

# Solution of a Mountain Pass Problem for the Isomerization of a Molecule with One Free Atom

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**Abstract.** In this paper, we continue the mathematical study of adiabatic chemical reactions, started in a previous work (Ann. Henri Poincaré 5, 477–521, 2004). We consider a molecule with one free atom, the latter having two distinct possible stable positions. We then look for a mountain pass point between these two local minima in the non-relativistic Schrödinger framework.

We prove the existence of a mountain pass point without any assumption on the molecules at infinity, improving our previous results for this model. This critical point is interpreted as a transition state in Quantum Chemistry.

## 1 Introduction

In the present work, we continue the mathematical study of adiabatic chemical reactions, started in a previous paper [7]. Namely, we consider, in the linear non-relativistic Schrödinger framework, a neutral molecule that possesses two distinct stable positions for its nuclei and look for a mountain pass point between these two configurations. Such a stationary state is interpreted as a transition state in Quantum Chemistry, for its energy is the lowest threshold for passing from one configuration to the other. An optimal path leading from one minimum to the other and passing through the mountain pass point is then interpreted as an adiabatic reaction, called isomerization.

A very classical example [11] is the HCN molecule which also exists in the form CNH. During the reaction process, the H atom simply turns around the CN molecule, and passes through a mountain pass point at which the H–C bond changes into a N–H bond. The computation of the transition state and its energy are both very important in practice [12, 4].

In [7], we first described the behavior of the non compact minimaxing paths, proving that in this case of lack of compactness the mountain pass energy corresponds to a system which is broken into independent parts, the electrons being shared among them and at their ground state. Then we proved the existence of the mountain pass only for specific cases, under reasonable assumptions on the configurations at infinity. More precisely, we assumed either that the molecules at infinity are charged, or that they are polarized. Since it involves an H atom (which has no dipole), the isomerization of HCN mentioned as an example before is not covered by this results.

Our goal in this paper is to show the existence of the mountain pass point without any assumption at infinity, in the special case of a molecule that possesses only one free atom, like HCN or many other practical cases.

Although we use here results and methods from [7], the main part of the proof is different from the one of [7]. Instead, we use ideas from a celebrated paper of Lieb and Thirring [8] to show that attractive long-distance Van Der Waals forces always exist between an atom and a molecule, independently of the orientation of the molecule. In [8], this attractive force is shown to exist only for a certain (unknown) orientation of each system, a restriction which is adapted to minimizing sequences but not to the study of paths.

In the next section we define the model and state our main result. The last section is devoted to the proof of our theorem.

## 2 Model and Main Result

We consider a neutral quantum system containing one free atom. We use here mainly the notation of [7]. Namely, the molecule is placed at 0 whereas the single atom is located at a distance  $\alpha$  along a fixed axis in the direction  $\vec{v}$ , with  $\|\vec{v}\| = 1$ . The parameters for the position of the nuclei are the distance  $\alpha$  and the orientation of the molecule, represented by a rotation  $u \in SO_3(\mathbb{R})$ .

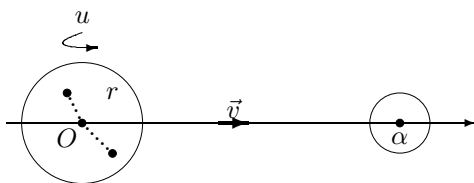


Figure 1. An atom interacting with a molecule.

The nuclei of the first molecule are represented as pointwise charges within the Born-Oppenheimer approximation, with relative locations  $r = (0, r_2, \dots, r_m) \in (\mathbb{R}^3)^m$ ,  $r_i \neq r_j$  for  $i \neq j$ , and charges  $z = (z_1, \dots, z_m) \in (0; \infty)^m$ . The charge of the single atom is  $z'$ .

We now introduce, for  $\alpha \in \mathbb{R}^*$  and  $u \in SO_3(\mathbb{R})$ ,

$$R(\alpha, u) = (\alpha \vec{v}, u r) \in (\mathbb{R}^3)^{m+1}, \quad Z = (z', z) \in (0; \infty)^{m+1},$$

where we have used the notation  $u r = (u r_i)_{i=1}^m$ . This system of nuclei creates a Coulomb potential  $V_{(R(\alpha, u), Z)}$  where by definition

$$V_{(R, Z)}(x) = - \sum_{j=1}^M \frac{Z_j}{|x - R_j|}$$

when  $R = (R_1, \dots, R_M) \in (\mathbb{R}^3)^M$  and  $Z = (Z_1, \dots, Z_M) \in (0; \infty)^M$  (in our case  $M = m + 1$ ).

The electrons are described by the purely Coulombic  $N$ -body Hamiltonian

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

acting on the  $N$ -body space  $L_a^2((\mathbb{R}^3)^N, \mathbb{C})$ , with domain  $H_a^2((\mathbb{R}^3)^N, \mathbb{C})$  and quadratic form domain  $H_a^1((\mathbb{R}^3)^N, \mathbb{C})$ . Throughout the paper, the subscript  $a$  indicates that we consider wavefunctions  $\Psi$  which are antisymmetric under interchanges of variables

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

due to the Pauli principle and the fermionic nature of electrons. We refer the reader to, e.g., [7, Theorem 1], for a description of the known properties of  $H^N(R, Z)$ .

Notice that, like in [7], we consider complex-valued wavefunctions, which is important for the proof. We have neglected the spin but our result can be easily extended to the case of spin-dependent wavefunctions.

