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Solutions of the Multiconfiguration Equations 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.

1. Introduction

We want to prove here some results concerning the multiconfiguration (MC) methods in molecular quantum chemistry.

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

$$\mathcal{E}_N(\Psi) = \langle \Psi, \mathcal{H}\Psi \rangle = \sum_{i=1}^{N} \int_{\mathbb{R}^{3N}} \left(\frac{1}{2} |\nabla_{x_i} \Psi(x)|^2 + V(x_i) |\Psi(x)|^2 \right) dx + \sum_{1 \leqq i < j \leqq N} \int_{\mathbb{R}^{3N}} \frac{|\Psi(x)|^2}{|x_i - x_j|}\, dx, \tag{1}$$

where $x = (x_1, \ldots, x_N) \in (\mathbb{R}^3)^N$, 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), $\Psi \in H^1_a(\mathbb{R}^{3N}, \mathbb{R})$ is such that $\|\Psi\|_{L^2} = 1$. The subscript a on the Sobolev space H^1_a indicates that we consider functions Ψ which are antisymmetric under interchanges of variables (expression of the Pauli exclusion principle):

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

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

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

For the sake of simplicity, we restrict ourselves to real-valued functions and do not take the spin into account. Of course, everything in this article can be trivially adapted to the case of complex-valued (spin-dependent) functions. In what follows, we denote by $Z = \sum_{m=1}^{M} z_m$ the total nuclear charge. We refer the reader to [4, 21] 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 [14]): it is bounded from below, $\sigma_{\text{ess}}(\mathcal{H}) = [\Sigma; +\infty)$ where $\Sigma \leqq 0$, 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 $E_N < \Sigma$ corresponds to the physical property of the nuclei being 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 [33] (see also [9]) that when $Z > N - 1$,

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

where $(\lambda_i)_{i \geqq 1}$ are eigenvalues strictly below Σ and whose eigenfunctions are called *excited states*. Throughout this article, 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 we need 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), it might be thought 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 $M^1 \subset \dots \subset M^K \subset \dots \subset H$ 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 method of rank K* (see [17, 9] for a mathematical set-up and for instance [30] for chemical and numerical aspects), the set of admissible wavefunctions is limited to the Ψ which are a linear combination of Slater determinants built with K functions $\phi_1, \dots, \phi_K$ in $H^1(\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$:

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

where

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

and

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

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

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

The set of the functions Ψ that can be written in 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

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

that is to say,

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

It can easily be proved (see [24, 9] and Lemma 1) that Ψ is of the form (3) if and only if $\mathrm{rank}(\Gamma_\Psi) \leqq K$ and $\mathrm{Range}(\Gamma_\Psi) \subset \mathrm{span}(\phi_i)$. The *total electronic charge density* is defined on $\mathbb{R}^3$ by $\rho_\Psi(x) = \gamma_\Psi(x, x)$ and we have $\mathrm{Tr}(\Gamma_\Psi) = \int_{\mathbb{R}^3} \rho(x)\, dx = N$.

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

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

Since every wavefunction 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 [21–23, 11]: 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 Lieb & Simon in [22].

In [23], 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 $E_N^N - E_N \geqq 0$ between the Hartree-Fock and the "exact" energy is called the *electron correlation energy* [17–19, 25]. 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, 12, 32]). In such situations, the HF method fails and chemists have to use the more accurate MC method.

In practice, chemists rarely work with an expansion of wavefunctions containing all Slater determinants built with $\phi_1, \ldots, \phi_K$ 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 [29–32]. In what follows, 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 $\mathrm{Range}(\Gamma_\Psi)$ is used.

For algebraic reasons (see [1, 5, 24, 9] and the Appendix), there do not exist N-body wavefunctions 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 LE BRIS [17] who considered the minimization over doubly excited configurations

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

He proved the existence of a minimum when $Z > N-1$ and obtained the inequality $E_N^{N+2} < E_N^N$ (see [10] for the generalization $E_N^{K+2} < E_N^K$, $K \geqq N$).

The existence of a minimum for E_N^K provided $K \geqq N$ and $Z > N - 1$ was recently proved by FRIESECKE in [9]. 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 [23], allows us 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 $K \geqq N$, we prove that there exists a sequence of distinct critical points of rank K, whose energy converges to 0.
2. For each $K \geqq N$, 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 $(\lambda_i)_{i \geqq 1}$ of the Hamiltonian $\mathcal{H}$).

The solutions of the multiconfiguration equations constructed in the first part are the analogue of LIONS' result for HF [23]. 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 $K \geqq N$, 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 [22, 23], 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" $H_a^1(\mathbb{R}^{3N})$. 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.

Finally, let us mention that some of the results proved here were outlined in [20].

