INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS:
PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

MOLECULAR BEAM TECHNIQUES & ATOMIC & MOLECULAR COLLISIONS: AN INTRODUCTION

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Molecular Beam Techniques and Atomic & Molecular Collisions: An Introduction

Concise Glossary	sources, detectors, state analyzers, ...
Phenomenological Potential Scattering	shadows, glories, rainbows, diffractions, orbiting & resonances
Electronic Energy Transfer	curve crossings, interferences, polarization effects
Angular Momentum Transfer	molecular rotations, Electron spin effects, Orbital alignment and polarization.
Dynamics on Molecular Potential Energy Surfaces	Hyperspherical description of chemical reactions; Angular momentum barriers; Resonances & unimolecular decay; Short wave (semi-classical) mechanics; How quantum mechanics avoids classical chaos and catastrophes.

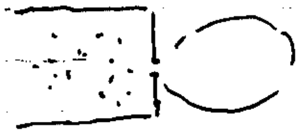
V. Aquilanti, Università di Perugia

(on the last topics, see also separate notes!)

Molecular beams: Sources

~~Effusive~~ Mean free path $\Lambda = \frac{1}{\pi\sigma^2 n} \approx 10^{-5}$ $\sigma = 3\times10^{-8}$, $n \approx 3\cdot10^{19}$ molec cm (1 Atm)

Effusive: slit dimension $\lesssim \Lambda$

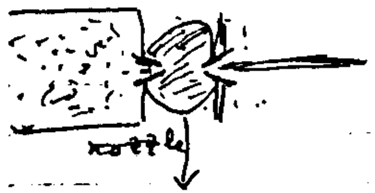


$\bar{v}_{M.B.}$

M Boltzmann distribution

Supersonic slit $\gtrsim \Lambda$

nozzle skimmer



~~nozzle~~

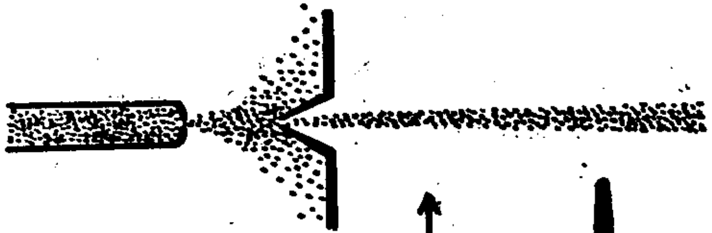
big pumps

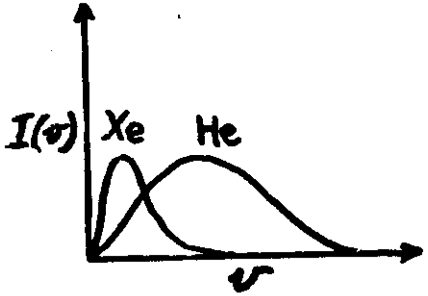
$v > \bar{v}_{Maxwell-B}$

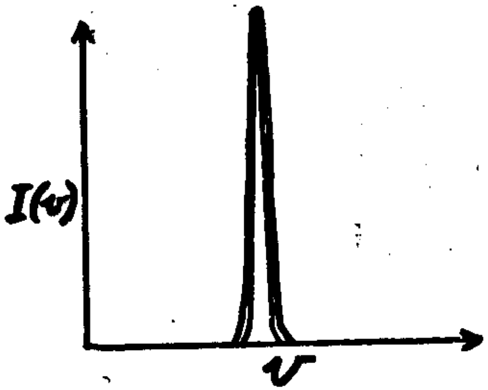
Seeding

Pulsed etc.

SEEDED BEAMS







$$\frac{1}{2}\bar{m}v^2 + \frac{5}{2}kT = \frac{1}{2}\bar{m}v'^2 + \frac{5}{2}kT'$$

$$\frac{1}{2}\bar{m}v^2 \rightarrow 0 \qquad \frac{5}{2}kT' \rightarrow 0$$

$$\frac{1}{2}\bar{m}v'^2 = \frac{5}{2}kT$$

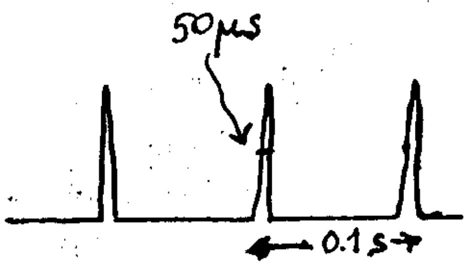
$$\frac{1}{2}Mv'^2 = \frac{1}{2}\bar{m}v'^2\left(\frac{M}{\bar{m}}\right)$$

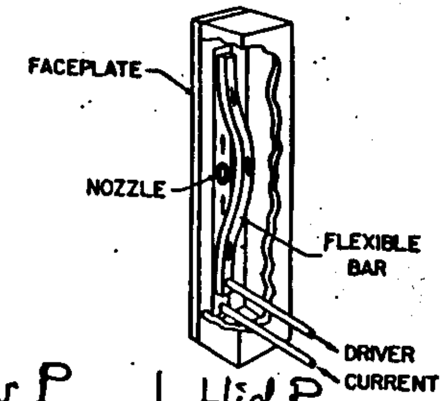
$$= \left(\frac{M}{\bar{m}}\right)\left(\frac{5}{2}kT\right)$$

$$\approx \frac{M_{Xe}}{m_{He}}\left(\frac{5}{2}kT\right)$$

PULSED BEAMS

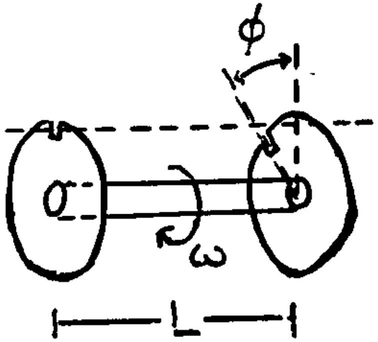
Gentry and Giese, 1978



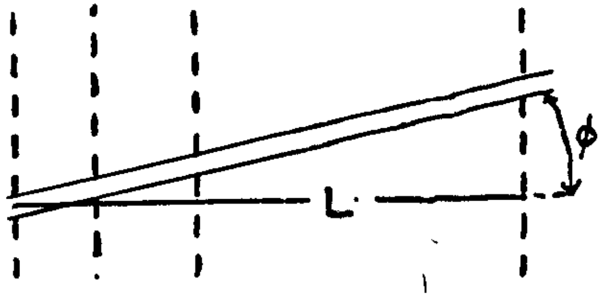


	Low P		High P	
	cont.	pulsed	cont.	pulsed
Source pressure (bar)	1	1	200	200
Pumping speed (ℓ/s)	5000	5000	350	5000
Background pressure (torr)	10^{-3}	$5\cdot10^{-8}$	1	10^{-5}
Nozzle diameter (cm)	0.01	0.05	0.003	0.05
Mach N° (arb)	7.6	38	460	76,000
Duty Factor	1	$5\cdot10^{-4}$	1	5×10^{-4}
Gas consumption (torr·cm²)	0.076	0.001	1.4	0.19

Velocity selection: Fizeau

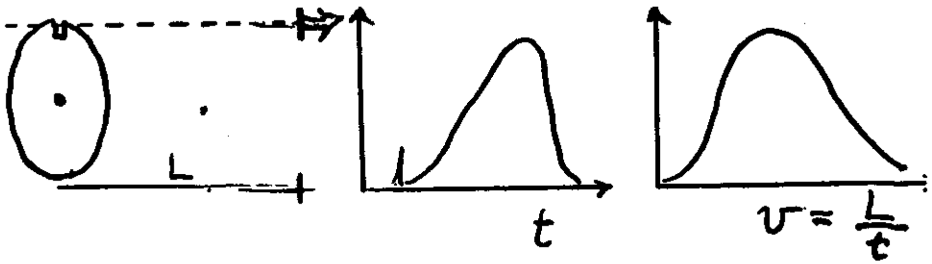


$$v = \frac{L}{\Delta t} = \frac{L\,\omega}{\phi}$$



for ~50% transmission: <u>several disks</u>!

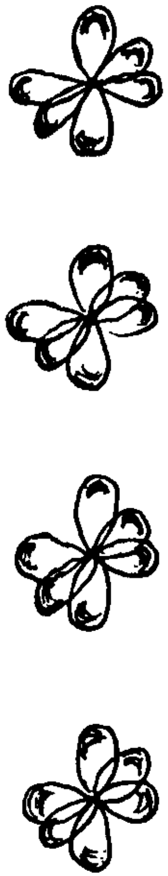
Velocity analysis: time of flight

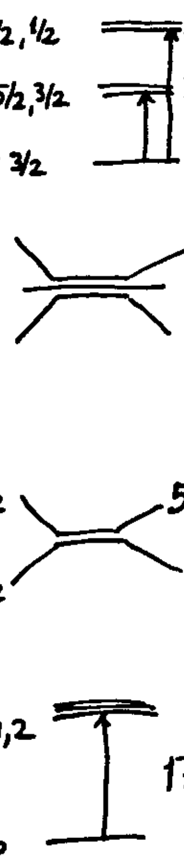


$$v = \frac{L}{t}$$

for 50% transmission: <u>cross correlation</u>!

