

La química del estado de transición

F. Borondo

Departamento de Química
Instituto de Ciencias Matemáticas (ICMAT)
Universidad Autónoma de Madrid

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9 Noviembre 2016

- 1 Motivación
- 2 Comienzos de la teoría del estado de transición
- 3 (Un poco de) Historia de la Química reciente
- 4 Avances teóricos recientes en la teoría del ET

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MENSAJE: Las reacciones químicas son sistemas dinámicos

- Matemáticas – Dinámica Nolineal y Teoría del Caos
- Química – Aplicaciones

Ejemplo:

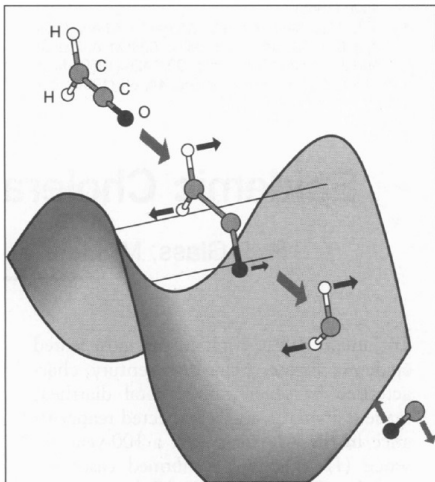
Skiing the Reaction Rate Slopes

R. A. Marcus

SCIENCE • VOL. 256 • 12 JUNE 1992

On the way from reactants to products, a chemical reaction passes through what chemists term the transition state—for a brief moment, the participants in the reaction may look like one large molecule ready to fall apart. The nature of this elusive state is the subject of a number of exciting recent developments that involve theory and experiment in the study of chemical reaction rates

Ejemplo:



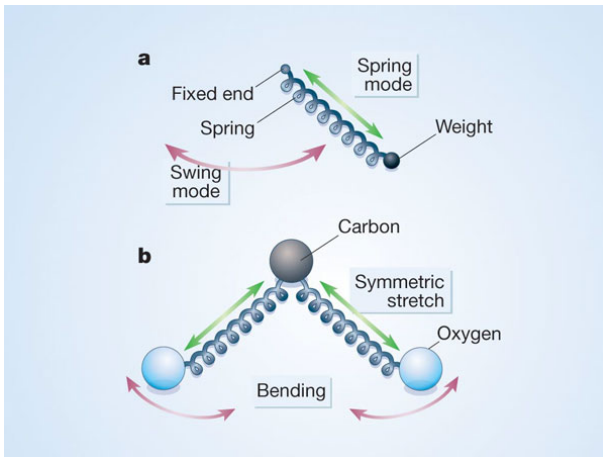
Over the hump. Schematic diagram of the unimolecular dissociation of ketene (CH_2CO) (see cover illustration also). The ketene molecule is prepared in a vibrationally excited state by absorption of laser light, which is followed by a localization of energy in the C-C bond. At the transition state (the saddle point of the energy surface) the CH_2 and CO repel, converting potential energy into translational and rotational energy of the fragments, which can be observed with laser-induced fluorescence. As more energy is pumped into the transition state complex, stepwise increases in dissociation rate are observed. This is consistent with RRKM theory, which assumes that the dissociation rate is controlled by quantized transition state thresholds.

Aproximación de Born-Oppenheimer



- Separación de los movimientos de núcleos y electrones
- ¿Por qué? Porque los núcleos son más pesados (más de 1800 veces) que los electrones
- **Resultado:** Los núcleos se mueven en el potencial creado por los electrones

Vibraciones moleculares



Topografía del potencial (Reaction landscapes)

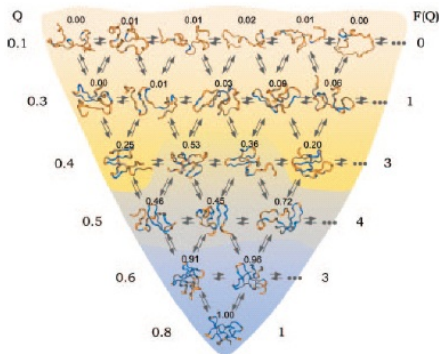


Fig. 1. A schematic representation of the ordering of protein structures as

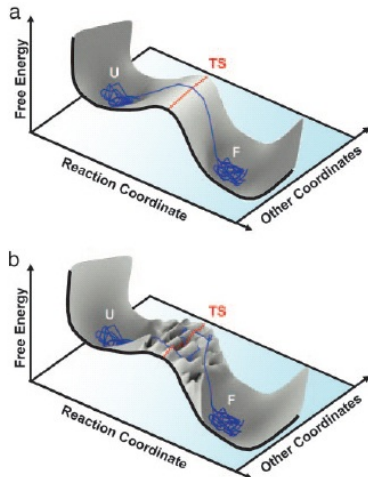
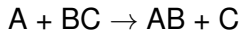


Fig. 2. Schematics depicting two possible trajectories of protein folding. (a) A single crossing of the transition state as predicted by TST. (b) Multiple crossings of the transition state in the limiting case of high friction due to ruggedness.

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- **Velocidad de reacción:**



$$v = \frac{dc_A}{dt} = \frac{dc_{BC}}{dt} = -\frac{dc_{AB}}{dt} = -\frac{dc_C}{dt}$$

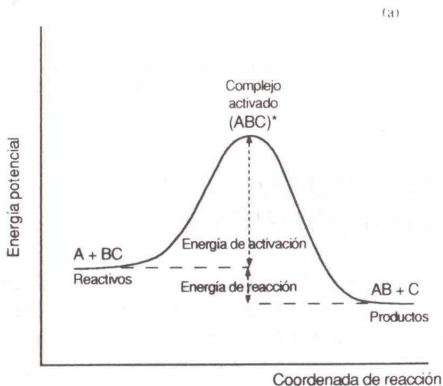
- **Svante Arrhenius**

Premio Nobel 1903 por sus contribuciones a la Electroquímica
(Fué el primero en estimar el efecto invernadero del CO₂)

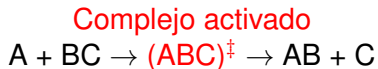


Ley de Arrhenius: $v = Ae^{-E_a/RT}$

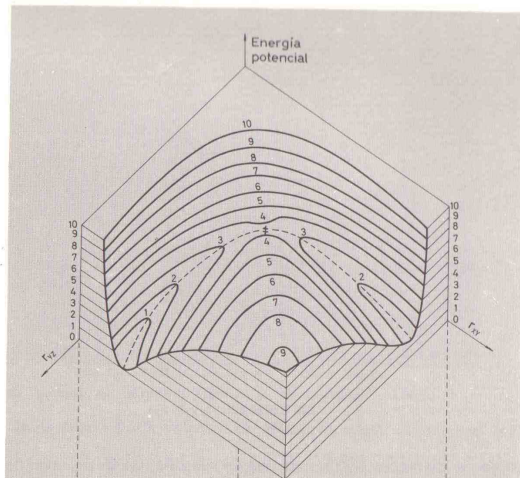
Energía de activación



Perfil de energía potencial a lo largo de la coordenada de reacción.



