A Mountain Pass for Reacting Molecules

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Abstract

In this paper, we consider a neutral molecule that possesses two distinct stable positions for its nuclei, and look for a mountain pass point between the two minima in the non-relativistic Schrödinger framework.

We first prove some properties concerning the spectrum and the eigenstates of a molecule that splits into pieces, a behaviour which is observed when the Palais-Smale sequences obtained by the mountain pass method are not compact. This enables us to identify precisely the possible values of the mountain pass energy and the associated "critical points at infinity" (a concept introduced by Bahri [2]) in this non-compact case.

We then restrict our study to a simplified (but still relevant) model: a molecule made of two interacting parts, the geometry of each part being frozen. We show that this lack of compactness is impossible under some natural assumptions about the configurations "at infinity", proving the existence of the mountain pass in these cases. More precisely, we suppose either that the molecules at infinity are charged, or that they are neutral but with dipoles at their ground state.

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Contents

Introduction

In this paper, we study in the non-relativistic quantum Schrödinger framework the case of a molecule that possesses two distinct stable positions for its nuclei, as this is for instance the case for HCN and CNH. Our purpose is somewhat simple: can we obtain a critical point of the energy by using the classical mountain pass method between the two minima ? Experiment suggests that this is the case (at least for the HCN↔CNH reaction). Indeed, such mountain pass points are frequently computed by chemists who need to understand the possible behaviour of the molecule: it corresponds to a "transition state" during an infinitely slow reaction leading from one minimum to the other. But as far as we know, this problem has never been tackled from the mathematical point of view for the N-body quantum problem, or even in the context of the classical Hartree or Thomas-Fermi type models which are approximations of the exact theory.

For a neutral molecule, the proof that there is a *minimum* with regards to the position of the nuclei can be found in the fundamental work of E.H. Lieb and W. E. Thirring [25] for the Schrödinger model, and in a series of papers by I. Catto and P.-L. Lions [4, 5, 6, 7] for approximate models (Hartree or Thomas-Fermi type), the latter being really more complicated due to the non linearity of these models. In these two works, the authors had to prove that minimizing sequences are compact, the non-compactness behaviour being related to the fact that the molecule can split into parts, each moving away from the others. Remark that binding does not occur for the Thomas-Fermi model (see the works of E. Teller [31], E.H. Lieb and B. Simon [24], and the references in [4]) and that the result is not known for the Hartree-Fock model, except in very special cases [7].

Let us make some comment on a tool used in these proofs that cannot be simply adapted to our setting. A common idea in these two works is to average over all the possible orientations of each piece in order to simplify the computation of the interaction energy between them, by suppressing the multipoles. To show that the energy can be lower than the energy at infinity, a new term using the correlation between the electrons is then created in [25] to obtain a Van Der Waals term of the form $-C/R^6$ (R is the distance between the molecules), while a very detailed computation of the (exponentially small) combined energy is done in [4, 5, 6, 7] to conclude that the system can bind. Because of the preliminary averaging, the conclusion is that there exists some orientation of the molecules for which this is true, but this position is unknown *a priori*.

In the case of the mountain pass method that we propose here, the non-compactness is obviously also due to a possible splitting of the molecule. However, we want to insist on the fact that we cannot use in this setting the same idea of averaging over all the rotations of the molecules, because we have to pull down the energy *along a path*. In other words, a comparison between the energies is not sufficient to conclude, and a precise information on the directions on which the energy decreases is needed.

This is why we failed to treat the problem in its full generality and we had to add some hypothesis about the configurations "at infinity". Nevertheless, we wish to ameliorate this first work in the future, and hope that it will stimulate further results.

The results proved in this paper are the following.

First, we study the spectrum and the eigenfunctions of the Hamiltonian when a molecule splits into parts. We obtain some bounds on the eigenvalues and the bottom of the essential spectrum which allow to show that the "electrons remain in the vicinity of the nuclei" when a fixed excited state is studied.

In other words, no electron is lost during the process. This is obtained by a non-isotropic exponential decay of the electronic density, which is shown to be uniform when the distance between the molecules grows. We also specify the behaviour of the associated wavefunctions and define the "critical points at infinity", a concept introduced by A. Bahri [2]. Some parts of this first result are necessary for our min-max problem.

Then, we prove a result that enables to identify the possible behaviour of the non-compact min-maxing paths. As it is suggested by the intuition, it is shown that the optimal energy of the mountain pass corresponds in this case to a system where the molecule is split into independent parts (the electrons are shared among them), each being at its ground state. This Morse information on the critical points at infinity is rather intuitive.

As announced, we were unable to treat the general case and we end this article by showing that this non-compactness behaviour is impossible in the special case of two interacting molecules with fixed nuclei. This is done under the hypothesis that we are in the easy case of two charged molecules at infinity, or in the more difficult case of two neutral molecules at infinity, but with dipoles at their ground state. This enables to obtain the required result for many practical situations. As explained before, the crucial step is to evaluate the interaction energy between the molecules and we use here a multipolar expansion, even for wavefunctions that are not a simple tensor product of two ground states as in [25]. Finally, the expected result is deduced from the fact that the critical points of the dipole/dipole interaction energy which have a nonnegative energy have a Morse index which is at least 2.

From a practical point af view, the study of this mountain pass method is really important. As mentionned above, the main idea is that a path leading from one minimum to the other represents an infinitely slow chemical reaction. The mountain pass energy is then interpreted as the lowest energy threshold for the reaction to happen. The numerical computation of this energy and of the optimum (even the whole path) is then really a prime necessity for chemists, who have to understand the possible behaviours of the molecule (see for instance [28, 9] for chemical and numerical aspects).

However, chemists only consider paths on which the molecule is at its ground state all along it, which leads to obvious problems of smoothness in the case of degeneracy of the first eigenvalue of the Hamiltonian, and can obstruct convergence. For mathematical reasons, we were thus forced to abandon this hypothesis and relax the problem by considering that the wavefunction can vary independently of the nuclear geometry, in order to obtain a critical point with respect to nuclei's variations. Since we shall show that our min-max energy is in fact the same that the one used in practice, this approach could also be interesting for numerical computations.

We conclude with a few words on the mathematical tools used in this paper. As in [4, 5, 6, 7], the proof is guided by P.-L. Lions' Concentration-Compactness ideas [26], although the localization of the electrons is given by the uniform exponential decay of Theorem 2, and not by this theory. Let us remark that the physical intuition is somewhat often related to the behaviour of the electronic density. For instance, when the molecule splits into parts, the latter becomes a sum of functions localized near the nuclei. But this point of view is not sufficient to understand the problem since the main object is not the density, but the wavefunction. The latter will not split into sums, but into sums of tensor products of wavefunctions in lower dimensions (see the work of G. Friesecke [10] for a very clear explanation of this phenomenon). Therefore, we use a variant of N-body geometric methods for Schrödinger operators [30, 29, 18] that enables to relate the behaviour of the wavefunction to those of the associated electronic density. This method is used in [10] and enabled G. Friesecke to notice an interesting link between the celebrated HVZ Theorem [18, 32, 33] and the Concentration-Compactness method [26].

Moreover, the HVZ Theorem (which enables to identify the bottom of the spectrum as the ground state energy of the same system but with an electron removed), and Zhislin's Theorem (which states the existence of excited states for positive or neutral molecules) are abundantly used in this article.

Finally, we use the results and methods developed by G. Fang and N. Ghoussoub [8, 14] which enable to obtain Morse information on the Palais-Smale sequences, related to the fact that the deformed object are paths (i.e. deformations of $[0;1]$). We also use the duality theory developed in [14] which permits to locate critical points.

The paper is organized as follows. In the next section, we describe the model in detail and recall known results on the Hamiltonian and its eigenfunctions. Then, in section 2, we present our results without proof: for the sake of clarity, we have brought all the proofs together in the last section.

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1 The model

1.1 Framework

We consider here a positive or neutral molecule with N non relativistic electrons, and M nuclei of charges $Z_1 + \cdots + Z_M \geq N$. The nuclei are supposed to be correctly described by a classical model (Born-Oppenheimer approximation) and are thus represented as pointwise charges at $R_1 \cdots R_M \in \mathbb{R}^3$. In what follows, we let

$$R = (R_1, ..., R_M) \in \Omega := (\mathbb{R}^3)^M \setminus (\cup_{i \neq j} \{R_i = R_j\})$$

and

$$Z = (Z_1, ..., Z_M) \in (\mathbb{N}^*)^M, \quad |Z| = Z_1 + \cdots + Z_M \geq N.$$

The quantum energy of the system in the state $\Psi \in L^2_a(\mathbb{R}^{3N},\mathbb{C}) := \bigwedge_1^N L^2(\mathbb{R}^3,\mathbb{C})$ is

$$\begin{aligned}\mathcal{E}^N(R,\Psi) &= \langle \Psi, H^N(R,Z)\Psi\rangle \\ &= \sum_{i=1}^N \int_{\mathbb{R}^{3N}} \frac{1}{2}|\nabla_{x_i}\Psi(x)|^2 dx - \sum_{i=1}^N\sum_{j=1}^M \int_{\mathbb{R}^{3N}} \frac{Z_j|\Psi(x)|^2}{|x_i-R_j|}dx \\ &\quad + \sum_{1\le i<j\le N}\int_{\mathbb{R}^{3N}} \frac{|\Psi(x)|^2}{|x_i-x_j|}dx + \sum_{1\le i<j\le M}\frac{Z_iZ_j}{|R_i-R_j|}.\end{aligned}$$

$H^N(R,Z)$ is the purely coulombic N-body Hamiltonian

$$H^N(R,Z) = \sum_{i=1}^N\left(-\frac{1}{2}\Delta_{x_i} + V_R(x_i)\right) + \sum_{1\le i<j\le N}\frac{1}{|x_i-x_j|} + \sum_{1\le i<j\le M}\frac{Z_iZ_j}{|R_i-R_j|},$$

$$V_R(u) = -\sum_{j=1}^M \frac{Z_j}{|u-R_j|}.$$

Its operator domain is the Sobolev space $H^2_a(\mathbb{R}^{3N},\mathbb{C})$, and its quadratic form domain is $H^1_a(\mathbb{R}^{3N},\mathbb{C})$. In all this paper, the subscript a indicates that we consider wavefunctions Ψ which are antisymmetric under interchanges of variables (expression of the Pauli exclusion principle):

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

We refer the reader to [22, 3] for a description of this model and a detailed explanation of the Born-Oppenheimer approximation. The properties of $H^N(R,Z)$ and its eigenfunctions are recalled below. For the sake of simplicity, we have neglected the spin and the dynamic of the nuclei, as in [25]. We would like also to mention that all the results in this paper can be adapted to the case of smeared nuclei, that is to say when the Coulomb potential $\frac{1}{|x-R_i|}$ is replaced by $\int_{\mathbb{R}^3}\frac{1}{|x-y-R_i|}d\mu_i(y)$ where μ_i is a probability measure on $\mathbb{R}^3$. Of course, $\frac{1}{|R_i-R_j|}$ has to be replaced by $\iint_{\mathbb{R}^6}\frac{1}{|R_i+y-(R_j+z)|}d\mu_i(y)d\mu_j(z)$. Remark that, in opposition to many other papers dealing with minimization, we work here with complex-valued wavefunctions, an hypothesis that plays a role in our results (see for instance Theorem 4 and the associated remarks).

Z and N being fixed such that $N \le |Z|$, for each $R\in\Omega$, the problem

$$E^N(R,Z) = \min\{\mathcal{E}^N(R,\Psi),\ \|\Psi\|_{L^2}=1\}$$

has a solution Ψ, which is the ground state of the N electrons interacting with the M nuclei localized at the R_i.

For neutral molecules ($N=|Z|$), it is also known that the problem

$$E^N = \min_{R\in\Omega} E^N(R,Z)$$

admits a solution [25], proving the stability of neutral molecules.

We shall assume that (R, Ψ) and (R', Ψ') are two local minima of $\mathcal{E}^N$. We then consider the classical mountain pass method

$$c = \inf_{\gamma \in \Gamma} \max_{t \in [0;1]} \mathcal{E}^N(\gamma(t)) \tag{1}$$

where

$$\Gamma = \{\gamma \in \mathcal{C}^0([0;1], \Omega \times SH^1_a(\mathbb{R}^{3N})),\ \gamma(0) = (R, \Psi),\ \gamma(1) = (R', \Psi')\}$$

$$SH^1_a(\mathbb{R}^{3N}) = \{\Psi \in H^1_a(\mathbb{R}^{3N}),\ \|\Psi\|_{L^2} = 1\}$$

and want to show that c is a critical value of $\mathcal{E}^N$.

As mentionned in introduction, the physical interpretation of this min-max method is that paths $\gamma \in \Gamma$ represent an infinitely slow reaction leading from one minimum to the other. c is thus interpreted as the lowest energy threshold for passing from (R, Ψ) to (R', Ψ').

In practice, the following definition is used

$$c' = \inf_{r \in \mathcal{R}} \max_{t \in [0;1]} E^N(r(t), Z)$$

where

$$\mathcal{R} = \{r \in \mathcal{C}^0([0;1], \Omega),\ r(0) = R,\ r(1) = R'\}.$$

As explained in introduction, the function $R \mapsto E^N(R, Z)$ is continuous but not necessary differentiable and this is why we shall study the min-max method (1). However, it will be shown that in fact $c = c'$.

1.2 Properties of $H^N(R, Z)$

Let us now recall some well-known facts about the spectrum of $H^N(R, Z)$. We introduce

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

In the sequel, we shall denote for all $d \geq 1$

$$E^0(R, Z) = \lambda^0_d(R, Z) := \sum_{1 \leq i < j \leq M} \frac{Z_i Z_j}{|R_i - R_j|}, \quad \Sigma^0(R, Z) = +\infty.$$

For a wavefunction Ψ, the electronic density and the electronic kinetic energy density are respectively defined by

$$\rho_\Psi(x) = N \int_{R^{3(N-1)}} |\Psi(x, x_2, ..., x_N)|^2 dx_2 ... dx_N$$

$$t_\Psi(x) = N \int_{R^{3(N-1)}} |\nabla \Psi(x, x_2, ..., x_N)|^2 dx_2 ... dx_N.$$

We have brought together the main results known in the following

Theorem 1. *We assume $N \geq 1$. The following results are known :*

1. **(Self-Adjointness [20])** *$H^N(R,Z)$ is self-adjoint on $L^2_a(\mathbb{R}^{3N})$ with operator domain $H^2_a(\mathbb{R}^{3N})$ and quadratic form domain $H^1_a(\mathbb{R}^{3N})$.*

2. *We have [19]*

$$\sigma_{ess}\left(H^N(R,Z)\right) = [\Sigma^N(R,Z);+\infty)$$

$$\forall d \geq 1,\ \lambda^N_d(R,Z) \leq \Sigma^N(R,Z) \leq \sum_{1\leq i<j\leq M} \frac{Z_iZ_j}{|R_i - R_j|}$$

3. **(HVZ Theorem [18, 32, 33, 19])** *$\Sigma^N(R,Z)$ is the lowest energy threshold for breaking the N-electrons system into independent parts, that is to say, to remove one electron :*

$$\Sigma^N(R,Z) = E^{N-1}(R,Z).$$

4. **(Compactness Below The Essential Spectrum [10])** *If $\lambda^N_d(R,Z) < \Sigma^N(R,Z)$, then $\lambda^N_d(R,Z)$ is an eigenvalue of finite multiplicity and in particular, there exists a $\Psi_d \in H^2_a(\mathbb{R}^{3N})$ such that*

$$H^N(R,Z)\Psi_d = \lambda^N_d(R,Z)\Psi_d.$$

It is locally lipschitz [21], i.e.

$$\Psi_d \in \mathcal{C}^0(\mathbb{R}^{3N}) \qquad \text{and} \qquad |\nabla\Psi_d| \in L^\infty_{loc}(\mathbb{R}^{3N}),$$

and real analytic [13] on $U^N \setminus \{x_i = x_j\}$, where $U = \mathbb{R}^3 \setminus \{R_i\}_{i=1}^M$. If ρ_d is the associated electronic density, then [13]

$$\rho_d \in \mathcal{C}^\omega(U) \cap \mathcal{C}^{0,1}(\mathbb{R}^3).$$

5. **(Zhislin Theorem [33])** *For positive and neutral molecules $N \leq |Z|$, then*

$$\lambda^N_d(R,Z) < \Sigma^N(R,Z)$$

for all $d \geq 1$, so that

$$\sigma\left(H^N(R,Z)\right) = \{\lambda^N_1(R,Z) \leq \cdots \leq \lambda^N_d(R,Z) \leq \cdots\} \cup [\Sigma^N(R,Z);+\infty).$$

6. **(Negative Molecules [23])** *For negative molecules $N > |Z|$, there exists a δ such that $\lambda^N_\delta(R,Z) = \Sigma^N(R,Z)$, and $\delta = 1$ when $N \geq 2|Z| + M$.*

Note that the functions $\Sigma^N(R,Z)$ and $\lambda^N_d(R,Z)$ ($d \geq 1$) are continuous with respect to R.

2 The results

In this section, we present the results that we have obtained concerning the mountain pass method defined above. As mentionned, all the proofs are postponed to the next section.

2.1 The spectrum of a molecule that splits into pieces

We begin the study by some general results about the spectrum and the behaviour of the eigenstates when the molecule splits into pieces, that is to say when $|R_i - R_j| \to +\infty$ for some i and j. As mentionned above, this splitting of the molecule will be shown to be the main reason for the possible lack of compactness of Palais-Smale sequences.

Although only the case of ground states will be necessary for the sequel, we tackle here arbitrary excited states. In this section, we consider a positive or neutral molecule ($N \leq |Z|$).