For a fixed configuration of the nuclei, we define the *electronic ground state energy*

$$E^N(R, Z) = \inf \{ \langle \Psi, H^N(R, Z) \Psi \rangle, \Psi \in SH_a^1((\mathbb{R}^3)^N, \mathbb{C}) \},$$

where  $\Psi \in SH_a^1((\mathbb{R}^3)^N, \mathbb{C})$  means  $\Psi \in H_a^1((\mathbb{R}^3)^N, \mathbb{C})$  and  $\|\Psi\|_{L^2((\mathbb{R}^3)^N, \mathbb{C})} = 1$ . In our case, the total energy of the system is then given by

$$\mathcal{E}^N(\alpha, u, \Psi) := \langle \Psi, H^N(R(\alpha, u), Z) \Psi \rangle$$

for  $\alpha \in \mathbb{R}^*$ ,  $u \in SO_3(\mathbb{R})$  and  $\Psi \in SH_a^1((\mathbb{R}^3)^N, \mathbb{C})$ . We also introduce the notation

$$I(\alpha, u) := E^N(R(\alpha, u), Z) \tag{1}$$

for the electronic ground state energy of our molecule in the configuration  $(\alpha, u) \in \mathbb{R}^* \times SO_3(\mathbb{R})$ .

In the following, we want to consider a neutral molecule, i.e.,

$$N = z' + |z|,$$

where  $|z| := z_1 + \dots + z_m$ . In this case, it has been shown by Lieb and Thirring [8] that  $\mathcal{E}^N$  possesses a minimizer  $M \in \mathbb{R}^* \times SO_3(\mathbb{R}) \times SH_a^1((\mathbb{R}^3)^N, \mathbb{C})$ . In the present work, we consider a molecule which possesses two local minima  $M = (\alpha_M, u_M, \Psi_M)$  and  $M' = (\alpha_{M'}, u_{M'}, \Psi_{M'})$  of  $\mathcal{E}^N$  on  $\mathbb{R}^* \times SO_3(\mathbb{R}) \times SH_a^1((\mathbb{R}^3)^N, \mathbb{C})$ . Up to a rotation of the system, we may assume that  $\alpha_M, \alpha_{M'} \in (0, \infty)$ . This allows us to define the following mountain pass method [7], in the spirit of A. Ambrosetti and P.H. Rabinowitz [1],

$$c = \inf_{\gamma \in \Gamma} \max_{t \in [0;1]} \mathcal{E}^N(\gamma(t)) \tag{2}$$

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

As explained in [7], the physical interpretation of (2) is that a path  $\gamma \in \Gamma$  represents an infinitely slow (adiabatic) reaction leading from  $M$  to  $M'$ . The number  $c$  is thus the lowest energy threshold for passing from one local minimum to the other. In Quantum Chemistry, the function  $\Psi$  is usually kept to be a ground state of the  $N$ -body Hamiltonian all along the path, but here we add no such constraint on  $\Psi$ . In [7, Theorem 4], we showed that the generalized min-max method (2) is indeed a mathematical tool which allows to obtain exactly the same energy as in practice and avoid problems of smoothness in case of degeneracy of the ground state.

Our main goal is to prove the existence of a mountain pass at the level  $c$ , interpreted as a *transition state* in Chemistry. In [7], the case of two molecules was considered and we proved the existence of the mountain pass under restricting assumptions on the configurations at infinity. In the special case considered here, namely when one of these two subsystems is a single atom, we are able to show the existence of the mountain pass in full generality.

**Theorem 1 (Existence of a transition state)** *Let be  $N = z' + |z|$ . Then there exists a critical point  $(\bar{\alpha}, \bar{u}, \bar{\Psi}) \in \mathbb{R}^* \times SO_3(\mathbb{R}) \times SH_a^1((\mathbb{R}^3)^N, \mathbb{C})$  of  $\mathcal{E}^N$  at the level  $c$ , such that*

$$c = I(\bar{\alpha}, \bar{u}),$$

*the electronic ground state energy of  $H^N(R(\bar{\alpha}, \bar{u}), Z)$ .*

Remark that an electronic ground state is obtained in Theorem 1, which really corresponds to the fact that we are dealing with adiabatic reactions.

The rest of the paper is devoted to the proof of this result. It uses ideas from both [8] and [7].

### 3 Proof of Theorem 1

Notice that we may assume  $c > \max\{\mathcal{E}^N(M), \mathcal{E}^N(M')\}$ . Indeed, if for instance  $c = \mathcal{E}^N(M)$ , then  $M$  is a critical point which is a solution of the problem.

Let us first recall results of [7]. In this paper, we proved the following alternative [7, Theorems 4 and 5]

- **either** we can construct a minimaxing sequence  $(\alpha_n, u_n, \Psi_n)$ , with  $\alpha_n$  bounded, which is known to converge, up to a subsequence, to a critical point  $(\bar{\alpha}, \bar{u}, \bar{\Psi})$  of  $\mathcal{E}^N$  at the level  $c$ , such that  $\bar{\Psi}$  is a ground state of  $H^N(R(\bar{\alpha}, \bar{u}), Z)$ ;
- **or** we have

$$c = \min \{E^{n_1}(0, z') + E^{n_2}(r, z), n_1 + n_2 = N\} \quad (3)$$

and there exists  $a_n \rightarrow +\infty$  and a sequence of paths  $(\gamma_n) \in \Gamma$ ,  $\gamma_n(t) = (\alpha_n(t), u_n(t), \Psi_n(t))$  for  $t \in [0; 1]$ , such that

$$\begin{aligned} c &\leq \max_{t \in [0; 1]} \mathcal{E}^N(\gamma_n(t)) \leq c + \frac{1}{n} \\ \alpha_n(t) \leq a_n &\implies \mathcal{E}^N(\gamma_n(t)) < c. \end{aligned} \quad (4)$$

To prove this alternative, we used in [7] the duality theory developed by Ghoussoub in [5] and Palais-Smale sequences with Morse-type information which can be obtained by the result of Fang and Ghoussoub [3, 5]. In the second case of the alternative, the interpretation is that it is necessary to break the molecule into pieces (i.e., to pass through a critical point at infinity [7, 2]) in order to solve the mountain pass problem.

We emphasize that showing that the second case does not occur indeed corresponds to proving that a lack of compactness due to *dichotomy* is impossible, in the usual language of the locally compact concentration-compactness method of P.L. Lions [9].