$R_{AB} \rightarrow$



$\leftarrow R_{BC}$

Trayectorias clásicas

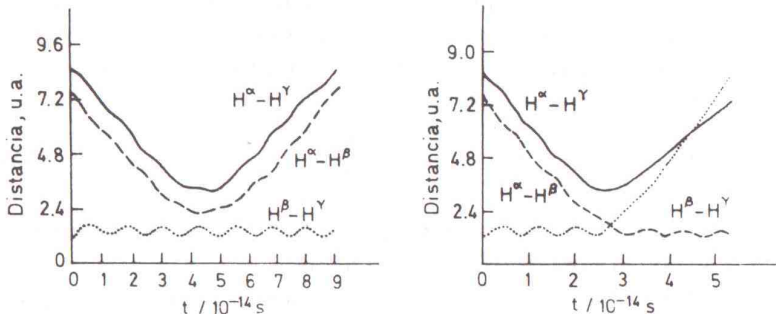
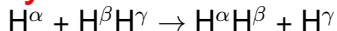


Figura 15. Representación de trayectorias para la colisión $\text{H}^{\alpha} + \text{H}^{\beta} - \text{H}^{\gamma}$: (a) colisión no reactiva; (b) colisión reactiva. (Adaptado de K. J. Laidler (1969): *Theories of Chemical Reaction Rates*. N. Y.: McGraw Hill).

'Potencia' del concepto de ET—Reglas de Polanyi

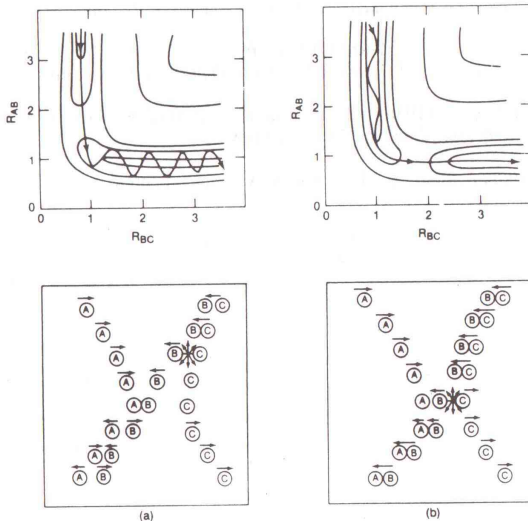
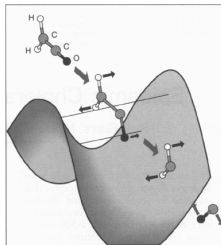


Figura 16. Representación esquemática de la distribución de energía en los productos para reacciones con superficie de energía potencial de barrera: (a) temprana y (b) tardía. En (a) la energía liberada va a parar a la vibración de AB, mientras que en (b) aparece como traslación. Ver más detalles en el texto. (Adaptada de J. C. Polanyi (1972) *Acc. Chem. Res.*, 5, 161).

Teoría del estado de transición

- Eyring y Polanyi, 1935

- Sitúa el ET en el punto de silla de la superficie de potencial.
- Se basa en criterios termodinámicos (equilibrio).



- Wigner, 1938

- Enfoque más dinámico/flujo a través del ET

- PROBLEMA:** Recruzamiento

- Avances recientes, venidos de la mano de las técnicas de la Mecánica Celeste, han solucionado este problema.

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Experimentos

- El estudio detallado de la dinámica química implicó importantes avances técnicos Muchos (alto vacío, láseres, etc.) llegaron a partir de la Segunda Guerra Mundial
- Pero, finalmente es un problema de **cronometraje**
- Un problema similar se dió a finales del XIX:
Cuando un caballo galopa ¿levanta simultáneamente las 4 patas del suelo?
- Solución: Fotografía de alta velocidad ...

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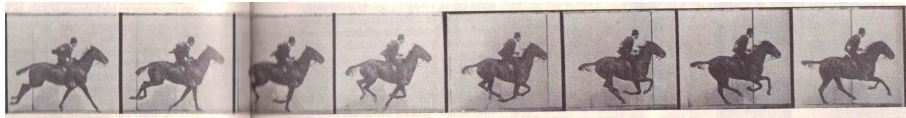
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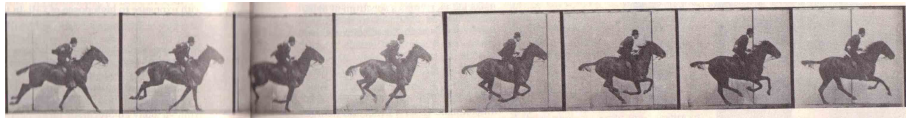
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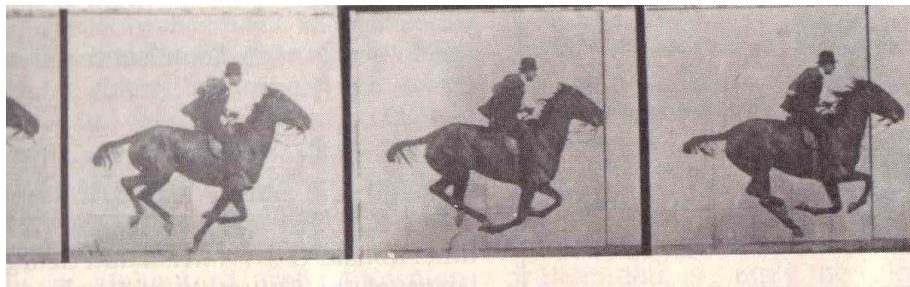
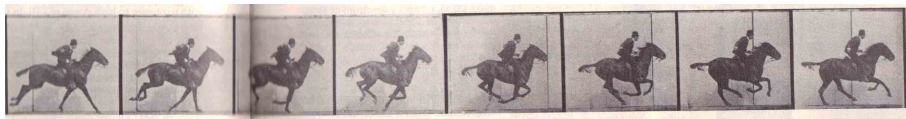
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- Y las reacciones químicas, ¿cómo son de rápidas?
¿de que orden es la dinámica del ET?
- Del orden del **FEMTOSEGUNDO** = 10^{-15} seg.
- Muy rápido si tenemos en cuenta que en F1 las 'pole positions' se dirimen sólo por milésimas de seg.



- Se inicia la 'caza' del ET

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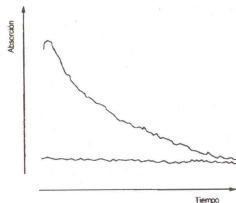
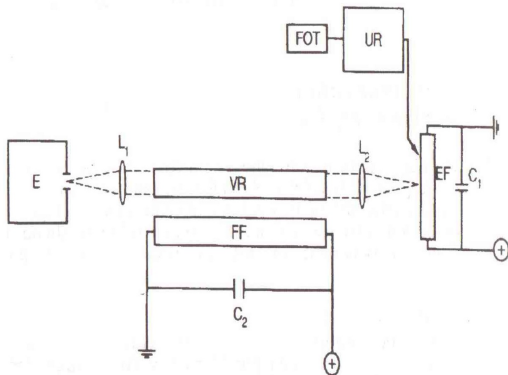


- Se inicia la '**caza**' del ET

Primer paso: Fotólisis de Flash

10^{-6} – 10^{-3} seg

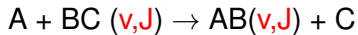
Norrish y Porter en 1950, Premio Nobel 1967



Aparato para Fotólisis de Flash. FOT, fotocélula; UR, unidad electrónica de retardo; FF, fotoflash o flash principal; EF espectroflash o flash secundario; VR, vasija de reacción; C₁, C₂, condensadores; L₁ y L₂, lentes; E, espectrógrafo.