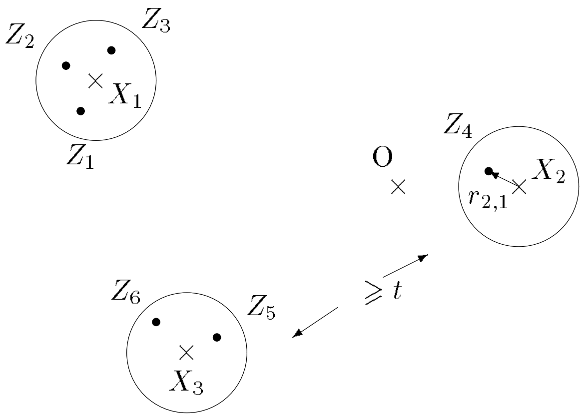


Figure 1: An example with $M = 6$, $p = 3$, $m_1 = 3$, $m_2 = 1$ and $m_3 = 2$.

We fix a $2 \leq p \leq M$ (number of pieces).

Let $X_1, ..., X_p : \mathbb{R}^+ \mapsto \mathbb{R}^3$ be p functions that satisfy $|X_i(t) - X_j(t)| \geq t$ for all $i \neq j$ and t large enough. Let be $m = (m_1, ..., m_p) \in (\mathbb{N}^*)^p$ such that $\sum_{j=1}^p m_j = M$. We fix a positive constant R_0 and some $r_{j,k} \in \mathbb{R}^3$ and $z_{j,k} \in \mathbb{N}$ for $j = 1, ..., p$ and $k = 1, ..., m_j$ such that $|Z| := \sum_{j=1}^p \sum_{k=1}^{m_j} z_{j,k} \geq N$, $|r_{j,k}| \leq R_0$ and $r_{j,k} \neq r_{j,l}$ when $k \neq l$. We then let

$$z_j = (z_{j,1}, ..., z_{j,m_j}), \quad Z = (z_1, ..., z_p), \quad r_j = (r_{j,1}, ..., r_{j,m_j}),$$

$$\tilde{r}_j(t) = (X_j(t) + r_{j,1}, ..., X_j(t) + r_{j,m_j}), \quad R(t) = (\tilde{r}_1(t), ..., \tilde{r}_p(t))$$

We also introduce

$$\omega_j = \{(r_k) \in B(0, R_0)^{m_j}, \ r_{k_1} \neq r_{k_2} \text{ if } k_1 = k_2\}.$$

and

$$\mathcal{U}(R) = \mathbb{R}^3 \setminus \left(\bigcup_{j=1}^{p} \overline{B(X_j, R)} \right).$$

2.1.1 Spectrum and uniform exponential decay

We have the following result:

Theorem 2 (Spectrum and uniform exponential decay). *For all* $1 \leq N \leq |Z|$ *and all* $d \geq 1$, *we have*

1. $$\lim_{t\to+\infty} E^N(R(t),Z) = \min\left\{\sum_{j=1}^{p} E^{N_j}(r_j,z_j),\ N_1+...+N_p=N\right\}.$$

2. $$\limsup_{t\to+\infty} \lambda_d^N(R(t),Z) \leq \min\left\{\sum_{j=1}^{p} \lambda_{\delta_j}^{N_j}(r_j,z_j),\ N_1+...+N_p=N,\ \prod_{j=1}^{p}\delta_j = d\right\}.$$

3. $$\inf_{r_j\in\omega_j}\liminf_{t\to+\infty}\left(\Sigma^N(R(t),Z) - \lambda_d^N(R(t),Z)\right) > 0.$$

4. *Let* Ψ_R *be an eigenfunction associated to the eigenvalue* $\lambda_d^N(R,Z)$, *with associated densities* ρ_R *and* t_R. *Then there exist positive constants* R_1, C *and* α, *depending only on* N, d, R_0, p *such that*

   $$\rho_R(x) \leq Cexp(-\alpha\delta(x)) \quad \text{and} \quad t_R(x) \leq Cexp(-\alpha\delta(x)) \quad \text{on} \ \ \mathcal{U}(R_1)$$

   where $\delta(x) = \min\{|x-X_j|,\ j=1,...,d\}$.

The interpretation of this result is that if a neutral or positively charged molecule splits into parts, then for a fixed excited state, the electrons remain in the vicinity of the nuclei.

For the sake of simplicity, let us denote, for $r=(r_1,...,r_p)$ and $z=(z_1,...,z_p)$

$$\Lambda_d^N(r,z) := \min\left\{\sum_{j=1}^{p}\lambda_{\delta_j}^{N_j}(r_j,z_j),\ N_1+...+N_p=N,\ \prod_{j=1}^{p}\delta_j = d\right\}.$$

2.1.2 Behaviour of the wavefunctions, critical points at infinity

Now that we have some bounds on the eigenvalues and the bottom of the essential spectrum, we want to prove a result describing the behaviour of the eigenfunctions. This will enable us to define the "critical points at infinity" of the model, a concept that was introduced by A. Bahri [2].

The right hand side of Theorem 2 - 1), or more generally an equality like

$$c = \sum_{j=1}^{p}\lambda_{\delta_j}^{N_j}(r_j,z_j), \tag{3}$$

is rather standard from P.-L. Lions' Concentration-Compactness point of view: when the molecule splits into pieces, then the energy of an electronic excited states becomes a sum of excited states energies of the pieces. In other words, a "critical point at infinity" would be a system constituted by p molecules in some excited state, each being infinitely far from the others, so that the interactions between them vanish.

Let us consider a sequence $t_n \to +\infty$, some $r = (r_1, ..., r_p) \in \bigotimes_{j=1}^p \omega_j$, and denote by $R^n = R(t_n) := (X_1(t_n) + r_1, ..., X_p(t_n) + r_p)$, $X_j^n = X_j(t_n)$. For the electronic density, such a configuration is then clearly obtained in the case of dichotomy, that is to say $\rho^n \simeq \sum_{j=1}^p \rho_j^n$ where ρ_j^n is essentially supported in the vicinity of X_j^n (see the exponential decay of Theorem 2). But the behaviour of the wavefunction Ψ^n is less simple since these functions will not split into sum of functions, but into sums of antisymmetric tensor products of wavefunctions in lower dimensions. In other words, a simple way to represent these non interacting molecules in terms of the wavefunction is to take

$$\Psi^n = \tau_{X_1^n} \cdot \psi_1 \wedge \cdots \wedge \tau_{X_p^n} \cdot \psi_p \tag{4}$$

where each ψ_j is an eigenfunction of $H^{N_j}(r_j, z_j)$ associated to the eigenvalue $\lambda_{\delta_j}^{N_j}(r_j, z_j)$. We have used here the notation

$$\tau_v \cdot \Psi(x_1, ..., x_N) := \Psi(x_1 - v, ..., x_N - v)$$

and we recall that the tensor product is defined for $\psi \in L_a^2(\mathbb{R}^{3N_1})$ and $\psi' \in L_a^2(\mathbb{R}^{3N_2})$ by

$$\psi \wedge \psi'(x_1, ..., x_{N_1+N_2}) = \frac{1}{\sqrt{N!N_1!N_2!}} \sum_{\sigma \in S_N} \varepsilon(\sigma) \psi(x_\sigma^1) \psi'(x_\sigma^2).$$

where $x_\sigma^1 := (x_{\sigma(1)}, ..., x_{\sigma(N_1)})$ and $x_\sigma^2 = (x_{\sigma(N_1+1)}, ..., x_{\sigma(N)})$.

With (4), one easily sees that $\rho^n = \sum_{j=1}^p \tau_{X_j^n} \cdot \rho_j$ with obvious notations, and that

$$H^N(R^n, Z)\Psi^n - c\Psi^n \to 0$$

in $L^2(\mathbb{R}^{3N})$ as $n \to +\infty$.

When a $\lambda_{\delta_j}^{N_j}(r_j, z_j)$ is degenerated, we can obtain the same behaviour by taking a wavefunction which is a sum of such antisymmetric tensor products

$$\Psi^n \in \bigwedge_{j=1}^p \tau_{X_j^n} \cdot ker\left(H^{N_j}(r_j, z_j) - \lambda_{\delta_j}^{N_j}(r_j, z_j)\right).$$

To simplify notations, we shall denote $\tau_n \cdot (\psi_1 \wedge \cdots \wedge \psi_p) := \tau_{X_1^n} \cdot \psi_1 \wedge \cdots \wedge \tau_{X_p^n} \cdot \psi_p$, so that $\Psi^n = \tau_n \cdot \Psi$ where $\Psi \in \bigwedge_{j=1}^p ker\left(H^{N_j}(r_j, z_j) - \lambda_{\delta_j}^{N_j}(r_j, z_j)\right)$.

Suppose now that a molecule splits into two identical pieces: $r_1 = r_2$ and $z_1 = z_2$, and that $N_1 \neq N_2$. At infinity, we shall obtain two molecules with the same configurations of the nuclei, but not the same number of electrons. Since there is no reason to distinguish the two states obtained by inverting the electrons between the two molecules, a wavefunction can be *a sum* of these two states with the same energies. We are thus led to introduce the following definition.

Definition 1. *Let* $r^n = (r_1^n, ..., r_p^n) \in \bigotimes_{j=1}^p \omega_j$ *be such that* $r_j^n \to r_j \in \omega_j$, *and* $R^n = R(t_n) := (X_1(t_n) + r_1, ..., X_p(t_n) + r_p)$, $X_j^n = X_j(t_n)$, *for some* $t_n \to +\infty$. *Let* c *be such that the set*

$$\mathcal{A}_c^N(r,z) = \left\{ (N_j, \delta_j) \in (\mathbb{N}^p)^2,\ N_1 + \cdots + N_p = N,\ \sum_{j=1}^{p} \lambda_{\delta_j}^{N_j}(r_j, z_j) = c \right\} \tag{5}$$

is not empty. The sequence (R^n, Ψ^n) *in* $\Omega \times SH_a^1(\mathbb{R}^{3N})$ converges to a critical point at infinity of energy c *if there exists some*

$$\Psi \in \sum_{(N_j,\delta_j) \in \mathcal{A}_c^N(r,z)} \left(\bigwedge_{j=1}^{p} ker\left(H^{N_j}(r_j, z_j) - \lambda_{\delta_j}^{N_j}(r_j, z_j) \right) \right) \tag{6}$$

such that

$$\|\Psi^n - \tau_n \cdot \Psi\|_{H_a^1(\mathbb{R}^{3N})} \to 0. \tag{7}$$

To justify the term *critical point*, we remark that one can prove

Lemma 1. *Let be* c *and* Ψ *that satisfy* (5) *and* (6). *Then*

$$(H^N(R^n, Z) - c)(\tau_n \cdot \Psi) \to 0$$

in $L^2(\mathbb{R}^{3N})$.

Details will be given later on.

Saying differently, a *critical point at infinity* is a class

$$\tau_K(r, \Psi) = \left\{ \tau_{X_1,...,X_p}(r, \Psi),\ X_j \in \mathbb{R}^3,\ |X_i - X_j| \geq K \right\}$$

where $\Psi \in \sum_{(N_j,\delta_j) \in \mathcal{A}_c^N(r,z)} \left(\bigwedge_{j=1}^{p} ker\left(H^{N_j}(r_j, z_j) - \lambda_{\delta_j}^{N_j}(r_j, z_j) \right) \right)$, $r_j \in \omega_j$ and $\tau_{X_1,...,X_p}$ is defined on each $\Omega \times \bigwedge_{j=1}^p H_a^1(\mathbb{R}^{3N_j})$ by

$$\tau_{X_1,...,X_p} \cdot r = (X_1 + r_1, \cdots, X_p + r_p)$$

$$\tau_{X_1,...,X_p} \cdot (\psi_1 \wedge \cdots \wedge \psi_p) = (\tau_{X_1} \psi_1) \wedge \cdots \wedge (\tau_{X_p} \psi_p).$$

A sequence (R^n, Ψ^n) converges to this critical point at infinity when there exists a $K_n \to +\infty$ such that

$$\lim_{n \to +\infty} d[(R^n, \Psi^n); \tau_{K_n}(r, \Psi)] = 0.$$

Let us now fix a sequence $t_n \to +\infty$ and some $r^n = (r_1^n, ..., r_p^n) \in \bigotimes_{j=1}^p \omega_j$ such that $r_j^n \to r_j \in \omega_j$, and denote $R^n = R(t_n)$, $X_j^n = X_j(t_n)$. We then have the following result concerning the behaviour of the eigenfunctions

Theorem 3. *We assume $1 \leq N \leq |Z|$ and $d \geq 1$. Let (Ψ^n) be a sequence of wavefunctions such that*

$$H^N(R^n, Z) \cdot \Psi^n = \lambda_d^N(R^n, Z) \cdot \Psi^n.$$

Then, up to a subsequence, we have $\lim_{n \to +\infty} \lambda_d^N(R^n, Z) := c$ with

$$\Lambda_1^N(r, z) \leq c = \sum_{j=1}^{p} \lambda_{\delta'_j}^{N'_j}(r_j, z_j) \leq \Lambda_d^N(r, z)$$

for some N'_j and δ'_j, and (R^n, Ψ^n) converges to a critical point at infinity of energy c.

2.2 The mountain pass method: a general result

Let us now come back to our mountain pass method, and consider again a neutral molecule ($N = |Z|$). Recall that (R, Ψ) and (R', Ψ') are two local minima of $(R, \Psi) \mapsto \mathcal{E}^N(R, \Psi)$, and that c and c' are defined by

$$c = \inf_{\gamma \in \Gamma} \max_{t \in [0;1]} \mathcal{E}^N(\gamma(t)) \tag{8}$$

$$\Gamma = \{\gamma \in \mathcal{C}^0([0;1], \Omega \times SH_a^1(\mathbb{R}^{3N})),\ \gamma(0) = (R, \Psi),\ \gamma(1) = (R', \Psi')\}.$$

$$c' = \inf_{r \in \mathcal{R}} \max_{t \in [0;1]} E^N(r(t), Z)$$

$$\mathcal{R} = \{r \in \mathcal{C}^0([0;1], \Omega),\ r(0) = R,\ r(1) = R'\}.$$

The following result enables to identify c in the case of lack of compactness:

Theorem 4. *We assume $N = |Z|$. We have $c = c'$. There exists a min-maxing sequence $(R^n, \Psi^n) \in \Omega \times H_a^1(\mathbb{R}^{3N})$ such that:*

If $\sum_{i \neq j} |R_i^n - R_j^n|$ is bounded then, up to a translation, (R^n, Ψ^n) converges strongly in $\Omega \times H_a^1(\mathbb{R}^{3N})$ to some critical point (R, Ψ) of $\mathcal{E}^N$ such that

$$H^N(R, Z) \cdot \Psi = c \cdot \Psi, \quad c = \lambda_1^N(R, Z).$$

If $\sum_{i \neq j} |R_i^n - R_j^n|$ is not bounded, there exists a $2 \leq p \leq M$, some $X_j^n \in \mathbb{R}^3$ with $j = 1, \ldots, p$ and a $R_0 > 0$ such that, changing the indices if necessary, $R^n = (X_1^n + r_1^n, \ldots, X_p^n + r_p^n)$, $\|r_j^n\| \leq R_0$, $Z = (z_1, \ldots, z_p)$, and $\lim_{n \to +\infty} |X_i^n - X_j^n| = +\infty$, $r_j^n \to r_j$. Then

$$c = \Lambda_1^N(r, z) = \min\left\{\sum_{j=1}^{p} E^{N_j}(r_j, z_j),\ N_1 + \cdots + N_p = N\right\}$$

and (R^n, Ψ^n) converges up to a subsequence to a critical point at infinity of energy $c = \Lambda_1^N(r, z)$.

As a consequence, in the non-compact case, the molecule splits into pieces, the electrons being shared among them and at their ground state. We also believe that the r_j correspond to positions of the nuclei with a Morse index equal to 0, but this is not necessary for the sequel.

This result should be seen as the first step towards concluding the existence of a critical point of energy c, by proving that the second case in Theorem 4 does not happen. Unfortunately, we met with serious difficulties when trying to solve this general problem. This is why the compactness will be shown in the next section for the special case of two interacting molecules with fixed nuclei.

Remark – In all this paper, we work with complex-valued wavefunctions Ψ. Although in other situations (minimization for instance) one often works with real-valued functions without any change, this is not the case here. In particular, the equality $c = c'$ is very easily obtained in this setting, while one can prove that this is also true for real-valued wavefunctions, but for well-chosen ground states Ψ and Ψ' only. See the proof for more details.

2.3 Compactness in the case of two interacting molecules

Now that we have identified the critical points at infinity for the mountain pass method, the next step is to show that min-maxing paths cannot approach these critical points. We study here the case of two interacting molecules with fixed nuclei. The parameters are then

- the distance between the two molecules (denoted by α in the sequel),
- the orientation of each molecule (represented by two rotations u and u'),
- the electronic wavefunction.

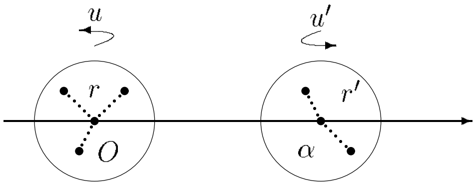


Figure 2: Two molecules with fixed nuclei.

So we consider $r = (r_1, ..., r_m) \in B(0, R_0)^m$ and $r' = (r'_1, ..., r'_{m'}) \in B(0, R_0)^{m'}$ such that $r_1 = r'_1 = 0$, $r_i \neq r_j$ and $r'_i \neq r'_j$ for $i \neq j$, and some $z = (z_1, ..., z_m)$, $z' = (z'_1, ..., z'_{m'})$. We denote by $Z = (z, z')$, and introduce

$$R(\alpha, u, u') = (u \cdot r, \alpha \vec{v} + u' \cdot r').$$

where $\vec{v}$ is a fixed vector of norm 1, $\alpha \in \mathbb{R}$, and u, u' are rotations in $\mathbb{R}^3$. We have used the notation $u \cdot r = (u \cdot r_1, ..., u \cdot r_m)$. We suppose now that $N = |Z|$ and define

$$\mathcal{E}^N(\alpha, u, u', \Psi) := \mathcal{E}^N(R(\alpha, u, u'), \Psi).$$

In [25], it is proved that $\mathcal{E}^N$ admits a minimum on $\mathbb{R} \times (SO_3(\mathbb{R}))^2 \times SH^1_a(\mathbb{R}^{3N})$. As in the previous sections, we shall assume that $\mathcal{E}^N$ possesses two local minima M and M'. Up to a rotation of each molecule, we may suppose that $\alpha(M) > 0$ and $\alpha(M') > 0$. We then consider

$$c = \inf_{\gamma \in \Gamma} \max_{t \in [0;1]} \mathcal{E}^N(\gamma(t))$$

where Γ is the set of all the continuous functions $\gamma : [0;1] \to X := (0;+\infty) \times (SO_3(\mathbb{R}))^2 \times SH^1_a(\mathbb{R}^{3N})$ such that $\gamma(0) = M$ and $\gamma(1) = M'$.

