Compactness of reaction paths in quantum mechanics

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References

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[Lew-06] M.L. Solution of a mountain pass problem for the isomerization of a molecule with one free atom, *Ann. Henri Poincaré*, 2006

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Chemical reactions

▶ **Computing reaction paths**

is one of main goals in chemistry

▶ Born-Oppenheimer approximation

▶ **Example:** HCN → CNH
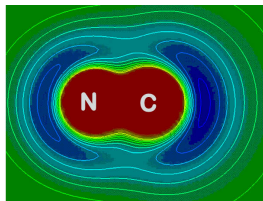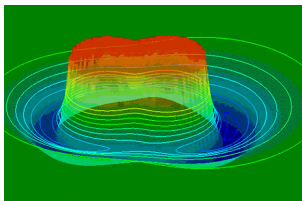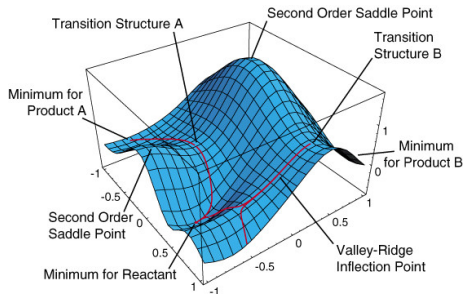
N-particle quantum Hamiltonian

$$H_N(Y,Z) := \sum_{j=1}^{N} -\Delta_{x_j} - \sum_{j=1}^{N} \sum_{m=1}^{M} \frac{z_m}{|x_j - y_m|} + \sum_{1 \leq j < k \leq N} \frac{1}{|x_j - x_k|} + \sum_{1 \leq \ell < m \leq M} \frac{z_m z_\ell}{|y_m - y_\ell|}$$

HVZ + Zhislin-Sigalov '60–65

$$E_N(Y,Z) := \min \sigma\big(H_N(Y,Z)\big) < \min \sigma_{\text{ess}}\big(H_N(Y,Z)\big) = E_{N-1}(Y,Z)$$

Theorem (All neutral molecules can bind in Born-Oppenheimer)

$N = |Z| := \sum_{m=1}^{M} z_m$. *There exist* $\bar{Y} = (\bar{y}_1, ..., \bar{y}_M) \in (\mathbb{R}^3)^M$ *such that*

$$E_N(\bar{Y}, Z) = \min_{Y \in (\mathbb{R}^3)^M} E_N(Y, Z).$$

More precisely: $\displaystyle \min_{Y \in (\mathbb{R}^3)^M} E_N(Y, Z) < \liminf_{\sum_{m \neq \ell} |y_m - y_\ell| \to \infty} E_N(Y, Z).$

Morgan-Simon '80, Lieb-Thirring '86

Assume molecule dissociates in two parts: $Y = (Y_1, Y_2 + Le_1)$, $Z = (Z_1, Z_2)$

Theorem (Morgan-Simon '80)

$$\lim_{L\to\infty} E_N(Y_1, Y_2 + Le_1, Z) = \min_{N_1+N_2=N} \left\{ E_{N_1}(Y_1,, Z_1) + E_{N_2}(Y_2, Z_2) \right\}$$

Conjecture: min for $N_1 = |Z_1|$ and $N_2 = |Z_2|$ (neutral case).

If not, using trial state $\Psi_1 \wedge \Psi_2(\cdot - Le_1)$ gives upper bound

$$E_N(Y_1, Y_2 + Le_1, Z) \leq E_{N_1}(Y_1,, Z_1) + E_{N_2}(Y_2, Z_2) - \frac{(N_1 - |Z_1|)(|Z_2| - N_2)}{L} + o\left(\frac{1}{L}\right)$$

In general, sign of interaction depends on orientation of the two molecules

Theorem (Van der Waals, Lieb-Thirring '86)

$$\iint_{SO(3)^2} E_N(UY_1, VY_2 + Le_1, Z)\, dU dV \leq E_{|Z_1|}(Y_1,, Z_1) + E_{|Z_2|}(Y_2, Z_2) - \frac{C_{VdW}}{L^6} + o\left(\frac{1}{L^6}\right)$$

Anapolitanos-Sigal '16–17: computation of exact C_{VdW} for atoms, no average

Chemical reaction = mountain pass

We assume $Y \mapsto E_N(Y, Z)$ has two strict local minima $\bar{Y}_0$ and $\bar{Y}_1$.