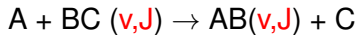
Fotólisis de láser – 10^{-9} (picoseg)– 10^{-6} seg

En Química se necesita más información que la dinámica.



- Quimiluminiscencia infrarroja
- Haces moleculares

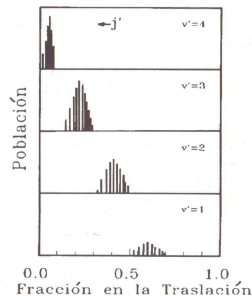
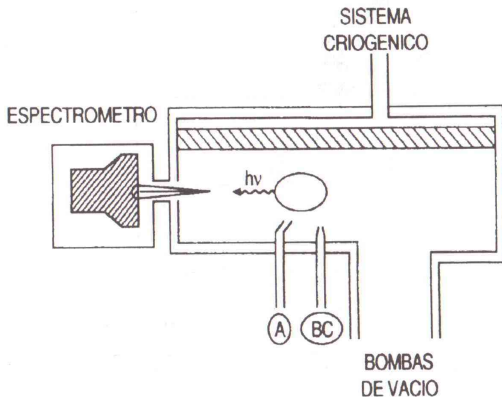
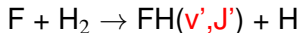
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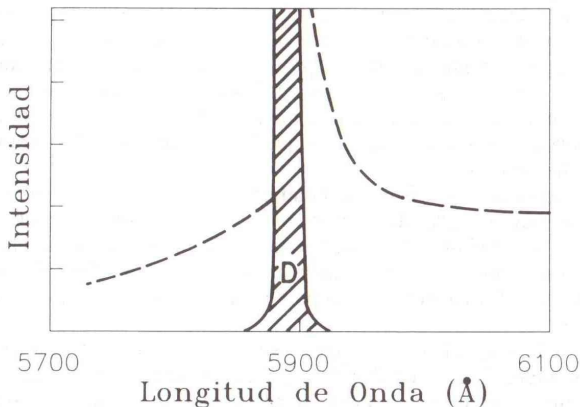
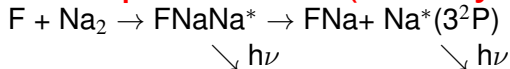
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Quimiluminiscencia infrarroja

J.C. Polanyi en 1972, Premio Nobel 1986



Espectroscopía del ET (Polanyi-1982)

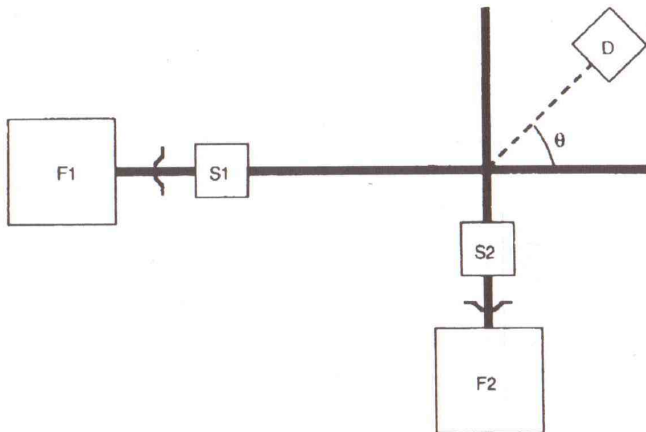


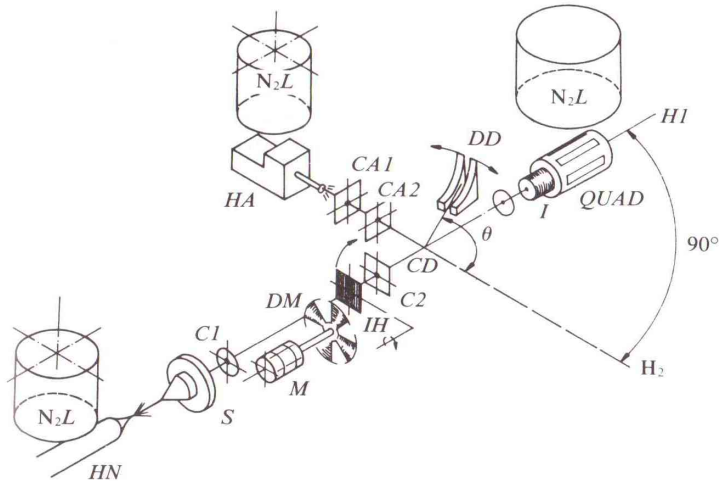
Espectroscopía del estado de transición. Quimiluminiscencia de la reacción $\text{F} + \text{Na}_2 \rightarrow \text{FNa} + \text{Na}^*$. (Adaptado de Foth, Polanyi y Telle (1982): *J. Phys. Chem.*, 86, 5027).

Haces moleculares

D. Herschbach y Y.T. Lee, Premio Nobel 1986

R. Bernstein





8.6. Máquina de haces moleculares cruzados para la medida de la dispersión reactiva. *H1* y *H2*, haces supersónicos y térmicos; *HA* y *HN*, horno de alcalinos y «nozzle»; *C1*, *I* y *CA2*, colimadores; *N₂L*, depósitos de hidrógeno líquido; *S*, Skimer; *M*, motor; *DM*, modulador; *IH*, interruptor de haz; *CD*, centro de dispersión; *DD*, detector de dispersión; *I* y *QUAD*, ionizador de cuadrupolo. (Adaptado de la referencia 13.)

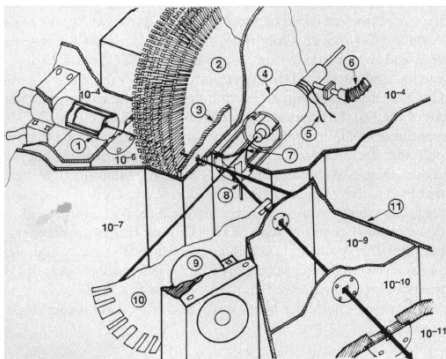


Fig. 2. Experimental arrangement for $F + D_2 \rightarrow DF + D$ and $F + H_2 \rightarrow HF + H$ reactive scattering. Pressures (in torr) for each region are indicated. Components shown by numbers are: (1) effusive fluorine atom beam source made of nickel, resistively heated; (2) velocity selector; (3) cold trap cooled with liquid nitrogen; (4) D_2 or H_2 beam source, supersonic expansion; (5) heater; (6) liquid nitrogen feed line; (7) skimmer; (8) tuning fork chopper; (9) synchronous motor; (10) cross-correlation chopper for time-of-flight velocity analysis; and (11) ultrahigh vacuum, triply differentially pumped, mass spectrometric detector chamber.

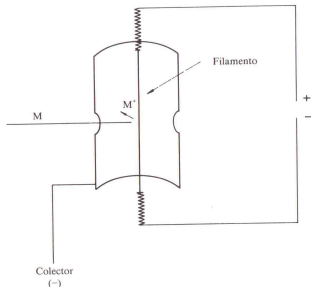


Figura 8.3. Esquema simple de detector de ionización superficial.