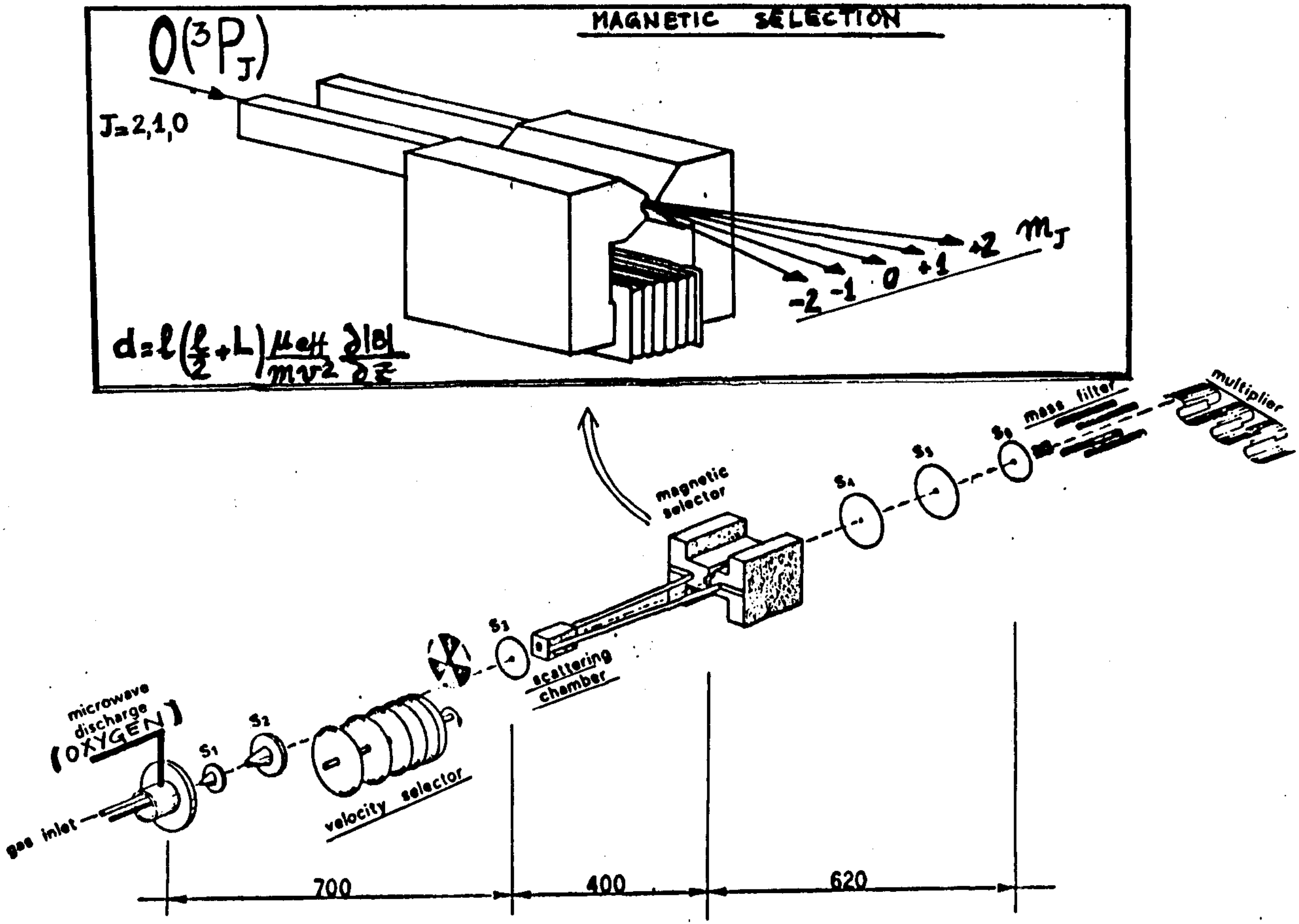
INTEGRAL CROSS SECTIONS AT THERMAL ENERGIES AS A FUNCTION OF VELOCITY, FOR FIRST ROW ATOMS WITH RARE GASES (glory range, magnetic analysis)



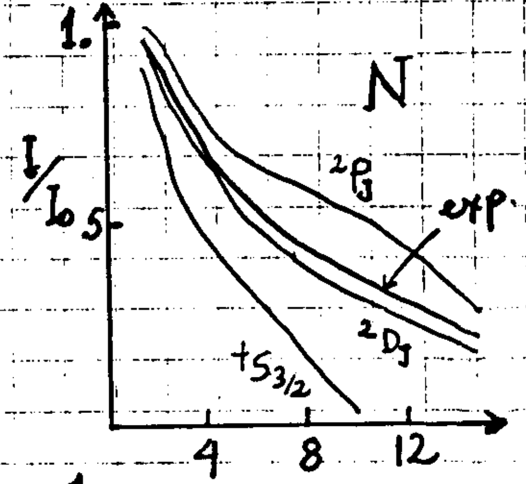


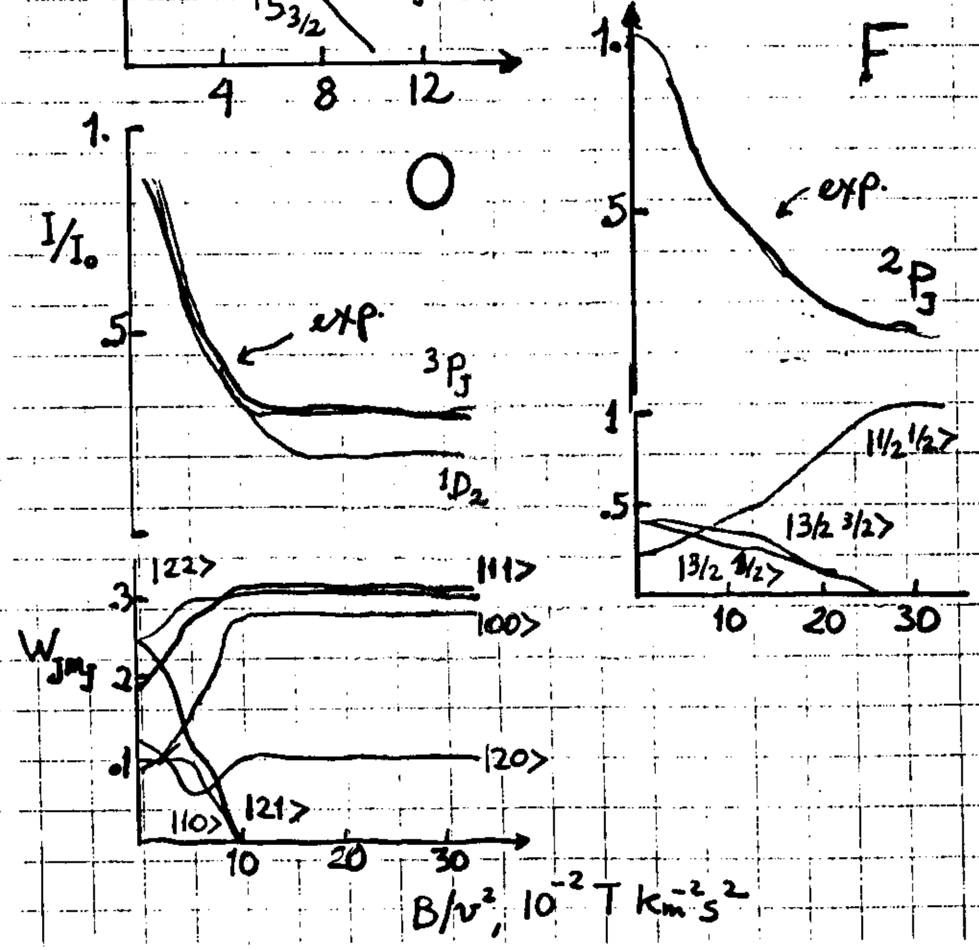
2p orbitals		L	S	$^{2S+1}L_j$	
	N	1	1/2	$^2P_{3/2,1/2}$	3.82 eV
		2	1/2	$^2D_{5/2,3/2}$	2.38 eV
		0	3/2	$^4S_{3/2}$	0
	O	1	1	$^3P_0$	28.1 meV
				$^3P_1$	19.6 meV
				$^3P_2$	0
	F	1	1/2	$^2P_{1/2}$	50.1 meV
				$^2P_{3/2}$	0
	Ne	1	1	$^3P_{0,1,2}$	17 eV
		0	0	$^1S_0$	

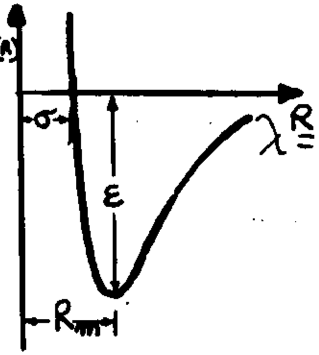
 filled  half filled


MAGNETIC SELECTION
O(3PJ)
J=2,1,0
d=l(l/2+L) μeff/mv2 ∂|B|/∂z
mJ
-2 -1 0 +1 +2
magnetic selector
S4
S5
S6
mass filter
multiplier
S3
scattering chamber
microwave discharge
(OXYGEN)
S1
S2
velocity selector
gas inlet
700
400
620

Magnetic analysis of atomic beams





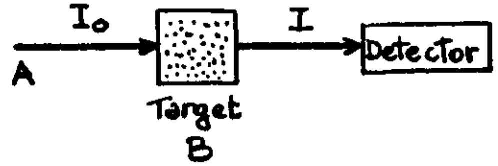


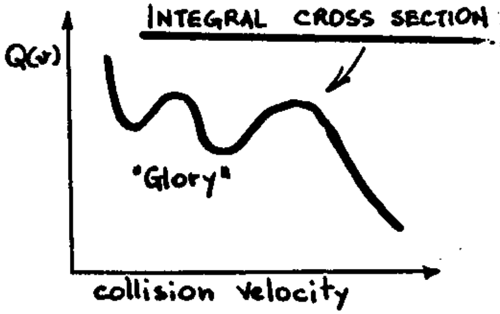
6×10^{-27} erg

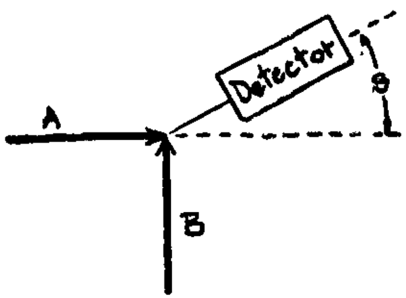
$$\lambda = \frac{h}{mv} \approx 3\times10^{-8}\ \text{cm}$$

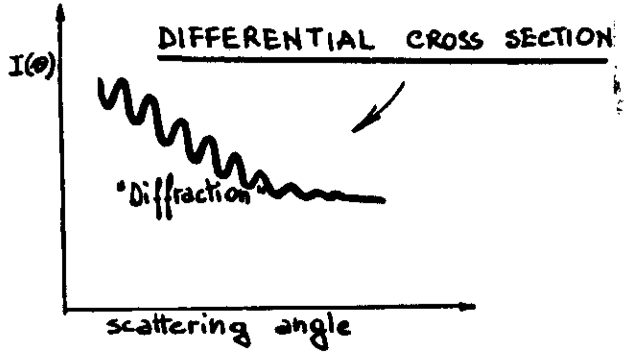
5×10^{-4} cm s^{-1}

5.10^{-23} g (air)





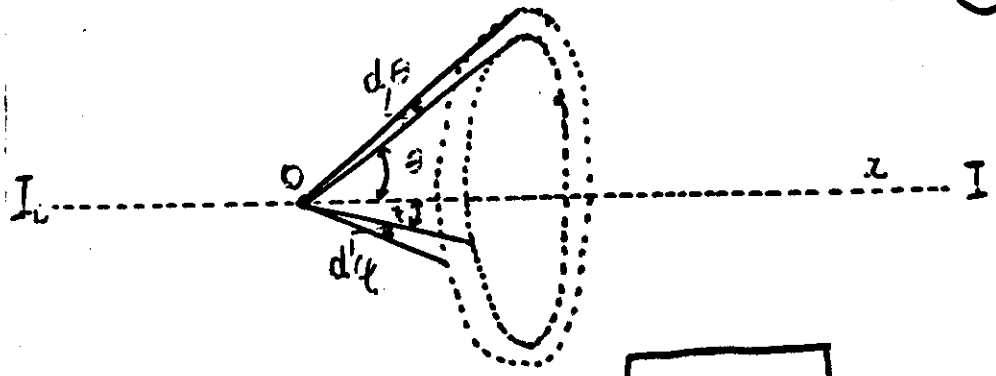




Absolute value of Q(v) ⟶ long range
"Glory" structure ⟶ ~ εR_m
"Diffraction" structure ⟶ ~ σ