In [7, Theorem 6], we proved that in the case of charged molecules at infinity, i.e., if there exist  $n_1 \neq z'$  and  $n_2 \neq |z|$  solving the right-hand side of (3), then the second case of the alternative is impossible. It thus remains to show that this is also impossible for neutral systems at infinity, i.e., when  $c = E^{z'}(0, z') + E^{|z|}(r, z)$ , which we will do in the particular situation (a molecule with one free atom) of this paper.

Let  $t_n$  and  $t'_n$  be the minimum and the maximum of  $\{t, \alpha_n(t) \geq a_n\}$ , where  $\alpha_n$  and  $a_n$  satisfy (4). By the definition of  $c$ , we have  $0 < t_n < t'_n < 1$ . Let us introduce  $M_n = \gamma_n(t_n)$  and  $M'_n = \gamma_n(t'_n)$ . Like in [7, Proof of Theorem 6], the general idea is to connect  $M_n$  and  $M'_n$  by a path on which  $\alpha(t)$  is constant ( $\alpha_n(t) \equiv a_n$ ), and with a maximum energy below  $c$ , which will be a contradiction. For charged molecules at infinity, the path linking  $M_n$  and  $M'_n$  was simply constituted in [7] by tensor products of ground states. Since we are dealing here with neutral molecules, the path will be constructed on a different set.

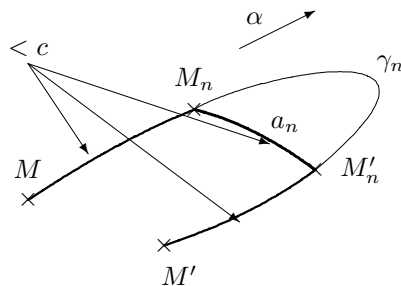


Figure 2. General idea of the proof.

Let us write  $M_n = (a_n, u_n, \Psi_n)$  and  $M'_n = (a_n, u'_n, \Psi'_n)$ , and notice that  $\mathcal{E}^N(M_n) < c$  and  $\mathcal{E}^N(M'_n) < c$  by definition of  $a_n$ . One can always find a path linking  $\Psi_n$  and a ground state of  $H^N(R(a_n, u_n), Z)$ , on which the energy is not higher than  $\mathcal{E}^N(M_n) < c$  (see, e.g., [7, Lemma 10]). Therefore, we can assume, without any loss of generality, that  $\Psi_n$  (resp.  $\Psi'_n$ ) is a ground state of  $H^N(R(a_n, u_n), Z)$  (resp.  $H^N(R(a_n, u'_n), Z)$ ).

We want to construct a path between  $M_n$  and  $M'_n$ , with a maximal energy lower than the mountain pass level  $c$ . Since  $SO_3(\mathbb{R})$  is pathwise connected, there

exists a continuous path  $v_n(t) \in \mathcal{C}^0([t_n; t'_n], SO_3(\mathbb{R}))$  such that  $v_n(t_n) = u_n$  and  $v_n(t'_n) = u'_n$ . In the following, we fix the part of the path  $t \mapsto (a_n, v_n(t))$  corresponding to the positions of the nuclei, and we only allow variations of the wavefunction  $\Psi$ .

We therefore consider the following minimax principle

$$c_n = \inf_{\Psi(t) \in \Gamma'_n} \max_{t \in [t_n; t'_n]} \mathcal{E}^N(a_n, v_n(t), \Psi(t)), \tag{5}$$

where

$$\Gamma'_n = \{ \Psi(t) \in \mathcal{C}^0([t_n; t'_n], SH_a^1((\mathbb{R}^3)^N, \mathbb{C})) \mid \Psi(t_n) = \Psi_n, \Psi(t'_n) = \Psi'_n \}. \tag{6}$$

Notice that (5) has not the form of a usual mountain pass variational problem, for the energy to be optimized depends on the parameter  $t$  of the path  $\Psi(t)$ , via  $v_n(t)$ . For each  $\Psi \in \Gamma'_n$ , the path  $\gamma$  defined by

$$\gamma(t) = \begin{cases} (a_n, v_n(t), \Psi(t)) & \text{if } t \in [t_n; t'_n] \\ (a_n, v_n(t), \Psi_n(t)) & \text{if } t \in [0; t_n] \cup [t'_n; 1] \end{cases}$$

belongs to  $\Gamma$  defined in (2). Therefore, by definition of  $c$ , we obtain for each  $n$ ,

$$c \leq c_n. \tag{7}$$

We shall need the following two results, whose proof will be postponed until the end of the proof of Theorem 1. The first states that  $c_n$  equals the maximum value of the *first* eigenvalue of  $H^N(R(a_n, v_n(t)), Z)$  when  $t \in [t_n; t'_n]$ .

**Lemma 1** *One has*

$$c_n = \max_{t \in [t_n; t'_n]} I(a_n, v_n(t)). \tag{8}$$

The proof of Lemma 1 uses the fact that the wavefunction  $\Psi$  is complex-valued. The second theorem is an improved version of a result due to Lieb and Thirring [8]. It states the existence of attractive Van Der Waals forces in the special case where one of the two considered systems is a single atom, *independently of the orientation of the other subsystem*.

**Theorem 2 (Van Der Waals forces between an atom and a molecule)** *There exists a constant  $C > 0$  such that*

$$\max_{u \in SO_3(\mathbb{R})} I(\alpha, u) \leq E^{z'}(0, z') + E^{|z|}(r, z) - \frac{C}{\alpha^6} + O\left(\frac{1}{\alpha^7}\right).$$

It is easy to see that (8) and Theorem 2 allow to end the proof of Theorem 1, since one then infers

$$\begin{aligned} c_n &\leq E^{z'}(0, z') + E^{|z|}(r, z) - \frac{C}{(a_n)^6} + O\left(\frac{1}{(a_n)^7}\right) \\ &= c - \frac{C}{(a_n)^6} + O\left(\frac{1}{(a_n)^7}\right), \end{aligned}$$

which contradicts (7) as  $a_n \rightarrow \infty$ . It therefore only rests to prove Lemma 1 and Theorem 2.