2.3.1 The mountain pass method

We begin this section by stating a result which is the analogue of Theorem 4 in this special setting.

Theorem 5. *We have*

- *either there exists a critical point* (α, u, u', Ψ) *of* $\mathcal{E}^N$ *on* X, *such that*
$$H^N(R(\alpha, u, u'), Z) \cdot \Psi = c \cdot \Psi, \quad c = \lambda_1^N(R(\alpha, u, u'), Z),$$
- *or*
$$c = \min\left\{E^{N_1}(r, z) + E^{N_2}(r', z'),\ N_1 + N_2 = N\right\}.$$

Roughly speaking, the non compactness of min-maxing sequences is related to the existence of two gradient lines going from a local minimum to some critical point at infinity of index 0. The idea is that an "optimal path" has to follow these lines, and then to connect the two critical points at infinity. Since the molecule is split here into two independent parts, the problem is now to find two mountain pass paths connecting each configuration of the two molecules – two similar problems of lower dimension. When the position of the nuclei in each molecule is fixed, these paths can be obtained by only applying some rotations. In other words, the minima always belong to the same connected component and this is why the situation will be simpler in this setting. When the position is not fixed, even if we may assume the existence of such paths (by induction), the situation is much more complicated and we hope to come back to this more general issue in the future.

The proof of Theorem 5 is very similar to the one of Theorem 4, and will be ommitted.

In order to prove that the second case in Theorem 5 does not happen, we need some information on the directions on which the energy decreases near the critical points at infinity. We shall thus need an expansion of the interaction energy between the two molecules when α grows. The terms involving in these expansion are classical. Let us first recall the definitions of the first multipoles.

Definition 2. *Let be* $R = (R_1, ..., R_M) \in \Omega$, $Z = (Z_1, ..., Z_M)$, *and* $\rho \in L^1(\mathbb{R}^3) \cap \mathcal{S}(\mathbb{R}^3 \setminus \{R_j\})$ *a non negative function such that* $\int_{\mathbb{R}^3} \rho = N > 0$. *Then*

1. *the* total density of charge *is the measure* $\tilde{\rho} := \rho - \sum_{j=1}^M Z_j \delta_{R_j}$. *The* total charge *is* $q := \int_{\mathbb{R}^3} \tilde{\rho} = N - |Z|$,
2. *the* dipole moment *is the vector* $P := \int_{\mathbb{R}^3} x\tilde{\rho}(x)\,dx = \int_{\mathbb{R}^3} x\rho(x)\,dx - \sum_{j=1}^M Z_j R_j$,
3. *the* quadrupole moment *is the matrix* $Q := \int_{\mathbb{R}^3} \left(xx^T - \frac{1}{3}|x|^2 I\right) \tilde{\rho}(x)\,dx$.

When ρ is the electronic density associated to some eigenstate Ψ, we shall use the notations ρ_Ψ, $\tilde{\rho}_\Psi$, P_Ψ and Q_Ψ.

This multipoles will be used in the expansion of the interaction energy. To illustrate this point, we give here the following

Lemma 2. *We assume that* N_1 *and* N_2 *are such that* $N_1 + N_2 = N$, $E^{N_1}(r, z) < \Sigma^{N_1}(r, z)$ *and* $E^{N_2}(r', z') < \Sigma^{N_2}(r', z')$. *Let* ψ_1 *and* ψ_2 *be two ground states of respectively* $H^{N_1}(r, z)$ *and* $H^{N_2}(r', z')$. *Denoting*

$$\Psi(\alpha, u, u') = (u \cdot \psi_1) \wedge (\tau_{\alpha\vec{v}} \cdot u' \cdot \psi_2),$$

we have

$$\begin{aligned}\mathcal{E}^N \left(R(\alpha, u, u'), \Psi(\alpha, u, u')\right) &= E^{N_1}(r, z) + E^{N_2}(r', z') \\ + \frac{q_1 q_2}{\alpha} + q_2 \frac{uP_1 \cdot \vec{v}}{\alpha^2} - q_1 \frac{u'P_2 \cdot \vec{v}}{\alpha^2} &+ \frac{(uP_1) \cdot (u'P_2) - 3(uP_1 \cdot \vec{v})(u'P_2 \cdot \vec{v})}{\alpha^3} \\ &+ \frac{3(q_2 u Q_1 u^T + q_1 u' Q_2 u'^T) v \cdot v}{2\alpha^3} + O\left(\frac{1}{\alpha^4}\right)\end{aligned}$$

for all $u, u' \in SO_3(\mathbb{R})$ *and when* α *goes to* $+\infty$.

In this result, q_k, P_k and Q_k are respectively the total charge, the dipole and the quadrupole moment associated to the electronic densities ρ_k of the states ψ_k.

The terms of this expansion can be interpreted respectively as the energies of the molecules, and the interaction energy between them, which decomposes into the charge/charge ($1/\alpha$), dipole/charge ($1/\alpha^2$), dipole/dipole and charge/quadrupole ($1/\alpha^3$) terms.

We are now able to state our main compactness results. As mentionned above, we had to add some hypothesis about the molecules "at infinity", concerning their multipoles in their ground state.

2.3.2 The case of charged molecules at infinity

Our first result will concern the case of monopoles at infinity, that is to say when the molecules are charged.

Theorem 6 (Charged molecules at infinity). *Let us assume that*

$$E^{N_1}(r,z)+E^{N_2}(r',z')=\min\left\{E^{n_1}(r,z)+E^{n_2}(r',z'),\ n_1+n_2=N\right\} \qquad (9)$$

for some N_1 and N_2 with $(N_1-|z|)(N_2-|z'|)\neq 0$.

Then the case 2) in Theorem 5 does not happen. Therefore c is a critical value of $\mathcal{E}^N$ on X.

Remark – By (9), we have for instance

$$\mu := E^{N_1}(r,z)-E^{|z|}(r,z) < E^{|z'|}(r',z')-E^{N_2}(r',z') := \mu'$$

for some N_1, N_2 such that $N_1+N_2=N$ and $N_1<|z|$. This can be viewed as a comparison between oxydo-reduction potentials. So (9) will be probably true if one molecule is a oxydant and the other is a reductor.

2.3.3 The case of neutral molecules with dipole moments at infinity

If the two molecules at infinity are neutral, the first term involving in the expansion of the interaction energy is the dipole/dipole term. This is why we shall now consider the case of molecules that possess some dipole moment in their ground state (experiment suggests that this is the case for every non symmetric molecule).

Let us introduce the following definition

Definition 3. *Let be $R=(R_1,...,R_M)\in\Omega$, $Z=(Z_1,...,Z_M)$ and $N>0$ such that $\lambda_1^N(R,Z)<\Sigma^N(R,Z)$. We shall say that the molecule (R,Z,N) possesses a dipole moment at its ground state if $P_\Psi\neq 0$ for all ground state Ψ.*

Since $V := ker\left(H^N(R,Z)-E^N(R,Z)\right)$ is finite dimensional, let us notice that this implies $\min\{|P_\Psi|,\ \Psi\in V,\ \|\Psi\|_{L^2}=1\}>0$.

We then have the following result:

Theorem 7 (Neutral molecules with dipole moments at infinity). *Let us assume that*

(H1) $E^{|z|}(r,z)+E^{|z'|}(r',z')<E^{N_1}(r,z)+E^{N_2}(r',z')$ for all N_1, N_2 such that $N_1+N_2=N$ and $(N_1-|z|)(N_2-|z'|)\neq 0$,

(H2) the two molecules $(r,z,|z|)$ and $(r',z',|z'|)$ possess a dipole moment at their ground state,

(H3) $E^{|z|}(r,z)$ or $E^{|z'|}(r',z')$ is non-degenerated.

Then the case 2) in Theorem 5 does not happen. Therefore c is a critical value of $\mathcal{E}^N$ on X.

Remark – *(H3)* is a purely mathematical restriction that simplifies the proof.

Let us explain the general idea of the proof. Recall that the dipole/dipole interaction energy can be written $F(P,P')/\alpha^3$ (see Lemma 2). It is shown in Appendix 2 that the critical points of F which have a non-negative energy have a Morse index which is at least one. If a path approaches a critical point at infinity then, to pull down the energy along the path, one may use either the rotations of the molecules if the dipole/dipole interaction energy is positive (thanks to this Morse index information on F), or the distance between them if it is negative (because $\alpha \mapsto F(P,P')/\alpha^3$ is then increasing). This is why min-maxing paths do not approach the critical points at infinity, and give thus a compact Palais-Smale sequence. Obviously, this general idea does not suffice to lead the proof and there are some other difficulties (essentially due to the complexity of the model) that are explicited in the next section.

Remark – This general information on the Morse index is probably true for the others multipoles interaction energies, a fact that could be used to treat the general case.

3 Proofs

3.1 Proof of Theorems 2 and 3

3.1.1 Preliminaries

We shall use the following lemma, which is an adaptation of results in [15, 16, 11, 12, 13], and which is proved in Appendix 1.

Lemma 3. *Let Ψ_R be an eigenfunction associated to the eigenvalue $\lambda_d^N(R,Z)$ and ρ_R be the electronic density. We introduce $\epsilon_R = \Sigma^N(R,Z) - \lambda_d^N(R,Z)$. Then*

1. *ρ_R satisfies the inequation*

$$-\frac{1}{2}\Delta\rho_R + V_R\rho_R + \epsilon_R\rho_R \leq 0. \tag{10}$$

2. *With $R_1(\epsilon) := max\left(R_0+1, R_0+\frac{2Np}{\epsilon}\right)$ and $C(\epsilon) := \cup_{j=1}^p\{x,\ |x-X_j| = R_1(\epsilon)\}$, and if $r > 2R_1(\epsilon_R)$, then we have*

$$\begin{aligned}\rho_R(x) &\leq \|\rho_R\|_{L^\infty(C(\epsilon_R))}\sum_{j=1}^p e^{-\sqrt{\epsilon_R/p}(|X_j-x|-R_1(\epsilon_R))}\\ &\leq p\|\rho_R\|_{L^\infty(C(\epsilon_R))}e^{-\sqrt{\epsilon_R/p}(\delta(x)-R_1(\epsilon_R))}\\ &\leq Me^{-\sqrt{\epsilon_R/p}(\delta(x)-R_1(\epsilon_R))},\end{aligned} \tag{11}$$

   on $\mathcal{U}(R_1(\epsilon_R))$, where $\delta(x) = \min\{|x-X_j|,\ j=1,\ldots,d\}$, and $M = M(p,N,R_1(\epsilon_R))$.

The explicit bound (11) has been written in order to show the dependence of all the constants with regard to ϵ_R. It is clearly not optimal. It shows a non-isotropic exponential decay of the electronic density, which will be uniform if $\epsilon_R \nrightarrow 0$. This type of bounds is studied in the work of Agmon [1] and we do not know if one can use his formalism to obtain the same result. Isotropic exponential bounds for N-body eigenfunctions are frequently seen in the literature, but surprising is the fact that such non-isotropic bounds has not yet been noticed.

Lemma 4. *For all $\alpha > 0$, there exists a constant $M = M(\alpha, N, R_0)$ such that*

$$t_R(x) \leq M \int_{B(x,\alpha)} \rho_R(y)\, dy$$

on $\mathcal{U}(R_0 + 1/2 + \alpha)$.

Proof of Lemma 4 – see [16]. ☐

Lemma 5. *For all $j = 1, ..., p$, $d \geq 1$ and $n \leq |z_j|$, we have*

$$\inf_{r_j \in \omega_j} (\Sigma^n(r_j, z_j) - \lambda_d^n(r_j, z_j)) > 0.$$

Proof – We have

$$\Sigma^n(r_j, z_j) - \lambda_d^n(r_j, z_j) = \tilde{\Sigma}^n(r_j, z_j) - \tilde{\lambda}_d^n(r_j, z_j)$$

where $\tilde{\lambda}_d^n(r_j, z_j)$ and $\tilde{\Sigma}^n(r_j, z_j)$ are the d^{th} eigenvalue and the bottom of the essential spectrum of the Hamiltonian with the nuclei interaction removed

$$\tilde{H}^n(r_j, z_j) = \sum_{i=1}^{n} \left(-\frac{1}{2}\Delta_{x_i} + V_{r_j}(x_i) \right) + \sum_{1 \leq i < j \leq n} \frac{1}{|x_i - x_j|}.$$

By Zhislin's Theorem, it is known that

$$\tilde{\Sigma}^n(r_j, z_j) - \tilde{\lambda}_d^n(r_j, z_j) > 0$$

for all $r_j \in \overline{\omega_j}$ and, since this function is continuous with regard to r_j,

$$\inf_{r_j \in \omega_j} (\Sigma^n(r_j, z_j) - \lambda_d^n(r_j, z_j)) > 0.$$

☐

Lemma 6. *If the minimum*

$$\min \left\{ \sum_{j=1}^{p} \lambda_{\delta_j}^{N_j}(r_j, z_j),\ N_1 + ... + N_p = N,\ \prod_{j=1}^{p} \delta_j = d \right\}.$$

is attained for $N_1, ..., N_j$ and $\delta_1, ..., \delta_p$, then necessarily

$$\lambda_{\delta_j}^{N_j}(r_j, z_j) < \Sigma_{\delta_j}^{N_j}(r_j, z_j)$$

for all $j = 1, ..., p$.

Proof of Lemma 6 – Remark that by definition $\lambda^0_{\delta_j}(r_j, z_j) < \Sigma^0(r_j, z_j) = +\infty$ for all δ_j. We argue by contradiction and suppose that there exists a k such that $N_k > 0$ and $\lambda^{N_k}_{\delta_k}(r_k, z_k) = \Sigma^{N_k}(r_k, z_k) = E^{N_k-1}(r_k, z_k)$. Theorem 1 implies $N_k \geq |z_k| + 1$. Since $\sum_{j=1}^p (N_k - |z_k|) = N - |Z| \leq 0$, there exists a $l \neq k$ such that $N_l < |z_l|$. We then let $\delta'_j = \delta_j$, $N'_j = N_j$ for $j \notin \{k, l\}$, $\delta'_k = 1$, $N'_k = N_k - 1$, $\delta'_l = \delta_k \delta_l$, and $N'_l = N_l + 1$. We obtain

$$\begin{aligned}
\sum_{j=1}^p \lambda^{N_j}_{\delta_j}(r_j, z_j) - \sum_{j=1}^p \lambda^{N'_j}_{\delta'_j}(r_j, z_j) &= \lambda^{N_l}_{\delta_l}(r_l, z_l) - \lambda^{N_l+1}_{\delta'_l}(r_l, z_l) \\
&\geq E^{N_l}(r_l, z_l) - \lambda^{N_l+1}_{\delta'_l}(r_l, z_l) \\
&= \Sigma^{N_l+1}(r_l, z_l) - \lambda^{N_l+1}_{\delta'_l}(r_l, z_l) \\
&> 0
\end{aligned}$$

since $N_l + 1 \leq |z_l|$ (Zhislin Theorem), which is a contradiction. □

3.1.2 Proof of Theorem 2

We are now able to prove Theorem 2.

We first prove 2). Suppose that the right hand side is attained for some $N_1, ..., N_j$ and $\delta_1, ..., \delta_p$ such that $N_1 + ... + N_p = N$ and $\prod_{j=1}^p \delta_j = p$. For the sake of simplicity, we may assume that $N_j > 0$ for all $j = 1, ..., p$. By Lemma 6 and Theorem 1, there exist eigenfunctions $\Psi_j^k \in L^2_a(\mathbb{R}^{3N_j})$ satisfying

$$H^{N_j}(r_j, z_j)\Psi_j^k = \lambda_k^{N_j}(r_j, z_j)\Psi_j^k, \quad \int_{\mathbb{R}^{3N_j}} \Psi_j^k \Psi_j^l = \delta_{kl}$$

for all $j = 1, ..., p$ and $k = 1, ..., \delta_j$. If

$$V_j = span(\Psi_j^k,\ k = 1, ..., \delta_j) \subset L^2_a(\mathbb{R}^{3N_j})$$

then we have

$$\max_{\Psi \in V_j,\ \|\Psi\|^2_L = 1} \langle H^{N_j}(r_j, z_j)\Psi, \Psi\rangle = \lambda^{N_j}_{\delta_j}(r_j, z_j).$$

We now consider a sequence $t_n \to +\infty$ such that $\lim_{n\to+\infty} \lambda_d^N(R(t_n), Z) = \limsup_{t\to+\infty} \lambda_d^N(R(t), Z)$. If $\Psi \in L^2(\mathbb{R}^{3N})$, we introduce

$$\Psi_j^{k,n} = \tau_{X_j(t_n)} \cdot \Psi_j^k$$

$$\tilde{V}_j^n = span(\Psi_j^{k,n},\ k = 1, ..., \delta_j) \subset L^2_a(\mathbb{R}^{3N_j}).$$

(we recall that τ_v is the translation by v).