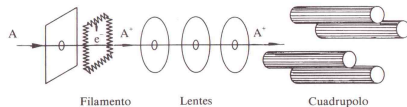


Figura 8.7. Esquema de detector universal formado por un ionizador, lentes eléctricas y un cuadrupolo que hace de selector o filtro de masas y un colector de iones.

¿Qué se aprende con los haces moleculares?

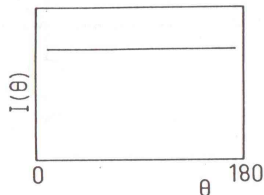


Figura 12. a) Distribución angular de productos esquemática para una reacción con un complejo de larga vida.

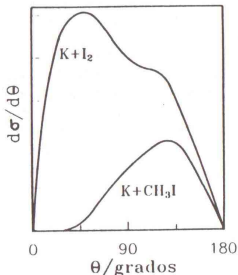


Figura 12. b) Distribución angular de KI en las reacciones de mecanismo directo $K + I_2$ y $K + CH_3I$, para una energía traslacional de ≈ 12 kJ/mol. (Adaptado de R. B. Bernstein y col. (1971): *J. Chem. Phys.*, 54, 2831; (1972) 57, 5497.

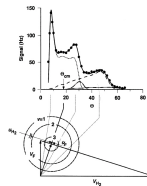


Fig. 3. Laboratory angular distribution for $F + \text{para-H}_2$, for a collision energy of 3.8 kcal/mol. The velocity diagram is shown below. Both the data (●) and calculated laboratory distributions are shown. (—) Data, (---) total calculated distribution. (---) $v = 1$ component, (---) $v = 2$ component, (---) $v = 3$ component. (---) $\phi = 0^\circ$, (---) $\phi = 45^\circ$, (---) $\phi = 90^\circ$, (---) $\phi = 135^\circ$, (---) $\phi = 180^\circ$. ϕ is the angle of the velocity vector of the center of mass of the reactants measured from F .

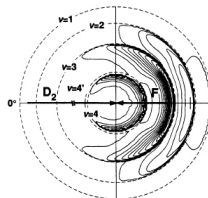


Fig. 1. Center-of-mass velocity flux contour map for the $F + D_2 \rightarrow DF + D$ reaction. Fluorine atoms and D_2 molecules move toward each other at a collision energy of 1.82 kcal/mol, with the fluorine atoms moving from right to left.

Haces moleculares en la actualidad

Superfluid Helium Droplets: A Uniquely Cold Nanomatrix for Molecules and Molecular Complexes

J. Peter Toennies* and Andrey F. Vilesov



J.P. Toennies

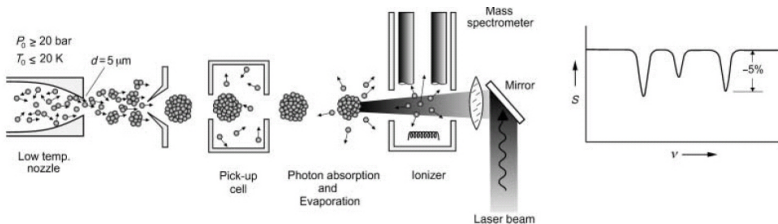
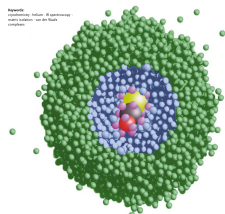
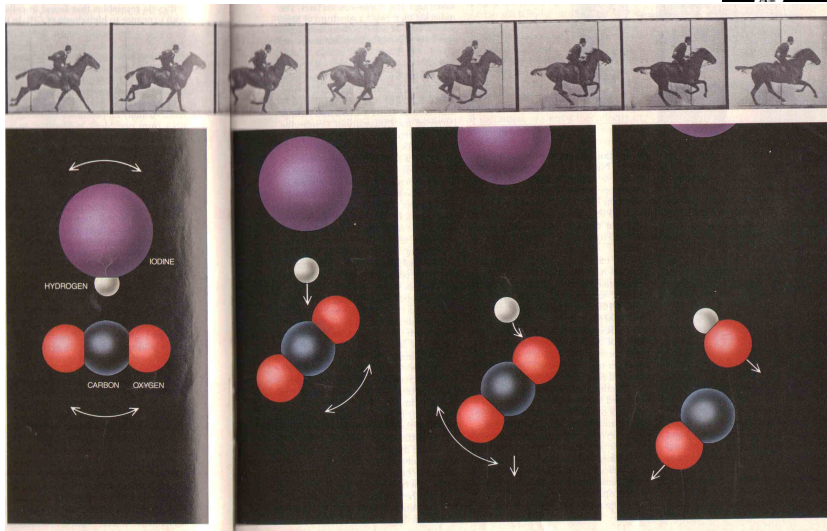


Figure 7. Schematic representation of the laser-depletion apparatus used for the pick-up and depletion spectroscopy of molecules inside helium droplets.^[9] After the adsorption of a laser photon the droplet size decreases as a result of evaporative loss of helium atoms as the photon energy deposited in the chromophore relaxes and temporarily heats the droplet. The absorption signal is detected as a decrease (D_{rel}) of the mass spectrometer signal S .

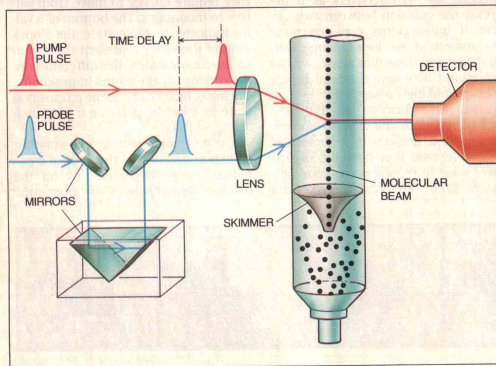
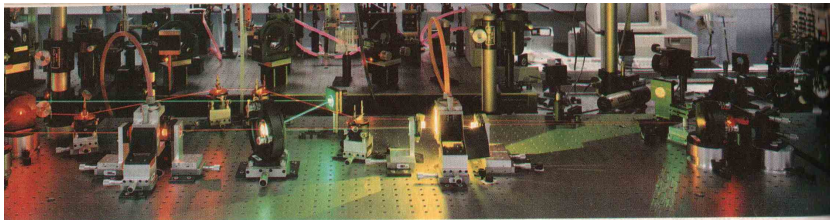
Femtoquímica

Seguimiento de las reacciones tiempo real

A.H. Zewail, Premio Nobel 1999



Femtoland, Caltech, CA, USA



FEMTOSECOND PHOTOGRAPHY captures the dynamics of molecular reactions in real time. The laser system (above) generates a pump pulse and a probe pulse. As shown in the illustration (left), the pump pulse and the probe pulse leave the laser system at the same time. The probe pulse is diverted so that a time delay of a few femtoseconds is introduced between the two pulses. When the pump pulse hits a molecule in the molecular beam, it initiates a chemical reaction. The probe pulse strikes the molecule a few femtoseconds later. The molecule then emits a spectrum of light, which can be analyzed to determine the dynamics of the atoms in real time.