**Proof of Lemma 1** The idea is to explicitly construct a path  $\Psi(t) \in \Gamma'_n$  such that  $\Psi(t)$  is, for any  $t \in [t_n; t'_n]$ , *almost* a ground state of the  $N$ -body Hamiltonian  $H^N(R(a_n, v_n(t)), Z)$ . If its first eigenvalue  $I(a_n, v_n(t))$  is non-degenerated for any  $t \in [t_n; t'_n]$ , it is indeed very easy to construct a continuous path  $\Psi(t)$  of ground states (see below). However, when it degenerates for some  $t$ , this may be impossible due to the lack of regularity of the eigenspaces. Therefore, our goal will be to construct for any fixed  $\epsilon > 0$  a path  $\Psi(t)$  which is such that

$$\forall t \in [t_n; t'_n], \quad \mathcal{E}^N(a_n, v_n(t), \Psi(t)) \leq I(a_n, v_n(t)) + \epsilon, \quad (9)$$

which exactly proves that

$$c_n \leq \max_{t \in [t_n; t'_n]} I(a_n, v_n(t)) + \epsilon.$$

This will end the proof of Lemma 1 since, of course, the reverse inequality

$$c_n \geq \max_{t \in [t_n; t'_n]} I(a_n, v_n(t))$$

is always true.

Recall that the wavefunction  $\Psi$  is complex-valued which means that we indeed have to find two real functions  $\Psi_1(t), \Psi_2(t) \in C^0([t_n; t'_n], L^2(\mathbb{R}^3, \mathbb{R}))$  such that  $\Psi = \Psi_1 + i\Psi_2$  is in  $\Gamma'_n$  and satisfies (9). Since the  $N$ -body Hamiltonian is real, it acts separately on the real and the imaginary parts of the wavefunction and one has, when  $\Psi = \Psi_1 + i\Psi_2$ ,

$$\langle H^N(R, Z)\Psi, \Psi \rangle = \langle H^N(R, Z)\Psi_1, \Psi_1 \rangle + \langle H^N(R, Z)\Psi_2, \Psi_2 \rangle$$

which, in matrix notation, can be written as

$$\langle H^N(R, Z)\Psi, \Psi \rangle = \left\langle \begin{pmatrix} H^N(R, Z) & 0 \\ 0 & H^N(R, Z) \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}, \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} \right\rangle$$

Therefore, in order to construct our path, we can consider the  $N$ -body Hamiltonian  $H^N(R, Z)$  as an operator acting on the real space  $L^2(\mathbb{R}^3, \mathbb{R}) \oplus L^2(\mathbb{R}^3, \mathbb{R})$ . Its spectrum is then the same as when it acts on  $L^2(\mathbb{R}^3, \mathbb{C})$  seen as a  $\mathbb{C}$ -vector space, but each of its eigenvalue now has an even multiplicity. This additional property will be used to construct the path  $\Psi(t) = \Psi_1(t) + i\Psi_2(t)$ .

For the sake of clarity, we denote by  $H(t)$  the operator  $H^N(R(a_n, v_n(t)), Z)$  defined on  $L^2(\mathbb{R}^3, \mathbb{R}) \oplus L^2(\mathbb{R}^3, \mathbb{R})$  and by  $\lambda_p(t)$ ,  $p \geq 0$ , the nondecreasing sequence of its eigenvalues. According to what we have just said above, one has  $\lambda_{2k}(t) = \lambda_{2k+1}(t)$  for any  $t \in [t_n; t'_n]$  and  $k \in \mathbb{N}$ . The functions  $\lambda_p(t)$  are known to be continuous [6] but they are not necessarily smoother in case of degeneracy.

We now fix some  $\epsilon > 0$  and denote by  $\kappa$  the smallest integer which is such that

$$\forall t \in [t_n; t'_n], \quad I(a_n, v_n(t)) = \lambda_0(t) < \lambda_{2\kappa}(t).$$

To see that such a  $\kappa$  exists, it suffices to notice that  $\lambda_0(t) < \Sigma(t)$  and that the functions  $\lambda_p$  are continuous and converge to  $\Sigma$  as  $p \rightarrow \infty$  uniformly on  $[t_n; t'_n]$ , where  $\Sigma(t)$  is the bottom of the essential spectrum of  $H(t)$ .

We now treat two different cases, depending whether the first eigenvalue  $\lambda_0(t)$  can have a multiplicity greater than 2 or not.

**First case:**  $\kappa = 1$ . In this case, the eigenspace  $V_0(t)$  associated with  $\lambda_0(t)$  has a dimension 2 for any  $t \in [t_n; t'_n]$ . Indeed, it can be written  $V_0(t) = E_0(t) \oplus E_0(t)$  where  $E_0(t)$  is the eigenspace of  $H^N(R(a_n, v_n(t)), Z)$  seen as an operator acting only on  $L^2(\mathbb{R}^3, \mathbb{R})$ . By the usual Kato's regularity Theorem [6, Thm 5.1],  $V_0(t)$  varies continuously. This means that there exists an orthonormal basis  $(\psi_1, \psi_2)$  of  $V_0(t_n)$  and a one parameter path of rotations  $U(t)$  such that  $(U(t)\psi_1, U(t)\psi_2)$  is an orthonormal basis of  $V_0(t)$  for any  $t \in [t_n; t'_n]$ . By definition, one has  $\Psi_n \in V_0(t_n)$  and  $\Psi'_n \in V_0(t'_n)$ , where we recall that  $\Psi_n$  and  $\Psi'_n$  are the wavefunctions appearing in (6). Since then

$$\Psi_n = \cos(\beta)\psi_1 + \sin(\beta)\psi_2 \quad \text{and} \quad \Psi'_n = \cos(\beta')U(t'_n)\psi_1 + \sin(\beta')U(t'_n)\psi_2,$$

we can simply take the following path of ground states

$$\Psi(t) = \cos(\beta(t))U(t)\psi_1 + \sin(\beta(t))U(t)\psi_2$$

where  $\beta(t)$  is a continuous function such that  $\beta(t_n) = \beta$  and  $\beta(t'_n) = \beta'$ . One then has  $\mathcal{E}^N(a_n, v_n(t), \Psi(t)) = \lambda_0(t)$  for all  $t \in [t_n; t'_n]$  and therefore  $c_n = \max_{t \in [t_n; t'_n]} I(a_n, v_n(t))$ .