Now, let be

$$W_n = \tilde{V}_1^n \wedge \cdots \wedge \tilde{V}_p^n = span(\Psi_1^{k_1,n} \wedge \cdots \wedge \Psi_p^{k_p,n},\ 1 \leq k_j \leq \delta_j)$$

which is a space of dimension $\prod_{j=1}^{d} \delta_j = d$. If

$$\Psi = \sum_{1 \le k_j \le \delta_j} c_{k_1,\dots,k_p} \Psi_1^{k_1,n} \wedge \cdots \wedge \Psi_p^{k_p,n} \in W_n,$$

and $\sum |c_{k_1,\dots,k_p}|^2 = 1$, we have

$$\langle H^N(R,Z)\Psi, \Psi\rangle = \sum_{j=1}^{p} \sum_{1 \le k_j \le \delta_j} |c_{k_1,\dots,k_p}|^2 \langle H^{N_j}(r_j, z_j)\Psi_j^{k_j,n}, \Psi_j^{k_j,n}\rangle + e_n$$

where e_n is the interaction energy between the p molecules. It is the sum of three terms

$$e_n = e_n^1 + e_n^2 + e_n^3.$$

e_n^1 is the interaction between electrons in different molecules, and contains terms like

$$\iint \frac{(\Psi_{j_1}^{k_{j_1}} \Psi_{j_1}^{k'_{j_1}})(x,\dots)\Psi_{j_2}^{k_{j_2}} \Psi_{j_2}^{k'_{j_2}})(y,\dots)}{|x - y + X_{j_2}(t_n) - X_{j_1}(t_n)|} \, dx \, dy.$$

with $j_1 \neq j_2$. e_n^2 is the interaction between electrons and nuclei of different molecules, and contains terms like

$$\iint \frac{z_{j_2,i}(\Psi_{j_1}^{k_{j_1}} \Psi_{j_1}^{k'_{j_1}})(x,\dots)}{|x - r_{j_2,i} + X_{j_2}(t_n) - X_{j_1}(t_n)|} \, dx \, dy$$

with $j_1 \neq j_2$. Finally, e_n^3 is the interaction between nuclei of different molecules

$$e_n^3 = \sum_{j_1 < j_2} \sum_{1 \le k_j \le m_j} \frac{z_{j_1,k_{j_1}} z_{j_2,k_{j_1}}}{|r_{j_1,k_{j_1}} - r_{j_2,k_{j_2}} + X_{j_2}(t_n) - X_{j_1}(t_n)|}.$$

It is now easy to see that each of this term tends to 0 as $n \to +\infty$.

By definition, we have

$$\begin{aligned}
\lambda_d^N(R,Z) &\le \max_{\sum |c_{k_1,\dots,k_p}|^2 = 1} \langle H^N(R,Z)\Psi, \Psi\rangle \\
&\le \sum_{j=1}^{p} \max_{\sum |c_{k_1,\dots,k_p}|^2 = 1} \sum_{1 \le k_j \le \delta_j} |c_{k_1,\dots,k_p}|^2 \lambda_{k_j}^{N_j}(r_j, z_j) + \max e_n \\
&\le \sum_{j=1}^{p} \lambda_{\delta_j}^{N_j}(r_j, z_j) + \max e_n.
\end{aligned}$$

We may now pass to the limit as $n \to +\infty$ in this inequality and obtain the bound

$$\limsup_{t \to +\infty} \lambda_d^N(R(t), Z) \le \min \left\{ \sum_{j=1}^{p} \lambda_{\delta_j}^{N_j}(r_j, z_j),\ N_1 + \dots + N_p = N,\ \prod_{j=1}^{p} \delta_j = d \right\}.$$

We then prove simultaneously 1) 3) 4) by induction on $N = 1, ..., |Z|$.

For $N = 1$, it is known that

$$\Sigma^1(R, Z) = E^0(R, Z) = \sum_{1 \le i < j \le M} \frac{Z_i Z_j}{|R_i - R_j|},$$

and so

$$\lim_{t \to +\infty} \Sigma^1(R(t), Z) = \sum_{j=1}^{p} \sum_{1 \le k < l \le m_j} \frac{z_{j,k} z_{j,l}}{|r_{j,k} - r_{j,l}|} = \sum_{j=1}^{p} E^0(r_j, z_j).$$

As a consequence

$$\begin{aligned} &\liminf_{t \to +\infty} \left(\Sigma^1(R(t), Z) - \lambda_d^1(R(t), Z)\right) \\ &\qquad \ge \sum_{j=1}^{p} E^0(r_j, z_j) - \left(\lambda_d^1(r_1, z_1) + \sum_{j=2}^{p} E^0(r_j, z_j)\right) \\ &\qquad\qquad = E^0(r_1, z_1) - \lambda_d^1(r_1, z_1) = \Sigma^1(r_1, z_1) - \lambda_d^1(r_1, z_1) \end{aligned}$$

and

$$\inf_{r_i \in \omega_i} \liminf_{t \to +\infty} \left(\Sigma^1(R(t), Z) - \lambda_d^1(R(t), Z)\right) \ge \inf_{r_1 \in \omega_1} \left(\Sigma^1(r_1, z_1) - \lambda_d^1(r_1, z_1)\right) > 0$$

by lemma 5. The uniform exponential decay is then a consequence of lemmas 3 and 4.

Let $t_n \to +\infty$ be such that $\lim_{n \to +\infty} E^1(R(t_n), Z) = \liminf_{t \to +\infty} E^1(R(t), Z)$, and $\phi^n \in L^2(\mathbb{R}^3)$ be such that

$$H^1(R(t_n), Z)\phi^n = E^1(R(t_n), Z)\phi^n.$$

By the uniform exponential decay, we may write $\phi^n = \sum_{j=1}^{p} \phi_j^n + \alpha_n$ where $supp(\phi_j^n) \subset B(X_j, r_n/3)$, and $\|\alpha_n\|_{H^1} \to 0$. Then

$$\langle H^1(R(t_n), Z)\phi^n, \phi^n\rangle = \sum_{j=1}^{p} \langle \tilde{H}^1(r_j, z_j)\phi_j^n, \phi_j^n\rangle + \sum_{j=1}^{p} \sum_{1 \le k < l \le m_j} \frac{z_{j,k} z_{j,l}}{|r_{j,k} - r_{j,l}|} + e_n$$

where $\tilde{H}$ is the Hamiltonian with the nuclei interaction removed, and $e_n \to 0$. We have

$$\begin{aligned} \sum_{j=1}^{p} \langle \tilde{H}^1(r_j, z_j)\phi_j^n, \phi_j^n\rangle &\ge \sum_{j=1,\dots,p} \tilde{E}^1(r_j, z_j) \|\phi_j^n\|_{L^2}^2 \\ &\ge \min_{j=1,\dots,p} \tilde{E}^1(r_j, z_j) \left(\sum_{j=1,\dots,p} \|\phi_j^n\|_{L^2}^2\right) \end{aligned}$$

so

$$\begin{aligned}\langle H^1(R(t_n),Z)\phi^n,\phi^n\rangle &\geq \min_{j=1,\ldots,p}\tilde{E}^1(r_j,z_j)+\sum_{j=1}^{p}\sum_{1\leq k<l\leq m_j}\frac{z_{j,k}z_{j,l}}{|r_{j,k}-r_{j,l}|}\\ &= \min\left\{\sum_{j=1}^{p}E^{N_j}(r_j,z_j),\ N_1+\ldots+N_p=1\right\}\end{aligned}$$

and finally

$$\lim_{t\to+\infty}E^1(R(t),Z)=\min\left\{\sum_{j=1}^{p}E^{N_j}(r_j,z_j),\ N_1+\ldots+N_p=1\right\}.$$

Let us now assume that 1) 3) 4) have been proved for $N-1<|Z|$. We have $\Sigma^N(R,Z)=\lambda_1^{N-1}(R,Z)$ so

$$\begin{aligned}\lim_{t\to+\infty}\Sigma^N(R(t),Z) &= \min\left\{\sum_{j=1}^{p}E^{N_j}(r_j,z_j),\ N_1+\ldots+N_p=N-1\right\}\\ &= \sum_{j=1}^{p}E^{N_j}(r_j,z_j)\end{aligned}$$

for some $N_1,\ldots,N_p$. But $\sum_{j=1}^{p}(|z_j|-N_j)=|Z|-(N-1)>0$ so there exists a k such that $N_k<|z_k|$. We then have, for all $d\geq 1$,

$$\begin{aligned}&\liminf_{t\to+\infty}\left(\Sigma^N(R(t),Z)-\lambda_d^N(R(t),Z)\right)\\ &\qquad\geq\sum_{j=1}^{p}E^{N_j}(r_j,z_j)-\left(\lambda_d^{N_k+1}(r_k,z_k)+\sum_{j=1,\ j\neq k}^{p}E^{N_j}(r_j,z_j)\right)\\ &\qquad=E^{N_k}(r_k,z_k)-\lambda_d^{N_k+1}(r_k,z_k)=\Sigma^{N_k+1}(r_k,z_k)-\lambda_d^{N_k+1}(r_k,z_k)\end{aligned}$$

and

$$\begin{aligned}&\inf_{r_i\in\omega_i}\liminf_{t\to+\infty}\left(\Sigma^N(R(t),Z)-\lambda_d^N(R(t),Z)\right)\\ &\qquad\qquad\geq\inf_{\substack{j=1,\ldots,p\\ n\leq|z_j|}}\inf_{r_j\in\omega_j}\left(\Sigma^n(r_j,z_j)-\lambda_d^n(r_j,z_j)\right)>0\end{aligned}$$

by lemma 5. The uniform exponential decay 4) is then a consequence of lemmas 3 and 4.

We now prove the inequality

$$\liminf_{t\to+\infty}E^N(R(t),Z)\geq\min\left\{\sum_{j=1}^{p}E^{N_j}(r_j,z_j),\ N_1+\ldots+N_p=N\right\}$$

by using a variant of classical N-body geometric methods for Schrödinger operators [30, 29, 19], which is used in [10].

Let $t_n \to +\infty$ be such that $\lim_n E^N(R(t_n), Z) = \liminf_t E^N(R(t), Z)$, and Ψ_n an associated sequence of ground states, with densities ρ_{Ψ_n} and t_{Ψ_n}. We denote $R^n = R(t_n)$ and $X_j^n = X_j(t_n)$. Due to the uniform exponential decay, one has

$$\lim_{n\to+\infty} \int_{\mathcal{U}(t_n/3)} \rho_{\Psi_n} = \lim_{n\to+\infty} \int_{\mathcal{U}(t_n/3)} t_{\Psi_n} = 0. \tag{12}$$

Let $\xi_n \in \mathcal{C}^\infty(\mathbb{R}^3, [0;1])$ be a cutoff function such that $\xi_n \equiv 0$ on $\mathcal{U}(t_n/3)$, $\xi_n \equiv 1$ on $\mathbb{R}^3 \setminus \mathcal{U}(t_n/3 - 1)$, and $\|\nabla \xi_n\|_\infty \leq 1$, $\|\Delta \xi_n\|_\infty \leq 2$. We then introduce $\chi_n(x_1, ..., x_N) = \prod_{i=1}^N \xi_n(x_i)$ and $\tilde{\Psi}_n = \chi_n \Psi_n$. Using (12), it is then easy to see that $\|\Psi_n - \tilde{\Psi}_n\|_{H^1} \to 0$, and

$$\begin{aligned} H^N(R^n, Z) \cdot \tilde{\Psi}_n - \lambda_1^N(R^n, Z) \cdot \tilde{\Psi}_n &= -\sum_{i=1}^N (2\nabla_{x_i}\chi_n \cdot \nabla_{x_i}\Psi_n + \Psi_n \Delta_{x_i}\chi_n) \\ &\to 0 \quad \text{in } L^2(\mathbb{R}^{3N}), \end{aligned}$$

$$\mathcal{E}^N(R^n, \tilde{\Psi}_n) - \lambda_1^N(R^n, \Psi_n)\|\tilde{\Psi}_n\|_{L^2(\mathbb{R}^{3N})} = \sum_{i=1}^N \int |\Psi_n|^2 |\nabla_{x_i}\chi_n|^2 \to 0.$$

Now, we may write $\xi_n = \sum_{j=1}^p \xi_n^j$ where $Supp(\xi_n^j) \subset B(X_j, t_n/3)$, and

$$\tilde{\Psi}_n = \sum_{1 \leq k_j \leq p} \xi_n^{k_1}(x_1) \cdots \xi_n^{k_N}(x_N) \Psi_n := \sum_{1 \leq k_j \leq p} \Psi_n^{k_1, ..., k_N}.$$

Since the $\Psi_n^{k_1,...,k_N}$ have disjoint supports,

$$|\tilde{\Psi}_n|^2 = \sum_{1 \leq k_j \leq p} |\Psi_n^{k_1,...,k_N}|^2, \quad \mathcal{E}^N(R^n, \tilde{\Psi}_n) = \sum_{1 \leq k_j \leq p} \mathcal{E}^N(R_n, \Psi_n^{k_1,...,k_N}),$$

$$\left(H^N(R^n, Z) - \lambda_1^N(R^n, Z)\right) \cdot \Psi_n^{k_1,...,k_N} \to 0$$

in $L^2(\mathbb{R}^{3N})$ for all $k_1, ...k_N$. To end the proof of Theorem 2, it suffices to underestimate $\mathcal{E}^N(R^n, \tilde{\Psi}_n)$. We now fix $k_1, ..., k_N$ and introduce $C_j = \{i,\ k_i = j\}$, $N_j = |C_j|$. Remark that $\Psi_n^{k_1,...,k_N}$ is antisymmetric in $(x_i)_{i \in C_j}$ for all $j = 1, ..., p$. Then

$$\begin{aligned} \mathcal{E}^N(R^n, \Psi_n^{k_1,...,k_N}) &= \sum_{j=1}^p \left(\sum_{i \in C_j} \int \frac{1}{2} |\nabla_{x_i} \Psi_n^{k_1,...,k_N}|^2 - \sum_{i \in C_j} \int V_{\tilde{r}_j}(x_i) |\Psi_n^{k_1,...,k_N}|^2 \right. \\ &\quad \left. + \sum_{k,l \in C_j} \int \frac{|\Psi_n^{k_1,...,k_N}|^2}{|x_k - x_l|} + E^0(r_j, z_j) \right) + e_n \end{aligned}$$

where

$$e_n = \sum_{1 \leq j \neq j' \leq p} \left(\sum_{i \in C_j} \int V_{\tilde{r}_{j'}}(x_i) |\Psi_n^{k_1,...,k_N}|^2 + \sum_{i \in C_j} \sum_{i' \in C_{j'}} \int \frac{|\Psi_n^{k_1,...,k_N}|^2}{|x_i - x_{i'}|} \right) + e_n',$$

e'_n being the interaction energy between nuclei in different molecules, which easily tends to 0 as $n \to +\infty$. Now

$$|e_n| \le \sum_{1 \le j \ne j' \le p} \left(\sum_{i \in C_j} \int \frac{3|z_j|}{t_n} |\Psi_n^{k_1,\dots,k_N}|^2 + 3 \sum_{i \in C_j} \sum_{i' \in C_{j'}} \int \frac{|\Psi_n^{k_1,\dots,k_N}|^2}{t_n} \right) + e'_n \to 0$$

as $n \to +\infty$. Finally, since $\Psi_n^{k_1,\dots,k_N}$ is antisymmetric in $(x_i)_{i \in C_j}$ for all $j = 1, \dots, p$ and thanks to the translation invariance of the Hamiltonian,

$$\mathcal{E}^N(R^n, \Psi_n^{k_1,\dots,k_N}) \ge \left(\sum_{j=1}^{p} E^{N_j}(r_j, z_j) \right) \|\Psi_n^{k_1,\dots,k_N}\|_{L^2}^2 + e_n.$$

Passing to the limit, we obtain

$$\lim_{n \to +\infty} \mathcal{E}^N(R^n, \tilde{\Psi}_n) \ge \min \left\{ \sum_{j=1}^{p} E^{N_j}(r_j, z_j),\ N_1 + \cdots N_p = N \right\}$$

which ends the proof of Theorem 2. $\square$

3.1.3 Proof of Theorem 3

The proof uses exactly the same N-body geometric method as the end of the proof of Theorem 2, but with $\lambda_1^N(R^n, Z)$ replaced by $\lambda_d^N(R^n, Z)$. If we suppose that $\lim_{n \to +\infty} \lambda_d^N(R^n, Z) = c$, then passing to the limit and using Theorem 2

$$c \le \limsup_{n \to +\infty} \lambda_d^N(R^n, Z) \le \Lambda_d^N(r, z).$$

We have

$$\left(H^N(R^n, Z) - c \right) \cdot \Psi_n^{k_1,\dots,k_N} \to 0$$

in $L^2(\mathbb{R}^{3N})$ for all $k_1, \dots k_N$. Since all the interaction terms tend to 0 (see the proof of Theorem 2), we obtain

$$\left(\sum_{j=1}^{p} H^{N_j}(X_j^n + r_j^n, z_j)_{C_j} - c \right) \cdot \Psi_n^{k_1,\dots,k_N} \to 0$$

where the Hamiltonian $H^{N_j}(X_j^n + r_j^n, z_j)_{C_j}$ acts on the variables $(x_i)_{i \in C_j}$. Due to the translation invariance, we obtain

$$\left(\sum_{j=1}^{p} H^{N_j}(r_j^n, z_j)_{C_j} - c \right) \cdot \tilde{\Psi}_n^{k_1,\dots,k_N} \to 0$$

where $\tilde{\Psi}_n^{k_1,\dots,k_N}(x_1, \dots, x_N) = \Psi_n^{k_1,\dots,k_N}(X_{k_i}^n + x_i)$. But due to the exponential decay of Ψ_n, $\tilde{\Psi}_n^{k_1,\dots,k_N}$ is precompact in $H^1(\mathbb{R}^{3N})$ and converges up to a subsequence to some $\tilde{\Psi}^{k_1,\dots,k_N}$ such that

$$\left(\sum_{j=1}^{p} H^{N_j}(r_j, z_j)_{C_j} \right) \tilde{\Psi}^{k_1,\dots,k_N} = c \cdot \tilde{\Psi}^{k_1,\dots,k_N}.$$

We thus have either c is an eigenvalue of $\left(\sum_{j=1}^p H^{N_j}(r_j,z_j)_{C_j}\right)$ on the tensor product $\bigotimes_{j=1}^p L_a^2(\mathbb{R}^{3N_j})_{C_j}$ (with an obvious notation), or $\tilde{\Psi}^{k_1,\dots,k_N}=0$.

