Solution of a mountain pass problem for the isomerization of a molecule with one free atom

Mathieu LEWIN*

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 [6]. 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 [9] 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

*I would like to thank Éric Séré for helpful advice. I also acknowledge support through the European Union's IHP network *Analysis & Quantum* HPRN-CT-2002-00277.

H–C bond changes into a N–H bond. The computation of the transition state and its energy are both very important in practice [10, 4].

In [6], we first described the behaviour 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 a 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 [6], the main part of the proof is different from the one of [6]. Instead, we use ideas from a celebrated paper of Lieb and Thirring [7] 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 [7], this attractive force in 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. Like in [6], we also use the results by G. Fang and N. Ghoussoub [5, 3], which enable to obtain Morse-type information on minimaxing Palais-Smale sequences.

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 [6]. Namely, the molecule is placed at 0 whereas the single atom is located at a distance α along a fixed axis in the direction $\vec{v}$, with $\|\vec{v}\| = 1$. The parameters for the position of the nuclei are the distance α and the orientation of the molecule, represented by a rotation $u \in SO_3(\mathbb{R})$.

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

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

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

where we have used the notation $u \cdot r = (u \cdot r_i)_{i=1}^m$. This system of nuclei

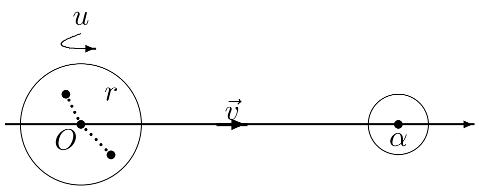

Figure 1: An atom interacting with a molecule.

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

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

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

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

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

due to the Pauli principle and the fermionic nature of electrons. We refer the reader to, e.g., [6, Theorem 1], for a description of the known properties of $H^N(R,Z)$.

Notice that, like in [6], 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*

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

where $\Psi \in SH^1_a((\mathbb{R}^3)^N, \mathbb{C})$ means $\Psi \in H^1_a((\mathbb{R}^3)^N, \mathbb{C})$ 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 $\Psi \in SH^1_a((\mathbb{R}^3)^N, \mathbb{C})$. We also introduce the notation

$$E(\alpha, u) := E^N(R(\alpha, u), Z)$$

for the electronic ground state energy of our molecule with one free atom.

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

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

where $|z| := z_1 + \cdots + z_m$. In this case, it has been shown by Lieb and Thirring [7] that $\mathcal{E}^N$ possesses a minimizer $M \in \mathbb{R}^* \times SO_3(\mathbb{R}) \times SH^1_a((\mathbb{R}^3)^N, \mathbb{C})$. In the present work, we consider a molecule which possesses two local minima $M = (\alpha, u, \Psi)$ and $M' = (\alpha', u', \Psi')$ of $\mathcal{E}^N$ on $\mathbb{R}^* \times SO_3(\mathbb{R}) \times SH^1_a((\mathbb{R}^3)^N, \mathbb{C})$. Up to a rotation of the system, we may assume that $\alpha, \alpha' \in (0; \infty)$. This allows us to define the following mountain pass method [6], in the spirit of A. Ambrosetti and P.H. Rabinowitz [1],

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

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

As explained in [6], the physical interpretation of (1) 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 Ψ 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 Ψ. In [6, Theorem 4], we showed that the generalized min-max method (1) 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 [6], 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 $(\alpha, u, \Psi) \in \mathbb{R}^* \times SO_3(\mathbb{R}) \times SH^1_a((\mathbb{R}^3)^N, \mathbb{C})$ of $\mathcal{E}^N$ at the level c, such that*

$$c = E(\alpha, u),$$

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

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 [7] and [6].

3 Proof of Theorem 1

Notice that we may assume $c > \max\{\mathcal{E}^N(M), \mathcal{E}^N(M')\}$.