**Second case:**  $\kappa > 1$ . In this case, we isolate the points on which the multiplicity of  $\lambda_0(t)$  is greater than 2, by introducing the following non empty compact subset of  $[t_n; t'_n]$

$$K := \{t \in [t_n; t'_n] \mid \lambda_0(t) = \lambda_{2(\kappa-1)}(t)\}.$$

Then, we cover  $K$  by finitely many intervals on which  $\lambda_{2(\kappa-1)}$  stays close to  $\lambda_0$ . More precisely, there exist

$$t_n \leq s_1 < s'_1 < s_2 < s'_2 < \dots < s_k < s'_k \leq t'_n$$

such that

$$K \subset \bigcup_{i=1}^k (s_i; s'_i),$$

$$\forall t \in \bigcup_{i=1}^k [s_i; s'_i], \quad \lambda_{2(\kappa-1)}(t) \leq \lambda_0(t) + \epsilon \quad \text{and} \quad \lambda_{2(\kappa-1)}(t) < \lambda_{2\kappa}(t).$$



We now choose for each  $i = 1 \dots k$  two ground states  $\tilde{\Psi}_i$  and  $\tilde{\Psi}'_i$  of respectively  $H(s_i)$  and  $H(s'_i)$  (of course, if  $s_1 = t_n$  we take  $\tilde{\Psi}_1 = \Psi_n$  and similarly if  $s'_k = t'_n$ ). We then construct the path  $\Psi(t)$  separately on each interval  $[s_i; s'_i]$  or  $[s'_i; s_{i+1}]$ .

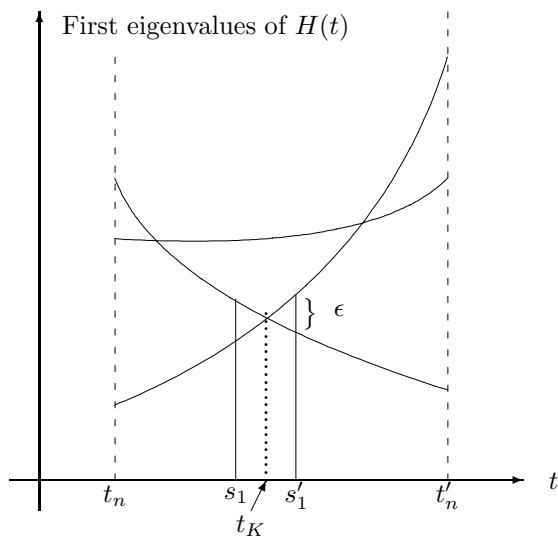


Figure 3. Proof of Lemma 1, an example in which  $\kappa = 2$  and  $K$  is a single point  $\{t_K\}$ .

Let us start with  $[s_1; s'_1]$ . On this interval, we have  $\lambda_{2(\kappa-1)}(t) < \lambda_{2\kappa}(t)$  and therefore, applying the usual Kato's regularity Theorem [6, Thm 5.1], the direct sum  $W(t)$  of the eigenspaces associated with the eigenvalues smaller than  $\lambda_{2\kappa}(t)$  is continuous in  $t$ , in the sense recalled above. Of course  $\dim W(t) = 2\kappa > 2$  and, arguing similarly as in the first case above, we can construct a path  $\Psi(t)$  of normalized functions in  $W(t)$  such that  $\Psi(s_1) = \tilde{\Psi}_1 \in W(s_1)$  and  $\Psi(s'_1) = \tilde{\Psi}'_1 \in W(s'_1)$ . By definition of  $s_1, s'_1$  and  $W(t)$ , one then has

$$\forall t \in [s_1; s'_1], \quad \mathcal{E}^N(a_n, v_n(t), \Psi(t)) \leq \lambda_{2(\kappa-1)}(t) \leq \lambda_0(t) + \epsilon.$$

The same procedure can be done on all the other intervals  $[s_i, s'_i]$ .

Eventually, one has to construct the path  $\Psi(t)$  on the intervals  $[t_n; s_1]$ ,  $[s'_i; s_{i+1}]$  for  $i = 1 \dots k-1$  and  $[s'_k; t'_n]$ . But on these intervals, one has by definition  $\lambda_0(t) < \lambda_{2(\kappa-1)}(t)$  and it therefore suffices to iterate all the above procedure by induction on  $\kappa$ .

As a conclusion, one can construct in finitely many steps a path  $\Psi(t)$  which satisfies

$$\forall t \in [t_n; t'_n], \quad \mathcal{E}^N(a_n, v_n(t), \Psi(t)) \leq \lambda_0(t) + \epsilon.$$

This ends the proof of Lemma 1. □

**Remark** A careful analysis of the proof of Lemma 1 indeed shows that Theorem 1 is still true when the wavefunction is only assumed to be real, but provided that the ground states  $\Psi_M$  and  $\Psi_{M'}$  used for the end points of the main mountain pass lemma (2) are adequately chosen.

**Proof of Theorem 2** Since the function  $v \mapsto I(\alpha, v)$  is continuous on the compact set  $SO_3(\mathbb{R})$ , there exists a  $u_\alpha \in SO_3(\mathbb{R})$  (depending on  $\alpha$ ), such that  $I(\alpha, u_\alpha) = \max_{v \in SO_3(\mathbb{R})} I(\alpha, v)$ .