Lemma 7. *We have* $\sigma\left(\sum_{j=1}^p H^{N_j}(r_j,z_j)_{C_j}\right)=\sum_{j=1}^p \sigma\left(H^{N_j}(r_j,z_j)_{C_j}\right)$ *so that* $\sigma_{ess}\left(\sum_{j=1}^p H^{N_j}(r_j,z_j)_{C_j}\right)=[\Sigma;+\infty)$ *with*

$$\begin{aligned}\Sigma &= \min\left\{\sum_{j\neq j_0} E^{N_j}(r_j,z_j)+\Sigma^{N_{j_0}}(r_{j_0},z_{j_0}),\ 1\leq j_0\leq p\right\}\\ &> \Lambda_d^N(r,z)\end{aligned}$$

for all $d\geq 1$.

Proof of Lemma 7 – The fact that the spectrum of $\sum_{j=1}^p H^{N_j}(r_j,z_j)_{C_j}$ is the sum $\sum_{j=1}^p \sigma\left(H^{N_j}(r_j,z_j)_{C_j}\right)$ is standard (see for instance [27], Theorem VIII-33). Suppose now that $\Sigma=\sum_{j\neq j_0} E^{N_j}(r_j,z_j)+\Sigma^{N_{j_0}}(r_{j_0},z_{j_0})$ for some $1\leq j_0\leq p$. If $\lambda_d^{N_{j_0}}(r_{j_0},z_{j_0})<\Sigma^{N_{j_0}}(r_{j_0},z_{j_0})$ then obviously $\Sigma>\Lambda_d^N(r,z)$. If $\lambda_d^{N_{j_0}}(r_{j_0},z_{j_0})=\Sigma^{N_{j_0}}(r_{j_0},z_{j_0})$ then $\Sigma>\Lambda_d^N(r,z)$ by lemma 6. $\square$

As a consequence, if c is an eigenvalue of $\left(\sum_{j=1}^p H^{N_j}(r_j,z_j)_{C_j}\right)$, it is necessary below its essential spectrum. It is then easy to see that this implies

$$\tilde{\Psi}^{k_1,\dots,k_N}\in\bigotimes_{j=1}^p ker\left(H^{N_j}(r_j,z_j)-\lambda_{\delta_j}^{N_j}(r_j,z_j)\right)_{C_j}$$

for some $\lambda_{\delta_j}^{N_j}(r_j,z_j)<\Sigma^{N_j}(r_j,z_j)$.

Now, we have $\|\Psi^n-\tau_n\cdot\Psi\|_{H_a^1(\mathbb{R}^{3N})}\to 0$ where $\Psi=\sum_{k_1,\dots,k_N}\tilde{\Psi}^{k_1,\dots,k_N}$. $\square$

3.2 Proof of Theorem 4

We may suppose $c>\max(\mathcal{E}^N(R,\Psi),\mathcal{E}^N(R',\Psi'))$.

Let us first prove the equality $c=c'$. Indeed, $c'\leq c$ is obvious. Let be $r_n\in\mathcal{R}$ a sequence such that $m_n:=\max_{t\in[0;1]}E^N(r_n(t),Z)\to c'$ as $n\to+\infty$. For each $n\in\mathbb{N}$, we define

$$c_n=\min_{\psi\in\Gamma_\Psi}\max_{t\in[0;1]}\mathcal{E}^N(r_n(t),\psi(t))$$

$$\Gamma_\Psi=\left\{\psi\in\mathcal{C}^0([0;1],SH_a^1(\mathbb{R}^{3N})),\ \psi(0)=\Psi,\ \psi(1)=\Psi'\right\}.$$

We may now apply the methods of [8] to obtain some sequences $t_k\in[0;1]$ and $(\Psi_k)_{k\geq 1}$ such that

1. $\lim\limits_{k\to+\infty}\mathcal{E}^N(r^n(t_k),\Psi_k)=c_n$,

2. $H^N(r_n(t_k), Z)\cdot\Psi_k - \mathcal{E}^N(r_n(t_k), \Psi_k)\cdot\Psi_k \to 0$ in $L^2(\mathbb{R}^{3N})$,

3. $\mathcal{E}^N(r_n(t_k), \Psi_k) \le \lambda_1^N(r_n(t_k), Z) + \epsilon_k, \quad \lim_{k\to+\infty} \epsilon_k = 0$

1, 2) correspond to the classical fact that one can obtain min-maxing sequences that are almost critical. On the other hand, 3) is a consequence of the less-known fact that one can obtain Palais-Smale sequences with Morse-type information related to the dimension of the homotopy-stable class used in the min-max method, which is 1 here (paths are deformations of [0; 1]). Since we are in $\mathbb{C} = \mathbb{R}^2$, eigenvectors always have an even Morse index and this is why λ_1^N appears in 3) and not λ_2^N.

The fact that such a sequence (Ψ_k) is precompact in $H_a^1(\mathbb{R}^{3N})$ is now a simple consequence of Theorem 1 - 4). Indeed, the compactness below the essential spectrum is nothing else but the Palais-Smale condition of $\mathcal{E}^N$ with Morse-type information introduced in [14]. We have the following general lemma, whose proof is postponed until the end of the proof of Theorem 4.

Lemma 8. *We assume that* $Z = (Z_1, ..., Z_M)$ *is such that* $N \le |Z|$. *Let* (R^n, Ψ^n) *be a sequence in* $\Omega \times SH_a^1(\mathbb{R}^{3N})$ *such that*

1. $R^n \to R \in \Omega$

2. $\lim_{n\to+\infty} \mathcal{E}^N(R^n, \Psi^n) = c$,

3. $H^N(R^n, Z)\cdot\Psi^n - \mathcal{E}^N(R^n, \Psi^n)\cdot\Psi^n \to 0$ *in* $L^2(\mathbb{R}^{3N})$,

4. there exist $d_0 \ge 1$ *and* $\epsilon_n \to 0$ *such that* $\mathcal{E}^N(R^n, \Psi^n) \le \lambda_{d_0}^N(R^n, Z) + \epsilon_n$.

Then (Ψ^n) *is precompact in* $H_a^1(\mathbb{R}^{3N})$ *and converges, up to a subsequence, to an eigenfunction* Ψ *of* $H^N(R, Z)$ *associated to* $\lambda_d^N(R, Z)$ *with* $d \le d_0$.

Applying this result, we obtain, by passing to the limit as $k \to +\infty$,

$$c \le c_n = \lambda_1^N(r_n(t_n), Z) \le m_n$$

for some $t_n \in [0; 1]$ and so $c = c'$.

We now prove the alternative of the Theorem. We introduce

$$\mathcal{F}_c(R_0) = \left\{ (R, \Psi) \in \Omega \times SH_a^1(\mathbb{R}^{3N}),\ \sum_{i\neq j} |R_i - R_j| \le R_0,\ \mathcal{E}^N(R, \Psi) \ge c \right\}$$

$$\Gamma(\alpha) = \left\{ \gamma \in \Gamma,\ \max_{t\in[0;1]} \mathcal{E}^N(\gamma(t)) \le c + \alpha \right\}.$$

We have the following alternative:

either there exist $R_0 > 0$ and $\alpha > 0$ such that, $\mathcal{F}_c(R_0) \cap \gamma([0; 1]) \neq \emptyset$ for all $\gamma \in \Gamma(\alpha)$,

or for all $R_0 > 0$ there exists a min-maxing sequence $\gamma_n \in \Gamma$ such that $\mathcal{F}_c(R_0) \cap \gamma_n([0;1]) = \emptyset$.

First Case : there exist $R_0 > 0$ and $\alpha > 0$ such that, $\mathcal{F}_c(R_0) \cap \gamma([0;1]) \neq \emptyset$ for all $\gamma \in \Gamma(\alpha)$.

Since (R, Ψ) and (R', Ψ') do not belong to $\mathcal{F}_c(R_0)$, we may apply the methods of [14] ($\mathcal{F}_c(R_0)$ is a set which is dual to the homotopy-stable class $\Gamma(\alpha)$ with boundary $B = \{(R, \Psi), (R', \Psi')\}$) to obtain a sequence $(R^n, \Psi^n) \in \Omega \times SH^1_a(\mathbb{R}^{3N})$ such that

1. $\lim\limits_{n \to +\infty} d((R^n, \Psi^n), \mathcal{F}_c(R_0)) = 0,$
2. $\lim\limits_{n \to +\infty} \mathcal{E}^N(R^n, \Psi^n) = c,$
3. $\lim\limits_{n \to +\infty} \nabla_R \mathcal{E}^N(R^n, \Psi^n) = 0,$
4. $H^N(R^n, Z) \cdot \Psi^n - \mathcal{E}^N(R^n, \Psi^n) \cdot \Psi^n \to 0$ in $L^2(\mathbb{R}^{3N})$,
5. $\mathcal{E}^N(R^n, \Psi^n) \leq \lambda_1^N(R^n, Z) + \epsilon_n, \quad \lim\limits_{n \to +\infty} \epsilon_n = 0$

Remark that $2, 3, 4, 5$) correspond to the fact that one can obtain min-maxing sequences that are almost critical, and with Morse-type information. On the other hand, 1) is the consequence of the duality theory developed in [14] that enables to locate the critical points.

Due to 1), $\sum_{i \neq j} |R_i^n - R_j^n|$ is bounded. Up to a translation, we may suppose $R^n \to R \in \Omega$ (since $\lambda_1^N(R^n, Z) \to +\infty$ when $d(R^n, \partial\Omega) \to 0$ due to the nuclei/nuclei repulsion). Now Ψ^n converges up to a subsequence to a Ψ in $H^1(\mathbb{R}^{3N})$ by lemma 8.

Second Case : for all $R_0 > 0$ there exists a min-maxing sequence $\gamma_n \in \Gamma$ such that $\mathcal{F}_c(R_0) \cap \gamma_n([0;1]) = \emptyset$.

Let (r_n) be a sequence in $\mathbb{R}$ such that $r_n \to +\infty$. For each r_n, there exists a γ_n such that, for instance,

$$c \leq \max_{t \in [0;1]} \mathcal{E}^N(\gamma_n(t)) \leq c + \frac{1}{n}$$

and $\mathcal{F}_c(r_n) \cap \gamma_n([0;1]) = \emptyset$. We now write $\gamma_n(t) = (R_n(t), \tilde{\Psi}_n(t))$ and fix n. The set $K_n = \{t \in [0;1], \sum |R_i^n(t) - R_j^n(t)| \leq r_n\}$ is a compact subset of $[0;1]$ such that $\max \mathcal{E}^N(\gamma(K_n)) < c$. We now introduce

$$\Gamma_\Psi = \left\{ \psi \in \mathcal{C}^0([0;1], SH^1_a(\mathbb{R}^{3N})), \ \psi_{|K_n} \equiv \tilde{\Psi}^n_{|K_n} \right\}$$

which is an homotopy-stable class of dimension 1 with boundary $\tilde{\Psi}^n(K_n)$, and

$$c_n = \min_{\psi \in \Gamma_\Psi} \max_{t \in [0;1]} \mathcal{E}^N(R_n(t), \psi(t)) \tag{13}$$

so that

$$c \leq c_n \leq c + \frac{1}{n}.$$

Applying the methods of [14], we may find a sequence $t_k \in [0;1] \setminus K_n$ and $\Psi_n^k \in SH_a^1(\mathbb{R}^{3N})$ such that $t_k \to \bar{t}$ and

1. $\sum_{i \neq j} |R_{n,i}(t_k) - R_{n,j}(t_k)| \geq r_n$
2. $\lim_{k \to +\infty} \mathcal{E}^N(R_n(t_k), \Psi_n^k) = c_n$
3. $H^N(R_n(t_k), Z) \cdot \Psi_n^k - \mathcal{E}^N(R_n(t_k), \Psi_n^k) \cdot \Psi_n^k \to 0 \quad \text{in } L^2(\mathbb{R}^{3N})$
4. $\mathcal{E}^N(R_n(t_k), \Psi_n^k) \leq \lambda_1^N(R_n(t_k), Z) + \alpha_k \quad \text{with} \lim_{k \to +\infty} \alpha_k = 0$

By lemma 8, $(\Psi_n^k)_{k \in \mathbb{N}}$ is precompact in $H_a^1(\mathbb{R}^{3N})$ and converges, up to a subsequence, to some Ψ^n such that

1. $\sum_{i \neq j} |R_i^n - R_j^n| \geq r_n$
2. $\lim_{n \to +\infty} \mathcal{E}^N(R^n, \Psi^n) = c$
3. $H^N(R^n, Z) \cdot \Psi^n = \lambda_1^N(R^n, Z) \cdot \Psi^n$

where $R^n := R_n(\bar{t})$.

Since $\sum_{i \neq j} |R_i^n - R_j^n| \to +\infty$, there exists a $2 \leq p \leq M$, some $X_j^n \in \mathbb{R}^3$ with $j = 1, ..., p$ and a $R_0 > 0$ such that (changing the indices if necessary and up to a subsequence) $R^n = (X_1^n + r_1^n, ..., X_p^n + r_p^n)$, $\|r_j^n\| \leq R_0$, $Z = (z_1, ..., z_p)$, and $\lim_{n \to +\infty} |X_i^n - X_j^n| = +\infty$, $r_j^n \to r_j$.

Passing to the limit, we obtain, by Theorem 2

$$c = \lim_{n \to +\infty} \lambda_1^N(R^n, Z) = \Lambda_1^N(r, z).$$

We now simply apply Theorem 3 to obtain the convergence to a critical point at infinity of energy c, as defined in the corresponding section. □

Let us now prove Lemma 8.

Proof of Lemma 8 – Let m be an integer such that $\lambda_m^N(R, Z) > \lambda_{m-1}^N(R, Z) = \lambda_{d_0}^N(R, Z)$. Due to the fact that $\lambda_d^N(R^n, Z) \to \lambda_d^N(R, Z)$ as $n \to +\infty$, we have $\lambda_m^N(R^n, Z) > \lambda_{d_0}^N(R, Z) \geq c$ for n large enough.

Let be $V_n = \bigoplus_{i=1}^{m-1} ker\left(H(R^n, Z) - \lambda_i^N(R^n, Z)\right)$, and $(\psi_1^n, ..., \psi_{m-1}^n)$ an orthonormal basis of V^n, ψ_i^n being eigenfunctions of $H^N(R^n, Z)$ (Theorem 1 - 4)). Due for instance to the uniform exponential decay of Theorem 2, one easily sees that each ψ_i^n is precompact and converges up to a subsequence in $H_a^1(\mathbb{R}^{3N})$ to a ψ_i, with $span(\psi_i) = \bigoplus_{i=1}^{m-1} ker\left(H(R, Z) - \lambda_i^N(R, Z)\right)$.

Now we can write $\Psi^n = \Psi_{V^n} + \Psi_{(V^n)^\perp}$ with an obvious definition. Since $\mathcal{E}^N(R^n, \Psi^n)$ is bounded, it is a classical fact that (Ψ^n) is bounded in $H_a^1(\mathbb{R}^{3N})$ and so, up to a subsequence, $\Psi^n \rightharpoonup \Psi$ weakly in $H_a^1(\mathbb{R}^{3N})$. Since $dim(V_n) = m - 1$, (Ψ_{V_n}) is precompact in $H^1(\mathbb{R}^{3N})$ and converges to a $\Psi_V \in V$. By difference, $\Psi_{(V^n)^\perp} \rightharpoonup \Psi_{(V)^\perp}$ weakly in $H^1(\mathbb{R}^{3N})$.

Since $\lim_{n\to+\infty} \mathcal{E}^N(R^n, \Psi^n) = c$, $H^N(R^n, Z)\cdot\Psi^n - c\cdot\Psi^n \to 0$ in $L^2(\mathbb{R}^{3N})$, so we obtain

$$(H^N(R^n, Z) - c)\cdot\Psi_{V_n} + (H^N(R^n, Z) - c)\cdot\Psi_{(V_n)^\perp} \to 0$$

which implies $(H^N(R^n, Z) - c)\cdot\Psi_{V_n} \to 0$ and $(H^N(R^n, Z) - c)\cdot\Psi_{(V_n)^\perp} \to 0$ in $L^2(\mathbb{R}^{3N})$. Finally,

$$\mathcal{E}^N(R^n, \Psi_{(V_n)^\perp}) - c\|\Psi_{(V_n)^\perp}\|^2_{L^2(\mathbb{R}^{3N})} \to 0.$$

Because $\min \mathcal{E}^N(R^n, S(V_n)^\perp) = \lambda^N_m(R^n, Z) > \lambda^N_{d_0}(R^n, Z) \geq c$, this implies $\|\Psi_{(V_n)^\perp}\|_{L^2} \to 0$ and then $\|\Psi_{(V_n)^\perp}\|_{H^1} \to 0$. Thus Ψ^n converges in $H^1(\mathbb{R}^{3N})$ to a $\Psi = \Psi_V$ which is an eigenfunction of $H^N(R, Z)$ that belongs to V. □

3.3 The case of two interacting molecules

3.3.1 Proof of Lemma 2

We shall use the following lemma:

Lemma 9 (Multipole expansion). *There exists a constant* C *such that, for all* R *and* $h \in \mathbb{R}^3$ *with* $R + h \neq 0$,

$$\left|\frac{1}{|R+h|} - \left(\frac{1}{|R|} - \frac{e_R\cdot h}{|R|^2} + \frac{3(e_R\cdot h)^2 - |h|^2}{2|R|^3}\right)\right| \leq \frac{C\,|h|^3}{|R|^3|R+h|}$$

with $e_R = R/|R|$.

Proof of Lemma 9 – It suffices to show

$$\left|\frac{1}{\sqrt{1-2xt+t^2}} - \left(1 + xt + \frac{t^2}{2}(3x^2-1)\right)\right| \leq \frac{C|t|^3}{\sqrt{1-2xt+t^2}}$$

for all $t \in \mathbb{R}$ and $x \in [-1;1]$ (take $x = -(e_R\cdot h)/|h|$ and $t = |h|/|R|$). We thus introduce $f(x,t) = 1 - \sqrt{1-2xt+t^2}\left(1 + xt + \frac{t^2}{2}(3x^2-1)\right)$. One easily computes $\frac{\partial f}{\partial x}(x,t) = \frac{3t^3(5x^2-2xt-1)}{2\sqrt{1-2xt+t^2}}$, so that

$$\max_{x\in[-1;1]} |f(x,t)| \leq \max\{f_1(t), f_2(t), f_3(t), f_4(t)\}$$

where $f_1(t) = |f(x_1(t),t)|\mathbb{1}_{-1\leq x_1\leq 1}(t)$, $f_2(t) = |f(x_2(t),t)|\mathbb{1}_{-1\leq x_2\leq 1}(t)$, $f_3(t) = |f(-1,t)|$, $f_4(t) = |f(1,t)|$, $x_1(t) = \frac{t-\sqrt{t^2+5}}{5}$ and $x_2(t) = \frac{t+\sqrt{t^2+5}}{5}$. It is now easy to conclude that $|f(x,t)| \leq C|t|^3$ for some constant $C > 0$. □

We are now able to prove Lemma 2.