Step 1: Reduction to the case of neutral systems at infinity. Let us first recall results of [6]. In this paper, we proved the following alternative [6, Theorems 4 and 5]

• **either** we can construct a minimaxing sequence (α_n, u_n, Ψ_n), with α_n bounded, which is known to converge, up to a subsequence, to a critical point (α, u, Ψ) of $\mathcal{E}^N$ at the level c, such that Ψ is a ground state of $H^N(R(\alpha, u), Z)$;

• **or** we have

$$c = \min\left\{E^{n_1}(0, z') + E^{n_2}(r, z),\ n_1 + n_2 = N\right\} \tag{2}$$

and there exists $a_n \to +\infty$ 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

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

$$\alpha_n(t) \leq a_n \Longrightarrow \mathcal{E}^N(\gamma_n(t)) < c. \tag{3}$$

To prove this alternative, we used in [6] the duality theory developed in [5] and Palais-Smale sequences with Morse-type information which can be obtained by the result of [3]. In the second case of the alternative, the interpretation is that it is necessary to break the molecule (i.e. to pass through a critical point a infinity [6, 2]) in order to solve the mountain pass problem.

In [6, 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 (2), 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 α_n and a_n satisfy (3). 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 [6, 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 [6] by tensor products of ground states. Since we are dealing here with neutral molecules, the path will be constructed on a different set.

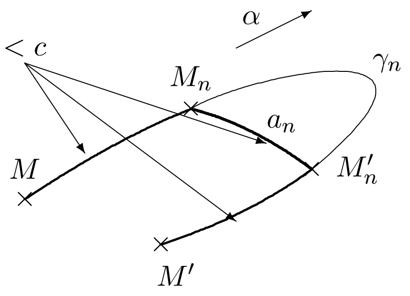

Figure 2: General idea of the proof.

Step 2: Existence of attractive Van der Waals forces, independently of the orientation of the molecule. We now state a modified version of the result due to Lieb and Thirring [7].

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

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

It is crucial here that one of the two considered systems is a single atom; such a result cannot be true in general. The proof of Theorem 2 will be postponed until the end of the proof of Theorem 1.

Step 3: Conclusion. We end the proof using Theorem 2. We may write $M_n = (a_n, u_n, \Psi_n)$ and $M_n' = (a_n, u_n', \Psi_n')$. Notice that $\mathcal{E}^N(M_n) < c$ and $\mathcal{E}^N(M_n') < c$ by definition of a_n. To end the proof, it remains to build 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 $v_n(t_n') = u_n'$. We now consider the following minimax principle

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

where

$$\Gamma_n' = \left\{ \Psi(t) \in \mathcal{C}^0([t_n; t_n'], SH^1_a((\mathbb{R}^3)^N, \mathbb{C})) \mid \Psi(t_n) = \Psi_n,\ \Psi(t_n') = \Psi_n' \right\}.$$

For each $\Psi \in \Gamma'_n$, the path γ 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 Γ defined in (1). Therefore, by definition of c, we obtain for each n,

$$c \leq c_n. \tag{4}$$

In particular, we infer $\max\{\mathcal{E}^N(M_n), \mathcal{E}^N(M'_n)\} < c_n$. Hence, applying the methods of [5, 3], we may find, for each n, sequences $(t^k) \in (t_n; t'_n)$ and $(\Psi^k) \in SH^1_a((\mathbb{R}^3)^N, \mathbb{C})$ such that

a. $t^k \to \bar{t} \in (t_n; t'_n)$,

b. $\lim_{k\to\infty} \mathcal{E}^N(a_n, v_n(t^k), \Psi^k) = c_n$,

c. $H^N(R(a_n, v_n(t^k)), Z)\cdot\Psi^k - \mathcal{E}^N(a_n, v_n(t^k), \Psi^k)\cdot\Psi^k \to 0$ in $L^2((\mathbb{R}^3)^N, \mathbb{C})$,

d. $\mathcal{E}^N(a_n, v_n(t^k), \Psi^k) \leq E(a_n, v_n(t^k)) + \epsilon_k$, with $\lim_{k\to\infty} \epsilon_k = 0$.