We now use ideas from [8]. Namely, we consider real-valued ground states  $\phi_1$  and  $\phi_2$  of  $H^{z'}(0, z')$  and  $H^{|z|}(r, z)$ , which are known to exist by Zhislin Theorem [13]. It is also known that  $\phi_1$  and  $\phi_2$  decay exponentially [10]. Let  $\chi$  be a real smooth function such that  $\chi(x) = 1$  if  $x \in [0; 1]$ ,  $\chi(x) = 0$  if  $x \geq 2$  and  $\chi(x) \in [0; 1]$  if  $x \in [1; 2]$ . We define

$$\begin{aligned} \phi_1^\alpha(x_1, \dots, x_{z'}) &:= k_1^\alpha \phi_1(x_1, \dots, x_{z'}) \prod_{i=1}^{z'} \chi(5|x_i|/\alpha) \\ \phi_2^\alpha(x_1, \dots, x_{|z|}) &:= k_2^\alpha \phi_2(x_1, \dots, x_{|z|}) \prod_{i=1}^{|z|} \chi(5|x_i|/\alpha) \end{aligned}$$

where  $k_i^\alpha$  are real numbers such that  $\|\phi_i^\alpha\|_{L^2} = 1$  for  $i = 1, 2$ .

Like in [8], we take a trial function of the form

$$\Psi_\epsilon^{p,q,u} = \tau_{\alpha\bar{v}} u \phi_1^\alpha \wedge u_\alpha \phi_2^\alpha + \epsilon [(p \cdot \nabla) \tau_{\alpha\bar{v}} u \phi_1^\alpha] \wedge [(q \cdot \nabla) u_\alpha \phi_2^\alpha], \tag{10}$$

where we have used the notations

$$\begin{aligned} u\psi(x_1, \dots, x_N) &= \psi(u^{-1}x_1, \dots, u^{-1}x_N) \\ \tau_e\psi(x_1, \dots, x_N) &= \psi(x_1 - e, \dots, x_N - e), \\ (p \cdot \nabla)\psi &= \sum_{i=1}^N (p \cdot \nabla)_{x_i} \psi \end{aligned}$$

for any  $N$ -body wavefunction  $\psi$ , and where  $\wedge$  denotes the usual antisymmetric tensor product. It is defined for  $\psi \in L_a^2(\mathbb{R}^{3N_1})$  and  $\psi' \in L_a^2(\mathbb{R}^{3N_2})$  by

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

where  $x_\sigma^1 := (x_{\sigma(1)}, \dots, x_{\sigma(N_1)})$  and  $x_\sigma^2 = (x_{\sigma(N_1+1)}, \dots, x_{\sigma(N_1+N_2)})$ . In (10),  $u \in SO_3(\mathbb{R})$ ,  $p \in S^2$ ,  $q \in S^2$  ( $S^2$  being the sphere of  $\mathbb{R}^3$ ) and  $\epsilon \in [-1; 1]$  are parameters that will be chosen later on.

The energy of the trial function  $\Psi_\epsilon^{p,q,u}$  can be computed to get (details can be found in [8])

$$\begin{aligned}
 \mathcal{E}^N(\alpha, u_\alpha, \Psi_\epsilon^{p,q,u}) &= (E^{z'}(0, z') + E^{|z|}(r, z)) \|\Psi_\epsilon^{p,q,u}\|_{L^2}^2 \\
 &+ \frac{\epsilon^2}{2} (\mathcal{Q}_1(up) \|(q \cdot \nabla)\phi_2\|_{L^2}^2 + \mathcal{Q}_2(u_\alpha q) \|(p \cdot \nabla)\phi_1\|_{L^2}^2) \\
 &+ \iint_{\mathbb{R}^6} \frac{u\tilde{\rho}_1^\alpha(x)u_\alpha\tilde{\rho}_2^\alpha(y)}{|x-y+\alpha\vec{v}|} dx dy \\
 &+ \frac{\epsilon}{2} \iint_{\mathbb{R}^6} \frac{(p \cdot \nabla)_x u \rho_1^\alpha(x) (q \cdot \nabla)_y u_\alpha \rho_2^\alpha(y)}{|x-y+\alpha\vec{v}|} dx dy \\
 &+ \epsilon^2 \iint_{\mathbb{R}^6} \frac{T_1(up, u^{-1}x)T_2(u_\alpha q, u_\alpha^{-1}y)}{|x-y+\alpha\vec{v}|} dx dy + O(e^{-c\alpha})
 \end{aligned}
 \tag{11}$$

where  $\rho_1^\alpha$  and  $\rho_2^\alpha$  are the charge densities of  $\phi_1^\alpha$  and  $\phi_2^\alpha$  defined by

$$\begin{aligned}
 \rho_1^\alpha(x) &= z' \int \cdots \int |\phi_1^\alpha(x, x_2, \dots, x_{z'})|^2 dx_2 \dots dx_{z'} \\
 \rho_2^\alpha(x) &= |z| \int \cdots \int |\phi_2^\alpha(x, x_2, \dots, x_{|z|})|^2 dx_2 \dots dx_{|z|}, \\
 \tilde{\rho}_1^\alpha &= \rho_1^\alpha - z'\delta_0, \quad \tilde{\rho}_2^\alpha = \rho_2^\alpha - \sum_{j=1}^m z_j \delta_{r_j},
 \end{aligned}$$

$\mathcal{Q}_1$  and  $\mathcal{Q}_2$  are the quadratic forms

$$\begin{aligned}
 \mathcal{Q}_1(p) &= - \int_{\mathbb{R}^3} \frac{z'}{|x|} (p \cdot \nabla)^2 \rho_1(x) dx \\
 \mathcal{Q}_2(q) &= - \int_{\mathbb{R}^3} \left( \sum_{i=1}^m \frac{z_i}{|x-r_i|} \right) (q \cdot \nabla)^2 \rho_2(x) dx,
 \end{aligned}$$

$\rho_i$  being the density of charge associated with  $\phi_i$ , and where finally

$$\tilde{T}_i(p, x) = T_i(p, x) - z'\delta_0, \quad \tilde{T}_2(p, x) = T_2(p, x) - \sum_{j=1}^m z_j \delta_{r_j},$$

$T_i(p, x)$  being the density of charge of  $(p \cdot \nabla)\phi_i$ .