Proof of Lemma 2 – Let $\xi_\alpha \in \mathcal{C}^\infty(\mathbb{R}^3, [0;1])$ be a cut-off function such that $\xi_\alpha \equiv 0$ on $\mathbb{R}^3 \setminus B(O, \alpha/3)$, $\xi_\alpha \equiv 1$ on $B(O, \alpha/3 - 1)$, $\|\nabla\xi_\alpha\|_\infty \leq 1$, $\|\Delta\xi_\alpha\|_\infty \leq 2$. We introduce $\tilde{\psi}^\alpha_j(x_1, ..., x_{N_j}) = \prod_{k=1}^{N_j} \xi_\alpha(x_k)\psi_j(x_1, ..., x_{N_j})$, $\psi^\alpha_j = \tilde{\psi}^\alpha_j/\|\tilde{\psi}^\alpha_j\|_{L^2}$

and $\tilde{\Psi}(\alpha, u, u') = (u \cdot \psi_1^\alpha) \wedge (\tau_{\alpha\vec{v}} \cdot u' \cdot \psi_2^\alpha)$. Due to the exponential decay of Theorem 2, one has

$$\left|\mathcal{E}^N\left(R(\alpha, u, u'), \tilde{\Psi}(\alpha, u, u')\right) - \mathcal{E}^N\left(R(\alpha, u, u'), \Psi(\alpha, u, u')\right)\right| \leq Ce^{-a\alpha}$$

$$\left|E^{N_1}(r, z) - \mathcal{E}^{N_1}(r, \psi_1^\alpha)\right|, \ \left|E^{N_2}(r', z') - \mathcal{E}^{N_2}(r', \psi_2^\alpha)\right| \ \leq Ce^{-a\alpha}$$

for some $C, a > 0$. Let us recall that, by definition,

$$\psi \wedge \psi'(x_1, ..., x_N) = \sqrt{\frac{N_1!N_2!}{N!}} \sum_{|C|=N_1} \sigma(C)\psi(x_C)\psi'(x_{\overline{C}})$$

where $x_C = (x_{i_1}, ..., x_{i_{N_1}})$ when $C = \{i_1 < \cdots < i_{N_1}\}$, $\sigma(C) = \pm 1$. Applying this equality to $\tilde{\Psi}$, we obtain on the right functions with disjoint supports. We shall therefore only study the expansion of

$$\mathcal{E}^N\left(R(\alpha, u, u'), (u \cdot \psi_1^\alpha) \otimes (\tau_{\alpha\vec{v}} \cdot u' \cdot \psi_2^\alpha)\right).$$

We have (using the notation $x^1 = (x_1, ..., x_{N_1})$ and $x^2 = (x_{N_1+1}, ..., x_N)$)

$$\begin{aligned}
\mathcal{E}^N\left(R(\alpha, u, u'), (u\psi_1^\alpha) \otimes (\tau_{\alpha\vec{v}}u'\psi_2^\alpha)\right) &= \mathcal{E}^{N_1}(ur, u\psi_1^\alpha) + \mathcal{E}^{N_2}(\alpha\vec{v} + u'r', \tau_{\alpha\vec{v}}u'\psi_2^\alpha) \\
&+ \sum_{i=1}^{N_1}\sum_{j=1}^{N_2} \int_{\mathbb{R}^{3N}} \frac{|\psi_1^\alpha(x^1)|^2|\psi_2^\alpha(x^2)|^2}{|\alpha\vec{v} + u' \cdot x_j^2 - u \cdot x_i^1|} dx^1dx^2 + \sum_{i=1}^{m}\sum_{j=1}^{m'} \frac{z_i z_j'}{|\alpha\vec{v} + u' \cdot r_j' - u \cdot r_i|} \\
&- \int_{\mathbb{R}^{3N}} \left\{ \sum_{i=1}^{m}\sum_{j=1}^{N_2} \frac{z_i|\psi_1^\alpha(x^1)|^2|\psi_2^\alpha(x^2)|^2}{|\alpha\vec{v} + u' \cdot x_j^1 - u \cdot r_i|} + \sum_{i=1}^{N_1}\sum_{j=1}^{m'} \frac{z_j'|\psi_1^\alpha(x^1)|^2|\psi_2^\alpha(x^2)|^2}{|\alpha\vec{v} + u' \cdot r_j' - u \cdot x_i^1|} \right\} dx^1dx^2
\end{aligned}$$

so we obtain

$$\begin{aligned}
\mathcal{E}^N\left(R(\alpha, u, u'), (u\psi_1^\alpha) \otimes (\tau_{\alpha\vec{v}}u'\psi_2^\alpha)\right) &= \mathcal{E}^{N_1}(r, \psi_1^\alpha) + \mathcal{E}^{N_2}(r', \psi_2^\alpha) \\
&+ \iint_{\mathbb{R}^6} \frac{\rho_1^\alpha(x)\rho_2^\alpha(y)}{|\alpha\vec{v} + u' \cdot y - u \cdot x|} dx\, dy + \sum_{i=1}^{m}\sum_{j=1}^{m'} \frac{z_i z_j'}{|\alpha\vec{v} + u' \cdot r_j' - u \cdot r_i|} \\
&- N_1 \sum_{i=1}^{m} \int_{\mathbb{R}^3} \frac{z_i \rho_2^\alpha(y)}{|\alpha\vec{v} + u' \cdot y - u \cdot r_i|} dy - N_2 \sum_{j=1}^{m'} \int_{\mathbb{R}^3} \frac{z_j' \rho_1^\alpha(x)}{|\alpha\vec{v} + u' \cdot r_j' - u \cdot x|} dx
\end{aligned}$$

where the ρ_k^α are the electronic densities associated to ψ_k^α, and finally

$$\begin{aligned}
\mathcal{E}^N\left(R(\alpha, u, u'), (u\psi_1^\alpha) \otimes (\tau_{\alpha\vec{v}}u'\psi_2^\alpha)\right) &= \mathcal{E}^{N_1}(r, \psi_1^\alpha) + \mathcal{E}^{N_2}(r', \psi_2^\alpha) \\
&+ \iint_{\mathbb{R}^6} \frac{\tilde{\rho}_1^\alpha(x)\tilde{\rho}_2^\alpha(y)}{|\alpha\vec{v} + u' \cdot y - u \cdot x|} dx\, dy
\end{aligned}$$

where $\tilde{\rho}_1^\alpha(x) = \rho_1^\alpha(x) - \sum_{i=1}^m z_i\delta_{r_i}(x)$ and $\tilde{\rho}_2^\alpha(y) = \rho_2^\alpha(y) - \sum_{j=1}^{m'} z_i'\delta_{r_i'}(y)$ are the total densities of charge associated to the distributions ρ_1^α and ρ_2^α. Now, by lemma 9, we have

$$\iint_{\mathbb{R}^6} \frac{\tilde\rho_1^\alpha(x)\tilde\rho_2^\alpha(y)}{|\alpha\vec v + u'\cdot y - u\cdot x|}dx\,dy = \frac{q_1q_2}{\alpha} + q_2\frac{(uP_1^\alpha)\cdot\vec v}{\alpha^2} - q_1\frac{(u'P_2^\alpha)\cdot\vec v}{\alpha^2}$$
$$-\frac{3(uP_1^\alpha\cdot\vec v)(u'P_2^\alpha\cdot\vec v) - (uP_1^\alpha)\cdot(u'P_2^\alpha)}{\alpha^3} + \frac{3(q_2uQ_1u^T + q_1u'Q_2u'^T)v\cdot v}{2\alpha^3}$$
$$+O\left(\frac{1}{\alpha^3}\iint_{\mathbb{R}^6} \frac{|u'y-ux|^3|\tilde\rho_1^\alpha|(x)|\tilde\rho_2^\alpha|(y)}{|\alpha\vec v + u'\cdot y - u\cdot x|}dx\,dy\right)$$

But we have

$$\iint_{\mathbb{R}^6} \frac{|u'y-ux|^3|\tilde\rho_1^\alpha|(x)|\tilde\rho_2^\alpha|(y)}{|\alpha\vec v + u'\cdot y - u\cdot x|}dx\,dy \le \frac{3C}{\alpha}\int_{\mathbb{R}^3}|x|^3(|\tilde\rho_1|+|\tilde\rho_2|)(x)dx.$$

It suffices to notice that $|P_k^\alpha - P_k| \le Ce^{-a\alpha}$ and $|Q_k^\alpha - Q_k| \le Ce^{-a\alpha}$ for some $C, a > 0$ to end the proof. □

3.3.2 Proof of Theorem 6

Let us suppose that we are in the second case of Theorem 5, and that $c > \max\{\mathcal{E}^N(M), \mathcal{E}^N(M')\}$. By the proof of Theorem 4, we obtain a sequence $\alpha_n \to +\infty$ and paths γ_n such that

$$\Lambda_1^N \le c \le \max_{t\in[0;1]} \mathcal{E}^N(\gamma_n(t)) \le c + \frac{1}{n}$$

and $\mathcal{E}^N(\alpha(t), u(t), u'(t), \Psi(t)) < c$ when $\alpha(t) \le \alpha_n$. Let t_1^n and t_2^n be respectively the minimum and the maximum of $\{t,\ \alpha(t) \ge \alpha_n\}$. By the definition of c, we have $0 < t_1^n < t_2^n < 1$. For the sake of simplicity, we introduce $u_j^n = u(t_j^n)$, $u'^n_j = u'(t_j^n)$, and $\Psi_j^n = \Psi(t_j^n)$.

The idea of the proof is now to connect $M_1^n = (\alpha_n, u_1^n, u'^n_1, \Psi_1^n)$ and $M_2^n = (\alpha_n, u_2^n, u'^n_2, \Psi_2^n)$ by a path on which α is constant, with a maximum energy that is below c.

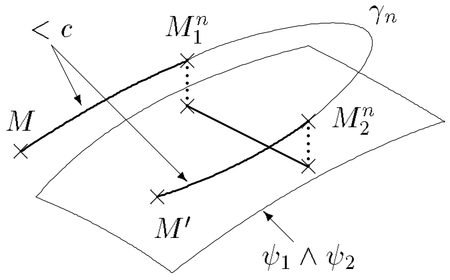


Figure 3: A schematic representation of the proof

We shall use the following lemma

Lemma 10. *We assume that* $(\alpha, u, u') \in (0; +\infty) \times (SO_3(\mathbb{R}))^2$ *is fixed, and we abbreviate* $R = R(\alpha, u, u')$. *Let* Ψ_1 *and* Ψ_2 *be two wavefunctions of* $SH^1_a(\mathbb{R}^{3N})$. *Then there exists a continuous path* $\Psi : [0; 1] \to SH^1_a(\mathbb{R}^{3N})$ *such that* $\Psi(0) = \Psi_1$, $\Psi(1) = \Psi_2$, *and for all* $t \in [0; 1]$

$$\mathcal{E}^N(R, \Psi(t)) \leq \max\{\mathcal{E}^N(R, \Psi_1), \mathcal{E}^N(R, \Psi_2)\}.$$

Proof of Lemma 10 – Let us denote by V the finite-dimensional eigenspace associated to the first eigenvalue $\lambda_1^N(R, Z)$ of $H^N(R, Z)$, and let P_V be the projection onto V. We may write $\Psi_1 = t_0 \Psi_V + \sqrt{1 - t_0^2}\Psi_{V^\perp}$, where $t_0 \in [0; 1]$, $\Psi_V = \frac{P_V(\Psi_1)}{\|P_V(\Psi_1)\|_{L^2}}$ if $P_V(\Psi_1) \neq 0$, and Ψ_V is an arbitrary normalized function of V if $P_V(\Psi_1) = 0$ (then $t_0 = 0$). This enables to define a path connecting Ψ_1 to Ψ_V, on which the energy decreases, by varying $t \in [t_0; 1]$.

We may find with the same method a path from Ψ_2 to some Ψ'_V in V, with a decreasing energy. It remains now to take an arbitrary path in the sphere of V to connect Ψ_V and Ψ'_V (the sphere of V being pathwise-connected since we are in $\mathbb{C}$), on which $\mathcal{E}^N(R, \cdot)$ is constant. □

Now, let N_1 and N_2 be such that

$$E^{N_1}(r, z) + E^{N_2}(r', z') = \min\left\{E^{n_1}(r, z) + E^{n_2}(r', z'),\ n_1 + n_2 = N\right\} := \Lambda_1^N$$

and $(N_1 - |z|)(N_2 - |z'|) \neq 0$.

By lemma 6, there exist ψ_1 and ψ_2, two ground states of respectively $H^{N_1}(r, z)$ and $H^{N_2}(r', z')$. We now introduce $\tilde{\Psi}_k^n = (u_k^n \cdot \psi_1) \wedge (\tau_{\alpha_n \vec{v}} \cdot u'^n_k \psi_2)$ for $k = 1, 2$. Since $SO_3(\mathbb{R})$ is pathwise connected, one may find two paths $U_n, U'_n : [0; 1] \to SO_3(\mathbb{R})$ such that $U_n(0) = u_1^n$, $U_n(1) = u_2^n$, $U'_n(0) = u'^n_1$ and $U'_n(1) = u'^n_2$. This enables to connect $\tilde{M}_1^n := (\alpha_n, u_1^n, u'^n_1, \tilde{\Psi}_1^n)$ and $\tilde{M}_2^n := (\alpha_n, u_2^n, u'^n_2, \tilde{\Psi}_2^n)$ by a path on which $\alpha \equiv \alpha_n$. Applying Lemma 10, we may connect M_1^n to $\tilde{M}_1^n$, and M_2^n to $\tilde{M}_2^n$. We finally obtain an admissible path $\tilde{\gamma}_n$ connecting M and M', with a maximum that is attained "between" $\tilde{M}_1^n$ and $\tilde{M}_2^n$. It is now a consequence of Lemma 2 that

$$\max_{t \in [0;1]} \mathcal{E}^N(\tilde{\gamma}_n(t)) = E^{N_1}(r, z) + E^{N_2}(r', z') + \frac{(N_1 - |z|)(N_2 - |z'|)}{\alpha_n} + O\left(\frac{1}{(\alpha_n)^2}\right).$$

Since $N_1 + N_2 = N = |z| + |z'|$, we have $(N_1 - |z|)(N_2 - |z'|) < 0$ and so

$$c \leq \max_{t \in [0;1]} \mathcal{E}^N(\tilde{\gamma}_n(t)) < E^{N_1}(r, z) + E^{N_2}(r', z')$$

for n large enough, which is a contradiction. □

3.3.3 Proof of Theorem 7

As in the previous proofs, we may suppose that $c > \max\{\mathcal{E}^N(M), \mathcal{E}^N(M')\}$, and that there exists a sequence $\alpha_n \to +\infty$ and paths γ_n such that

$$c \leq \max_{t \in [0;1]} \mathcal{E}^N(\gamma_n(t)) \leq c + \frac{1}{n}$$

and $\mathcal{E}^N(\alpha(t), u(t), u'(t), \Psi(t)) < c$ when $\alpha(t) \le \alpha_n$. We use the same definitions as above for t_1^n, t_2^n, $M_k^n = (u_k^n, {u'}_k^n, \Psi_k^n)$ for $k = 1, 2$. Applying Lemma 10 if necessary, we may also assume that Ψ_k^n is a ground state of $H^N(R(\alpha_n, u_k^n, {u'}_k^n), Z)$.

Up to a subsequence, we may assume that $u_k^n \to u_k$ and ${u'}_k^n \to {u'}_k$ as n goes to $+\infty$ and that each $(\Psi_k^n)_n$ converges to some critical point at infinity of energy c (by Theorem 3). But by *(H1), (H3)* (let us assume for instance that $E^{|z|}(r, z)$ is not degenerated), these points can be written $(u\psi) \wedge (u'\psi')$ where ψ is a fixed ground state of $H^{|z|}(r, z)$, and $\psi' \in ker\left(H^{|z'|}(r', z') - E^{|z'|}(r', z')\right)$, $\|\psi'\|_{L^2} = 1$. So finally, we may assume that each $(\Psi_k^n)_n$ converges to a critical point at infinity of the form $(u_k\psi) \wedge (u'_k\psi'_k)$.

Step 1: Rotating the molecules. As above, the idea is now to find a path from each M_k^n to some tensor product, with a non-increasing energy. But we cannot apply the method used before since a tensor product may now have an energy which is greater than c if the molecules have a 'bad' orientation. This is due to the fact that the first term in the expansion of the interaction energy will be the dipole/dipole term. Therefore, our first step will be to change the orientation of the molecules, so that the dipole/dipole interaction energy of a tensor product becomes negative.