Notice that (b) and (c) correspond to the classical fact that there exists a minimaxing Palais-Smale sequence which is almost critical. One the other hand, (d) is a Morse-type information, consequence of the theory developed in [5, 3]. More precisely, since we are considering paths (i.e. deformations of $[0; 1]$), the results of [5, 3] provide a sequence (Ψ^k) which satisfies

$$\mathcal{E}^N(a_n, v_n(t^k), \Psi^k) \leq \lambda_2^{\mathbb{R}}(a_n, v_n(t^k)) + \epsilon_k,$$

where $\lambda_2^{\mathbb{R}}(a_n, v_n(t^k))$ is the second eigenvalue of $H^N(R(a_n, v_n(t^k)), Z)$, as an operator acting on $L^2_a((\mathbb{R}^3)^N, \mathbb{R}) \otimes L^2_a((\mathbb{R}^3)^N, \mathbb{R}) \simeq L^2_a((\mathbb{R}^3)^N, \mathbb{C})$. Since the N-body Hamiltonian is real, it acts separately on the real and the imaginary part of wavefunctions, and therefore each of its eigenvalues has an even multiplicity. This is why $E(a_n, v_n(t^k)) = \lambda_2^{\mathbb{R}}(a_n, v_n(t^k))$ appears in the right hand side of (d). For this part of the proof, it is essential to work with complex-valued wavefunctions.

Since $v_n(t^k) \to v_n(\bar{t})$, we obtain, passing to the limit as $k \to \infty$,

$$c_n = E(a_n, v_n(\bar{t})).$$

Applying Theorem 2, we infer

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

which contradicts (4) as $a_n \to \infty$, and ends the proof of Theorem 1. $\square$

It rests to prove Theorem 2.

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

We now use ideas from [7]. Namely, we consider real-valued ground states ϕ_1 and ϕ_2 of $H^{z'}(0, z')$ and $H^{|z|}(r, z)$, which are known to exist by Zhislin Theorem [11]. It is also known that ϕ_1 and ϕ_2 decay exponentially [8]. Let χ 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

$$\phi_1^\alpha(x_1, ..., x_{z'}) := k_1^\alpha \phi_1(x_1, ..., x_{z'}) \prod_{i=1}^{z'} \chi(5|x_i|/\alpha)$$

$$\phi_2^\alpha(x_1, ..., x_{|z|}) := k_2^\alpha \phi_2(x_1, ..., x_{|z|}) \prod_{i=1}^{|z|} \chi(5|x_i|/\alpha)$$

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

Like in [7], we take a trial function of the form

$$\Psi_\epsilon^{p,q,u} = \tau_{\alpha \vec{v}} u \phi_1^\alpha \wedge u_\alpha \phi_2^\alpha + \epsilon \left[(p \cdot \nabla) \tau_{\alpha \vec{v}} u \phi_1^\alpha\right] \wedge \left[(q \cdot \nabla) u_\alpha \phi_2^\alpha\right], \tag{5}$$

where we have used the notations

$$u\psi(x_1, ..., x_N) = \psi(u^{-1}x_1, ..., u^{-1}x_N)$$

$$\tau_e \psi(x_1, ..., x_N) = \psi(x_1 - e, ..., x_N - e),$$

$$(p \cdot \nabla)\psi = \sum_{i=1}^{N} (p \cdot \nabla)_{x_i} \psi$$

for any N-body wavefunction ψ, 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

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

where $x_\sigma^1 := (x_{\sigma(1)}, ..., x_{\sigma(N_1)})$ and $x_\sigma^2 = (x_{\sigma(N_1+1)}, ..., x_{\sigma(N_1+N_2)})$. In (5), $u \in SO_3(\mathbb{R})$, $p \in S^2$, $q \in S^2$ (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 [7])