Some 40 years ago techniques were introduced to study chemical intermediates and fast kinetics for the first time. Ronald G. W. Norrish and George Porter of the University of Cambridge and Manfred Eigen of the Max Planck

Algunos resultados

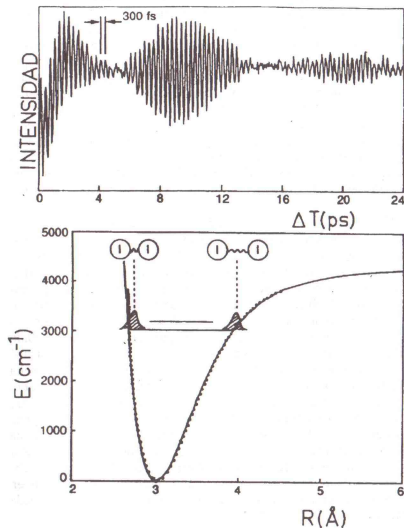


Figura 13. Movimiento vibracional de la molécula de I₂ determinado por espectroscopía de femtosegundo. (Adaptado de M. Grubele, G. Roberts, M. Dantus, R. M. Bowman y A. H. Zewail (1990), *Chem. Phys. Lett.*, 166, 459)

Atoquímica

- Son los desarrollos experimentales más recientes
- $t = 10^{-18}$ seg, $\ell = 10^{-10}$ m
- pulsos Rayos X

Atoquímica

TRUCO usar un solo electrón que se emite y se absorbe

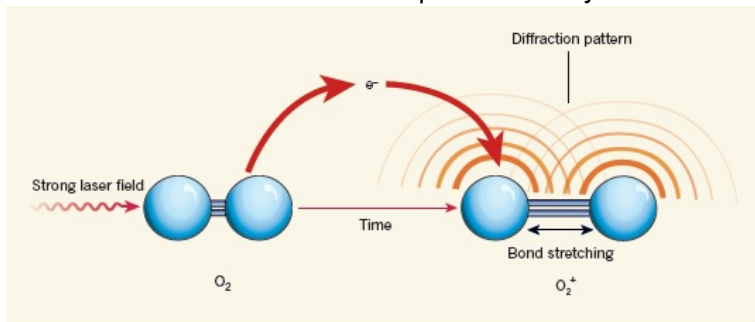


Figure 1 | Molecular movies. Blaga *et al.*⁴ have used laser-induced electron diffraction to ‘film’ single molecules in motion. In the authors’ technique, a molecule such as oxygen is irradiated with a strong infrared laser field, pulling away an electron (e^-) and causing the bond between the atoms in the molecule to stretch. The electron is accelerated in the laser field, then directed back towards the resulting ion. Collision of the electron with nuclei in the ion causes the electron to rebound and to generate a diffraction pattern — an electron spectrum. This spectrum contains information about the positions of the nuclei at the moment of collision. By performing a series of experiments in which the time delay between the electron’s departure from, and collision with, the molecule is varied, a series of snapshots (spectra) of the molecular motion can be taken, much like the frames of a movie.

Atoquímica

Imaging ultrafast molecular dynamics with laser-induced electron diffraction

Cosmin I. Blaga¹, Junliang Xu², Anthony D. DiChiara¹, Emily Sistrunk¹, Kaikai Zhang¹, Pierre Agostini¹, Terry A. Miller³, Louis F. DiMauro¹ & C. D. Lin²

NATURE | VOL 483 | 194 |

8 MARCH 2012

Atoquímica

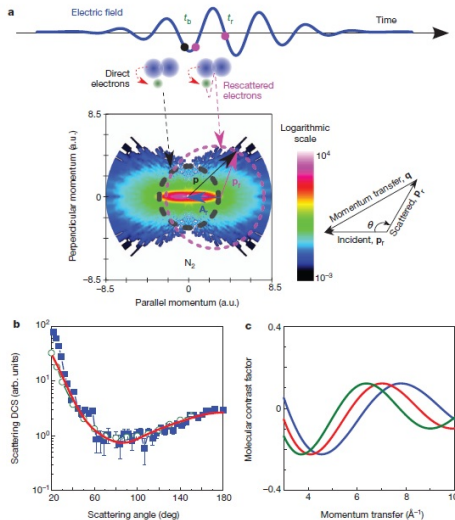


Figure 1 | The principle of laser-induced electron diffraction.

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Recruzamiento
- Recientes avances en la **Teoría del ET**
 - Berry, Komatsuzaki
 - Uzer, Jaffé, Farrelly, Wiggins, Waalkens, Bartsch, Hernandez Palacián, Yanguas
- **IDEA**: Buscar el cuello de botella del ET en el espacio de fases
'Normally Invariant Hyperbolic Manifolds'
(tomando prestadas técnicas de la Mecánica Celeste)
- **VENTAJA**: Soluciona el problema del recruzamiento

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- Recordar **PROBLEMA** con la Teoría del ET:
Recruzamiento
- Recientes avances en la **Teoría del ET**
 - Berry, Komatsuzaki
 - Uzer, Jaffé, Farrelly, Wiggins, Waalkens, Bartsch, Hernandez Palacián, Yanguas
- **IDEA**: Buscar el cuello de botella del ET en el espacio de fases
'Normally Invariant Hyperbolic Manifolds'
(tomando prestadas técnicas de la Mecánica Celeste)
- **VENTAJA**: Soluciona el problema del recruzamiento

Setup

Consider f -degree-of-freedom Hamiltonian system

$(\mathbb{R}^{2f}(p_1, \dots, p_f, q_1, \dots, q_f), \omega = \sum_{k=1}^f dp_k \wedge dq_k)$ and Hamilton function $\mathcal{H}$.

Assume that the Hamiltonian vector field

$$\begin{pmatrix} \dot{p} \\ \dot{q} \end{pmatrix} = \begin{pmatrix} -\frac{\partial \mathcal{H}}{\partial q} \\ \frac{\partial \mathcal{H}}{\partial p} \end{pmatrix} \equiv J D\mathcal{H}, \quad J = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

has **saddle-centre-...-centre equilibrium point** ('saddle' for short) at the origin, i.e.

$J D^2 \mathcal{H}$ has eigenvalues $\pm \lambda, \pm i\omega_2, \dots, \pm i\omega_f, \quad \lambda, \omega_k > 0$

Simplest case

Consider Hamilton function

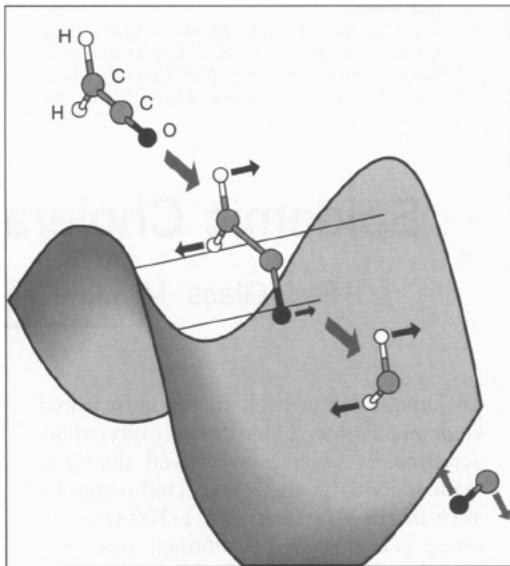
$$\begin{aligned}\mathcal{H} &= \frac{1}{2}p_x^2 - \frac{1}{2}\lambda^2 x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2 \\ &=: \mathcal{H}_x + \mathcal{H}_y\end{aligned}$$

