde{c}^n, \tilde{\Phi}^n) \in \mathcal{M}_N^{K,\mathcal{I}}$ such that

1. $\|\tilde{\Phi}^n - \Phi^n\|_{(H^1(\mathbb{R}^3))^K} \to 0$ and $|\tilde{c}_I^n - c_I^n| \to 0$ when $I \in \mathcal{I}$

2. there exists a sequence $(\hat{c}^n, \hat{\Phi}^n) \in \mathcal{M}_N^{K,\mathcal{I}}$ such that

$$\|\hat{\Phi}^n - \Phi^n\|_{(H^1(\mathbb{R}^3))^K} \to 0, \quad |\hat{c}_I^n - c_I^n| \to 0 \text{ when } I \in \mathcal{I}, \text{ and}$$

$$\forall n \in \mathbb{N}, \quad \mathcal{E}_N^K(\tilde{c}^n, \tilde{\Phi}^n) + \frac{1}{n}\mathcal{Q}_n(\tilde{c}^n, \tilde{\Phi}^n) = \min_{\mathcal{M}_N^{K,\mathcal{I}}} \left\{ \mathcal{E}_N^K + \frac{1}{n}\mathcal{Q}_n \right\}$$

where

$$\mathcal{Q}_n(c, \Phi) = \frac{1}{2}\left(\|c - \hat{c}_n\|^2 + \|\Phi - \hat{\Phi}_n\|^2 \right).$$

This new minimizing sequence $(\tilde{c}^n, \tilde{\Phi}^n)$ now satisfies the assumptions of Theorem 1, with $j = 0$. □

4.4 Proof of Theorem 3

We recall that we shall prove (i) and (ii) by using respectively the sequences $(\mu_d^{K,\mathcal{I}})_{d \geqslant 1}$ and $(\lambda_d^{K,\mathcal{I}})_{1 \leqslant d \leqslant |\mathcal{I}|}$, defined by the formulas (22) and (21).

Step 1 : Existence. We use here the Theorem of Fang-Ghoussoub [7, 10]. According to their terminology, we easily see that the min-max (21,22) are defined with $(\mathbb{Z}_2)_{c/\Phi}$-homotopic classes of dimension d for each d and, as in the Hartree-Fock case, we may thus obtain a sequence (c^n, Φ^n) that satisfies the assumptions of Theorem 1 with $j = d$. Therefore, one obtains the convergence of a subsequence in the sense of Theorem 1, and the existence of critical point (c', Φ') of $\mathcal{E}_N^{K'}$ on $\mathcal{M}_N^{K',\mathcal{I}'}$ with $K' \leqslant K$. One may add any $(\phi_{K'+1}, ..., \phi_K)$ to obtain solutions of (9) with a $\Lambda \geqslant 0$.

Step 2 : Study of $(\mu_d^{K,\mathcal{I}})_{d \geqslant 1}$. Our proof uses ideas of [22, 10]. Since in this step, $K \geqslant N$ and $\mathcal{I}$ are fixed, we shall forget these subscripts. We show that $-\infty < \mu_d \leqslant \mu_{d+1} < 0$ for all $d \geqslant 1$ and that $\lim_{d \to +\infty} \mu_d = 0$.

The fact that $-\infty < \mu_d \leqslant \mu_{d+1}$ is obvious. Let be $n_d = K \cdot d$. For each $d \geqslant 1$, by lemma 4, there exists a n_d-dimensional subspace V_d of $H^1(\mathbb{R}^3)$ and a $\delta > 0$ such that

$$\int_{\mathbb{R}^3} \frac{1}{2}|\nabla \phi|^2 + \left(V + m * \frac{1}{|r|} \right) \phi^2 \leqslant -\delta < 0$$