Mountain pass

$$c := \inf_{\substack{Y(t) \in C^0([0,1],(\mathbb{R}^3)^M) \\ Y(0) = \bar{Y}_0 \\ Y(1) = \bar{Y}_1}} \max_{t \in [0,1]} E_N\big(Y(t), Z\big).$$

Conjecture: all isomerizations without dissociation [Lew-04]

$N = |Z|$. There exists a min-maxing sequence of paths $\{Y_n(t)\}$ which is **compact** in the sense that the molecule does not dissociate: $|y_{n,j}(t) - y_{n,k}(t)| \leq R$, for all $j \neq k$, all $n \geq 1$ and all $t \in [0,1]$.

Difficulty: understand shape of E_N at infinity = Morse indices of "critical points at infinity". Not enough to know that energy decreases in **one** direction
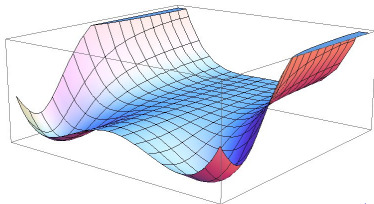
Existence of transition state

Theorem (Existence of transition state [Lew-04])

$N = |Z|$. Assume there exists a **compact** min-maxing sequence of paths $\{Y_n(t)\}$. Then there exist $t_n \in [0,1]$ and Ψ_n such that

$$\Big(H_N(Y_n(t_n), Z) - E_N(Y_n(t_n), Z) \Big) \Psi_n \to 0,$$

$$E_N(Y_n(t_n), Z) \to c, \qquad \big\langle \Psi_n, \nabla_Y H_N \big(Y_n(t_n), Z \big) \Psi_n \big\rangle \to 0.$$
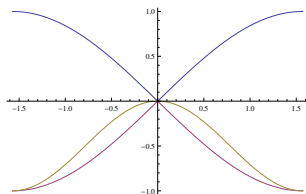
Extracting a subsequence and translating appropriately the whole system, we find in the limit a critical point $(\tilde{Y}, \tilde{\Psi})$ at mountain pass level

$$c = E_N(\tilde{Y}, Z), \quad H_N(\tilde{Y}, Z)\tilde{\Psi} = E_N(\tilde{Y}, Z)\tilde{\Psi}, \quad \big\langle \tilde{\Psi}, \nabla_Y H_N(\tilde{Y}, Z)\tilde{\Psi} \big\rangle = 0.$$
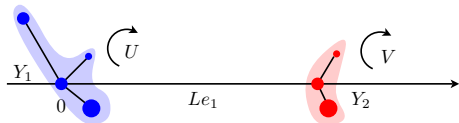
$$M(t) = \begin{pmatrix} \sin(t) & 0 \\ 0 & -\sin(t) \end{pmatrix}$$

$t \mapsto \lambda_1(M(t))$ not smooth, but $(x, t) \mapsto \langle x, M(t)x \rangle$ is

Rmk. existence of an optimal path more difficult
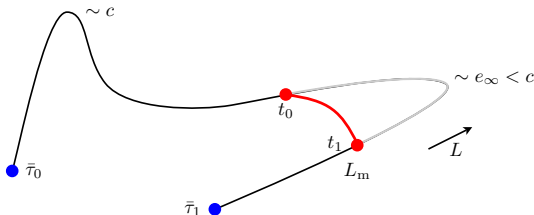
Conjecture in the case of two rigid molecules

Parameters: $L > 0$, $U, V \in SO(3)$

GS energy $= E(L, U, V)$

Theorem (First cases [Lew-04])

Assume there are two strict local min and let c be the mountain pass level. If

- $c \neq \min\{E_{N_1}(Y_1, Z_1) + E_{N_2}(Y_2, Z_2)\} := e_\infty$
- *or $c = \min\{E_{N_1}(Y_1, Z_1) + E_{N_2}(Y_2, Z_2)\}$ which is attained for some $N_1 \neq |Z_1|$*

then the conjecture is right. In particular, there is a transition state.

Multipolar expansion

Assumption: $c = E_{|Z_1|}(Y_1, Z_1) + E_{|Z_2|}(Y_2, Z_2) <$ non neutral

Theorem (Multipolar/Van der Waals expansion [AnaLew-18])

Ψ_1, Ψ_2 *(any) two ground states of the two sub-molecules.*

$$E(L, U, V) \leq E_1 + E_2 + \sum_{2 \leq n+m \leq 5} \frac{\mathcal{F}^{(n,m)}(U, V)}{L^{n+m+1}} - \frac{C_{\mathrm{VdW}}(U, V)}{L^6} + o\left(\frac{1}{L^6}\right)$$

where the $o(1/L^6)$ is uniform in $U, V \in SO(3)$. If in addition the two ground states are "non-degenerate", then there is equality.