- corresponding vector field is

$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = J D\mathcal{H} = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial p_x} \\ \frac{\partial \mathcal{H}}{\partial p_y} \\ \frac{\partial \mathcal{H}}{\partial x} \\ \frac{\partial \mathcal{H}}{\partial y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

- $\mathcal{H}_x$ and $\mathcal{H}_y$ are conserved individually,

$$\mathcal{H}_x = E_x \in \mathbb{R}, \quad \mathcal{H}_y = E_y \in [0, \infty), \quad \mathcal{H} = E = E_x + E_y \in \mathbb{R}$$



$E < 0$:

Rewrite energy equation $\mathcal{H} = E$ as

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}_{\simeq S^2 \text{ for } x \in (-\infty, -\frac{\sqrt{-2E}}{\lambda})}$$

or $x \in (\frac{\sqrt{-2E}}{\lambda}, \infty)$

$\Rightarrow$ Energy surface

$$\Sigma_E = \{\mathcal{H} = E\}$$

consists of two disconnected components which represent the
'reactants' and 'products'

$E > 0$:

$$\underbrace{E + \frac{1}{2}\lambda^2 x^2 = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}\omega_y^2 y^2}_{\simeq S^2 \text{ for all } x \in \mathbb{R}}$$

$\Rightarrow$ Energy surface

$$\Sigma_E = \{\mathcal{H} = E\} \simeq S^2 \times \mathbb{R} \quad (\text{spherical cylinder})$$

- $\Rightarrow \Sigma_E$ bifurcates at $E = 0$ (the energy of the saddle) from *two* disconnected components to a *single* connected component
- Consider projection of Σ_E to $\mathbb{R}^3(x, y, p_y)$, i.e. project out

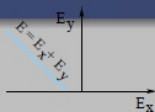
$$p_x = \pm \sqrt{2E - p_y^2 + \lambda^2 x^2 - \omega_y^2 y^2}$$

which gives two copies for the two signs of p_x

Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

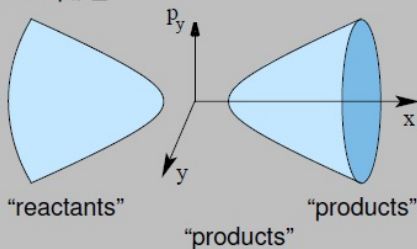
Σ_E for $E < 0$



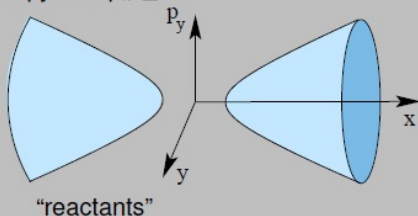
$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

- Σ_E consists of two components representing reactants and products

copy with $p_x \geq 0$



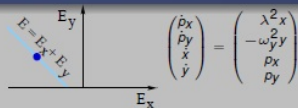
copy with $p_x \leq 0$



Phase Space Structures near a Saddle

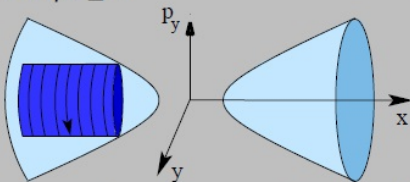
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E < 0$

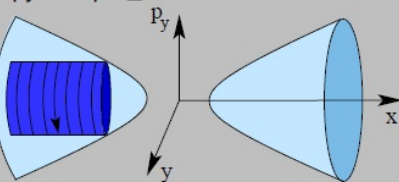


- all trajectories have $\mathcal{H}_x = E_x < 0$ and hence are non-reactive

copy with $p_x \geq 0$



copy with $p_x \leq 0$

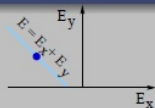


non-reactive trajectory on the side of reactants

Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

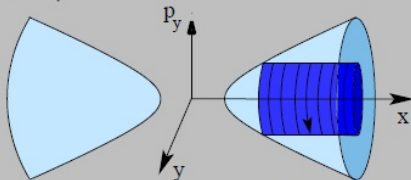
Σ_E for $E < 0$



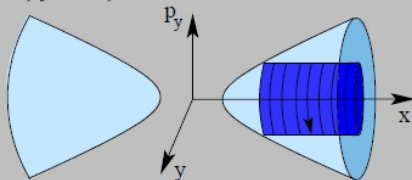
$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda^2 x \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

- all trajectories have $\mathcal{H}_x = E_x < 0$ and hence are non-reactive

copy with $p_x \geq 0$



copy with $p_x \leq 0$

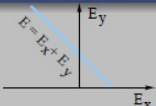


non-reactive trajectory on the side of products

Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

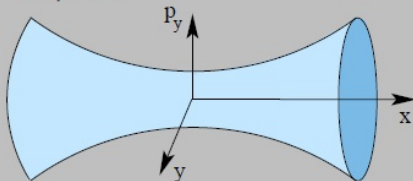
Σ_E for $E > 0$



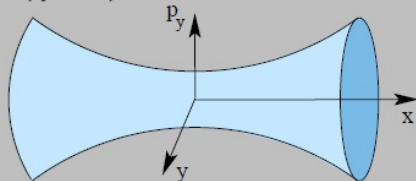
$$\begin{pmatrix} \dot{p}_x \\ \dot{p}_y \\ \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} \lambda_x^2 \\ -\omega_y^2 y \\ p_x \\ p_y \end{pmatrix}$$

• $\Sigma_E \simeq S^2 \times \mathbb{R}$

copy with $p_x \geq 0$



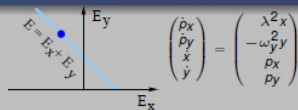
copy with $p_x \leq 0$



Phase Space Structures near a Saddle

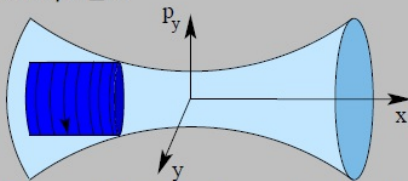
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$

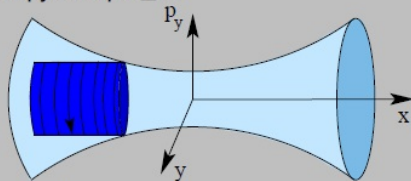


- Non-reactive trajectories have $\mathcal{H}_x = E_x < 0$

copy with $p_x \geq 0$



copy with $p_x \leq 0$

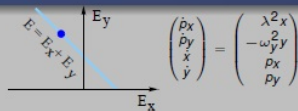


Non-reactive trajectory on the side of reactants

Phase Space Structures near a Saddle

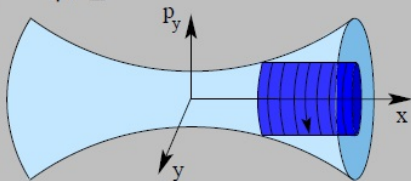
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$

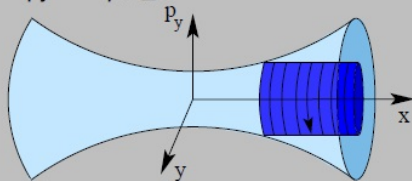


- Non-reactive trajectories have $\mathcal{H}_x = E_x < 0$

copy with $p_x \geq 0$



copy with $p_x \leq 0$

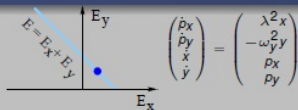


Non-reactive trajectory on the side of products

Phase Space Structures near a Saddle

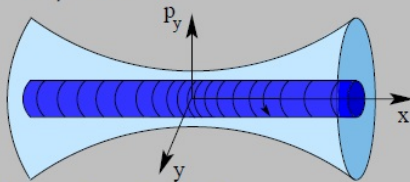
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