for all $\phi \in V_d$ with $\|\phi\|_{L^2(\mathbb{R}^3)} = 1$, and all bounded non-negative measure m on $\mathbb{R}^3$ which satisfies $m(\mathbb{R}^3) = N-1 < Z$. Let $(\phi_1, ..., \phi_{n_d})$ be a L^2-orthogonal basis of V_d, of radially symmetric functions in $\mathcal{D}(\mathbb{R}^3)$ with disjoints supports and such that $\int_{\mathbb{R}^3} (\phi_i)^2 = 1$. For the sake of simplicity, we may suppose that $\{1, ..., N\} \in \mathcal{I}$. We consider :

$$\begin{array}{rccc} f: & S^{d-1} & \longrightarrow & \mathcal{M}_N^{K,\mathcal{I}} \\ & (\alpha_1, ..., \alpha_d) & \longmapsto & \left(\begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \begin{pmatrix} \alpha_1 \phi_1 + \cdots + \alpha_d \phi_d \\ \vdots \\ \alpha_1 \phi_{d(K-1)+1} + \cdots + \alpha_d \phi_{Kd} \end{pmatrix} \right) \end{array}$$

f is a continuous $(\mathbb{Z}_2)_\Phi$-equivariant function and

$$\begin{aligned} \mathcal{E}_N^K(f(\alpha_1, ..., \alpha_d)) &= \mathcal{E}_N(|\alpha_1\phi_1 + \cdots + \alpha_d\phi_d, ..., \alpha_1\phi_{d(N-1)+1} + \cdots + \alpha_d\phi_{Nd}\rangle) \\ &= \mathcal{E}_N\left(\sum_{i_1=1}^{d} \cdots \sum_{i_N=(N-1)d+1}^{Nd} \alpha_{i_1} \cdots \alpha_{i_N-(N-1)d} |\phi_{i_1}, ..., \phi_{i_N}\rangle \right) \\ &= \sum_{i_1=1}^{d} \cdots \sum_{i_N=(N-1)d+1}^{Nd} (\alpha_{i_1} \cdots \alpha_{i_N-(N-1)d})^2 \mathcal{E}_N(|\phi_{i_1}, ..., \phi_{i_N}\rangle) \\ &\quad \text{since the } (\phi_i) \text{ have disjoint supports.} \\ &= \sum_{i_1=1}^{d} \cdots \sum_{i_N=(N-1)d+1}^{Nd} (\alpha_{i_1} \cdots \alpha_{i_N-(N-1)d})^2 \mathcal{E}^{HF}(\phi_{i_1}, ..., \phi_{i_N}). \end{aligned}$$

We recall that

$$\mathcal{E}^{HF}(\phi_1, ..., \phi_N) = \sum_{i=1}^{N} \int_{\mathbb{R}^3} \left(\frac{1}{2}|\nabla\phi_i|^2 + V(\phi_i)^2 \right)$$

$$+\frac{1}{2}\int_{\mathbb{R}^3} \left(\left(\sum_{j=1}^{N} (\phi_j)^2 \right) * \frac{1}{|r|} \right) \left(\sum_{i=1}^{N} (\phi_i)^2 \right) - \frac{1}{2} \sum_{i,j=1}^{N} \int_{\mathbb{R}^3} \left((\phi_i\phi_j) * \frac{1}{|r|} \right) (\phi_i\phi_j),$$

so that

$$\mathcal{E}^{HF}(\phi_1, ..., \phi_N) = \sum_{i=1}^{N} \int_{\mathbb{R}^3} \left(\frac{1}{2}|\nabla\phi_i|^2 + \left(V + m_i * \frac{1}{|r|} \right) (\phi_i)^2 \right)$$

$$-\frac{1}{2} \sum_{i \neq j=1}^{N} \int_{\mathbb{R}^3} \left((\phi_i\phi_j) * \frac{1}{|r|} \right) (\phi_i\phi_j)$$

where

$$m_i = \sum_{j=1,\ j\neq i}^{N} (\phi_j)^2 \quad \text{and} \quad \int_{\mathbb{R}^3} m_i = N-1.$$