In the next section, we introduce some notation and definitions in order to state properly the main results of this paper; they can be found in Section 3, with some comments 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 notation. Let Ψ be a wavefunction of rank K:

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

If we use the convention

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

(σ is the permutation of $[1; N]$ such that $i_{\sigma(1)} < \cdots < i_{\sigma(N)}$), 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:

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

This can be written in the compact form

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

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

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

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

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

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

We shall denote by $d\mathcal{E}_N^K$ its first derivative, and by $d_\Phi^2 \mathcal{E}_N^K$ 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

$$\left(\left(-\frac{\Delta}{2} + V \right) \Gamma + 2W_\Phi \right) \cdot \Phi + \Lambda \cdot \Phi = 0, \quad (9)$$

$$H_\Phi \cdot c = \beta \cdot c. \quad (10)$$

The first equation (9) is a system of K nonlinear partial differential equations – the Euler-Lagrange equations for the ϕ_i, Λ being the Lagrange-multipliers matrix associated with 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 $\beta = \mathcal{E}_N^K(c, \Phi)$. The matrix $H_\Phi = (\langle \Phi_I, \mathcal{H}\Phi_J \rangle)_{I,J}$ is the $\binom{K}{N} \times \binom{K}{N}$ matrix of the Hamiltonian $\mathcal{H}$ on $\mathrm{span}(\Phi_I)$.

We shall see that the compact form of (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 $\mathcal{H}$:

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

Recall that since $Z > N - 1$, the $(\lambda_d)_{d \geq 1}$ are eigenvalues of finite multiplicity of $\mathcal{H}$ below the bottom of the essential spectrum Σ.

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 $H_a^1(\mathbb{R}^{3N})$ and the basic properties of rank K wavefunctions. We recall that Γ_Ψ is the one-body density operator defined previously.

Lemma 1 (Basic properties of rank K wavefunctions [24])**.**

(a) *Let $(\phi_i)_{i \in \mathbb{N}}$ be an orthonormal basis of $L^2(\mathbb{R}^3)$ (resp. $H^1(\mathbb{R}^3)$). Then $(|\phi_{i_1} \dots \phi_{i_N}\rangle)_{i_1 < \dots < i_N}$ is an orthonormal basis of $L_a^2(\mathbb{R}^{3N})$ (resp. $H_a^1(\mathbb{R}^{3N})$).*

(b) *Let Ψ be a wavefunction of rank K (i.e., $\mathrm{rank}(\Gamma_\Psi) = K$), and $(\phi_i)_{i=1}^K$ be an orthonormal basis of $\mathrm{Range}(\Gamma_\Psi)$. Then Ψ can be expanded as a linear combination of Slater determinants built with $(\phi_i)_{i=1}^K$. Conversely, every wavefunction which is a linear combination of Slater determinants is of finite rank.*

Assertion (b) of this lemma corresponds to the *Löwdin Expansion Theorem* [24], while assertion (a) is just the expression of the classical

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

When $(\phi_i)_{i=1}^K$ is an orthonormal basis of $\mathrm{Range}(\Gamma_\Psi)$, 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 wavefunction of rank K,

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

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

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

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 notation,*

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

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

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

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 with 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*:

$$\left(\left(-\frac{\Delta}{2}+V\right)\Gamma+2W_\Phi\right)\cdot\Phi+\Lambda\cdot\Phi=0, \tag{13}$$

$$H_\Phi^{\mathcal{I}}\cdot c_{\mathcal{I}}=\beta\cdot c_{\mathcal{I}}\,, \tag{14}$$

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 $\mathrm{span}(\Phi_I,\,I\in\mathcal{I})$.

Compared to the "full" MC method, the new difficulty is that we cannot choose any basis $(\phi_i)_{i=1}^K$ of $\mathrm{Range}(\Gamma_\Psi)$ for we need to preserve the form of the wavefunction. We introduce

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

Below, 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

- there exists $(c,\Phi)\in\mathcal{M}_N^{K,\mathcal{I}}$ which is of rank K;
- for all $(c,\Phi)\in\mathcal{M}_N^{K,\mathcal{I}}$ there exists a $U\in\mathcal{O}_{\mathcal{I}}$ such that Γ', associated with $(c',\Phi')=U\cdot(c,\Phi)$, 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 it can easily be seen that Γ_Ψ is always diagonal and this method is thus natural. As an example, we can quote the method studied by Le Bris in [17]:

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

  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 [29, 30]. 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 for estimating the correlation energy. They are thus described by a "Full" MC. Hence, an integer $N_v\in[0;N]$ is chosen and we take

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

In other words, the considered wavefunctions have the form

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

$N_v = N$ 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, we 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)**.** *Assume $Z > N - 1$, $K \geqq N$ 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 in $\mathcal{M}_N^{K,\mathcal{I}}$, with associated wavefunctions $(\Psi^n)_{n\in\mathbb{N}}$, such that*

(a1) $(\mathcal{E}_N^K(c^n, \Phi^n))_{n\in\mathbb{N}}$ *is bounded;*

(a2) $d_\Phi \mathcal{E}_N^K(c^n, \Phi^n) \to 0$ *in* $(L^2(\mathbb{R}^3))^K$, *and* $\frac{\partial \mathcal{E}_N^K}{\partial c_I}(c^n, \Phi^n) \to 0$ *for all* $I \in \mathcal{I}$;

(a3) *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, $d_\Phi^2(\mathcal{E}_N^K)(c^n, \Phi^n)$ *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),

(c1) $\forall n \in \mathbb{N}$, $\Gamma^n = \mathrm{diag}(\gamma_1^n, \dots, \gamma_K^n)$,

(c2) $\forall i = 1, \dots, K'$, $\gamma_i^n \to \gamma_i > 0$ *and* $\phi_i^n \to \phi_i$ *strongly in* $H^1(\mathbb{R}^3)$,