Differential cross section

2



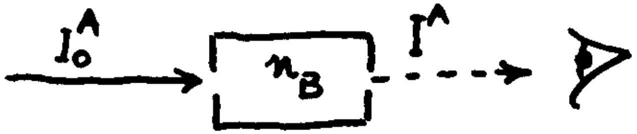
- $I(\omega)\,d\omega = \frac{d\dot{n}_c}{n_A n_B} v_{rel} V_{coll}$ $\boxed{\frac{I(\omega)}{I_0}}$
- $d\omega = 2\pi \sin\theta \, d\theta$
- $I(\omega) \longrightarrow I(\theta)$

$$\boxed{Q = \int I(\omega)\,d\omega = 2\pi \int_0^{\pi} I(\theta) \sin\theta \, d\theta}$$

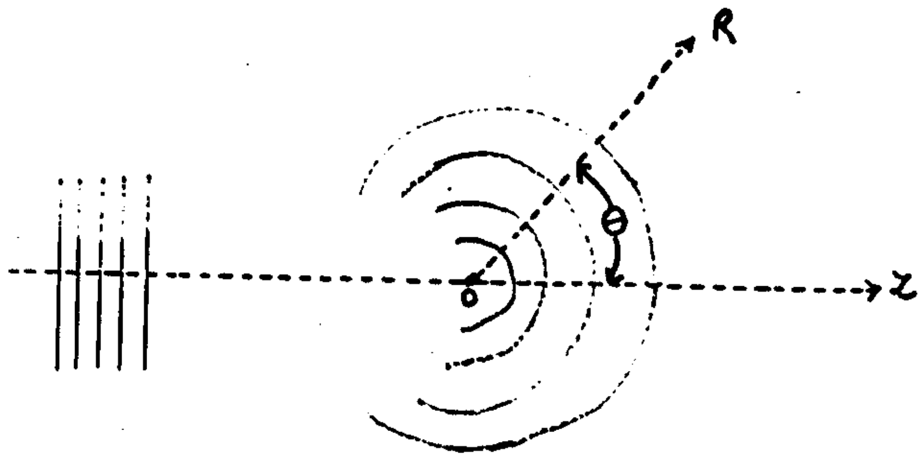
integral cross section

$I^A = I_0^A e^{-Q n_B l}$

e.g. attenuation experiment



3



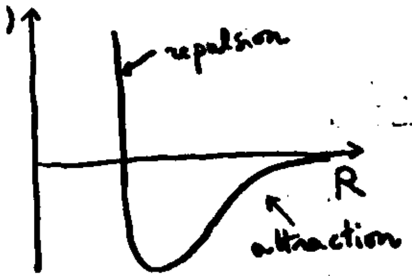
$\psi(R,\theta) \sim e^{ikz} + \frac{f(\theta)}{R} e^{ikR}$ $k = \frac{\mu v}{\hbar}$

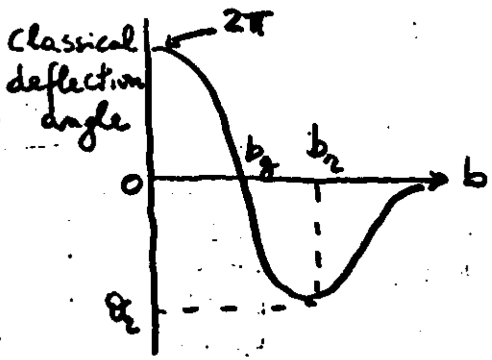
$\nabla^2 \psi + [k^2 - U(R)]\psi = 0$ $U(R) = \frac{2\mu}{\hbar} V(R)$

- $f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)\left(e^{2i\eta_l} - 1\right) P_l(\cos\theta)$
- $I(\theta) = |f(\theta)|^2 = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l+1) e^{i\eta_l} \sin\eta_l \, P_l(\cos\theta) \right|^2$

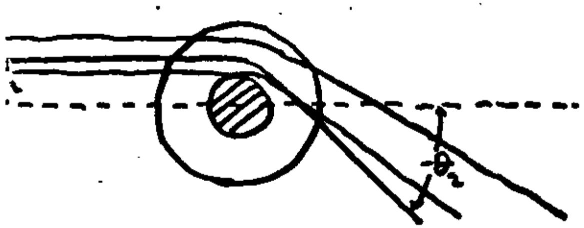
$Q = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l$

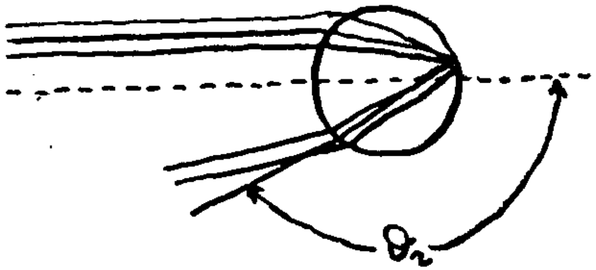
WAVE PHENOMENA IN ATOMIC SCATTERING





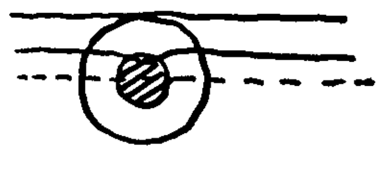
RAINBOW effect for atomic scattering





Descartes construction for RAINBOW due to water droplets

GLORY effect for atomic scattering



SEMICLASSICAL PHASE SHIFT

de Broglie wave $\left\{ \begin{matrix} \sin \\ \cos \end{matrix} 2\pi \nu t \right\}$ $\qquad \lambda_r = \dfrac{h}{\mu v_r}$

$$\eta = \int_{\text{with } V} 2\pi\nu \, dt - \int_{\text{without } V} 2\pi \nu_0 \, dt \qquad \nu = \frac{v_r}{\lambda_r} = \frac{d}{dt}$$

$$= \frac{\mu v}{\hbar} \left\{ \int_{r_0}^{\infty} \left[1 - \frac{V}{E} - \frac{b^2}{r^2} \right]^{1/2} dr - \int_b^{\infty} \left[1 - \frac{b^2}{r^2} \right]^{1/2} dr \right.$$

WKB phase shift

"High" energy: $\dfrac{V}{E} \ll 1 - \dfrac{b^2}{r^2}$

expanding the square root and

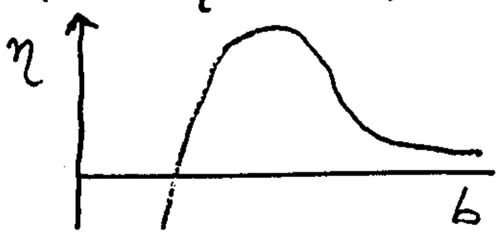
$r_0 \approx b$ ["linear" trajectory $r^2 = b^2 + v^2 t^2$]

$$\eta_{JB} = -\frac{1}{\hbar v} \int_b^{\infty} V(r) \left[1 - \frac{b^2}{r^2} \right]^{-1/2} dr$$

For $V = C_n / r^n$ closed form $\eta \propto -C_n / v / b^{n-}$

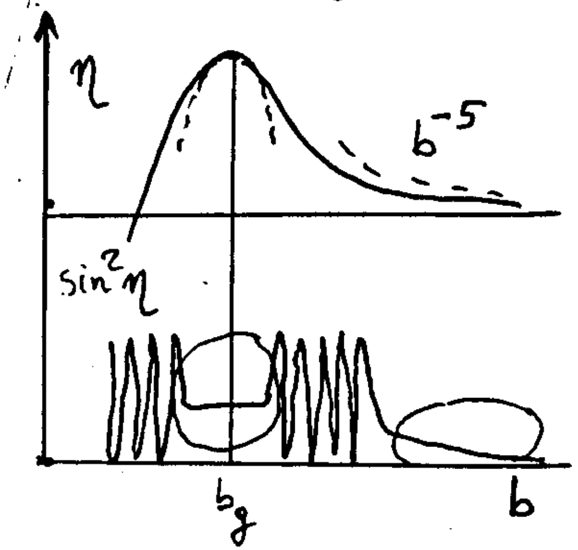
For L.J. (12,6)

$$\eta(b) = \frac{1}{v} \left[\frac{\alpha}{b^5} - \frac{\beta}{b^{11}} \right]$$



GLORY OSCILLATIONS in INTEGRAL CROSS SECTIONS

$$Q(v) = 8\pi \int_0^\infty \sin^2 \eta(v,b)\, b\, db$$



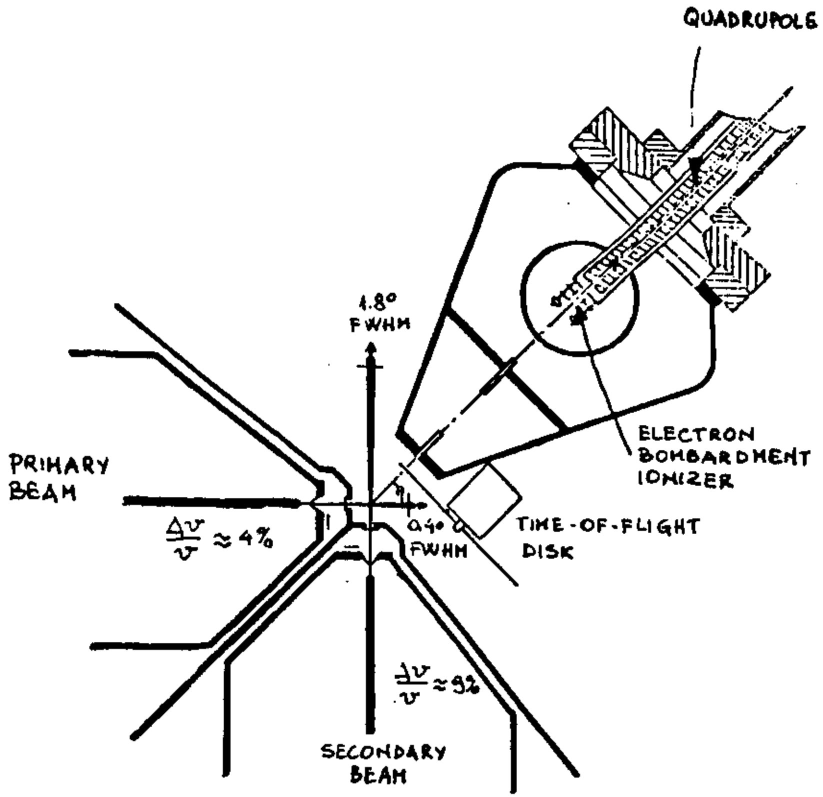
$$\eta \simeq \frac{1}{v}\left(\frac{\alpha}{b^5} - \frac{\beta}{b^{11}}\right)$$