Since $\int_{\mathbb{R}^3}\left((\phi_i\phi_j)*\frac{1}{|r|}\right)(\phi_i\phi_j)\geqslant 0$ for all $i\neq j$, we finally obtain

$$\begin{aligned}\mathcal{E}_N^K(f(\alpha_1,...,\alpha_d)) &\leqslant \sum_{i_1=1}^{d}\cdots\sum_{i_N=1}^{d}(\alpha_{i_1}\cdots\alpha_{i_N})^2(-N\delta)\\ &= -N\delta<0\end{aligned}$$

for all $(\alpha_1,...,\alpha_d)\in S^{d-1}$, which shows that $\mu_d\leqslant \max_{f(S^{d-1})}\mathcal{E}_N^K<0$.

To show that $\lim_{d\to+\infty}\mu_d=0$, we classically consider a sequence (V_d) of finite dimensional subspaces of $(H^1(\mathbb{R}^3))^K$ such that $dimV_d=d$ and $\bigcup_d V_d$ is dense in $(H^1(\mathbb{R}^3))^K$, and denote $W_d=V_d^{\perp}$. Since for all $d\geqslant 1$, $\mu_d<0$, there exists a $(\mathbb{Z}_2)_\Phi$-equivariant continuous f_d such that

$$\mu_d\leqslant \max_{f_d(S^{d-1})}\mathcal{E}_N^K<\frac{\mu_d}{2}.$$

By the Borsuk-Ulam Theorem, there exists $(c_d,\Phi_d)\in f_d(S^{d-1})$ such that $\Phi_d\in W_{d-1}$ and

$$\mathcal{E}_N^K(c_d,\Phi_d)\leqslant\frac{\mu_d}{2}<0.$$

Since (c_d) is bounded and $\Phi_d\rightharpoonup 0$ weakly in $(H^1(\mathbb{R}^3))^K$, we obtain by lemma 3

$$\liminf_{d\to+\infty}\mathcal{E}_N^K(c_d,\Phi_d)=0$$

which implies $\lim_{d\to+\infty}\mu_d=0$.

For each $d\geqslant 1$, there exists (c^d,Φ^d) and $\Lambda^d\geqslant 0$ such that $\mathcal{E}_N^K(c^d,\Phi^d)=\mu_d$ and

$$\left(\left(-\frac{\Delta}{2}+V\right)\Gamma^d+2W_{\Phi^d}\right)\cdot\Phi^d+\Lambda_d\cdot\Phi^d=0$$

This yields

$$\left\langle W_{\Phi^d}\cdot\Phi^d\,,\,\Phi^d\right\rangle+tr(\Lambda_d)=-\mathcal{E}_N^K(c^d,\Phi^d)=-\mu_d\longrightarrow_{d\to+\infty}0^+$$

and so

$$\left\langle W_{\Phi^d}\cdot\Phi^d\,,\,\Phi^d\right\rangle\to 0\quad\text{and}\quad\Lambda_d\to 0 \tag{27}$$

as $d\to+\infty$. By Lemma 3, $(\sqrt{\Gamma^d}\Phi^d)_d$ is bounded in $(H^1(\mathbb{R}^3))^K$, so one may suppose that $c_I^d\phi_i^d\rightharpoonup\phi_{I,i}$ weakly in $H^1(\mathbb{R}^3)$, strongly in $L^2_{loc}(\mathbb{R}^3)$ and a.e., for all $i=1,...,K$ and all I such that $i\in I$. But $\phi_{I,i}=0$ by (27) and this implies

$$\left\langle\left(-\frac{\Delta}{2}+V\right)\Gamma^d\cdot\Phi^d\,,\,\Phi^d\right\rangle\longrightarrow 0$$

as $d\to+\infty$. We now easily obtain $\sqrt{\Gamma^d}(\nabla\Phi^d)\to 0$ strongly in $(L^2(\mathbb{R}^3))^K$, thanks to the weakly lower semi-continuity of this last expression.