(c3) $\forall i = K'+1, \ldots, K$, $\gamma_i^n \to 0$ *and* $\sqrt{\gamma_i^n}\phi_i^n \to 0$ *strongly in* $H^1(\mathbb{R}^3)$.
(c4) *We define* $\mathcal{I}' = \mathcal{I} \cap \mathcal{A}_N^{K'}$, $c' = (c_I)_{I \in \mathcal{A}_N^{K'}}$ *and* $\Phi' = (\phi_1, \ldots, \phi_{K'})$. *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) *and* (14) *with a* $\Lambda > 0$.
(c5) *The sequence* $\Psi^n \to \Psi$ *strongly in* $H_a^1(\mathbb{R}^{3N})$, *where* Ψ *is the wavefunction associated with* (c', Φ').
(c6) *If* $\mathcal{I} = \mathcal{A}_N^K$ (*full MC*), *then* $K' \in \{K-1, K\}$.

Remark 1. The last claim $K' \in \{K-1, K\}$ is also true for some partial MC methods, including example (M_3) quoted in Section 2.3. See the proof in [10, 17]. In general, this depends on the method.

From the above result we obtain the existence of a minimizer:

Corollary 1 (Ground state for multiconfiguration methods)**.** *Let* $Z > N-1$. *For all* $K \geqq N$ *and any* $\mathcal{I}$ *that defines a natural method of rank* K, *there exists a minimizer of* $\mathcal{E}_N^K$ *on* $\mathcal{M}_N^{K,\mathcal{I}}$.

We now state our result concerning excited states:

Theorem 2 (Excited states for multiconfiguration methods)**.** *Assume* $Z > N-1$.

(i) *For all* $K \geqq N$ *and any* $\mathcal{I}$ *that defines a natural method of rank* K, *there exists a sequence* $(\tilde{c}^i, \tilde{\Phi}^i)_{i \geqq 1}$ *of distinct points of* $\mathcal{M}_N^{K,\mathcal{I}}$, *which are solutions of* (9) *with some* $\tilde{\Lambda}_i \geqq 0$. *In addition, if* $(\tilde{\Psi}^i)_{i \geqq 1}$ *is the associated sequence of wavefunctions, as* i *goes to infinity,*

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

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

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

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

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

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

We recall that λ_d is the d^{th} eigenvalue of $\mathcal{H}$ defined in (11). The two parts of Theorem 2 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 part (i), we show how an infinity can be exhibited. But, just a finite number of them, defined in part (ii), are 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, we need to work with a lot of Slater determinants so that $d \leqq |\mathcal{I}|$.

Remark 2. When $\mathcal{I} = \mathcal{A}_N^K$, we believe that the sequence $(\Psi_d^K)_{K \geq N}$ in Theorem 2(ii) is precompact in $H_a^1(\mathbb{R}^{3N})$ and converges, up to a subsequence, to an eigenfunction Ψ_d of $\mathcal{H}$ associated with the eigenvalue λ_d, but we were unable to prove it. This is true in the case of minimizing sequences ($d = 1$), see [9]. 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 1. *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 $\bigcap_{2 \leq p < 3} W^{2,p}(\mathbb{R}^3)$ and is real-analytic on $\Omega := \mathbb{R}^3 \setminus \{\bar{x}_1 \dots \bar{x}_M\}$. 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 electron-coalescence points, i.e., $(x_1, \dots, x_N) \in \Omega^N$ with $\prod_{i \neq j}(x_i - x_j) = 0$ [16, 13].

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 [23], 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 [8] (see also [11]) that deals with suitable min-max. Theorem 1 is thus the first step towards the existence of minima (Corollary 1) and saddle points (Theorem 2).

Therefore, our proof of Theorem 1 is largely inspired by the study of the Hartree-Fock functional in [23]. There are two main new difficulties.

The first is that we have lost the "crucial orthogonal invariance of the energy" (see [17]). It is linked to the fact that, in the Hartree-Fock theory, $\Gamma = I_N$ and so it may be supposed 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 $\Gamma' = U\Gamma U^T$, $W'_{\Phi'} = U W_\Phi U^T$. This implies $\Lambda' = U\Lambda U^T$ in (9). Hence, we may suppose either Γ or Λ to be 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 prove (c3), 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 $\Gamma^n \geqq \gamma I$ 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 $\Lambda^n \geqq \lambda I$. 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 1

Let us now give a sketch of the proof of Theorem 2.

As in [23, 11], 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 [23, 11, 27], 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

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

the natural projection from the one-body space into the N-body space. It can be proved 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 functions $f : S^{d-1} \to \mathcal{M}_N^K$, that is to say, $\Pi_N^K \circ f$ is odd. In standard theories, compact

symmetric sets are often used with $(-)\cdot(c,\Phi)=(-c,-\Phi)$, 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 us to construct only a finite number of critical points. To see this, let us introduce the projection

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

Then if $f: S^{d-1}\to\mathcal{M}_N^K$ is equivariant for this group action, $P\circ f: S^{d-1}\to S^{\binom{K}{N}-1}$ is odd. By the Borsuk-Ulam Theorem, we therefore obtain $\mathcal{C}_G(S^{d-1},\mathcal{M}_N^K)=\varnothing$ 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 $\mathcal{M}_N^K$:

$$(-)\cdot_c(c,\Phi)=(-c,\Phi), \tag{17}$$

$$(-)\cdot_\Phi(c,\Phi)=(c,-\Phi). \tag{18}$$

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

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

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

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

for all $d \geqq 1$.