$$\iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_{\mathrm{tot},1}(x)\rho_{\mathrm{tot},2}(y)\,dx\,dy}{|Ux - Uy - Le_1|} = \sum_{n+m \geq 2} \frac{\mathcal{F}^{(n,m)}(U, V)}{L^{n+m+1}}$$

$$C_{\mathrm{VdW}}(U, V) := \left\langle f_{(U,V)}\Psi_1 \otimes \Psi_2, (H_1 + H_2 - E_1 - E_2)_{\perp}^{-1} f_{(U,V)}\Psi_1 \otimes \Psi_2 \right\rangle > 0$$

$$f_{(U,V)}(x_1, ..., x_N) := \left\langle \sum_{j=1}^{|Z_1|} x_j - \sum_{m=1}^{M_1} z_m y_m, U^*(1 - 3|e_1\rangle\langle e_1|)\, V \sum_{j=|Z_1|+1}^{N} x_j - \sum_{m=M_1+1}^{M_1+M_2} z_m y_m \right\rangle$$

Feshbach-Schur: $\mathscr{A}\left\{1 - (H_1 + H_2 - E_1 - E_2)_{\perp}^{-1} f_{(U,V)}\right\}\Psi_1 \otimes \Psi_2(\cdot, \cdot + Le_1)/\|\cdot\|$

Case 1: Van der Waals dominates

Degenerate case: need to choose Ψ_1 and Ψ_2. Natural to take uniform average over $\ker(H_1 - E_1)$ and $\ker(H_2 - E_2) \rightsquigarrow$ multipoles with same symmetry property as the molecule

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Theorem (Compactness when Van der Waals dominates [AnaLew-18])

Let n_1 and $n_2 \in \mathbb{N} \cup \{\infty\}$ be the indices of the first non-vanishing 2^n–pole of the two molecules (uniformly averaged in case of degeneracy). If

$$n_1 + n_2 + 1 \geq 7$$

then the conjecture is true. In particular, there is a transition state.

Proof: VdW dominates $E(L, U, V) \leq E_1 + E_2 - CL^{-6}$ for $L \gg 1$.

Example: for an atom (H in HCN), $n_k = +\infty$. This was covered in [Lew-06]. All other cases are new.

Case 2: Multipolar interactions dominate

> ## Theorem (Compactness when multipolar dominates [AnaLew-18])
>
> *Assume that*
>
> $$n_1 + n_2 + 1 \in \{3, 4, 5\}$$
>
> *and that the two ground states are "non-degenerate". If $n_1 = 3$ or $n_2 = 3$, we make the additional non-degeneracy assumption on the octopole*
>
> $$\mathscr{O}(v, \cdot, \cdot) \equiv 0 \implies v = 0.$$
>
> *Then the conjecture is true. In particular, there is a transition state.*

Rmk:

- dipole-dipole, dipole-quadrupole, dipole-octopole, quadrupole-quadrupole
- cannot cover $n_1 + n_2 + 1 = 6$ where VdW and multipoles are of same order (cannot match the two completely different proofs!)
- need non-degeneracy (up to spin relabelling)
- $n_1 = n_2 = 1$ (dipole-dipole) covered in [Lew-04]

Idea of proof

Theorem (Mountain pass for $\mathcal{F}^{(n,m)}(U, V)$ [AnaLew-18])

Under the previous assumptions, the multipolar interactions $\mathcal{F}^{(n,m)}$ satisfy

- *any critical point of $\mathcal{F}^{(n,m)}$ on $SO(3)^2$ with positive Hessian (e.g. local min) has negative energy ;*
- *the sets $\{\mathcal{F}^{(n,m)} \leq -\delta < 0\}$ are pathwise connected for $\delta \ll 1$*

In other words, if $\mathcal{F}^{(n,m)}$ has two local min then the corresponding mountain pass level is < 0.

▶ **Example:** dipole-dipole interaction [Lew-04]
$$\mathcal{F}^{(1,1)}(U, V) = Up_1 \cdot Vp_2 - 3(Up_1 \cdot e_1)(Vp_2 \cdot e_1)$$

state	energy	Morse		state	energy	Morse
$\rightarrow\rightarrow$	$-2\|p_1\|\|p_2\|$	0		$\uparrow\uparrow$	$\|p_1\|\|p_2\|$	2
$\uparrow\downarrow$	$-\|p_1\|\|p_2\|$	1		$\rightarrow\leftarrow$	$2\|p_1\|\|p_2\|$	4

1. Flow to local min of $E(L, \cdot, \cdot)$ at first and last points where $L = L_m \gg 1$
2. Show $\nabla \mathcal{F}^{(n_1, n_2)} \simeq 0$ and Hess $\mathcal{F}^{(n_1, n_2)} \gtrsim 0$
3. Use one path for $\mathcal{F}^{(n_1, n_2)}$