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

where ρ_1^α and ρ_2^α are the charge densities of ϕ_1^α and ϕ_2^α defined by

$$
\rho_1^\alpha(x) = z'\int\cdots\int|\phi_1^\alpha(x,x_2,...,x_{z'})|^2dx_2\cdots dx_{z'}
$$

$$
\rho_2^\alpha(x) = |z|\int\cdots\int|\phi_2^\alpha(x,x_2,...,x_{|z|})|^2dx_2\cdots dx_{|z|},
$$

$$
\tilde{\rho}_1^\alpha = \rho_1^\alpha - z'\delta_0, \qquad \tilde{\rho}_2^\alpha = \rho_2^\alpha - \sum_{j=1}^m z_j\delta_{r_j},
$$

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

$$
\mathcal{Q}_1(p) = -\int_{\mathbb{R}^3}\frac{z'}{|x|}(p\cdot\nabla)^2\rho_1(x)\,dx
$$

$$
\mathcal{Q}_2(q) = -\int_{\mathbb{R}^3}\left(\sum_{i=1}^m\frac{z_i}{|x-r_i|}\right)(q\cdot\nabla)^2\rho_2(x)\,dx,
$$

ρ_i being the density of charge associated with ϕ_i, and where finally

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

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

Notice that in (6), we have used the fact that if ϕ is a ground state of $H^N(R,Z)$, then $u\phi$ is a ground state of $H^N(u\cdot R, Z)$. 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 $u\in SO_3(\mathbb{R})$. This last property of the ground states of atoms is a crucial point in the proof.

In [7], the formula (6) 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 1. *For any α, there exists a rotation $v_\alpha \in SO_3(\mathbb{R})$ such that*

$$\iint_{\mathbb{R}^6} \frac{v_\alpha \tilde{\rho}_1^\alpha(x) u_\alpha \tilde{\rho}_2^\alpha(y)}{|x-y+\alpha\vec{v}|} dx\, dy = 0. \tag{7}$$

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 $x' \in \mathbb{R}^3 \setminus B(0, 2\alpha/5)$, due to Newton's theorem. Therefore, there exists a $v_\alpha \in SO_3(\mathbb{R})$ such that (7) holds. $\square$

In the following, we therefore choose $u = v_\alpha$, given by Lemma 1. Let us now explain how q is chosen. Indeed, the trace of the quadratic form $\mathcal{Q}_2$ can be easily computed since, following [7, page 44],

$$\operatorname{tr}(\mathcal{Q}_2) = -\sum_{i=1}^{3} \int_{\mathbb{R}^3} \left(\sum_{j=1}^{m} \frac{z_j}{|x-r_j|} \right) \partial_{x_i}^2 \rho_2(x)\, dx = 4\pi \sum_{j=1}^{3} z_j \rho_2(r_j) \geq 0. \tag{8}$$

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 ϵ appropriately. To this end, we use [6, Lemma 9] which provides a uniform constant K such that

$$\left| \frac{1}{|R+h|} - \left(\frac{1}{|R|} - \frac{e_R \cdot h}{|R|^2} + \frac{3(e_R\cdot h)^2 - |h|^2}{2|R|^3} \right) \right| \leq \frac{K\,|h|^3}{|R|^3 |R+h|} \tag{9}$$

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

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

and

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

we obtain

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

$$\leq \frac{K}{\alpha^3}\iint_{\mathbb{R}^6} \frac{|x-y|^3|(p\cdot\nabla)_x v_\alpha \rho_1^\alpha(x)(u_\alpha^{-1}e_2\cdot\nabla)_y u_\alpha\rho_2^\alpha(y)|}{|x-y+\alpha\vec{v}|}dx\,dy$$

$$\leq \frac{5K}{\alpha^4}\iint_{\mathbb{R}^6} |x-y|^3|(p\cdot\nabla)_x v_\alpha \rho_1^\alpha(x)(u_\alpha^{-1}e_2\cdot\nabla)_y u_\alpha\rho_2^\alpha(y)|\,dx\,dy = O\left(\frac{1}{\alpha^4}\right)$$