$$Q = \overline{Q} + \Delta Q$$

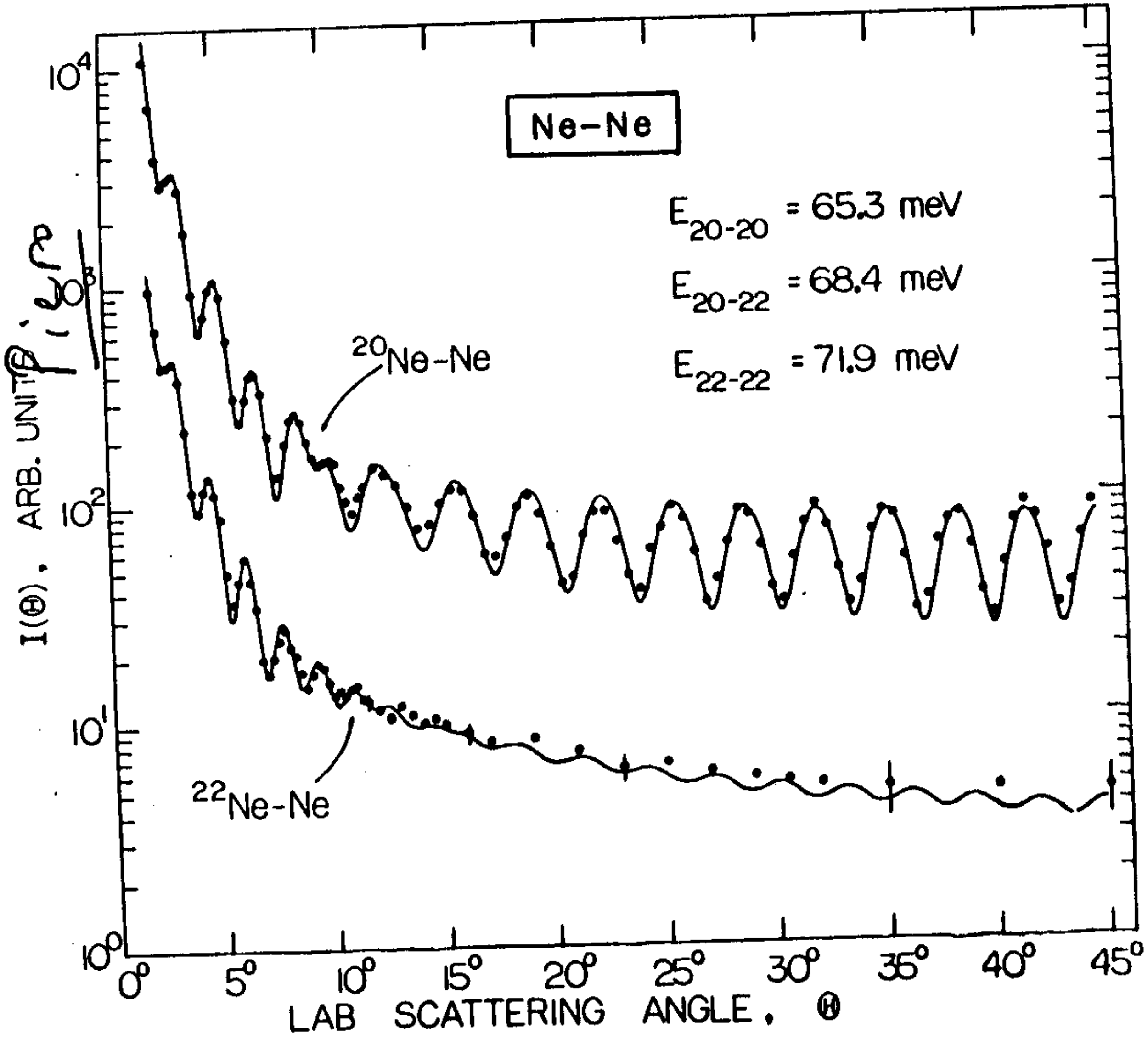
$$\overline{Q} \approx Q_{vdW} \approx 8.083\left(\frac{C_6}{\hbar v}\right)^{2/5}$$

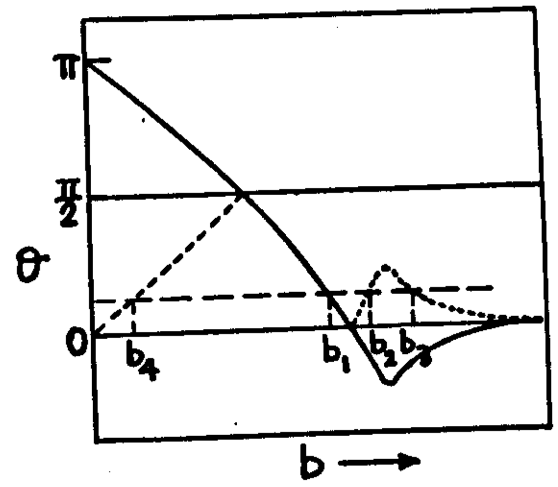
$$\Delta Q \propto -\cos\left[2\eta(b_g) - \frac{\pi}{4}\right]$$

CROSSED BEAM APPARATUS FOR DIFFERENTIAL SCATTERING CROSS SECTION



IDENTICAL PARTICLE SCATTERING (symmetry oscillations)