This argument 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

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

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

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

for all $d \geqq 1$.

In Section 4, we show that the variational principles underlying (21) and (22) yield solutions to the multiconfiguration equations, and that they allow us to prove respectively (ii) and (i) of Theorem 2.

Remark 3. The sequence $(\mu_d^{K,\mathcal{I}})_{d \geqq 1}$ is the natural generalization of the one that was used in the proof for $K = N$ (HF) in [23, 11] (see also [7] for the relativistic case), and its study will use exactly the same ideas.

Remark 4. We suppose here $\mathcal{I} = \mathcal{A}_N^K$. A basis $\mathcal{B} = (\phi_i)_{i \geqq 1}$ of $H^1(\mathbb{R}^3)$ being fixed, it is also natural to introduce, for all $K \geqq N$ and $d \geqq 1$ such that $\binom{K}{N} \geqq d$,

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

where $V_{\mathcal{B}}^K = \mathrm{span}(|\phi_{i_1}, \ldots, \phi_{i_N}\rangle,\ 1 \leqq i_k \leqq K)$. This method is called by chemists the Full Configuration Interaction method. It is very easy to see that

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

and we shall prove in Section 4.4 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 are a lot of different approaches, the general form of the numerical algorithms used to calculate the $(d-1)^{\text{th}}$ excited state with a fixed geometry can be summarized as follows (see for instance [30–32]):

1. Start with some $(c_{\mathcal{I}}, \Phi)$ obtained for instance 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 with $\mathcal{H}$ on the subspace $\mathrm{span}(\Phi_I,\ I \in \mathcal{I})$ where $\Phi_I = |\phi_{i_1}, \ldots, \phi_{i_N}\rangle$ if $I = \{i_1, \ldots, i_N\}$.

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

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

$$= \inf_{\substack{\Phi=(\phi_i)_{i=1}^K,\\ \int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij}}} \lambda_d(\Phi), \tag{24}$$

where $V^{K,\mathcal{I}}(\Phi) = \operatorname{span}(\Phi_I,\ I\in\mathcal{I})$ 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"* [30].

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

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

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

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

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 & SIMON [28]:

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

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 [28]), 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 $A'(0) = \left(\begin{smallmatrix} 1 & 1 \\ 1 & -1 \end{smallmatrix}\right)$ 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 above.

All these difficulties explain why we focused on the more "theoretical" 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.

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) (*Kato's inequality*) *Given* $\varepsilon > 0$ *there exists a constant* C_ε *such that*

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

for all $(c, \Phi) \in \mathcal{M}_N^K$ *with* $\Gamma = \mathrm{diag}(\gamma_1, \ldots, \gamma_K)$. *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 $(L^2_{\mathrm{loc}}(\mathbb{R}^3))^K$ and a.e., and that $\mathcal{E}_N^K(c^n, \Phi^n) \to L$. Since for all $k_2 \dots k_N$,

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

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

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

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

But Fatou's lemma yields

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

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

which easily concludes the proof of (i).

The proof of (25) is standard: by Kato's inequality, it is easily shown that

$$\langle \mathcal{H}\Psi, \Psi \rangle \geqq (1-\varepsilon) \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \Psi|^2 - C_\varepsilon$$

for all $\Psi \in H^1_a(\mathbb{R}^{3N})$ such that $\|\Psi\|_{L^2} = 1$ (see [9]). Given a $(c, \Phi) \in \mathcal{M}_N^K$ such that $\Gamma = \mathrm{diag}(\gamma_1 \dots \gamma_K)$, we may apply this inequality to the associated wavefunction and obtain

$$\mathcal{E}_N^K(c, \Phi) \geqq (1-\varepsilon) \sum_{i=1}^K \frac{\gamma_i}{2} \|\nabla \phi_i\|^2_{L^2(\mathbb{R}^3)} - C_\varepsilon$$

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 $U_n \Gamma^n U_n^T = \mathrm{diag}(\gamma_1^n \dots \gamma_K^n)$. 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 5. As has been pointed out by FRIESECKE in [9], $\mathcal{E}_N$ is not weakly lower semi-continuous on $H^1_a(\mathbb{R}^{3N})$. This shows the benefit of working in the one-body space $\mathcal{M}_N^K$.

4.1.2. About the inequality $Z > N - 1$. As in [22, 23, 11, 9], 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 $k \geqq 1$ and all $0 \leqq m < Z$, there exists a k-dimensional subspace $V_{k,m}$ of $H^1(\mathbb{R}^3)$ and a $\delta_{k,m} > 0$ such that*

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

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 $\mu(\mathbb{R}^3) \leqq m$.

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

In particular, the Hamiltonian

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

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

Proof. See the proof of a similar lemma in [23, 11]. □

4.2. Proof of Theorem 1

Our method of proof is in the spirit of [23], 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, $\Gamma^n = \mathrm{diag}(\gamma_1^n \ldots \gamma_K^n)$, with $0 \leqq \gamma_i^n \leqq 1$ and $\gamma_1^n \geqq \cdots \geqq \gamma_K^n$ (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 $\gamma_i \geqq 0$.