Notice that in (11), we have used the fact that if  $\phi$  is a ground state of  $H^N(R, Z)$ , then  $u\phi$  is a ground state of  $H^N(uR, Z)$ . In particular,  $u_\alpha\phi_2$  is a ground state of  $H^{|z|}(u_\alpha r, z)$  and  $u\phi_1$  is a ground state of  $H^{z'}(0, z')$  for all  $u \in SO_3(\mathbb{R})$ .

In [8], the formula (11) is integrated over all the rotations of each subsystem to kill the term  $\iint_{\mathbb{R}^6} \frac{u\tilde{\rho}_1^\alpha(x)u_\alpha\tilde{\rho}_2^\alpha(y)}{|x-y+\alpha\vec{v}|} dx dy$  and simplify the computation of the energy. In the case where one subsystem is an atom, this integration is not necessary since we can prove the

**Lemma 2** *For any  $\alpha$ , there exists a rotation  $v_\alpha \in SO_3(\mathbb{R})$  such that*

$$\iint_{\mathbb{R}^6} \frac{v_\alpha \tilde{\rho}_1^\alpha(x) u_\alpha \tilde{\rho}_2^\alpha(y)}{|x-y+\alpha\vec{v}|} dx dy = 0.
 \tag{12}$$

*Proof.* We have

$$\int_{SO_3(\mathbb{R})} dv \iint_{\mathbb{R}^6} \frac{v\tilde{\rho}_1^\alpha(x)u_\alpha\tilde{\rho}_2^\alpha(y)}{|x-y+\alpha\vec{v}|} dx dy = 0$$

since  $\mu_1^\alpha(x) = \int_{SO_3(\mathbb{R})} v\tilde{\rho}_1^\alpha(x) dv$  is a radial function and

$$\int_{\mathbb{R}^3} \frac{\mu_1^\alpha(x)}{|x-x'|} dx = 0$$

when  $x' \in \mathbb{R}^3 \setminus B(0, 2\alpha/5)$ , by Newton's theorem. Therefore, there exists a  $v_\alpha \in SO_3(\mathbb{R})$  such that (12) holds.  $\square$

In the following, we therefore choose  $u = v_\alpha$ , given by Lemma 2. Let us now explain how  $q$  is chosen. Indeed, the trace of the quadratic form  $\mathcal{Q}_2$  can be easily computed since, following [8, page 44],

$$\text{tr}(\mathcal{Q}_2) = - \sum_{i=1}^3 \int_{\mathbb{R}^3} \left( \sum_{j=1}^m \frac{z_j}{|x-r_j|} \right) \partial_{x_i}^2 \rho_2(x) dx = 4\pi \sum_{j=1}^3 z_j \rho_2(r_j) \geq 0. \tag{13}$$

Therefore,  $\mathcal{Q}_2$  possesses an eigenvector  $e_2$  with a non-negative eigenvalue  $\lambda_2 = \mathcal{Q}_2(e_2) \geq 0$ . We choose

$$q = u_\alpha^{-1} e_2.$$

To finish the proof, it remains to choose  $p$  and  $\epsilon$  appropriately. To this end, we use [7, Lemma 9] which provides a uniform constant  $K$  such that

$$\left| \frac{1}{|R+h|} - \left( \frac{1}{|R|} - \frac{e_R \cdot h}{|R|^2} + \frac{3(e_R \cdot h)^2 - |h|^2}{2|R|^3} \right) \right| \leq \frac{K|h|^3}{|R|^3|R+h|} \tag{14}$$

for any  $R$  and  $h \in \mathbb{R}^3$  with  $R+h \neq 0$ , and where we have used the notation  $e_R = R/|R|$ . Using the properties

$$\forall p', q' \in S^2, \quad \int_{\mathbb{R}^3} (p' \cdot \nabla) \rho_1^\alpha = \int_{\mathbb{R}^3} (q' \cdot \nabla) \rho_2^\alpha = 0$$

and

$$\forall p' \in S^2, i = 1, 2, \quad \int_{\mathbb{R}^3} x(p' \cdot \nabla) \rho_i^\alpha(x) dx = -p' \int_{\mathbb{R}^3} \rho_i^\alpha(x) dx,$$

we obtain

$$\begin{aligned} & \left| \iint_{\mathbb{R}^6} \frac{(p \cdot \nabla)_x v_\alpha \rho_1^\alpha(x) (u_\alpha^{-1} e_2 \cdot \nabla)_y u_\alpha \rho_2^\alpha(y)}{|x-y+\alpha\vec{v}|} dx dy - \frac{z'|z|\mathcal{D}(up, e_2)}{\alpha^3} \right| \\ & \leq \frac{K}{\alpha^3} \iint_{\mathbb{R}^6} \frac{|x-y|^3 |(p \cdot \nabla)_x v_\alpha \rho_1^\alpha(x) (u_\alpha^{-1} e_2 \cdot \nabla)_y u_\alpha \rho_2^\alpha(y)|}{|x-y+\alpha\vec{v}|} dx dy \\ & \leq \frac{5K}{\alpha^4} \iint_{\mathbb{R}^6} |x-y|^3 |(p \cdot \nabla)_x v_\alpha \rho_1^\alpha(x) (u_\alpha^{-1} e_2 \cdot \nabla)_y u_\alpha \rho_2^\alpha(y)| dx dy = O\left(\frac{1}{\alpha^4}\right) \end{aligned}$$

where  $\mathcal{D}$  is the dipole-dipole interaction

$$\mathcal{D}(p, q) = p \cdot q - 3(p \cdot \vec{v})(q \cdot \vec{v}) = p \cdot (q - 3(q \cdot \vec{v})\vec{v}),$$