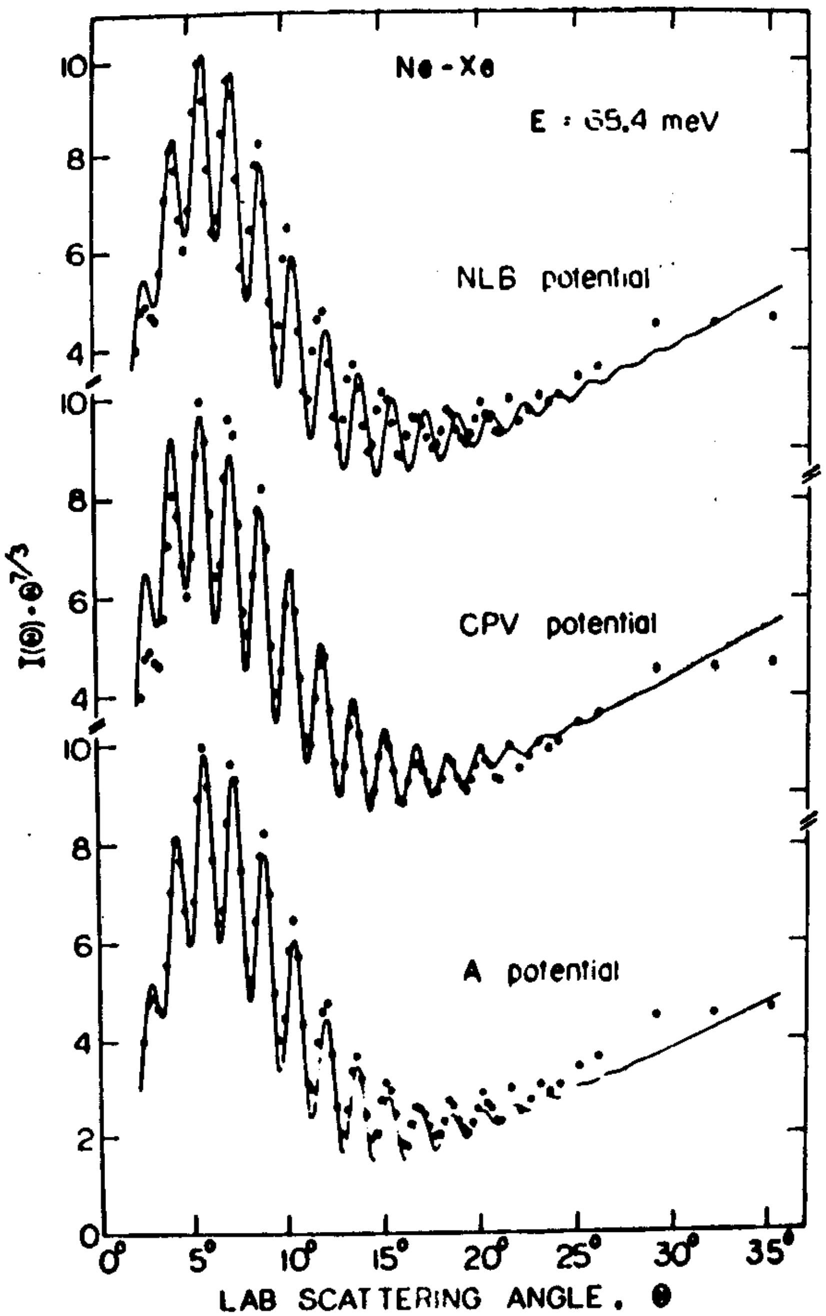


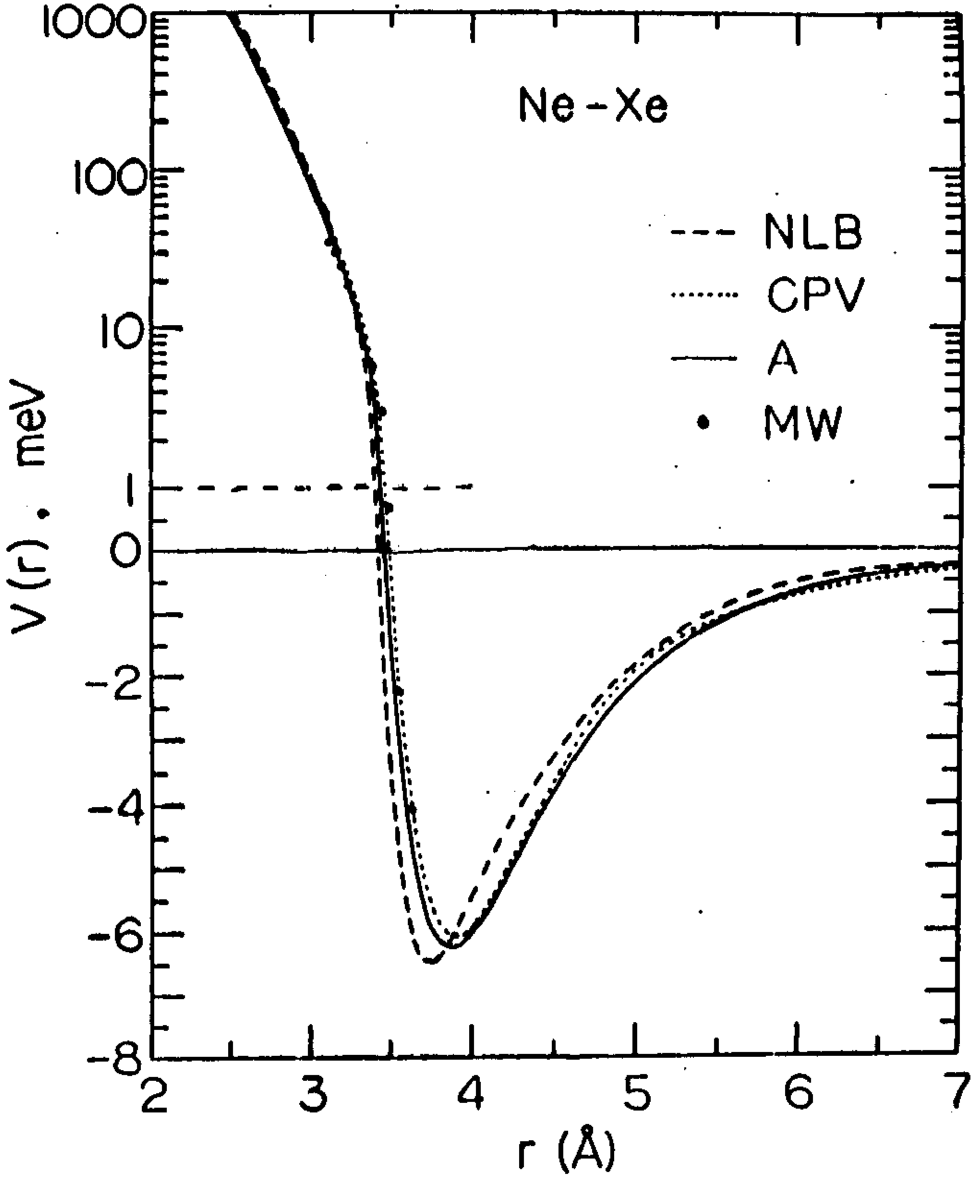


$$I(\theta) = \left| f(\theta) + f(\pi - \theta) \right|^2$$

(symmetry about $\theta = \frac{\pi}{2}$)

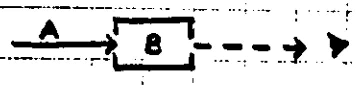
$$I(\theta) = \left| \sum_{\ell=0,2,4,\dots}^{\infty} (2\ell+1)\left(e^{2i\eta_\ell} - 1\right) P_\ell(\cos\theta) \right|^2$$


Ne-Xe
E = 65.4 meV
NLB potential
CPV potential
A potential
I(Θ)·Θ^7/3
LAB SCATTERING ANGLE, Θ


Ne-Xe
NLB
CPV
A
MW
V(r), meV
r (Å)

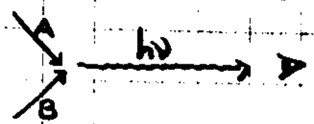
TOTAL CROSS SECTIONS

ELASTIC



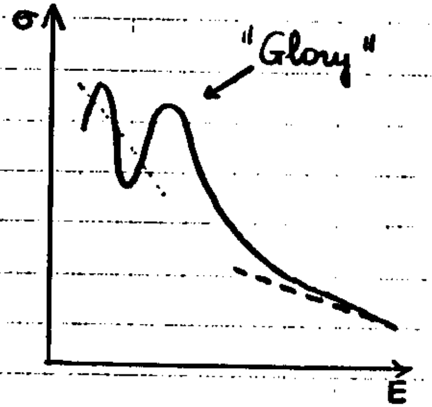
$$I_A = I_A^0 e^{-\sigma n_B l}$$

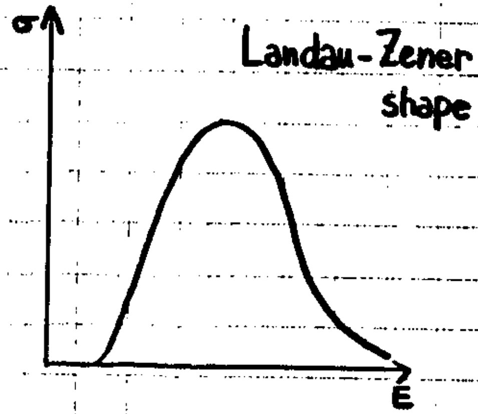
INELASTIC

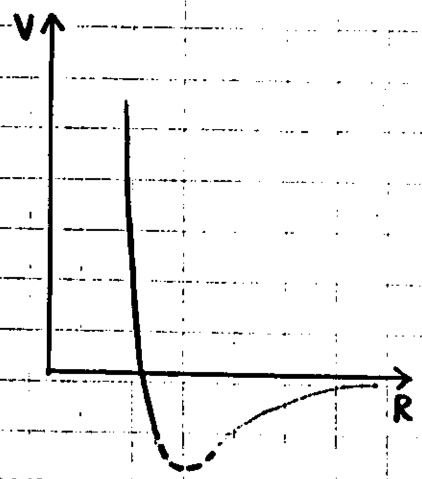


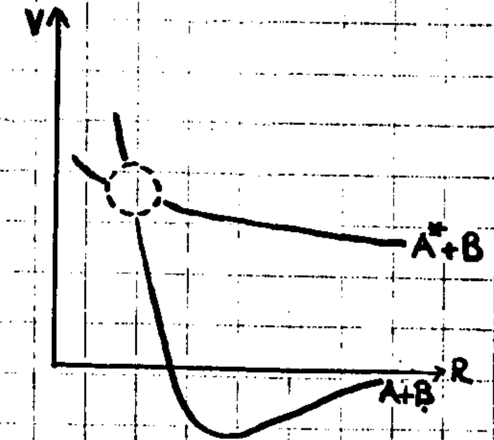
$$A + B \rightarrow A^* + B$$
$$A^* \xrightarrow{h\nu} A$$

$$I_{A^*} \propto \sigma_{A^*}$$









SEMICLASSICAL EQUATIONS

In a system of electrons & nuclei

$$H\Psi = \left\{ H_{el} + \Sigma K_{nucl} \right\} \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$H_{el}(\underset{\sim}{r}, \underset{\sim}{R}) \varphi_i(\underset{\sim}{r}, \underset{\sim}{R}) = E_i(\underset{\sim}{R}) \varphi_i(\underset{\sim}{r}, \underset{\sim}{R})$$

$\therefore$ φ_i molecular orbitals

Postulate $\underset{\sim}{R} = \underset{\sim}{R}(t)$ a classical trajectory for nuclei and expand $\Psi = \sum_i a_i(t) \varphi_i(\underset{\sim}{r}, \underset{\sim}{R}(t)) \exp\left\{-\frac{i}{\hbar}\int^t E_i(\underset{\sim}{R}(t))dt\right\}$

one gets

$$i\hbar \dot{a}_i = \sum_{j \neq i} V_{ij} a_j \exp\left\{-\frac{i}{\hbar}\int^t (E_j - E_i)dt\right\}$$

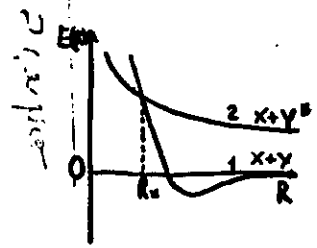
where

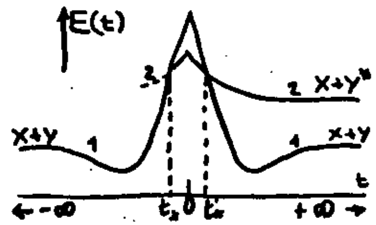
$$V_{ij} = \hbar \langle \varphi_i | \dot{\varphi}_j \rangle = \dot{R}^{-1} P_{ij}(R)$$

Adiabatic evolution on E_i described by phase shifts $\int^t E_i\,dt$, transitions (described by $|a_i(+\infty)|^2$) most likely take place when $E_j - E_i \lessapprox V_{ij}$

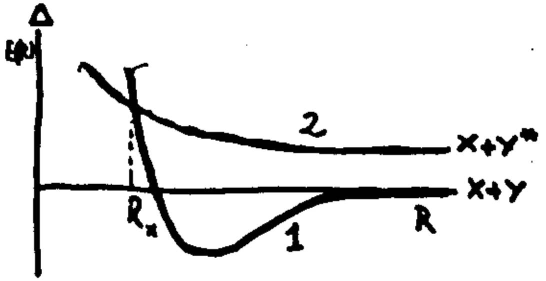
e.g.: two states, straight line trajectories

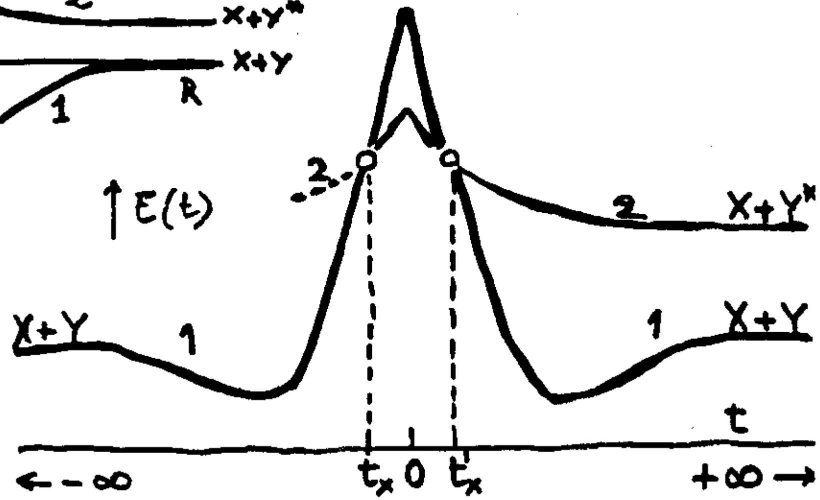
$R^2 = b^2 + v^2 t^2$.





2 STATE





LANDAU-ZENER-STÜCKELBERG (1932)

$$p(v,b) \approx \exp\left\{-\frac{2\pi V_{12}^2}{\hbar v_R \, d(E_1-E_2)/dR}\right\}_{R_x}$$

$$\gamma(v,b) \approx \pi/4$$

$$\begin{cases} i\hbar \dot{a}_1 = V_{12}\, a_2 \exp\left\{-\frac{i}{\hbar}\int^t (E_2-E_1)\,dt'\right\} \\ i\hbar \dot{a}_2 = V_{12}\, a_1 \exp\left\{+\frac{i}{\hbar}\int^t (E_2-E_1)\,dt'\right\}. \end{cases}$$

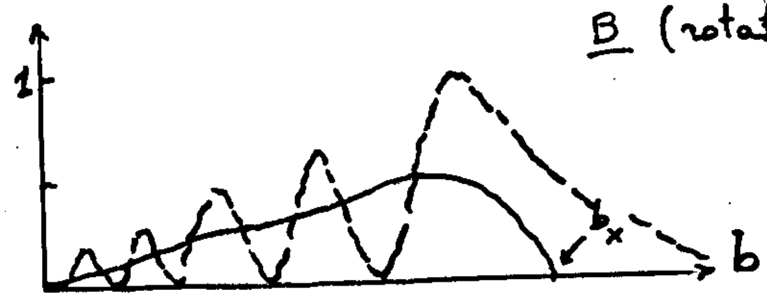
$$S_{11} = a_1(+\infty) = \left[p + (1-p)\exp\left\{-\frac{i}{\hbar}\int_{t_x}^{t'_x}(E_2-E_1)\,dt' + 2\gamma\right\}\right] \times$$
$$\times \exp\left\{-\frac{i}{\hbar}\int_{-\infty}^{+\infty} E_1\, dt'\right\}$$

$$S_{12} = a_2(+\infty) = 2i\, p^{1/2}(1-p)^{1/2} \sin\left\{-\frac{1}{2\hbar}\int_{t_x}^{t'_x}(E_2-E_1)\,dt + \gamma\right\} \times$$
$$\times \exp\left\{-\frac{i}{\hbar}\int_{-\infty}^{+\infty} E_2\, dt\right\}.$$

$$P_{12} = |a_2(+\infty)|^2 = 4\underline{p}(1-\underline{p}) \sin^2\left\{-\frac{i}{2\hbar}\int_{t_x}^{t'_x}(E_2-E_1)\,dt + \underline{\gamma}\right.$$

A (vibration-orbit, spin-orbit).