This ends the proof of (i).

Step 3 : Study of $(\lambda_d^{K,\mathcal{I}})_{1\leqslant d\leqslant|\mathcal{I}|}$. We first choose a sequence (Ψ_d) of eigenvectors of $\mathcal{H}$ associated to the eigenvalues (λ_d) such that $\int_{\mathbb{R}^{3N}}\Psi_i\Psi_j=\delta_{ij}$ and

$$\begin{aligned}\lambda_d=\mathcal{E}_N(\Psi_d) &= \max_{\substack{\Psi\,\in\, span(\Psi_1...\Psi_d),\\ \|\Psi\|_{L^2}=1}} \mathcal{E}_N(\Psi)\\ &= \min_{\substack{\Psi\,\in\, span(\Psi_1...\Psi_{d-1})^{\perp},\\ \|\Psi\|_{L^2}=1}} \mathcal{E}_N(\Psi).\end{aligned}$$

We denote by $V_d=span(\Psi_1...\Psi_d)$ and $W_d=(V_d)^{\perp}$ its orthogonal complements in $H^1_a(\mathbb{R}^{3N})$.

In the sequel, we fix a $d\geqslant 1$ and assume that K and $\mathcal{I}$ are such that $d\leqslant|\mathcal{I}|\leqslant\binom{K}{N}$. Let $f:S^{d-1}\to\mathcal{M}_N^{K,\mathcal{I}}$ be a $(\mathbb{Z}_2)_c$-equivariant continuous function. We have

$$\max_{f(S^{d-1})}\mathcal{E}_N^K=\max_{\Pi_N^K\circ f(S^{d-1})}\mathcal{E}_N$$

and since $\Pi_N^K\circ f$ is odd, $\Pi_N^K\circ f(S^{d-1})\cap W_{d-1}\neq\varnothing$. This implies

$$\max_{\Pi_N^K\circ f(S^{d-1})}\mathcal{E}_N\geqslant \min_{\substack{\Psi\,\in\,(V_{d-1})^{\perp},\\ \|\Psi\|_{L^2}=1}}\mathcal{E}_N(\Psi)=\lambda_d$$

for all $(\mathbb{Z}_2)_c$-equivariant continuous f, and so

$$\lambda_d\leqslant\lambda_d^{K,\mathcal{I}}. \tag{28}$$

We now assume $\mathcal{I}=\mathcal{A}_N^K$ and forget the subscript $\mathcal{I}$. We fix a basis $\mathcal{B}=(\phi_i)_{i\in\mathbb{N}^*}$ of $H^1(\mathbb{R}^3)$ such that $\int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij}$. We recall that every wave function Ψ can be expanded as a combination of Slater determinants built with (ϕ_i) :

$$\Psi=\sum_{1\leqslant i_1<...<i_N} c_I|\phi_{i_1}...\phi_{i_N}\rangle$$

where the sum converges in $H^1_a(\mathbb{R}^{3N})$. We then introduce

$$\begin{aligned}\mathcal{P}^K(\Psi) &= \frac{\displaystyle\sum_{1\leqslant i_1<...<i_N\leqslant K} c_I|\phi_{i_1}...\phi_{i_N}\rangle}{\sqrt{\displaystyle\sum_{1\leqslant i_1<...<i_N\leqslant K}(c_I)^2}} \text{ when } \sum_{1\leqslant i_1<...<i_N\leqslant K}(c_I)^2\neq 0\\ &= 0 \text{ either,}\end{aligned}$$

so that $rank(\Psi)\leqslant K$ and $Range(\Gamma_\Psi)\subset span(\phi_i)_{i=1}^K$.