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_α and v_α. Using also (9) or a simplified version for the last term in ϵ^2, we now arrive at

$$\begin{aligned}\mathcal{E}^N(\alpha,u_\alpha,\Psi_\epsilon^{p,u_\alpha^{-1}e_2,v_\alpha}) &= (E^{z'}(0,z')+E^{|z|}(r,z))\|\Psi_\epsilon^{p,u_\alpha^{-1}e_2,v_\alpha}\|_{L^2}^2 \\ &\quad+\frac{\epsilon^2}{2}\left(\mathcal{Q}_1(v_\alpha p)\|(e_2\cdot\nabla)\phi_2\|_{L^2}^2+\lambda_2\|(p\cdot\nabla)\phi_1\|_{L^2}^2\right) \\ &\quad+\epsilon\frac{z'|z|\mathcal{D}(v_\alpha p,e_2)}{2\alpha^3}+O\left(\frac{\epsilon}{\alpha^4}\right)+O\left(\frac{\epsilon^2}{\alpha}\right).\end{aligned} \tag{10}$$

Let us explain how we choose p.

Lemma 2. *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 (8), we find that $\mathrm{tr}(\mathcal{Q}_1)\geq 0$. 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 λ_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

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

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_α and v_α. If $b > 0$, we optimize the real function $\epsilon \mapsto \frac{\epsilon^2 b}{2} + \frac{\epsilon a}{\alpha^3}$ and choose, for α large enough, $\epsilon = -\frac{a}{b\alpha^3}$ to obtain

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

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 $b = 0$. □

References

[1] A. Ambrosetti, P.H. Rabinowitz. Dual variation methods in critical point theory and applications. *J. Funct. Anal.*, 14: 349–381, 1973.

[2] A. Bahri. *Critical Points at Infinity in some Variational Problems.* Pitman Research Notes in Mathematics Series, 182. Longman Scientific and Technical Ed., 1989.

[3] G. Fang, N. Ghoussoub. Morse-type information on Palais-Smale sequences obtained by min-max principles. *Manuscripta Math.*, 75 : 81–95, 1992.

[4] J. B. Foresman, A. Frisch. *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc, 1996. Chapter 3 and references therein.

[5] N. Ghoussoub. *Duality and perturbation methods in critical point theory.* Cambridge University Press, 1993.

[6] M. Lewin. A Mountain Pass for Reacting Molecules. *Ann. Henri Poincaré*, 5: 477–521, 2004.

[7] E. H. Lieb, W. E. Thirring. Universal Nature of Van Der Waals Forces for Coulomb Systems. *Phys. Rev. A*, 34 : 40–46, 1986.

[8] A. J. O'Connor. Exponential decay of bound state wave functions, *Commun. Math. Phys.*, 32: 319–340, 1973.

[9] P.K. Pearson, H.F. Schaefer III, U. Wahlgren. Potential energy surface for the model unimolecular reaction HNC $\rightarrow$ HCN. *J. Chem. Phys.*: 62(2), 350–354, 1975.

[10] H. B. Schlegel. In *Ab Inition Methods in Quantum Chemistry*, Lawley Ed, 1987. Vol 1, p 249–286 and references cited therein.

[11] G. M. Zhislin. Discussion of the spectrum of Schrödinger operators for systems of many particles. (In Russian). *Trudy Moskovskogo matematiceskogo obscestva*, 9 : 81–120, 1960.

Department of Mathematics,
University of Copenhagen,
Universitetsparken 5,
2100 Copenhagen Ø,
DENMARK

Email: `lewin@math.ku.dk`