By Lemma 3, for all $i = 1 \ldots K$, $\gamma_i^n \int_{\mathbb{R}^3} |\nabla\phi_i^n|^2$ 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 $i = 1, \ldots, N$ 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

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

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

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

$$\tilde{c}_I^n = \frac{c_I^n}{\sqrt{\sum_{J\subset\{1\dots K'\}}(c_J^n)^2}} \quad \text{for all } I \in \mathcal{A}_N^{K'}, \text{ and } \tilde{\Phi}^n = (\phi_1^n \dots \phi_{K'}^n)^T$$

so that $(\tilde{c}^n, \tilde{\Phi}^n) \in \mathcal{M}_N^{K',\mathcal{I}'}$. If $(\tilde{\Psi}^n)$ is the corresponding sequence of wavefunctions, 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 (a1)–(a3) of Theorem 1 on $\mathcal{M}_N^{K',\mathcal{I}'}$ and also $\tilde{\Gamma}^n \geqq \gamma I_{K'}$ 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

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

in $(L^2(\mathbb{R}^3))^K$. We now prove that there exists a $\lambda > 0$ such that $\Lambda^n \geqq \lambda I_{K'}$. Let U_n be an orthogonal matrix such that $\check{\Lambda}^n := U_n\Lambda U_n^T = \mathrm{diag}(\lambda_1^n \dots \lambda_{K'}^n)$. 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 $i = 1, \dots, K'$ and all ϕ in a closed subspace F_n of $H^1(\mathbb{R}^3)$ of codimension at most $K + j$

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

where $\varepsilon_i^n \to 0$ and

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

$$D_i^n = \sum_{k_3 \dots k_N} \int \int_{\mathbb{R}^6} \frac{1}{|x-y|} \left(\phi(x) \sum_k \check{\alpha}_{i,k,k_3 \dots,k_N}^n \check{\phi}_k^n(x) \right) \cdot \left(\phi(y) \sum_k \check{\alpha}_{i,k,k_3 \dots,k_N}^n \check{\phi}_k^n(y) \right) dxdy.$$

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

$$\frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi|^2 + \int_{\mathbb{R}^3} \left(V + \rho_i^n * \frac{1}{|r|} + \frac{\lambda_i^n}{\check{\gamma}_{ii}^n} + \varepsilon_i^n \right) \phi^2 \geqq 0 \tag{27}$$

for all $\phi \in F_n$.

We now use the method of [23] (see also [11]) which is based on the following simple lemma.

Lemma 5. *Let A be a self-adjoint operator on a Hilbert space H and let H_1, H_2 be two subspaces of H such that $H = H_1 \oplus H_2$, $\dim(H_1) = k < +\infty$ and $P_2 A P_2 \geqq 0$ (P_2 is the orthogonal projection onto H_2). Then A has at most k negative eigenvalues.*

Proof. See [23, 11]. □

By Lemma 5, we deduce that the Schrödinger operator $H_i^n := -\Delta/2 + V + \rho_i^n * \frac{1}{|r|}$ has at most $K + j$ eigenvalues strictly less than $-\frac{\lambda_i^n}{\check{\gamma}_{ii}^n} - \varepsilon_i^n$. On the other hand, 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 to find a $\delta > 0$ that does not depend on i such that H_i^n admits at least $K + j$ eigenvalues strictly below $-\delta$. We deduce that

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

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

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

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

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

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

Step 3. Since $\gamma_i^n \geqq \gamma > 0$, 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

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

by using the same argument 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 [17, 10] 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 1. This ends the proof of Theorem 1. □

4.3. Proof of Corollary 1

Let (c^n,Φ^n) be a minimizing sequence of $E_N^{K,\mathcal{I}}$. We use the minimization principle of BORWEIN & PREISS [3] (see also [11]) to obtain a new minimizing sequence $(\tilde{c}^n,\tilde{\Phi}^n)\in\mathcal{M}_N^{K,\mathcal{I}}$ such that

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

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

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 2

We recall that we shall prove (i) and (ii) by using the variational principles defining respectively the sequences $(\mu_d^{K,\mathcal{I}})_{d\geqq 1}$ and $(\lambda_d^{K,\mathcal{I}})_{1\leqq d\leqq|\mathcal{I}|}$ – formulas (22) and (21).

Step 1. Existence

We shall use here a theorem of FANG & GHOUSSOUB [8] (see also [11]) that enables us to obtain Palais-Smale sequences satisfying the assumptions of Theorem 1. Let us now present this result.

Let X be a complete $\mathcal{C}^2$-Riemannian manifold, and G a compact Lie group acting freely and differentiably on X and on $\mathbb{R}^d$ for some $d \geqq 1$. Let $\mathcal{F}$ be a G-homotopic family of dimension d, that is to say, a set of the form

$$\mathcal{F} = \{f(D),\ f \in \mathcal{C}_G(D, X)\},$$

where D is a fixed G-invariant compact subset of $\mathbb{R}^d$, and $\mathcal{C}_G(D, X)$ is the set of all G-equivariant continuous functions $f : D \to X$. We now have the following result, which is a simplified version of the original one in [8, 11].