B (rotation-orbit)



..., or ..

For the process $i \to f$, $a_i(-\infty) = 1$, $a_{j \neq i}(-\infty) = 0$

$$P_{if} = |a_f(+\infty)|^2 = |S^{(\ell)}_{if}|^2 .$$

$$Q_{if} = \frac{\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1) |S^{(\ell)}_{if}|^2 \longrightarrow 2\pi \int_0^{\infty} P_{if}(v,b)\, b\, db .$$

Experiments: Alkali ion-atom

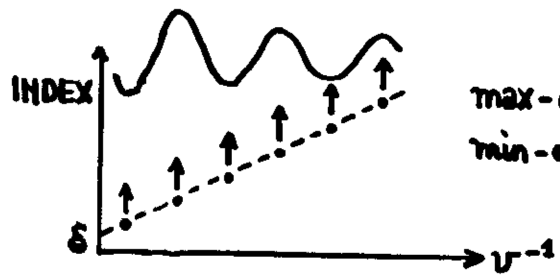
$Na^+ + Hg \to Hg^*$

interference oscillation and polarization effects

See: J. Chem. Phys. $\underline{64}$ 751 (1976)
$\underline{65}$ 5518 (1976)
$\underline{68}$ 1499 (1978)

② PHENOMENOLOGY OF OSCILLATIONS IN TOTAL CROSS SECTIONS

$$\Delta Q = -A(v) \cos\left[\frac{\langle \varepsilon \tau \rangle}{v} + \delta\right]$$

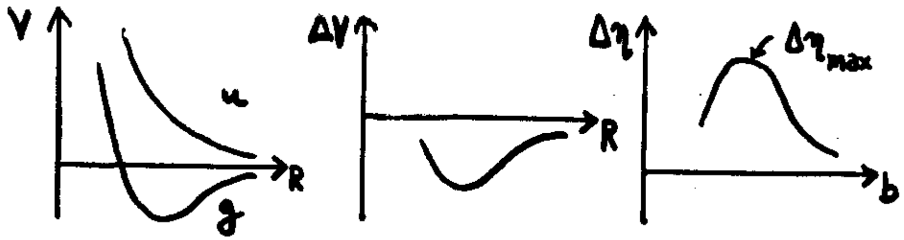


max-odd
min-even

1. Elastic "Glory"

$\delta = -\pi/4$ $\quad \frac{\langle \varepsilon \tau \rangle}{v} = 2\eta_{max}$ $\quad A(v) \propto v^{1/2}$

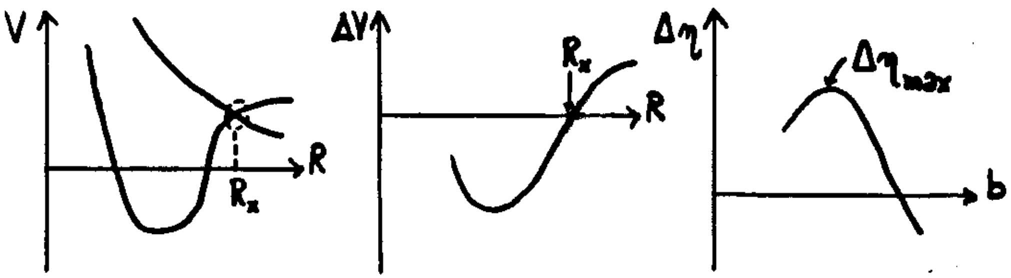
2. Resonant Charge-Transfer



$\delta = -\pi/4$ $\quad \frac{\langle \varepsilon \tau \rangle}{v} = 2\Delta\eta_{max}$ $\quad A(v) \propto v^{-1/2}$

$$\Delta Q = -A(v)\cos\left[\frac{\langle \varepsilon\tau \rangle}{v} + \delta\right]$$

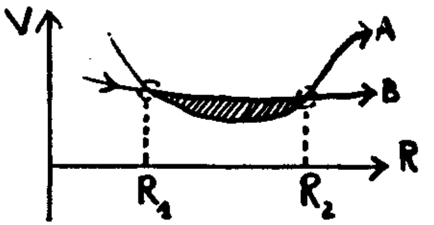
3. Inelastic "Glory"



$\delta \approx +\pi/4$ $\qquad \frac{\langle \varepsilon\tau \rangle}{v} = 2\Delta\eta_{max}$

$A(v)$ contains the probability of a nonadiabatic transition at R_x

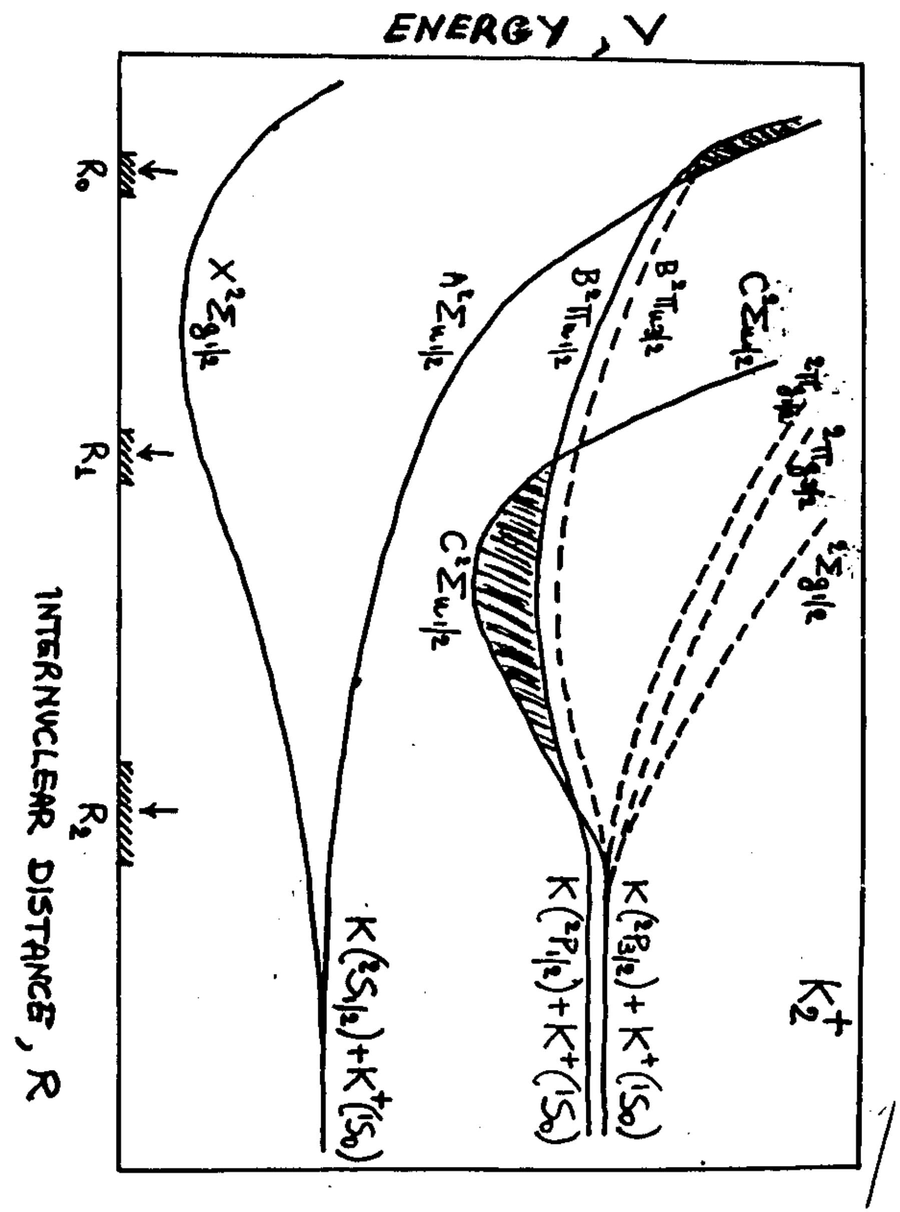
4. Long range interferences

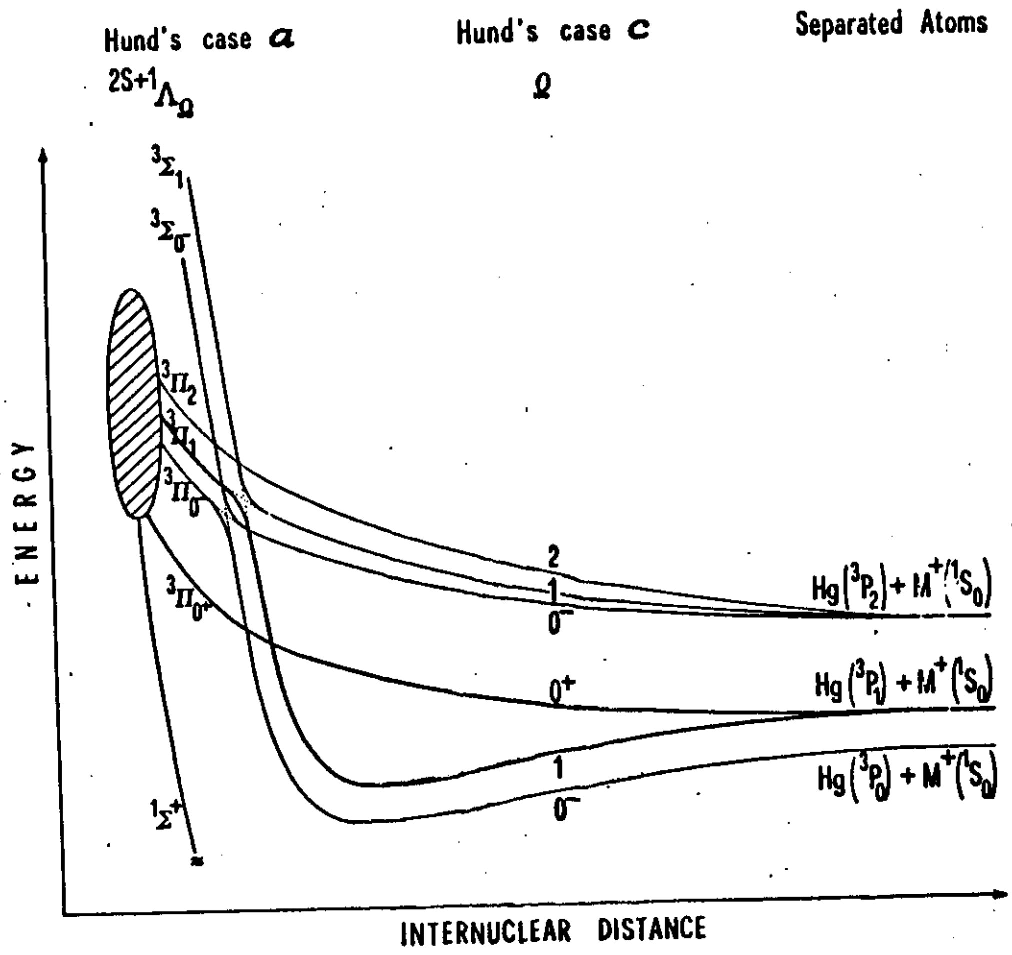


$\left.\begin{array}{ll} \Delta Q_A & \delta \approx +\pi/2 \\ \Delta Q_B & \delta \approx -\pi/2 \end{array}\right\}$ antiphase