Let $\xi_1^n \in \mathcal{C}^\infty(\mathbb{R}^3, [0;1])$ be a cut-off function such that $\xi_1^n \equiv 0$ on $\mathbb{R}^3 \setminus B(O, \alpha_n/3)$, $\xi_1^n \equiv 1$ on $B(O, \alpha_n/3 - 1)$, $\|\nabla\xi_1^n\|_\infty \le 1$, $\|\Delta\xi_1^n\|_\infty \le 2$, and let us denote by $\xi_2^n = \tau_{\alpha_n\vec{v}}\xi_1^n$ the translation of ξ_1^n, and by $\xi_3^n := 1 - \xi_1^n - \xi_2^n$. We now write as in the proof of Theorem 2

$$\Psi_k^n = \prod_{l=1}^{N}(\xi_1^n+\xi_2^n+\xi_3^n)(x_l)\Psi_k^n = \sum_{1\le k_l\le 3} \xi_{k_1}^n(x_1)\cdots\xi_{k_N}^n(x_N)\Psi_k^n := \sum_{1\le k_l\le 3} (\Psi_k^n)^{k_1,\dots,k_N}.$$

Since $k \in \{1, 2\}$ and n will be fixed during this step, we shall forget the subscripts and write $\Psi = \sum_{1\le k_l\le 3}\Psi^{k_1,\dots,k_N}$. We now introduce for all v_1, $v_2 \in SO_3(\mathbb{R})$,

$$\Psi_{(v_1,v_2)}(x_1, \dots x_N) := \sum_{1\le k_l\le 3} \Psi^{k_1,\dots,k_N}(w_{k_1}x_1, \dots w_{k_N}x_N),$$

$$M_{(v_1,v_2)} := (\alpha_n, v_1u, v_2u', \Psi_{(v_1,v_2)})$$

where $w_1 = v_1^T$, $w_3 = v_3 = I$ and $w_2(x) = v_2^T(x - \alpha_n\vec{v}) + \alpha_n\vec{v}$. We have also forgotten the indices k and n for the sake of simplicity. Obviously, $M_{(I,I)} = M_k^n$.

Lemma 11. *There exists a path* $V : [0, 1] \to (SO_3(\mathbb{R}))^2$ *such that* $V(0) = (I, I)$, $V(1)$ *is a critical point of* $(v_1, v_2) \mapsto \mathcal{E}^N(M_{(v_1,v_2)})$, *and* $\mathcal{E}^N(M_{V(t)}) \le \mathcal{E}^N(M_{I,I})$ *for all* $t \in [0; 1]$.

Proof of Lemma 11 – Since Ψ_k^n is locally Lipschitz by Theorem 1, one easily shows that $F : (v_1, v_2) \mapsto \mathcal{E}^N(M_{(v_1,v_2)})$ is $\mathcal{C}^2$ on $(SO_3(\mathbb{R}))^2$. We then simply consider the associated gradient flow to conclude. $\square$

Applying this lemma, we may obtain some $X = (\alpha_n, vu, v'u', \tilde{\Psi})$, connected to M_k^n by a path with a non-increasing energy, and which is a critical point with respect to the rotation of the molecules as defined before. Indeed it is a critical point of the function

$$(H_1, H_2) \mapsto \mathcal{E}^N \left(\alpha_n, e^{H_1} v, e^{H_2} v', (\tilde{\Psi})_{(e^{H_1}, e^{H_2})} \right)$$

defined on the space $A_3(\mathbb{R}) \times A_3(\mathbb{R})$, $A_3(\mathbb{R})$ being the space of 3×3 antisymmetric real matrices.

Step 2: Expression and expansion of the energy and its derivative. Now, we have

$$|\tilde{\Psi}|^2_{(e^{H_1}, e^{H_2})} = \sum_{1 \leq k_l \leq 2} |\tilde{\Psi}^{k_1, \ldots, k_N}_{(e^{H_1}, e^{H_2})}|^2 + \phi$$

with $\|\phi\|_{H^1} \leq C e^{-a\alpha_n}$ (by Theorem 2), so we obtain

$$\mathcal{E}^N \left(\alpha_n, e^{H_1} v, e^{H_2} v', \Psi_{(e^{H_1}, e^{H_2})} \right) = \\ \sum_{1 \leq k_l \leq 2} \mathcal{E}^N \left(\alpha_n, e^{H_1} v, e^{H_2} v', \tilde{\Psi}^{k_1, \ldots, k_N}_{(e^{H_1}, e^{H_2})} \right) + O\left(e^{-a\alpha_n}\right).$$

Let us fix $1 \leq k_1, \ldots, k_N \leq 2$ and denote $C_l = \{i,\ k_i = l\}$, $x^1 = (x_i)_{i \in C_1}$, $x^2 = (x_i)_{i \in C_2}$, $N_l = |C_l|$. We then have

$$\mathcal{E}^N \left(\alpha_n, e^{H_1} v, e^{H_2} v', \tilde{\Psi}^{k_1, \ldots, k_N}_{(e^{H_1}, e^{H_2})} \right) = \\ \langle H^{N_1}(r, z)_{C_1} \Psi^{k_1, \ldots, k_N}, \Psi^{k_1, \ldots, k_N} \rangle + \langle H^{N_2}(r', z')_{C_2} \Psi^{k_1, \ldots, k_N}, \Psi^{k_1, \ldots, k_N} \rangle \\ + \int_{\mathbb{R}^{3N}} |(\tau_{-\alpha_n \vec{v}})_{x^2} \tilde{\Psi}^{k_1, \ldots, k_N}|^2 \left(\sum_{i \in C_1,\ j \in C_2} \frac{1}{|\alpha_n \vec{v} + e^{H_2} x_j - e^{H_1} x_i|} \right. \\ - \sum_{i \in C_1} \sum_{j=1}^{m'} \frac{z'_j}{|\alpha_n \vec{v} + e^{H_2} r_j - e^{H_1} x_i|} - \sum_{i=1}^{m} \sum_{j \in C_2} \frac{z_i}{|\alpha_n \vec{v} + e^{H_2} x_j - e^{H_1} r_i|} \\ \left. + \sum_{i=1}^{m} \sum_{j=1}^{m'} \frac{z_i z'_j}{|\alpha_n \vec{v} + e^{H_2} r_j - e^{H_1} r_i|} \right) dx^1 dx^2.$$

Differentiating this expression with regard to $H = (H_1, H_2)$, we find

$$d_{H=0} \mathcal{E}^N \left(\alpha_n, e^{H_1} v, e^{H_2} v', \tilde{\Psi}^{k_1, \ldots, k_N}_{(e^{H_1}, e^{H_2})} \right) (H_1, H_2) = \\ - \int_{\mathbb{R}^{3N}} |(\tau_{-\alpha_n \vec{v}})_{x^2} \tilde{\Psi}^{k_1, \ldots, k_N}|^2 \left(\sum_{i \in C_1,\ j \in C_2} \frac{e_{\alpha_n \vec{v} + x_j - x_i} \cdot (H_2 x_j - H_1 x_i)}{|\alpha_n \vec{v} + x_j - x_i|^2} \right. \\ - \sum_{i \in C_1} \sum_{j=1}^{m'} \frac{z'_j e_{\alpha_n \vec{v} + r_j - x_i} \cdot (H_2 r_j - H_1 x_i)}{|\alpha_n \vec{v} + r_j - x_i|^2} - \sum_{i=1}^{m} \sum_{j \in C_2} \frac{z_i e_{\alpha_n \vec{v} + x_j - r_i} \cdot (H_2 x_j - H_1 r_i)}{|\alpha_n \vec{v} + x_j - r_i|^2} \\ \left. + \sum_{i=1}^{m} \sum_{j=1}^{m'} \frac{z_i z'_j e_{\alpha_n \vec{v} + r_j - r_i} \cdot (H_2 r_j - H_1 r_i)}{|\alpha_n \vec{v} + r_j - r_i|^2} \right) dx^1 dx^2.$$

Now, we obtain, using lemma 2,

$$\nabla_{H_1=0}\mathcal{E}^N\left(\alpha_n, e^{H_1}v, e^{H_2}v', \tilde{\Psi}^{k_1,\dots,k_N}_{(e^{H_1},e^{H_2})}\right) =$$

$$-\frac{(N_2-|z'|)}{(\alpha_n)^2}\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2\left(\sum_{i\in C_1}x_i-\sum_{i=1}^{m}z_jr_j\right)\vec{v}^T dx^1dx^2$$

$$-\frac{(N_2-|z'|)}{(\alpha_n)^3}\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2(I-3\vec{v}\vec{v}^T)\left(\sum_{i\in C_1}x_ix_i^T-\sum_{i=1}^{m}z_ir_ir_i^T\right)dx^1dx^2$$

$$-\frac{1}{(\alpha_n)^3}\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2(I-3\vec{v}\vec{v}^T)\cdot$$

$$\cdot\left(\sum_{i\in C_1}x_i-\sum_{i=1}^{m}z_ir_i\right)\left(\sum_{j\in C_2}x_j-\sum_{j=1}^{m'}z'_jr'_j\right)^T dx^1dx^2+O\left(\frac{\int_{\mathbb{R}^{3N}}|\tilde{\Psi}^{k_1,\dots,k_N}|^2}{(\alpha_n)^4}\right),$$

and a similar expansion for the gradient with regard to H_2.

We may now expand the energy with a similar method and obtain

$$\mathcal{E}^N\left(\alpha_n, v, v', \tilde{\Psi}^{k_1,\dots,k_N}\right) = \langle H^{N_1}(r,z)_{C_1}\Psi^{k_1,\dots,k_N},\Psi^{k_1,\dots,k_N}\rangle +$$

$$\langle H^{N_2}(r',z')_{C_2}\Psi^{k_1,\dots,k_N},\Psi^{k_1,\dots,k_N}\rangle+\frac{(N_1-Z_1)(N_2-Z_2)}{\alpha_n}\int_{\mathbb{R}^{3N}}|\tilde{\Psi}^{k_1,\dots,k_N}|^2$$

$$+\frac{(N_2-|z'|)}{(\alpha_n)^2}e_{\vec{v}}\cdot\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2\left(\sum_{i\in C_1}x_i-\sum_{i=1}^{m}z_ir_i\right)dx^1dx^2$$

$$-\frac{(N_1-|z|)}{(\alpha_n)^2}e_{\vec{v}}\cdot\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2\left(\sum_{j\in C_2}x_j-\sum_{j=1}^{m'}z'_jr'_j\right)dx^1dx^2$$

$$-\frac{(N_2-|z'|)}{2(\alpha_n)^3}\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2\left(\sum_{i\in C_1}(I-3\vec{v}\vec{v}^T)x_i\cdot x_i\right.$$

$$\left.-\sum_{i=1}^{m}z_i(I-3\vec{v}\vec{v}^T)r_i\cdot r_i\right)dx^1dx^2$$

$$-\frac{(N_1-|z|)}{2(\alpha_n)^3}\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2\left(\sum_{j\in C_2}(I-3\vec{v}\vec{v}^T)x_j\cdot x_j\right.$$

$$\left.-\sum_{j=1}^{m'}z'_i(I-3\vec{v}\vec{v}^T)r'_j\cdot r'_j\right)dx^1dx^2$$

$$+\frac{1}{(\alpha_n)^3}\int_{\mathbb{R}^{3N}}|(\tau_{-\alpha_n\vec{v}})_{x^2}\tilde{\Psi}^{k_1,\dots,k_N}|^2(I-3\vec{v}\vec{v}^T)\left(\sum_{i\in C_1}x_i-\sum_{i=1}^{m}z_ir_i\right)\cdot$$

$$\cdot\left(\sum_{j\in C_2}x_j-\sum_{j=1}^{m'}z'_jr'_j\right)dx^1dx^2+O\left(\frac{\int_{\mathbb{R}^{3N}}|\tilde{\Psi}^{k_1,\dots,k_N}|^2}{(\alpha_n)^4}\right).$$

With a similar computation, on can prove that

$$|\nabla_{H=0}\langle H^N(R^n,Z)\tilde{\Psi}^{k_1,\dots,k_N},\tilde{\Psi}^{k'_1,\dots,k'_N}\rangle| = O\left(e^{-a\alpha_n}\right)$$

when $k'_l = 3$ for some l.

As a conclusion, we obtain, by summing these expressions,

$$\mathcal{E}^N\left(\alpha_n, e^{H_1}v, e^{H_2}v', \tilde{\Psi}^n_k\right) = A_n - \frac{B_n}{\alpha_n} + \frac{C_n}{(\alpha_n)^2} + \frac{D_n+E_n}{(\alpha_n)^3} + O\left(\frac{1}{(\alpha_n)^4}\right)$$

where

$$A_n = \sum_{N_1+N_2=N}\sum_{|C_1|=N_1}\langle\left(H^{N_1}(r,z)_{C_1} + H^{N_2}(r',z')_{C_2}\right)\Psi^{C_1,C_2},\Psi^{C_1,C_2}\rangle$$

$$B_n = -\sum_{N_1+N_2=N}\sum_{|C_1|=N_1}(N_1-|z|)(N_2-|z'|)\|\tilde{\Psi}^{C_1,C_2}\|^2_{L^2} \geq 0$$

and with similar definitions for C_n, D_n, E_n (D_n contains the two terms involving $(N_1-|z|)$ and $(N_2-|z'|)$, and E_n is the third term).

Step 3: A boot-strap argument. We have

$$\begin{aligned}
A_n &\geq \sum_{N_1+N_2=N}\left(E^{N_1}(r,z)+E^{N_2}(r',z')\right)\sum_{|C_1|=N_1}\|\tilde{\Psi}^{C_1,C_2}\|^2_{L^2}\\
&= c\sum_{|C_1|=|z|}\|\tilde{\Psi}^{C_1,C_2}\|^2_{L^2}\\
&\quad + \sum_{\substack{N_1+N_2=N\\ N_1\neq|z|}}\left(E^{N_1}(r,z)+E^{N_2}(r',z')\right)\sum_{|C_1|=N_1}\|\tilde{\Psi}^{C_1,C_2}\|^2_{L^2}\\
&= c+O\left(e^{-a\alpha_n}\right) + \sum_{\substack{N_1+N_2=N\\ N_1\neq|z|}}\left(E^{N_1}(r,z)+E^{N_2}(r',z')-c\right)\sum_{|C_1|=N_1}\|\tilde{\Psi}^{C_1,C_2}\|^2_{L^2}\\
&\geq c+O\left(e^{-a\alpha_n}\right)+\epsilon\sum_{\substack{N_1+N_2=N\\ N_1\neq|z|}}\sum_{|C_1|=N_1}\|\tilde{\Psi}^{C_1,C_2}\|^2_{L^2}\\
&\geq c+\epsilon' B_n + O\left(e^{-a\alpha_n}\right)
\end{aligned}$$

where $\epsilon = \min\{E^{N_1}(r,z)+E^{N_2}(r',z'),\ N_1+N_2=N,\ N_1\neq|z|\} - c > 0$ *(H1)*. Now, we have by the definition of M^n_k and X^n_k,

$$\mathcal{E}^N\left(\alpha_n, e^{H_1}v, e^{H_2}v', \tilde{\Psi}^n_k\right) < c$$

so we obtain, for n large enough,

$$0 \leq \frac{\epsilon'}{2}B_n \leq \left(\epsilon' - \frac{1}{\alpha_n}\right)B_n \leq -\frac{C_n}{(\alpha_n)^2} - \frac{D_n+E_n}{(\alpha_n)^3} + O\left(\frac{1}{(\alpha_n)^4}\right). \qquad (14)$$

Using the fact that $\tilde{\Psi}^n_k$ converges to some critical point at infinity, one easily sees that A_n, B_n, C_n and D_n are bounded as n goes to $+\infty$, and finally $B_n =$

$O\left(\frac{1}{(\alpha_n)^2}\right)$. But we may write for instance, for $1 \leq k_l \leq 2$ with $|C_1| := N_1 \neq |z|$, by (14)

$$\left|(N_2 - |z'|)e_{\vec{v}} \cdot \int_{\mathbb{R}^{3N}} |(\tau_{-\alpha_n \vec{v}})_{x^2} \tilde{\Psi}^{k_1,\dots,k_N}|^2 \left(\sum_{i \in C_1} x_i - \sum_{i=1}^{m} z_i r_i\right) dx^1 dx^2\right|$$
$$\leq |N_2 - |z'||(N_1 + |z|)\alpha_n \int_{\mathbb{R}^{3N}} |(\tau_{-\alpha_n \vec{v}})_{x^2} \tilde{\Psi}^{k_1,\dots,k_N}|^2 dx^1 dx^2$$
$$= \alpha_n |N_2 - |z'||O\left(\|\tilde{\Psi}^{k_1,\dots,k_N}\|_{L^2}^2\right)$$

and so one can easily prove

$$C_n = O\left(\alpha_n B_n\right), \quad D_n = O\left((\alpha_n)^2 B_n\right). \tag{15}$$

Now $C_n = O\left(\frac{1}{\alpha_n}\right)$ and by (14), $B_n = O\left(\frac{1}{(\alpha_n)^3}\right)$. Using one more time (15), we obtain $C_n = O\left(\frac{1}{(\alpha_n)^2}\right)$ and $D_n = O\left(\frac{1}{\alpha_n}\right)$. As a consequence,

$$\mathcal{E}^N\left(\alpha_n, e^{H_1}v, e^{H_2}v', \tilde{\Psi}_k^n\right) = A_n + \frac{E_n}{(\alpha_n)^3} + O\left(\frac{1}{(\alpha_n)^4}\right).$$

Using the same estimates, we also obtain an expansion of the form

$$\nabla_{H_1=0}\mathcal{E}^N\left(\alpha_n, e^{H_1}v, e^{H_2}v', \tilde{\Psi}_{(H_1,H_2)}\right) = \frac{E'_n}{(\alpha_n)^3} + O\left(\frac{1}{(\alpha_n)^4}\right) = 0$$

where E'_n corresponds to the derivative of the dipole/dipole term. But now it is known that

$$\mathcal{P}_{\mathcal{A}_3(\mathbb{R})^\perp}\left[\nabla_{H_1=0}\mathcal{E}^N\left(\alpha_n, e^{H_1}v, e^{H_2}v', \tilde{\Psi}_{(H_1,H_2)}\right)\right] = 0$$

where $\mathcal{P}_{\mathcal{A}_3(\mathbb{R})^\perp}$ is the orthogonal projection onto $\mathcal{A}_3(\mathbb{R})^\perp$. We thus have $\mathcal{P}_{\mathcal{A}_3(\mathbb{R})^\perp}E'_n = O\left(\frac{1}{\alpha_n}\right)$ and so $\mathcal{P}_{\mathcal{A}_3(\mathbb{R})^\perp}E'_n \to 0$ as n goes to $+\infty$. A same result holds for the derivative with respect to H_2. Recall now that in fact $v = v_k^n$, $v' = v'^n_k$, $u = u_k^n$ and $u' = u'^n_k$. As above we may assume by extracting a sequence if necessary that v_k^n and v'^n_k converge to some v_k and v'_k as $n \to +\infty$.