We thus have $\mathcal{P}^K(\Psi)\to\Psi$ in $H^1_a(\mathbb{R}^{3N})$ as $K\to+\infty$. We now introduce

$$V_d^K=span(\mathcal{P}^K(\Psi_1),\cdots,\mathcal{P}^K(\Psi_d)) \text{ and } W_d^K=(V_d^K)^{\perp}.$$

We recall (see a previous remark) that $V_{\mathcal{B}}^K=span(|\phi_{i_1},...,\phi_{i_N}\rangle,\ 1\leqslant i_k\leqslant K)$ and so V_d^K is a subspace of $V_{\mathcal{B}}^K$. We have the following lemma

Lemma 5. *One has $dim(V_d^K) = d$ for K large enough, and*

$$\max_{\substack{\Psi \in V_d^K, \\ \|\Psi\|_{L^2} = 1}} \mathcal{E}_N(\Psi) \to \lambda_d$$

as $K \to +\infty$.

Proof of Lemma 5. – We introduce $G^K = Gram(\mathcal{P}^K(\Psi_i))$, i.e. $G_{ij}^K = \int_{\mathbb{R}^{3N}} \mathcal{P}^K(\Psi_i)\mathcal{P}^K(\Psi_j)$. $G^K \to I_d$, so $dim(V_d^K) \to d$. The end of the proof is easy, thanks to the continuity of $\mathcal{E}_N$. □

We now assume that K is large enough so that $dim(V_d^K) = d$. Let $(\psi_1', ..., \psi_d')$ be an basis of V_d^K such that $\int_{\mathbb{R}^{3N}} \psi_i'\psi_j' = \delta_{ij}$, and $c^1, ..., c^d \in S^{\binom{K}{N}-1}$ be such that

$$\psi_k' = \sum_{1 \leqslant i_1 < ... < i_N \leqslant K} c_I^k |\phi_{i_1} ... \phi_{i_N}\rangle.$$

When $(\alpha_1, ..., \alpha_d) \in S^{d-1}$, we have

$$\sum_{k=1}^d \alpha_k \psi_k' = \sum_{1 \leqslant i_1 < ... < i_N \leqslant K} \left(\sum_{k=1}^d \alpha_k c_I^k \right) |\phi_{i_1} ... \phi_{i_N}\rangle$$

and $\| \sum_{k=1}^d \alpha_k \psi_k' \|_{L^2(\mathbb{R}^{3N})} = 1$.

We thus introduce the continuous $(\mathbb{Z}_2)_c$-equivariant function

$$\begin{array}{rccc} f: & S^{d-1} & \longrightarrow & \mathcal{M}_N^K \\ & (\alpha_1, ..., \alpha_d) & \longmapsto & \left(\sum_{k=1}^d \alpha_k c^k, \begin{pmatrix} \phi_1 \\ \vdots \\ \phi_K \end{pmatrix} \right) \end{array}.$$

By the definition of λ_d^K, we obtain

$$\lambda_d^K \leqslant \lambda_{\mathcal{B},d}^K \leqslant \max_{f(S^{d-1})} \mathcal{E}_N^K = \max_{\Pi_N^K \circ f(S^{d-1})} \mathcal{E}_N = \max_{\substack{\Psi \in V_d^K, \\ \|\Psi\|_{L^2} = 1}} \mathcal{E}_N(\Psi).$$

Hence we have proved, by (28),

$$\lambda_d \leqslant \lambda_d^K \leqslant \lambda_{\mathcal{B},d}^K \leqslant \max_{\substack{\Psi \in V_d^K, \\ \|\Psi\|_{L^2} = 1}} \mathcal{E}_N(\Psi)$$

and so, by Lemma 5,

$$\lim_{K \to +\infty} \lambda_d^K = \lambda_d \quad \text{and} \quad \lim_{K \to +\infty} \lambda_{\mathcal{B},d}^K = \lambda_d.$$