and where our  $O\left(\frac{1}{\alpha^4}\right)$  is uniform in  $p$ ,  $u_\alpha$  and  $v_\alpha$ . Using also (14) or a simplified version for the last term in  $\epsilon^2$ , we now arrive at

$$\begin{aligned} \mathcal{E}^N(\alpha, u_\alpha, \Psi_\epsilon^{p, u_\alpha^{-1}e_2, v_\alpha}) &= (E^{z'}(0, z') + E^{|z|}(r, z)) \|\Psi_\epsilon^{p, u_\alpha^{-1}e_2, v_\alpha}\|_{L^2}^2 \\ &+ \frac{\epsilon^2}{2} (\mathcal{Q}_1(v_\alpha p)) \|(e_2 \cdot \nabla)\phi_2\|_{L^2}^2 + \lambda_2 \|(p \cdot \nabla)\phi_1\|_{L^2}^2 \\ &+ \epsilon \frac{z'|z|\mathcal{D}(v_\alpha p, e_2)}{2\alpha^3} + O\left(\frac{\epsilon}{\alpha^4}\right) + O\left(\frac{\epsilon^2}{\alpha}\right). \end{aligned} \tag{15}$$

Let us explain how we choose  $p$ .

**Lemma 3** *There exists a vector  $e_1 \in S^2$  such that  $\mathcal{Q}(e_1) \geq 0$  and  $\mathcal{D}(e_1, e_2) \neq 0$ .*

*Proof.* Notice that  $e_2 - 3(e_2 \cdot \vec{v})\vec{v} \neq 0$  since  $\vec{v} \in S^2$ . By the same computation as (13), we find that  $\text{tr}(\mathcal{Q}_1) \geq 0$ . If  $\mathcal{Q}_1 = 0$ , it suffices to choose  $e_1 = \frac{e_2 - 3(e_2 \cdot \vec{v})\vec{v}}{\|e_2 - 3(e_2 \cdot \vec{v})\vec{v}\|}$ . If  $\mathcal{Q}_1 \neq 0$ , it possesses a positive eigenvalue  $\lambda_1$  and the set  $\{x \in S^2 \mid \mathcal{Q}_1(x) > 0\}$  is a non-empty open set of  $S^2$ . Since on the other hand  $\{x \in S^2 \mid \mathcal{D}(x, e_2) = 0\} = \{e_2 - 3(e_2 \cdot \vec{v})\vec{v}\}^\perp \cap S^2$  has an empty interior in  $S^2$ , it exists a  $e_1 \in S^2$  such that  $\mathcal{Q}_1(e_1) > 0$  and  $\mathcal{D}(e_1, e_2) \neq 0$ .  $\square$

Choosing now  $p = v_\alpha^{-1}e_1$ , we obtain

$$\begin{aligned} \mathcal{E}^N(\alpha, u_\alpha, \Psi_\epsilon^{v_\alpha^{-1}e_1, u_\alpha^{-1}e_2, v_\alpha}) &= (E^{z'}(0, z') + E^{|z|}(r, z)) \|\Psi_\epsilon^{v_\alpha^{-1}e_1, u_\alpha^{-1}e_2, v_\alpha}\|_{L^2}^2 \\ &+ \frac{\epsilon^2 b}{2} + \frac{\epsilon a}{\alpha^3} + O\left(\frac{\epsilon}{\alpha^4}\right) + O\left(\frac{\epsilon^2}{\alpha}\right). \end{aligned}$$

where

$$a = \frac{z'|z|\mathcal{D}(e_1, e_2)}{2} \neq 0,$$

$$b = \mathcal{Q}_1(e_1) \|(e_2 \cdot \nabla)\phi_2\|_{L^2}^2 + \lambda_2 \|(e_1 \cdot \nabla)\phi_1\|_{L^2}^2 \geq 0,$$

which are independent on  $u_\alpha$  and  $v_\alpha$ . If  $b > 0$ , we optimize the real function  $\epsilon \mapsto \frac{\epsilon^2 b}{2} + \frac{\epsilon a}{\alpha^3}$  and choose, for  $\alpha$  large enough,  $\epsilon = -\frac{a}{b\alpha^3}$  to obtain

$$\begin{aligned} \mathcal{E}^N(\alpha, u_\alpha, \Psi_{-a/(b\alpha^3)}^{v_\alpha^{-1}e_1, u_\alpha^{-1}e_2, v_\alpha}) &= (E^{z'}(0, z') + E^{|z|}(r, z)) \|\Psi_{-a/(b\alpha^3)}^{v_\alpha^{-1}e_1, u_\alpha^{-1}e_2, v_\alpha}\|_{L^2}^2 \\ &- \frac{a^2}{2b\alpha^6} + O\left(\frac{1}{\alpha^7}\right). \end{aligned}$$

If  $b = 0$ , we choose for instance  $\epsilon = -a/\alpha^3$  and obtain the same type of result.

This ends the proof of Theorem 2 since

$$\|\Psi_\epsilon^{v_\alpha^{-1}e_1, u_\alpha^{-1}e_2, v_\alpha}\|_{L^2}^2 = 1 + \epsilon^2 \|(e_1 \cdot \nabla)\phi_1\|_{L^2}^2 \|(e_2 \cdot \nabla)\phi_2\|_{L^2}^2$$

and therefore

$$\mathcal{E}^N \left( \alpha, u_\alpha, \frac{\Psi_\epsilon^{v_\alpha^{-1}e_1, u_\alpha^{-1}e_2, v_\alpha}}{\|\Psi_\epsilon^{v_\alpha^{-1}e_1, u_\alpha^{-1}e_2, v_\alpha}\|_{L^2}} \right) = E^{z'}(0, z') + E^{|z|}(r, z) - \frac{C}{\alpha^6} + O\left(\frac{1}{\alpha^7}\right)$$

with  $C = a^2/(2b) > 0$  if  $b > 0$  and  $C = a^2 > 0$  if  $b = 0$ . □

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