Theorem 3 (Fang and Ghoussoub [8, 11])**.** *Let ϕ be a G-invariant $\mathcal{C}^2$ functional on X with $d\phi$ and $d^2\phi$ Hölder-continuous on X, and consider*

$$c = \inf_{A\in\mathcal{F}} \max_{x\in A} \phi(x).$$

Then for every min-maxing sequence $(A_n)_n$ in $\mathcal{F}$, there exist sequences $(x_n)_n$ in X and $(\delta_n)_n$ in $\mathbb{R}^+$ with $\lim_{n\to+\infty} \delta_n = 0$ such that

(a) $x_n \in A_n$ *for each n,*
(b) $\lim_{n\to+\infty} \phi(x_n) = c$,
(c) $\lim_{n\to+\infty} d\phi(x_n) = 0$,
(d) *for each n, $d^2\phi(x_n)$ has at most d eigenvalues below $-\delta_n$.*

Now 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 (take $X = \mathcal{M}_N^K$ and $D = S^{d-1}$). Applying this result, we obtain a sequence (c^n, Φ^n) that satisfies the assumptions of Theorem 1 with $j = d$. Therefore, it converges up to a subsequence, in the sense of Theorem 1, to some critical point (c', Φ') of $\mathcal{E}_N^{K'}$ on $\mathcal{M}_N^{K',\mathcal{I}'}$ with $K' \leqq K$. We may add any $(\phi_{K'+1}, \ldots, \phi_K)$ to obtain solutions of (9) with a $\Lambda \geqq 0$.

Step 2. Study of $(\mu_d^{K,\mathcal{I}})_{d\geqq 1}$

Our proof uses ideas of [23, 11]. Since in this step, $K \geqq N$ and $\mathcal{I}$ are fixed, we shall forget these subscripts. We show that $-\infty < \mu_d \leqq \mu_{d+1} < 0$ for all $d \geqq 1$ and that $\lim_{d\to+\infty} \mu_d = 0$.

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

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

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 $(\phi_1, \dots, \phi_{n_d})$ be an 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 $\{1, \dots, N\} \in \mathcal{I}$. We consider

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

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

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

since the (ϕ_i) have disjoint supports.

We recall that

$$\begin{aligned} \mathcal{E}^{HF}(\phi_1, \dots, \phi_N) = \sum_{i=1}^{N} \int_{\mathbb{R}^3} \left(\frac{1}{2}|\nabla\phi_i|^2 + V(\phi_i)^2 \right) \\ + \frac{1}{2} \int_{\mathbb{R}^3} \left(\left(\sum_{j=1}^{N} (\phi_j)^2 \right) * \frac{1}{|r|} \right) \left(\sum_{i=1}^{N} (\phi_i)^2 \right) \\ - \frac{1}{2} \sum_{i,j=1}^{N} \int_{\mathbb{R}^3} \left((\phi_i\phi_j) * \frac{1}{|r|} \right) (\phi_i\phi_j), \end{aligned}$$

so that

$$\begin{aligned} \mathcal{E}^{HF}(\phi_1, \dots, \phi_N) = \sum_{i=1}^{N} \int_{\mathbb{R}^3} \left(\frac{1}{2}|\nabla\phi_i|^2 + \left(V + m_i * \frac{1}{|r|} \right) (\phi_i)^2 \right) \\ - \frac{1}{2} \sum_{i \neq j=1}^{N} \int_{\mathbb{R}^3} \left((\phi_i\phi_j) * \frac{1}{|r|} \right) (\phi_i\phi_j), \end{aligned}$$

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

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

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

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 $\dim V_d = d$ and $\bigcup_d V_d$ is dense in $(H^1(\mathbb{R}^3))^K$, and denote $W_d = V_d^{\perp}$. Since for all $d \geqq 1$, $\mu_d < 0$, there exists a $(\mathbb{Z}_2)_\Phi$-equivariant continuous f_d such that

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

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

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

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 $d \geqq 1$, there exists (c^d, Φ^d) and $\Lambda^d \geqq 0$ 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

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

and so

$$\left\langle W_{\Phi^d} \cdot \Phi^d\ ,\ \Phi^d \right\rangle \to 0 \quad \text{and} \quad \Lambda_d \to 0 \tag{28}$$

as $d \to +\infty$. By Lemma 3, $(\sqrt{\Gamma^d}\Phi^d)_d$ is bounded in $(H^1(\mathbb{R}^3))^K$, so we may suppose that $c_I^d \phi_i^d \rightharpoonup \phi_{I,i}$ weakly in $H^1(\mathbb{R}^3)$, strongly in $L^2_{\mathrm{loc}}(\mathbb{R}^3)$ and a.e., for all $i = 1, \dots, K$ and all I such that $i \in I$. But $\phi_{I,i} = 0$ by (28) 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 $(\lambda_d^{K,\mathcal{I}})_{1\leqq d\leqq|\mathcal{I}|}$

We first choose a sequence (Ψ_d) of eigenvectors of $\mathcal{H}$ associated with the eigenvalues (λ_d) such that $\int_{\mathbb{R}^{3N}}\Psi_i\Psi_j=\delta_{ij}$ and

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

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

In what follows, we fix a $d\geqq 1$ and assume that K and $\mathcal{I}$ are such that $d\leqq|\mathcal{I}|\leqq\binom{K}{N}$. 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

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

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

$$\lambda_d\leqq\lambda_d^{K,\mathcal{I}}. \tag{29}$$

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 wavefunction Ψ can be expanded as a combination of Slater determinants built with (ϕ_i):

$$\Psi=\sum_{1\leqq i_1<\dots<i_N}c_I|\phi_{i_1}\dots\phi_{i_N}\rangle,$$

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

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

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

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

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

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

Lemma 6. *For K large enough,* $\dim(V_d^K) = d$ *and*

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

as $K \to +\infty$.