□

4.5 Proof of Proposition 4

The assertion $\phi_i \in \bigcap_{2\leqslant p<3} W^{2,p}(\mathbb{R}^3)$ is obtained by standard arguments. To prove the analyticity of the orbitals, we introduce $\phi_{i,j} = (\phi_i\phi_j) * \frac{1}{|r|}$. Equations 9 can be written on the form

$$\begin{cases} \gamma_i \left(-\dfrac{\Delta}{2} + V\right)\phi_i + \displaystyle\sum_j \sum_{k<l} \beta^{i,j}_{k,l}\, \phi_{k,l}\phi_j + \sum_j \lambda_{i,j}\phi_j = 0, & i = 1, ..., K \\ -\Delta\phi_{k,l} = 4\pi\phi_k\phi_l, & 1 \leqslant k, l \leqslant K \end{cases}$$

with $\gamma_i > 0$.

Since $(\phi_i, \phi_{k,l})_{i,k,l}$ is a solution of an analytic non-linear elliptic system of partial differential equations, we may use for instance the results of [25] or the method of [14] to obtain the analyticity of the ϕ_i and $\phi_{k,l}$ on Ω.

We now assume $\Lambda > 0$ and prove that the electronic density $\rho = \sum_{i=1}^K \gamma_i(\phi_i)^2$ has an exponential fall-off, which will end the proof. To obtain an inequation for ρ, we multiply (15) by Φ to have

$$-\frac{1}{2}\sum_{i=1}^K \gamma_i(\Delta\phi_i)\phi_i + V\rho + 2(W_\phi \cdot \Phi, \Phi) + (\Lambda\Phi, \Phi) = 0$$

where (,) denotes the usual scalar product of $\mathbb{R}^K$. This yields

$$-\frac{1}{4}\Delta\rho + V\rho + (\Lambda\Phi, \Phi) = -2(W_\phi \cdot \Phi, \Phi) - \frac{1}{2}\sum_{i=1}^K \gamma_i|\nabla\phi_i|^2$$

and since $W_\Phi(x)$ is a non negative matrix for all x,

$$-\frac{1}{4}\Delta\rho + V\rho + (\Lambda\Phi, \Phi) \leqslant 0.$$

Now, since Λ and Γ are positive, there exists an $\alpha > 0$ such that $\Lambda \geqslant \alpha\Gamma$, and so

$$(\Lambda\Phi, \Phi) \geqslant \alpha(\Gamma\Phi, \Phi) = \alpha\rho$$

which yields

$$-\frac{1}{4}\Delta\rho + V\rho + \alpha\rho \leqslant 0.$$

For $\rho \geqslant 0$ in $H^1(\mathbb{R}^3)$, it is now standard that this implies, thanks to the maximum principle,

$$\rho(x) \leqslant C_\beta e^{-\sqrt{4\beta}|x|}$$

for all $0 < \beta < \alpha$. □

Appendix

In order to emphasize the key role of the partial method (M_2) quoted in section 2.3, we want to tackle here the classification of wave functions of rank K when $N = 2$ and $K = N + 2$. Existence and non-existence of those wave functions have been largely studied in the 50-60's (see [23, 1, 5]) but we do not know if their general form has never been written. We shall prove the following

Proposition 5.

(N=2). *For all 2-electrons wave function* Ψ *of finite rank, there exists a* $p \in \mathbb{N}^*$ *and* $(\phi_i)_{i=1}^{2p}$ *with* $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$ *such that*

$$\Psi = \sum_{i=1}^{p} c_i |\phi_{2i-1}\phi_{2i}\rangle. \tag{29}$$

In particular, all such Ψ *have an even rank.*

(K=N+2). *For all* N*-electrons wave function* Ψ *of rank* $K \leqslant N+2$*, there exists* $(\phi_i)_{i=1}^{N+2}$ *with* $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$ *and a* $p \geqslant 1$ *with* $2p \leqslant N+2$*, such that*

$$\Psi = \Psi' \wedge |\phi_{2p+1} \ldots \phi_{N+2}\rangle \quad \textit{where} \quad (\star\Psi') = -\sum_{i=1}^{p} c_i |\phi_{2i-1}\phi_{2i}\rangle. \tag{30}$$