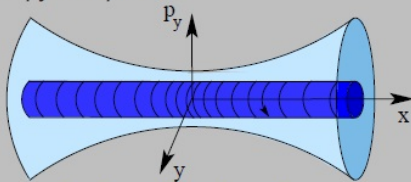
- Reactive trajectories have $\mathcal{H}_x = E_x > 0$

copy with $p_x \geq 0$



forward reactive trajectory

copy with $p_x \leq 0$

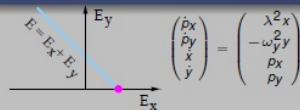


backward reactive trajectory

Phase Space Structures near a Saddle

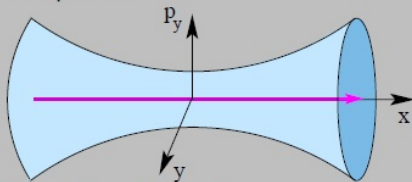
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



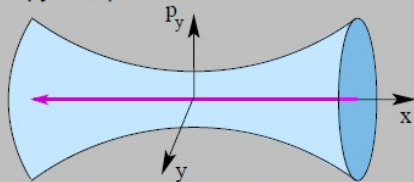
- Dynamical reaction paths have $\mathcal{H}_x = E_x = E$ (i.e. $\mathcal{H}_y = E_y = 0$)

copy with $p_x \geq 0$



forward reaction path

copy with $p_x \leq 0$

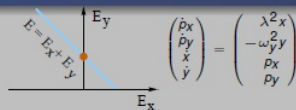


backward reaction path

Phase Space Structures near a Saddle

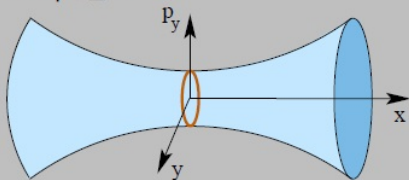
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$

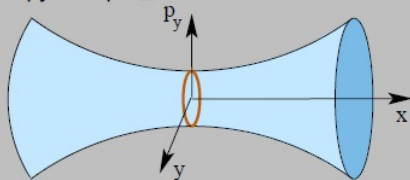


- Lyapunov periodic orbit $\simeq S^1$ has $\mathcal{H}_x = E_x = 0$ with $x = p_x = 0$

copy with $p_x \geq 0$



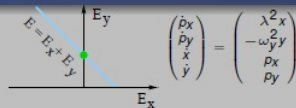
copy with $p_x \leq 0$



Phase Space Structures near a Saddle

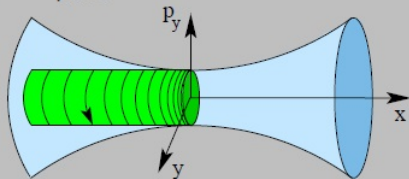
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



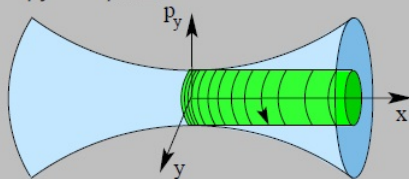
- Stable manifolds $W^s \simeq S^1 \times \mathbb{R}$ has $\mathcal{H}_x = E_x = 0$ with $p_x = -\lambda x$

copy with $p_x \geq 0$



reactants branch W_r^s

copy with $p_x \leq 0$

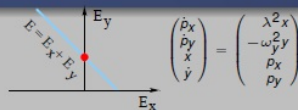


products branch W_p^s

Phase Space Structures near a Saddle

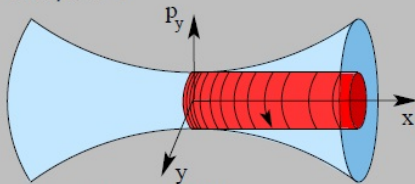
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



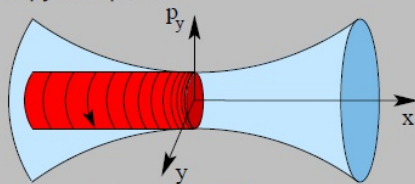
- Unstable manifolds $W^u \simeq S^1 \times \mathbb{R}$ has $\mathcal{H}_x = E_x = 0$ with $p_x = \lambda x$

copy with $p_x \geq 0$



products branch W_p^u

copy with $p_x \leq 0$

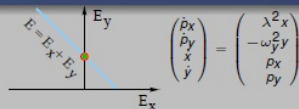


reactants branch W_r^u

Phase Space Structures near a Saddle

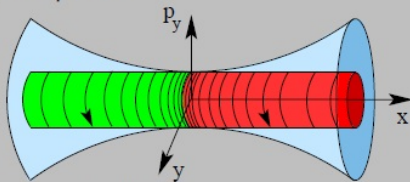
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



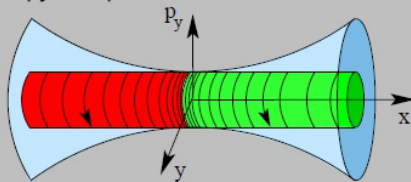
- *Forward cylinder* $W_r^s \cup W_p^u$ and *backward cylinder* $W_p^s \cup W_r^u$ enclose all the forward and backward reactive trajectories, respectively

copy with $p_x \geq 0$



forward cylinder

copy with $p_x \leq 0$

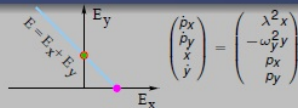


backward cylinder

Phase Space Structures near a Saddle

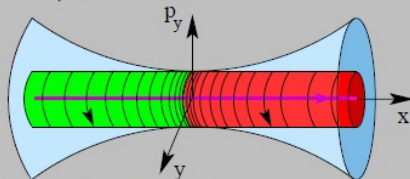
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



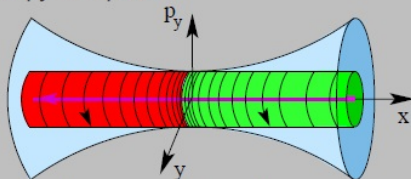
- Forward and backward **dynamical reaction paths** form the centreline of the forward and backward cylinders, respectively

copy with $p_x \geq 0$



forward reaction path

copy with $p_x \leq 0$

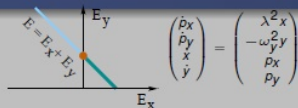


backward reaction path

Phase Space Structures near a Saddle

Linear vector field for $f = 2$ degrees of freedom

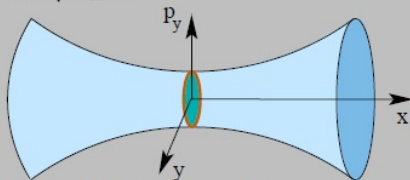
Σ_E for $E > 0$



- Dividing surface $\simeq S^2$ has $x = 0$,

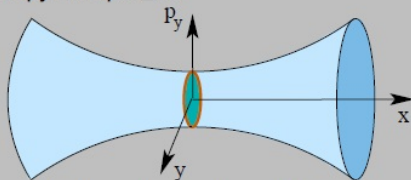
Lyapunov periodic orbit $\simeq S^1$ forms its equator and divides it into two hemispheres $\simeq B^2$

copy with $p_x \geq 0$



forward hemisphere B_f^2

copy with $p_x \leq 0$

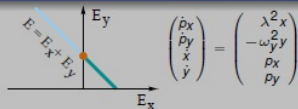


backward hemisphere B_b^2

Phase Space Structures near a Saddle

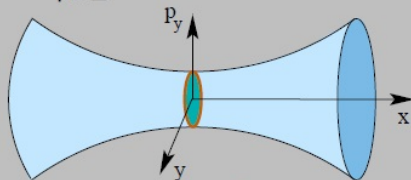
Linear vector field for $f = 2$ degrees of freedom