Proof. We introduce $G^K = \mathrm{Gram}(\mathcal{P}^K(\Psi_i))$, i.e. $G^K_{ij} = \int_{\mathbb{R}^{3N}} \mathcal{P}^K(\Psi_i)\mathcal{P}^K(\Psi_j)$. $G^K \to I_d$, 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 $(\psi'_1, \ldots, \psi'_d)$ be a basis of V_d^K such that $\int_{\mathbb{R}^{3N}} \psi'_i \psi'_j = \delta_{ij}$, and $c^1, \ldots, c^d \in S^{\binom{K}{N}-1}$ be such that

$$\psi'_k = \sum_{1 \leqq i_1 < \cdots < i_N \leqq K} c^k_I |\phi_{i_1} \ldots \phi_{i_N}\rangle.$$

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

$$\sum_{k=1}^d \alpha_k \psi'_k = \sum_{1 \leqq i_1 < \cdots < i_N \leqq K} \left(\sum_{k=1}^d \alpha_k c^k_I \right) |\phi_{i_1} \ldots \phi_{i_N}\rangle$$

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

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

By the definition of λ_d^K, we obtain

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

Hence we have proved, by (29),

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

and so, by Lemma 6,

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

4.5. *Proof of Proposition 1*

The assertion $\phi_i \in \bigcap_{2 \leqq p<3} W^{2,p}(\mathbb{R}^3)$ 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 in the form

$$\gamma_i \left(-\frac{\Delta}{2} + V\right) \phi_i + \sum_j \sum_{k<l} \beta_{k,l}^{i,j} \, \phi_{k,l} \phi_j + \sum_j \lambda_{i,j} \phi_j = 0, \qquad i = 1, \ldots, K,$$

$$-\Delta \phi_{k,l} = 4\pi \phi_k \phi_l, \quad 1 \leqq k, l \leqq K$$

with $\gamma_i > 0$.

Since $(\phi_i, \phi_{k,l})_{i,k,l}$ is a solution of an analytic nonlinear elliptic system of partial differential equations, we may use for instance the results of [26] or the method of [15] 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 inequality for ρ, we multiply (15) by Φ to give

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

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,

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

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

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

which yields

$$-\tfrac{1}{4} \Delta \rho + V\rho + \alpha \rho \leqq 0.$$

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

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

for all $0 < \beta < \alpha$. $\square$

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 wavefunctions of rank K when $N = 2$ and $K = N + 2$. Existence and non-existence of those wavefunctions have been largely studied in the 50's and 60's (see [24, 1, 5, 6]). Their general form is known by chemists in the case $N = 2$ [5, 6] but we do not know if the case $K = N + 2$ has never been written down. We shall however give here the proof for both cases, since they are quite similar.

Proposition 2 (N = 2 – COLEMAN [5, 6])**.** *For all 2-electron wavefunctions 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*

$$\Psi = \sum_{i=1}^{p} c_i |\phi_{2i-1}\phi_{2i}\rangle. \tag{30}$$

In particular, all such Ψ have an even rank.

($K = N + 2$). For all N-electron wavefunctions Ψ of rank $K \leqq N + 2$, there exists $(\phi_i)_{i=1}^{N+2}$ with $\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$ and a $p \geqq 1$ with $2p \leqq N + 2$, such that

$$\Psi = \Psi' \wedge |\phi_{2p+1} \dots \phi_{N+2}\rangle \quad \textit{where} \quad (\star\Psi') = -\sum_{i=1}^{p} c_i |\phi_{2i-1}\phi_{2i}\rangle. \tag{31}$$

In particular, there do not exist N-electron wavefunctions of rank $N + 1$.

Let us first recall the standard notation 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

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

whereas

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

means

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

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 us to limit significantly the number of determinants.

In (31), 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 LE BRIS in [17]:

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

Proof. Let us first consider the case $N = 2$. A basis $(\phi_i)_{i=1}^K$ of $\mathrm{Range}(\Gamma_\Psi)$ 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 $K = \mathrm{rank}(\Gamma) = \mathrm{rank}(A)$ 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 wavefunction $\Psi = \sum_I c_I |\phi_{i_1} \dots \phi_{i_N}\rangle$, we introduce $\beta_{ij} = (-1)^{i+j} c_I$ for $\{1 \dots K\} \setminus I = \{i < j\}$, 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 2. □

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References

1. ANDO, T.: Properties of Fermions Density Matrices. *Rev. Mod. Phys.* **35**, 690–702 (1963)
2. ATKINS, P.W., FRIEDMAN, R.S.: *Molecular Quantum Mechanics*. Third Edition. Oxford: Oxford University Press, 1997
3. BORWEIN, J., PREISS, D.: A smooth variational principle with applications to subdifferentiability and to differentiability of convex functions. *Trans. AMS* **303**, 517–527 (1987)
4. CANCÈS, E., *et al.*: *Computational quantum chemistry, a primer*. To appear in *Handbook of numerical analysis*. Elsevier, 2003
5. COLEMAN, A.J.: Structure of Fermions Density Matrices. *Rev. Mod. Phys.* **35**(3), 668–689 (1963)
6. COLEMAN, A.J., YUKALOV, V.I.: *Reduced Density Matrices: Coulson's Challenge*. Springer Verlag, 2000
7. ESTEBAN, M.J., SÉRÉ, E.: Solutions of the Dirac-Fock Equations for Atoms and Molecules. *Commun. Math. Phys.* **203**, 499–530 (1999)
8. FANG, G., GHOUSSOUB, N.: Morse-type information on Palais-Smale sequences obtained by min-max principles. *Manuscripta Math.* **75**, 81–95 (1992)