In particular, there does not exist N*-electrons wave functions of rank* $N+1$*.*

Let us first recall the standard notations used in this result. The bilinear operator

$$\wedge : H_a^1(\mathbb{R}^{3P}) \times H_a^1(\mathbb{R}^{3(N-P)}) \longrightarrow H_a^1(\mathbb{R}^{3N})$$

is defined by

$$|\phi_1, \ldots, \phi_P\rangle \wedge |\phi_{P+1}, \ldots, \phi_N\rangle = |\phi_1, \ldots, \phi_N\rangle,$$

whereas

$$(\star\Psi') = -\sum_{i=1}^{p} c_i |\phi_{2i-1}\phi_{2i}\rangle$$

means

$$\Psi' = \sum_{i=1}^{p} c_i |\phi_1\phi_2, \ldots, \phi_{2i-3}\phi_{2(i-1)}\phi_{2i+1}\phi_{2(i+1)}, \ldots, \phi_{2p-1}\phi_{2p}\rangle.$$

Hence, when $N = 2$ or $K = N + 2$, every wavefunction can be expressed in a form such that two determinants have at least two distinct orbitals, a method quoted as an example (M_2) in section 2.3. This allows to limit significantly the number of determinants.

In (30), the case $p = 1$ corresponds to the Hartree-Fock case (Ψ is a Slater determinant), and the case $p = 2$ corresponds to doubly excited configurations, also studied by C. Le Bris in [16]

$$\Psi = \alpha|\phi_1 \ldots \phi_N\rangle + \beta|\phi_1 \ldots \phi_{N-2}\phi_{N+1}\phi_{N+2}\rangle.$$

Proof of Proposition 5. – Let us first consider the case $N = 2$. A basis $(\phi_i)_{i=1}^{K}$ of $Range(\Gamma_\Psi)$ being fixed, we introduce the antisymmetric matrix $A = (\alpha_{ij})$ such that $\Psi = \sum \alpha_{ij} \phi_i \otimes \phi_j$. We have $\Gamma = 2AA^T$, so $K = rank(\Gamma) = rank(A)$ is even. By formula (12), $A' = UAU^T$ when $\Phi' = U \cdot \Phi$ and thus, we may find a $U \in \mathcal{O}_K(\mathbb{R})$ such that

$$A' = \begin{pmatrix} A_1 & & \\ & \ddots & \\ & & A_p \end{pmatrix} \quad \text{with } A_i = \begin{pmatrix} 0 & \alpha_i \\ -\alpha_i & 0 \end{pmatrix}, \ \alpha_i \in \mathbb{R}^*$$

which easily ends the proof of this first point.

The dual case $K = N + 2$ is very similar. Given a wave function $\Psi = \sum_I c_I|\phi_{i_1}...\phi_{i_N}\rangle$, we introduce $\beta_{ij} = (-1)^{i+j}c_I$ for $\{1...K\} \setminus I = \{i < j\}$, and the antisymmetric matrix $B = (\beta_{ij})$ (so $\beta_{ii} = 0$ and $\beta_{ji} = -\beta_{ij}$). Then, it is easy to see that $\Gamma = N(I_K - BB^T)$ and $B' = det(U)UBU^T$ when $\Phi' = U \cdot \Phi$. Now there exists a $U \in \mathcal{O}_K(\mathbb{R})$ such that

$$B' = \begin{pmatrix} B_1 & & & \\ & \ddots & & \\ & & B_p & \\ & & & 0 \end{pmatrix} \quad \text{with } B_i = \begin{pmatrix} 0 & \beta_i \\ -\beta_i & 0 \end{pmatrix}, \; \beta_i \in \mathbb{R}^*$$

which easily ends the proof of Proposition 5. □

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