Σ_E for $E > 0$



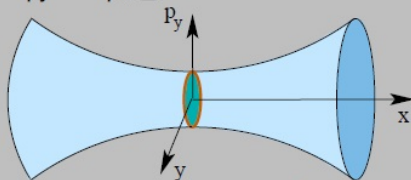
- Apart from its equator (which has $x = p_x = 0$) the **dividing surface** is transverse to the flow ($\dot{x} = p_x \neq 0$ for $p_x \neq 0$)

copy with $p_x \geq 0$



forward hemisphere B_f^2

copy with $p_x \leq 0$



backward hemisphere B_b^2

Phase Space Structures near a Saddle

General (nonlinear) case

- $f = 2$ degrees of freedom: dividing surface can be constructed from periodic orbit

Periodic Orbit Dividing Surface (PODS) (Pechukas, Pollak and McLafferty, 1970s)

- How can one construct a dividing surface for a system with an arbitrary number of
degrees of freedom? What are the phase space conduits for reaction in this case?

Phase Space Structures near a Saddle

General (nonlinear) case; $E > 0$

	2 DoF	3 DoF	f DoF
energy surface	$S^2 \times \mathbb{R}$	$S^4 \times \mathbb{R}$	$S^{2f-2} \times \mathbb{R}$
dividing surface	S^2	S^4	S^{2f-2}
normally hyperbolic invariant manifold (NHIM)	S^1	S^3	S^{2f-3}
(un)stable manifolds	$S^1 \times \mathbb{R}$	$S^3 \times \mathbb{R}$	$S^{2f-3} \times \mathbb{R}$
forward/backward hemispheres	B^2	B^4	B^{2f-2}
"flux" form $\Omega' = d\varphi$	ω	$\frac{1}{2}\omega^2$	$\frac{1}{(f-1)!}\omega^{f-1}$
"action" form φ	$p_1 dq_1 + p_2 dq_2$	$(p_1 dq_1 + p_2 dq_2 + p_3 dq_3) \wedge \frac{1}{2}\omega$	$\sum_{k=1}^f p_k dq_k \wedge \frac{1}{(f-1)!}\omega^{f-2}$

$$\text{Flux (rate): } N(E) = \int_{B_{\text{ds; forward}}^{2f-2}} \Omega' = \int_{S_{\text{NHIM}}^{2f-3}} \varphi$$

Dynamical hierarchy in transition states: Why and how does a system climb over the mountain?

Tamiki Komatsuzaki* and R. Stephen Berry^{†‡}

PNAS | July 3, 2001 | vol. 98 | 7666–7671

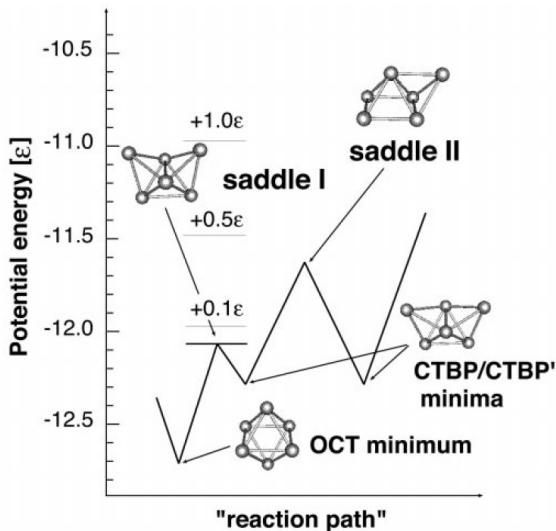
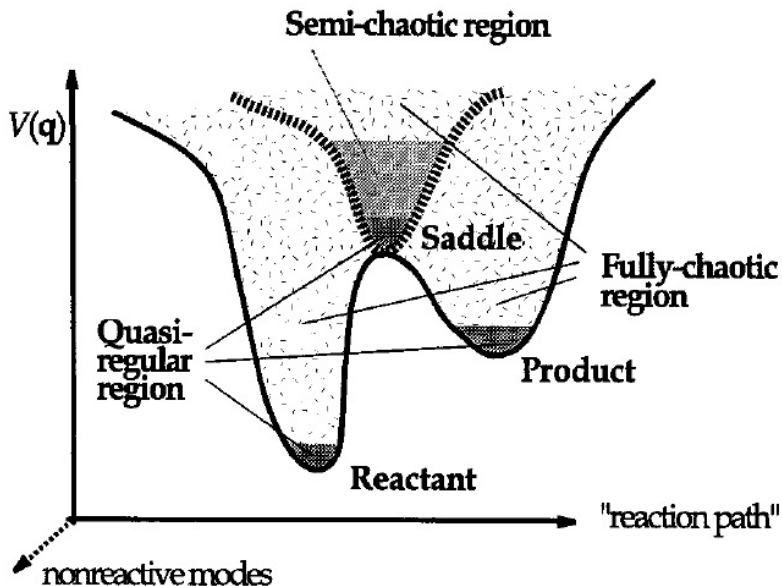


Fig. 1. Schematic picture of the potential energy surface of Ar_6 . Capped trigonal bipyramid (CTBP)' is a permutational isomer of the CTBP minimum neighboring on the octahedron (OCT) minimum. For argon, $\epsilon = 121$ K.



Definability of No-Return Transition States in the High-Energy Regime above the Reaction Threshold

Chun-Biu Li,^{1,*} Akira Shoujiguchi,² Mikito Toda,² and Tamiki Komatsuzaki^{1,3}

¹*Nonlinear Science Laboratory, Department of Earth and Planetary Sciences, Faculty of Science, Kobe University, JST/CREST, Nada, Kobe 657-8501 Japan*

²*Department of Physics, Faculty of Science, Nara Women's University, Nara, 630-8506 Japan*

³*Department of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*
(Received 26 January 2006; published 10 July 2006)

No-return transition states (TSs) defined in multidimensional phase space, where recrossing trajectories through the commonly used "configuration" TS pass only once, robustly exist up to a moderately high-energy regime above the reaction threshold, even when nonlinear resonances among the bath degrees of freedom perpendicular to the reaction coordinate result in local chaos. However, at much higher energy when global chaos appears in the bath space, the separability of the reaction coordinate from the bath degrees of freedom starts to lose locally. In the phase space near the saddles, it is found that the slower the system passes the TS, the more recrossing trajectories reappear. Their implications and mechanisms are discussed concerning to what extent one can define no-return TSs in the high-energy regime above the reaction threshold.



Gracias por la atención



¿Preguntas?