$\langle \varepsilon\tau \rangle \approx$ shaded area

$A(v)$ contains the transition probabilities at R_1 and R_2





~~Fig. 12~~ 27

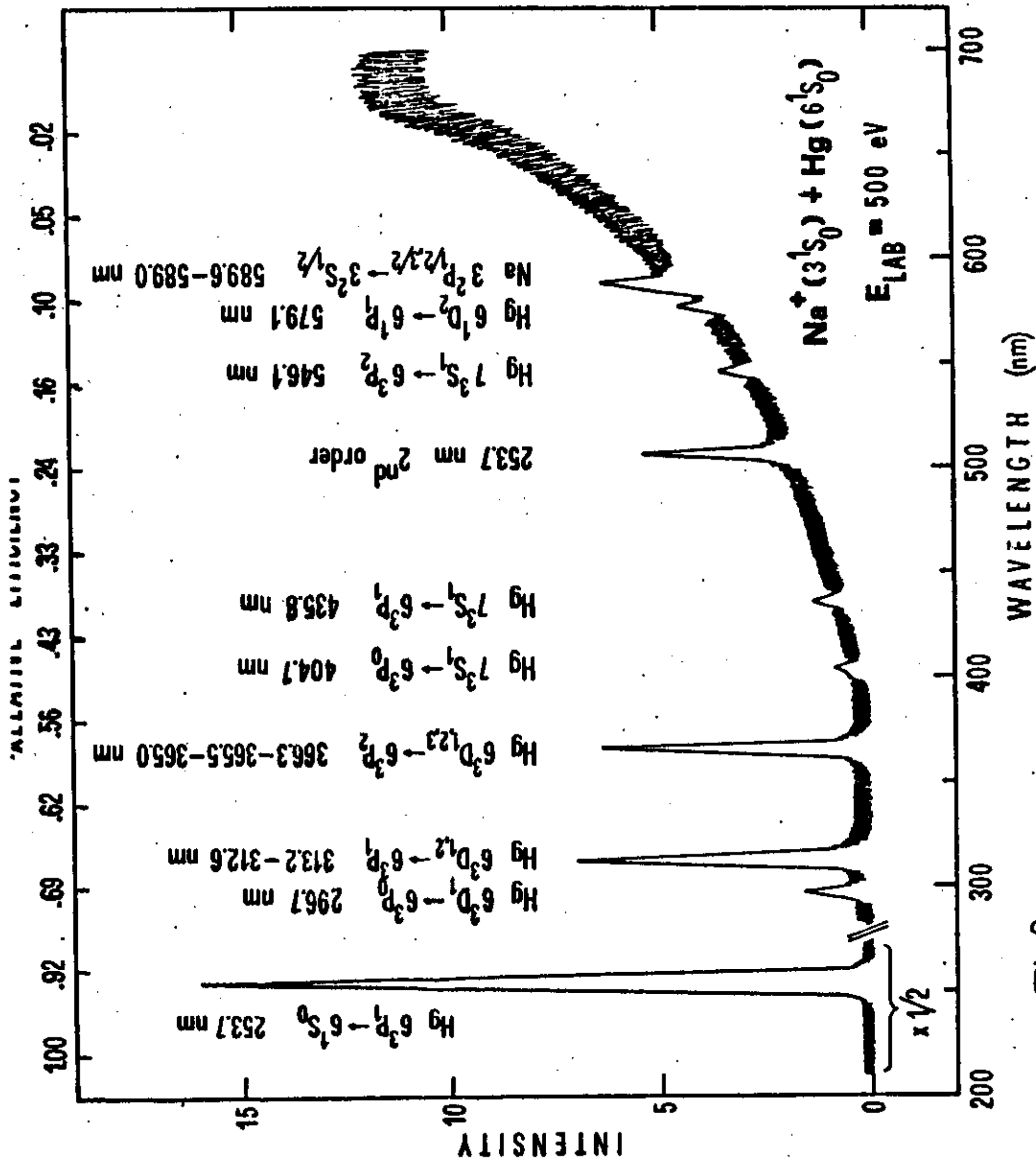


Fig. 2

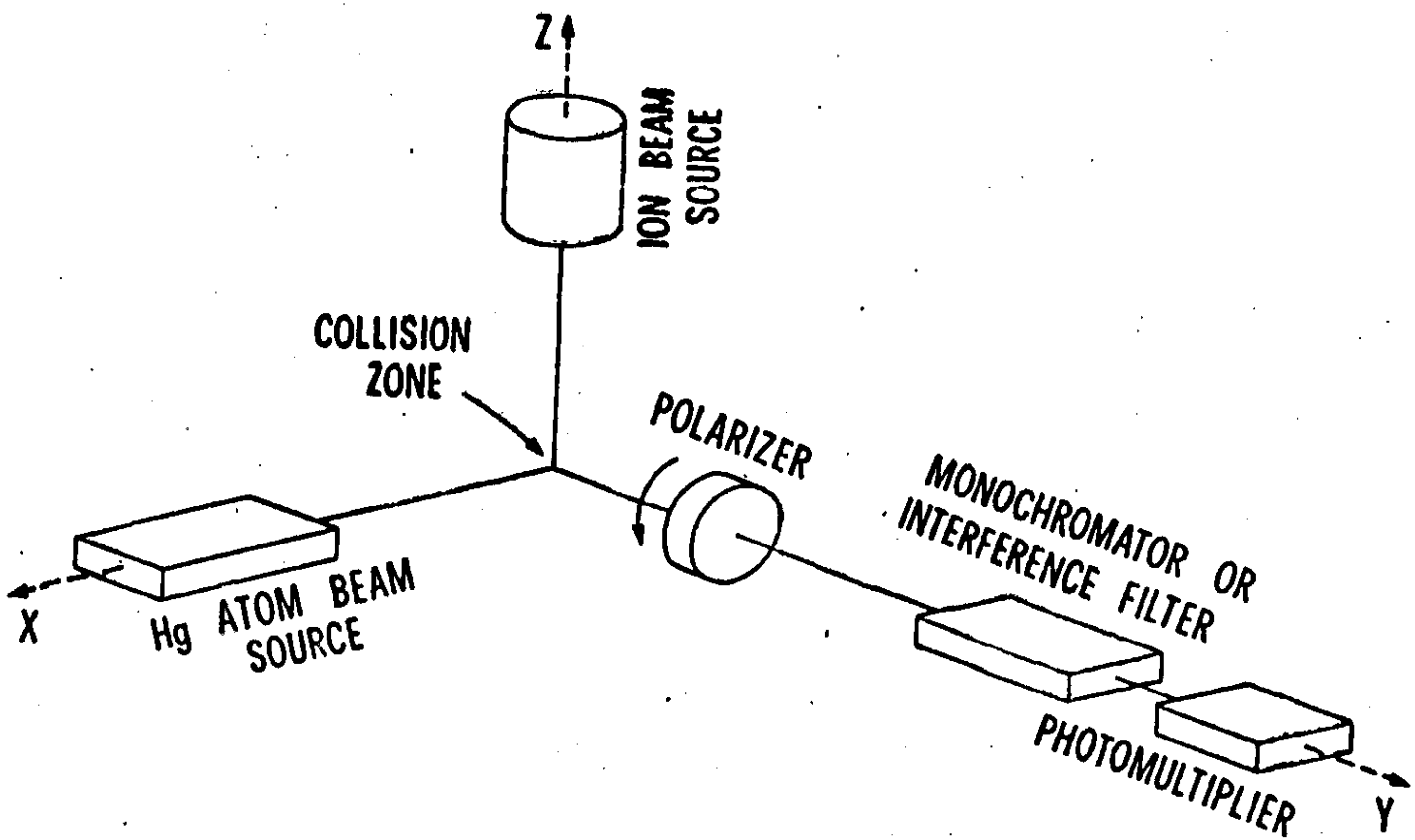

Z
ION BEAM SOURCE
COLLISION ZONE
POLARIZER
MONOCHROMATOR OR INTERFERENCE FILTER
X
Hg ATOM BEAM SOURCE
PHOTOMULTIPLIER
Y

Fig. 1

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Polarization fraction

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

Corrections for anisotropy for emission cross sections

$$Q(m \to n) = \frac{3 - P}{3(1 - P\cos^2\vartheta)}\, Q(m \to n, \theta)$$

Cascade contributions to excitation cross sections

$$Q(j) = \sum_{j > j'} Q(j \to j') - \sum_{j'' > j} Q(j'' \to j)$$

For

$$M^+(^1S_0) + Hg(^1S_0) \to M^+(^1S_0) + Hg(^3P_1)$$

$$Q(6^3P_1) = \frac{3-P}{3}\, Q(\underbrace{6^3P_1 \to 6^1S_0}_{253.7\,\mathrm{nm}}, \pi/2)$$

$$- Q(\underbrace{7^3S_1 \to 6^3P_1}_{313\,\mathrm{nm}}) - Q(\underbrace{6^3D_{1,2} \to 6^3P_1}_{436\,\mathrm{nm}})$$

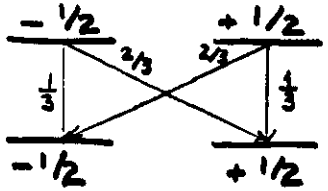
$\Delta m_j = 0 \Rightarrow I_{\parallel}$