9. FRIESECKE, G.: The multiconfiguration equations for atoms and molecules: charge quantization and existence of solutions. *Arch. Rational Mech. Anal.* **169**, 35–71 (2003)
10. FRIESECKE, G.: On the infinitude of nonzero eigenvalues of the single-electron density matrix for atoms and molecules. *Proc. Roy. Soc. London Ser. A* **459**, 47–52 (2003)
11. GHOUSSOUB, N.: *Duality and perturbation methods in critical point theory*. Cambridge University Press, 1993
12. HEAD-GORDON, M.: Quantum Chemistry and Molecular Processes. *J. Phys. Chem.* **100**, 13213–13225 (1996)
13. HOFFMANN-OSTENHOF, M., HOFFMANN-OSTENHOF, T., STREMNITZER, H.: Local properties of Coulombic wave functions. *Commun. Math. Phys.* **163**, 185–215 (1994)
14. HUNZIKER, W., SIGAL, I.M.: The Quantum N-Body Problem. *J. Math. Phys.* **41**, 3348–3509 (2000)
15. KATO, K.: New Idea for proof of Analyticity of Solutions to Analytic Non Linear Equations. *SUT Journal of Math.* **32**, 157–161 (1996)
16. KATO, T.: On the eigenfunctions of many particle systems in quantum mechanics. *Commun. Pure and Appl. Math.* **10**, 151–171 (1957)
17. LE BRIS, C.: A general approach for multiconfiguration methods in quantum molecular chemistry. *Ann. Inst. H. Poincaré Anal. Non Linéaire* **11**, 441–484 (1994)
18. LE BRIS, C.: Mathématiques Appliquées et Chimie Quantique. *Matapli – Bulletin de la Société de Mathématiques Appliquées et Industrielles* **58**, 25–36 (1999)
19. LE BRIS, C.: *Quelques problèmes mathématiques en chimie quantique moléculaire*. Thèse d'État, École Polytechnique, 1993
20. LEWIN, M.: The multiconfiguration methods in quantum chemistry: Palais-Smale condition and existence of minimizers. *C. R. Acad. Sci. Paris, Ser. I* **334**, 299–304 (2002)
21. LIEB, E.H.: The Stability of Matter: from Atoms to Stars. *Bull. Am. Math. Soc.* **22**, 1–49 (1990)
22. LIEB, E.H., SIMON, B.: The Hartree-Fock Theory for Coulomb Systems. *Commun. Math. Phys.* **53**, 185–194 (1977)
23. LIONS, P.L.: Solutions of Hartree-Fock Equations for Coulomb Systems. *Commun. Math. Phys.* **109**, 33–87 (1987)
24. LÖWDIN, P.O.: Quantum Theory of Many-Particle Systems, I: Physical Interpretations by Mean of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction. *Phys. Rev.* **97**, 1474–1489 (1955)
25. LÖWDIN, P.O.: Correlation Problem in Many-Electron Quantum Mechanics, I. Review of different approaches and discussion of some current ideas. *Adv. Chem. Phys.* **2**, 207–322 (1959)
26. MORREY, C.B.: On the analyticity of the solutions of analytic non-linear elliptic systems of partial differential equations. *Am. J. Math.* **80**, 198–218 (1958)
27. RABINOWITZ, P.H.: *Minimax methods in critical point theory with applications to differential equations.* Number 65 in Conference Board of the Mathematical Sciences, Regional Conference series in Mathematics. American Mathematical Society, 1986
28. REED, M., SIMON, B.: *Methods of Modern Mathematical Physics: IV – Analysis of Operators*. Academic Press, 1978
29. ROOS, B.O.: The Complete Active Space Self-Consistent Field method and its applications in electronic structure calculation. *Ab Initio Methods in Quantum Chemistry – II* in *Adv. Chem. Phys.* **69**, 399–446 (1987)
30. SHEPARD, R.: The multiconfiguration self-consistent field method. *Ab Initio Methods in Quantum Chemistry – II* in *Adv. Chem. Phys.* **69**, 63–200 (1987)
31. WERNER, H.-J.: Matrix-formulated direct Multiconfiguration Self-Consistent Field and Multiconfiguration Reference Configuration-Interaction methods. *Ab Initio Methods in Quantum Chemistry – II* in *Adv. Chem. Phys.* **69**, 1–62 (1987)

32. WERNER, H.-J., MEYER, W.: A quadratically convergent multiconfiguration-self-consistent field method with simultaneous optimization of orbitals and CI coefficients. *J. Chem. Phys.* **73**, 2342–2356 (1980)
33. ZHISLIN, G.M.: Discussion of the spectrum of Schrödinger operators for systems of many particles. *Trudy Moskovskogo matematiceskogo obscestva* **9**, 81–120 (1960) (In Russian)

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