We may now pass to the limit and obtain, by (14) and the convergence of $\tilde{\Psi}_k^n$,

$$\left\{\begin{array}{l} (v_k u_k P) \cdot (v'_k u'_k P'_k) - 3(v_k u_k P \cdot \vec{v})(v'_k u'_k P'_k \cdot \vec{v}) \leq 0 \\ \mathcal{P}_{\mathcal{A}_3(\mathbb{R})^\perp}\left[(I - 3\vec{v}\vec{v}^T)(v_k u_k P)(v'_k u'_k P'_k)^T\right] = 0 \\ \mathcal{P}_{\mathcal{A}_3(\mathbb{R})^\perp}\left[(I - 3\vec{v}\vec{v}^T)(v'_k u'_k P'_k)(v_k u_k P)^T\right] = 0 \end{array}\right. \tag{16}$$

for $k \in \{1, 2\}$, and where $P := P_\psi$ and $P_k := P_{\psi'_k}$.

Step 4: Study of the critical points of the dipole/dipole interaction. We have the following result, which is proved in Appendix 2.

Lemma 12. *Let be $P, P' \in \mathbb{R}^3 \setminus \{0\}$ and $e \in S^2$. The critical points of the function*

$$F^e_{P,P'} : (u, u') \mapsto (uP) \cdot (u'P') - 3(uP \cdot e)(u'P' \cdot e) = ((I - 3ee^T)(uP)) \cdot (u'P')$$

defined on $SO_3(\mathbb{R})^2$ are given by

1. *$u_0 P = \epsilon |P| e$, $u'_0 P' = \epsilon |P'| e$ with $\epsilon = \pm 1$. Then (u_0, u'_0) is a minimum of F, and $F^e_{P,P'}(u_0, u'_0) = -2|P|\,|P'|$.*
2. *$u_4 P = \epsilon |P| e$, $u'_4 P' = -\epsilon |P'| e$ with $\epsilon = \pm 1$. Then (u_4, u'_4) is a maximum of F with a Morse index equal to 4, and $F^e_{P,P'}(u_4, u'_4) = 2|P|\,|P'|$.*
3. *$u_1 P = |P| v$, $u'_1 P' = -|P'| v$ for some $v \in S^2 \cap (e)^\perp$. Then (u_1, u'_1) has a Morse index equal to 1, and $F^e_{P,P'}(u_1, u'_1) = -|P|\,|P'|$.*
4. *$u_2 P = |P| v$, $u'_2 P' = |P'| v$ for some $v \in S^2 \cap (e)^\perp$. Then (u_2, u'_2) has a Morse index equal to 2, and $F^e_{P,P'}(u_1, u'_1) = |P|\,|P'|$.*

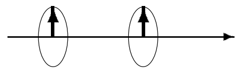
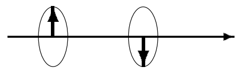
Index	Energy	
4	$2\|P\|\,\|P'\|$	
2	$\|P\|\,\|P'\|$	
1	$-\|P\|\,\|P'\|$	
0	$-2\|P\|\,\|P'\|$	

Figure 4: The critical points of the dipole/dipole interaction

By (16), $(v_k u_k, v'_k u'_k)$ is a critical point of $F^{\vec{v}}_{P,P'_k}$, with a non-positive energy. Since $P \neq 0$ and $P'_k \neq 0$ $(H1)$, we conclude by Lemma 12 that $F^{\vec{v}}_{P,P'_k}(v_k u_k, v'_k u'_k) \leq -|P||P'_k| < 0$.

As a consequence, applying Lemma 2, we obtain

$$\mathcal{E}^N\left(\alpha_n, v^n_k u^n_k, v'^n_k u'^n_k, (v^n_k u^n_k \cdot \psi) \wedge (\tau_{\alpha_n \vec{v}} \cdot v'^n_k u'^n_k \cdot \psi'_k)\right) = \\ c + \frac{F^{\vec{v}}_{P,P'_k}(v^n_k u^n_k, v'^n_k u'^n_k)}{(\alpha_n)^3} + O\left(\frac{1}{(\alpha_n)^4}\right) < c$$

for n large enough, since

$$\lim_{n \to +\infty} F^{\vec{v}}_{P,P'_k}(v^n_k u^n_k, v'^n_k u'^n_k) = F^{\vec{v}}_{P,P'_k}(v_k u_k, v'_k u'_k) < 0.$$

Let us now denote by

$$\tilde{M}_k^n := \left(\alpha_n, v_k^n u_k^n, v'^n_k u'^n_k, (v_k^n u_k^n \cdot \psi) \wedge (\tau_{\alpha_n \vec{v}} \cdot v'^n_k u'^n_k \cdot \psi'_k)\right).$$

For n large enough, we may now construct a path connecting X_k^n to $\tilde{M}_k^n$ $k \in \{1,2\}$, with an energy below c, by Lemma 10.

Step 5: Connecting the two tensor products. To end the proof, it remains to connect M_1^n and M_2^n by a path with a maximum energy below c. We fix here n and forget this subscript. Let us now introduce the function F defined by

$$F(\nu, \nu', \phi) = F^{\vec{v}}_{P,P_\phi}(\nu, \nu')$$

for $(\nu, \nu', \phi) \in W := SO_3(\mathbb{R})^2 \times V$ where V is the unit sphere of the finite dimensional space $ker\left(H^{|z'|}(r', z') - E^{|z'|}(r', z')\right)$. We now denote by $Y_k := (u_k v_k, u'_k v'_k, \psi_k)$ for $k \in \{1,2\}$. Notice that we have shown

$$\max(F(Y_1), F(Y_2)) \leq -\min_{\phi \in V}\{|P||P_\phi|\} < 0.$$

Now, let be

$$\tilde{c} := \min_{Y \in \Gamma'} \max_{t \in [0,1]} F(Y(t)) \tag{17}$$

where

$$\Gamma' = \{Y \in \mathcal{C}^0([0,1], W),\ Y(0) = Y_1,\ Y(1) = Y_2\}.$$

We have the following

Lemma 13. *We have* $\tilde{c} \leq -\min_{\phi \in V}\{|P||P_\phi|\} := C < 0$.

Proof of Lemma 13 – Suppose that $\tilde{c} > max(F(Y_1), F(Y_2))$. By the methods of [14], we may find a sequence $y_n \in W$ such that $F(y_n) \to \tilde{c}$, $\nabla F(y_n) \to 0$ and $d^2_{(\nu,\nu')} F \geq -e_n$ on a space of codimension at most 1, with $e_n \to 0$ as $n \to +\infty$. W being compact, up to a subsequence, $y_n = (\nu_n, \nu'_n, \phi_n)$ converges to a critical point $y = (\nu, \nu', \phi)$ of energy $\tilde{c}$, and with a Morse index with respect to (ν, ν') variations at most 1. By Lemma 12, we necessary have $F(y) \leq -|P||P_\phi|$. □

Let $Y_n \in \Gamma'$ be a path connecting Y_1 and Y_2 such that $\max_{t \in [0;1]} F(Y(t)) \leq \tilde{c} + \frac{1}{\alpha_n}$. We then have

$$\begin{aligned}
&\mathcal{E}^N\left(\alpha_n, \nu_n(t), \nu'_n(t), (\nu_n(t) \cdot \psi) \wedge (\tau_{\alpha_n \vec{v}} \cdot \nu'_n(t) \cdot \psi_n(t))\right) \\
&\qquad = c + \frac{F(Y_n(t))}{(\alpha_n)^3} + O\left(\frac{1}{(\alpha_n)^4}\right) \leq c + \frac{C}{(\alpha_n)^3} + O\left(\frac{1}{(\alpha_n)^4}\right) < c
\end{aligned}$$

for n large enough.

As a conclusion, we have built a path $\tilde{\gamma}_n$ for n large enough such that

$$\max_{t \in [0;1]} \mathcal{E}^N(\tilde{\gamma}_n(t)) < c$$

which is a contradiction and ends the proof of Theorem 7. □

Appendix 1: Non-isotropic exponential decay of the electronic density

We want to prove here Lemma 3, that we recall for the reader's convenience.

Lemma 14. *Let Ψ_R be an eigenfunction associated to the eigenvalue $\lambda_d^N(R,Z)$ and ρ_R be the electronic density. We introduce $\epsilon_R = \Sigma^N(R,Z) - \lambda_d^N(R,Z)$. Then*

1. *ρ_R satisfies the inequation*

$$-\frac{1}{2}\Delta\rho_R + V_R\rho_R + \epsilon_R\rho_R \leq 0. \tag{18}$$

2. *With $R_1(\epsilon) := max\left(R_0+1, R_0+\frac{2Np}{\epsilon}\right)$ and $C(\epsilon) := \cup_{j=1}^p\{x,\ |x-X_j| = R_1(\epsilon)\}$, and if $r > 2R_1(\epsilon_R)$, then we have*

$$\begin{aligned}\rho_R(x) &\leq \|\rho_R\|_{L^\infty(C(\epsilon_R))}\sum_{j=1}^p e^{-\sqrt{\epsilon_R/p}(|X_j-x|-R_1(\epsilon_R))}\\ &\leq p\|\rho_R\|_{L^\infty(C(\epsilon_R))}e^{-\sqrt{\epsilon_R/p}(\delta(x)-R_1(\epsilon_R))},\\ &\leq Me^{-\sqrt{\epsilon_R/p}(\delta(x)-R_1(\epsilon_R))}\end{aligned} \tag{19}$$

on $\mathcal{U}(R_1(\epsilon_R))$, where $\delta(x) = \min\{|x-X_j|,\ j = 1,...,d\}$, and $M = M(p,N,R_1(\epsilon_R))$.

Proof – The fact that ρ_R is a solution to (10) is essentially proved in [16] (the proof is written for atoms with no nuclei/nuclei interaction).

The proof of (19) follows ideas of [15]. We have

$$V_R(x) \geq -\sum_{j=1}^p \frac{N}{|x-X_j|-R_0}$$

for all $x \in \mathcal{U}(R_1(\epsilon_R))$, so that ρ_R satisfies

$$-\frac{1}{2}\Delta\rho_R + \sum_{j=1}^p\left(\frac{\epsilon_R}{p} - \frac{N}{|x-X_j|-R_0}\right)\rho_R \leq 0.$$

on $\mathcal{U}$. Let f be the radial positive solution of

$$-\frac{1}{2}\Delta f + \left(\frac{\epsilon_R}{p} - \frac{N}{|x|-R_0}\right)f = 0$$

on $\mathbb{R}^3 \setminus B(0, R_1(\epsilon_R))$, such that $f(x) = 1$ if $|x| = R_1(\epsilon_R)$ (f is a Whittaker function, see [15]). Then $f_j(x) = f(x-X_j)$ is a positive solution of

$$-\frac{1}{2}\Delta f_j + \left(\frac{\epsilon_R}{p} - \frac{N}{|x-X_j|-R_0}\right)f_j = 0$$

on $\mathbb{R}^3 \setminus B(X_j, R_1(\epsilon_R))$ and $F = \sum_{j=1}^p f_j$ is a solution of

$$-\frac{1}{2}\Delta F + \sum_{j=1}^{p} \left(\frac{\epsilon_R}{p} - \frac{N}{|x - X_j| - R_0} \right) F = 0.$$

such that $F(x) \geq 1$ if $x \in C(\epsilon_R)$.

Since $\rho_R \in \mathcal{C}^\infty(\mathcal{U}(R_1(\epsilon_R)))$ and $\lim_{|x| \to +\infty} \rho_R(x) = 0$, the maximum principle implies

$$\rho_R \leq \|\rho_R\|_{L^\infty(C(\epsilon_R))} F(x).$$

But, on $\mathbb{R}^3 \setminus B(X_j, R_1(\epsilon_R))$, we also have

$$\frac{\epsilon_R}{p} - \frac{N}{|x - X_j| - R_0} \geq \frac{\epsilon_R}{2p} > 0,$$

so that (maximum principle)

$$f_j(x) \leq \frac{R_1(\epsilon_R)}{|X_i - x|} e^{-\sqrt{\epsilon_R/p}(|x-X_j|-R_1(\epsilon_R))} \leq e^{-\sqrt{\epsilon_R/p}(|x-X_j|-R_1(\epsilon_R))}$$

on $\mathbb{R}^3 \setminus B(X_j, R_1(\epsilon_R))$ which implies

$$\begin{aligned} F(x) &\leq \sum_{j=1}^{p} e^{-\sqrt{\epsilon_R/p}(|x-X_j|-R_1(\epsilon_R))} \\ &\leq p e^{-\sqrt{\epsilon_R/p}\left(\frac{1}{p}\sum_{j=1}^{p} |x-X_j|-R_1(\epsilon_R)\right)} \\ &\leq p e^{-\sqrt{\epsilon_R/p}(\delta(x)-R_1(\epsilon_R))}. \end{aligned}$$

To end the proof, we now remark that since ρ_R is real analytic on $\mathcal{U}(R_0 + 1/2)$, there exists a constant M depending only on $R_1(\epsilon_R)$ such that

$$\|\rho_R\|_{L^\infty(C(\epsilon_R))} \leq M \|\rho_R\|_{L^1(\mathcal{U}(R_0+1/2)))} \leq M \|\rho_R\|_{L^1(\mathbb{R}^3)} = M \cdot N$$

and so

$$\rho_R \leq M N p e^{-\sqrt{\epsilon_R/p}(\delta(x)-R_1(\epsilon_R))}.$$

□

Appendix 2: Study of the critical points of the dipole/dipole interaction

We prove here Lemma 12 that we recall.

Lemma 15. *Let be $P, P' \in \mathbb{R}^3 \setminus \{0\}$ and $e \in S^2$. The critical points of the function*

$$F^e_{P,P'} : (u, u') \mapsto (uP) \cdot (u'P') - 3(uP \cdot e)(u'P' \cdot e) = ((I - 3ee^T)(uP)) \cdot (u'P')$$

defined on $SO_3(\mathbb{R})^2$ are given by

1. *$u_0 P = \epsilon|P|e$, $u'_0 P' = \epsilon|P'|e$ with $\epsilon = \pm 1$. Then (u_0, u'_0) is a minimum of F, and $F^e_{P,P'}(u_0, u'_0) = -2|P|\,|P'|$.*
2. *$u_4 P = \epsilon|P|e$, $u'_4 P' = -\epsilon|P'|e$ with $\epsilon = \pm 1$. Then (u_4, u'_4) is a maximum of F with a Morse index equal to 4, and $F^e_{P,P'}(u_4, u'_4) = 2|P|\,|P'|$.*
3. *$u_1 P = |P|v$, $u'_1 P' = -|P'|v$ for some $v \in S^2 \cap (e)^\perp$. Then (u_1, u'_1) has a Morse index equal to 1, and $F^e_{P,P'}(u_1, u'_1) = -|P|\,|P'|$.*
4. *$u_2 P = |P|v$, $u'_2 P' = |P'|v$ for some $v \in S^2 \cap (e)^\perp$. Then (u_2, u'_2) has a Morse index equal to 2, and $F^e_{P,P'}(u_1, u'_1) = |P|\,|P'|$.*

Proof – It is simpler to study the function

$$(x, y) \mapsto |P||P'|x \cdot y - 3(x \cdot e)(y \cdot e)$$

defined on $S^2 \times S^2$, but we shall not use here this expression, to keep the point of view imposed by the proof of Theorem 7.

If (u, u') is a critical point of $F^e_{P,P'}$, then $(0, 0)$ is a critical point of $f : (H, H') \mapsto F^e_{uP,u'P'}(e^H, e^{H'})$, defined on $\mathcal{A}_3(\mathbb{R}) \times \mathcal{A}_3(\mathbb{R})$. We may assume $u = u' = I$ and $|P| = |P'| = 1$ to simplify notations, and we denote by $M := I - 3ee^T$. Then we have

$$\left\{ \begin{array}{l} MP'P^T \in \mathcal{A}_3(\mathbb{R})^\perp \\ MP(P')^T \in \mathcal{A}_3(\mathbb{R})^\perp \end{array} \right. \iff \left\{ \begin{array}{l} MP'P^T = P(P')^T M \\ MP(P')^T = P'P^T M \end{array} \right. \tag{20}$$

Multiplying by M, we find for instance $M^2 P'P^T = P'P^T M^2$ and so $M^2 P' = (P^T M^2 P)P'$, showing that P and P' are eigenvectors of M^2. It is then easy to see that they are eigenvectors of M. Using (20), we obtain $P = \pm P'$. The critical points are thus those given in the Lemma.

The second derivative is given by

$$d^2 f_{P,P'}(H, H') = 2(MHP) \cdot (H'P') + (MH^2 P) \cdot P' + (M(H')^2 P') \cdot P.$$

Suppose for instance that $P = e$. Let (e_2, e_3) be an orthogonal basis of $e^\perp$. Then, in the basis $(e_1 = e, e_2, e_3)$, $M = diag(-2, 1, 1)$. We introduce $H_{ij} :=$

$e_i e_j^T - e_j e_i^T$, so that $(H_{ij})_{1\leq i<j\leq 3}$ is an orthogonal basis of $\mathcal{A}_3(\mathbb{R})$. The matrix of $d^2_{P,P} f$ is this basis is then

$$d^2_{P,P} f = \begin{pmatrix} 2 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 1 \\ 1 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 2 \end{pmatrix} \sim diag(1,1,3,3,0,0),$$

and obviously $d^2_{P,-P} f \sim diag(-1,-1,-3,-3,0,0)$.

If $P \perp e$, we use the same basis $(H_{ij})_{1\leq i<j\leq 3}$ but with $e_2 = P$ and find

$$d^2_{P,P} f = \begin{pmatrix} -1 & 0 & 0 & -2 & 0 & 0 \\ 0 & -1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -2 & 0 & 0 & -1 & 0 & 0 \\ 0 & -2 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \sim diag(1,-2,-3,0,0,0),$$

and obviously $d^2_{P,-P} f \sim diag(-1,2,3,0,0,0)$.

$\square$

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