$\Delta m_j = \pm 1 \Rightarrow I_{\perp}$

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

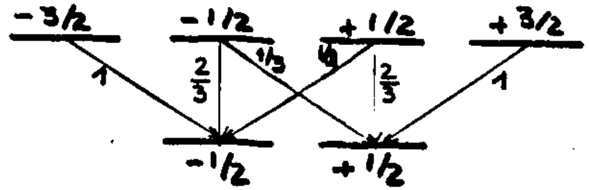
$j \to j'$

$\frac{1}{2} \to \frac{1}{2}$



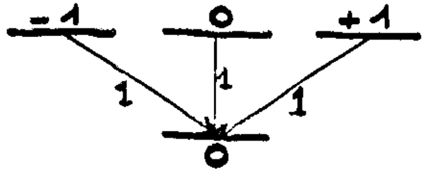
$P = 0$

$\frac{3}{2} \to \frac{1}{2}$



$$P = \frac{3(Q_{1/2} - Q_{3/2})}{3Q_{3/2} + 5Q_{1/2}}$$

$1 \to 0$



$$P = \frac{Q_0 - Q_1}{Q_0 + Q_1}$$

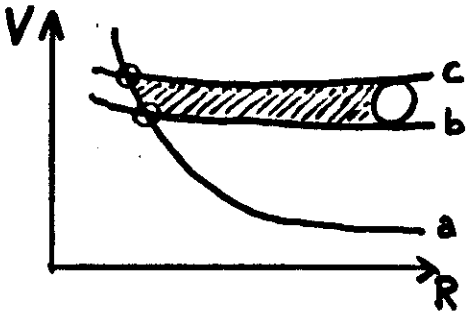
For $Hg(^3P_1 \to {}^1S_0)$ [70% $I=0$; 17% $I=\frac{1}{2}$; 13% $I=\frac{3}{2}$]

$$Q(^3P_1) = Q_{-1} + Q_0 + Q_1 = Q_0 + 2Q_1$$

$$P = 0.70 \cdot \frac{Q_0 - Q_1}{Q_0 + Q_1} + 0.17 \cdot \frac{3(Q_0 - Q_1)}{7Q_0 + 11Q_1} + 0.13 \cdot \frac{111(Q_0 - Q_1)}{337Q_0 + 563Q_1}$$

(6)

- Long-range interference model for oscillations in total inelastic cross sections



$$Q_{ab} = \bar{Q}_{ab} + \Delta Q$$
$$Q_{ac} = \bar{Q}_{ac} - \Delta Q$$
$$\Delta Q = A(v)\cos\left[\frac{\langle \varepsilon_R \rangle}{\hbar v} + \delta\right]$$

- Parametrize

$$Q_0 = \bar{Q}_0 + \Delta Q_0$$
$$Q_1 = \bar{Q}_1 + \Delta Q_1$$

- Take

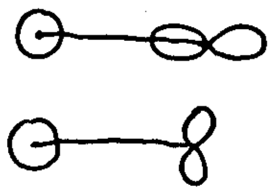
$\bar{Q}_0 \approx \bar{Q}_1$ (same threshold and similar average behavior)

$\Delta Q_0 \approx -2\Delta Q_1$ (flux lost by interference in Q_0 is divided equally between Q_1 and Q_{-1}, and viceversa)

- Deduce the interference term

OPEN SHELL ATOMS
BEYOND SPHERICAL INTERACTIONS

Simplest example : S atom + P atom
e.g.



V_Σ

V_π

Define $V_0 = \frac{1}{3}V_\Sigma + \frac{2}{3}V_\pi$ spherical

$V_2 = \frac{5}{3}(V_\Sigma - V_\pi)$ anisotropy

fine structure transitions, orientation and polarization effects determined by electrostatic interaction, spin-orbit and Coriolis coupling

<u>Theory</u> : Angular Momentum Coupling Schemes (Hund's cases)
J. Chem. Phys. <u>73</u>, 1165 (1980

Decoupling Approximations...
J. Chem. Phys. <u>73</u>, 1173 (198

Orientation and Polarization Effects
Nuovo Cim. <u>63B</u>, 7 (1981)

<u>Experimental</u> : O-Atoms (^3P) + Rare Gas
J. Chem. Phys. <u>73</u>, 1181 (1980)

F-Atoms (^2P) + Xenon
Chem. Phys. Lett. ...

ATOM-ATOM ELECTROSTATIC INTERACTION

$$V = \sum_\mu v_\mu(R)\, P_\mu(\cos\theta)$$

Mies (1973) Reid-Dalgarno (1969)

Generaliz'n to any L (JCP 1980)

$$v_\Lambda = \sum_\mu \langle L0, \mu 0 | L0\rangle \langle L\Lambda, \mu 0 | L\Lambda\rangle v_\mu$$

or

$$v_\mu = \sum_\Lambda \frac{(2\mu+1)\langle L\Lambda, \mu 0 | L\Lambda\rangle}{(2L+1)\langle L0, \mu 0 | L0\rangle} v_\Lambda$$

Explicitly, $L = 1$ (P atom)

$$v_\Sigma = v_0 + \frac{2}{5} v_2 \qquad v_\pi = v_0 - \frac{1}{5} v_2$$

or

$$v_0 = \frac{1}{3} v_\Sigma + \frac{2}{3} v_\pi \qquad v_2 = \frac{5}{3}(v_\Sigma - v_\pi)$$

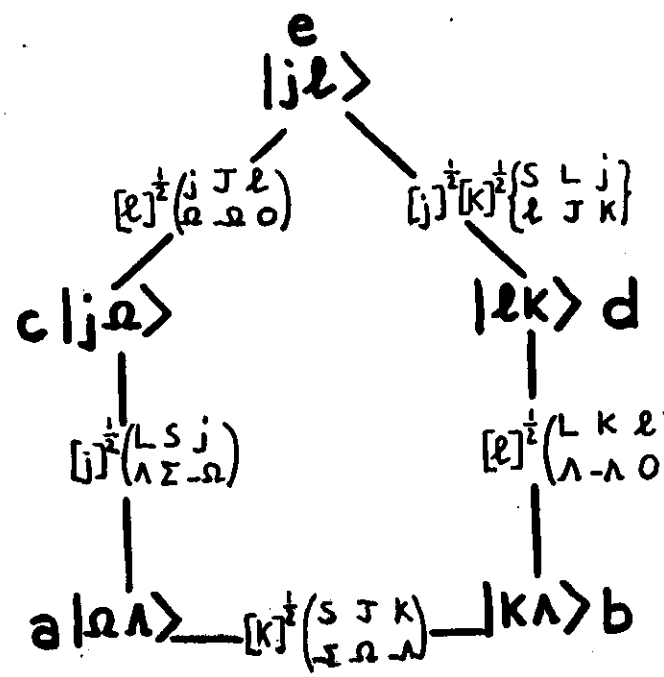
$L = 2$ (D atom)

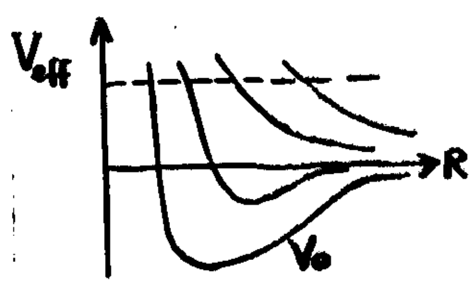
$$v_\Sigma = v_0 + \frac{2}{7} v_2 + \frac{2}{7} v_4 \qquad v_\pi = v_0 + \frac{1}{7} v_2 - \frac{4}{21} v_4$$

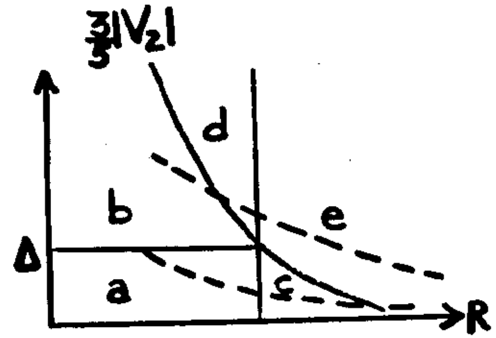
$$v_\Delta = v_0 - \frac{2}{7} v_2 + \frac{1}{21} v_4$$

$$v_0 = \frac{1}{5}(v_\Sigma + 2 v_\pi + 2 v_\Delta) \qquad v_2 = (v_\Sigma - v_\Delta) + (v_\pi - v_\Delta)$$

$$v_4 = \frac{9}{5}(v_\Sigma - v_\pi) + \frac{3}{5}(v_\Delta - v_\pi)$$







Δ = spin-orbit splitting

$$V_0 = \frac{1}{3}(V_\Sigma + 2V_\pi)$$

$$V_2 = \frac{5}{3}(V_\Sigma - V_\pi)$$

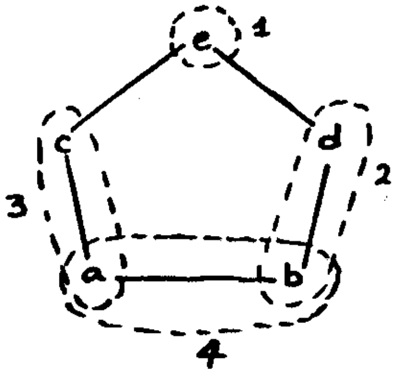
DECOUPLING SCHEMES

(1) $\underset{\sim}{V} = v_0 \underset{\sim}{1}$ atomic elastic
total decoupling in case (e)

(2) $\underset{\sim}{\mathcal{E}} = \mathcal{E}_0 \underset{\sim}{1}$ K-conserving (spin uncoupling)
partial decoupling cases (d) or (b)

3) $\underset{\sim}{\ell}^2 = \ell_0(\ell_0+1)\underset{\sim}{1}$ Ω-conserving (cf. j_z conserving)
partial decoupling cases (a) or (c)

4) (2) + (3) molecular elastic
total decoupling cases (a) or (b)



Angular momentum	Spin orbit	Routes
High	Low	(e) $\leftrightarrow$ (d) $\leftrightarrow$ (b)
Low	High	(e) $\leftrightarrow$ (c) $\leftrightarrow$ (a) $\leftrightarrow$ (b)

atomic $\leftrightarrow$ molecular representations via
space fixed $\leftrightarrow$ body fixed frame transformations

For each J: DIABATIC REPRESENTATIONS

$$\left[\left(\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + E\right)\underset{\sim}{1} - \underset{\sim}{U}(R)\right]\underset{\sim}{u}(R) = 0$$

$$\underset{\sim}{U} = \underset{\sim}{\mathcal{E}} + \frac{\hbar^2 \underset{\sim}{\ell}^2}{2\mu R^2} + \underset{\sim}{V}(R)$$

$\underset{\sim}{\mathcal{E}}$ eigenvalues $\mathcal{E}_j$ where $\vec{j} = \vec{L} + \vec{S}$

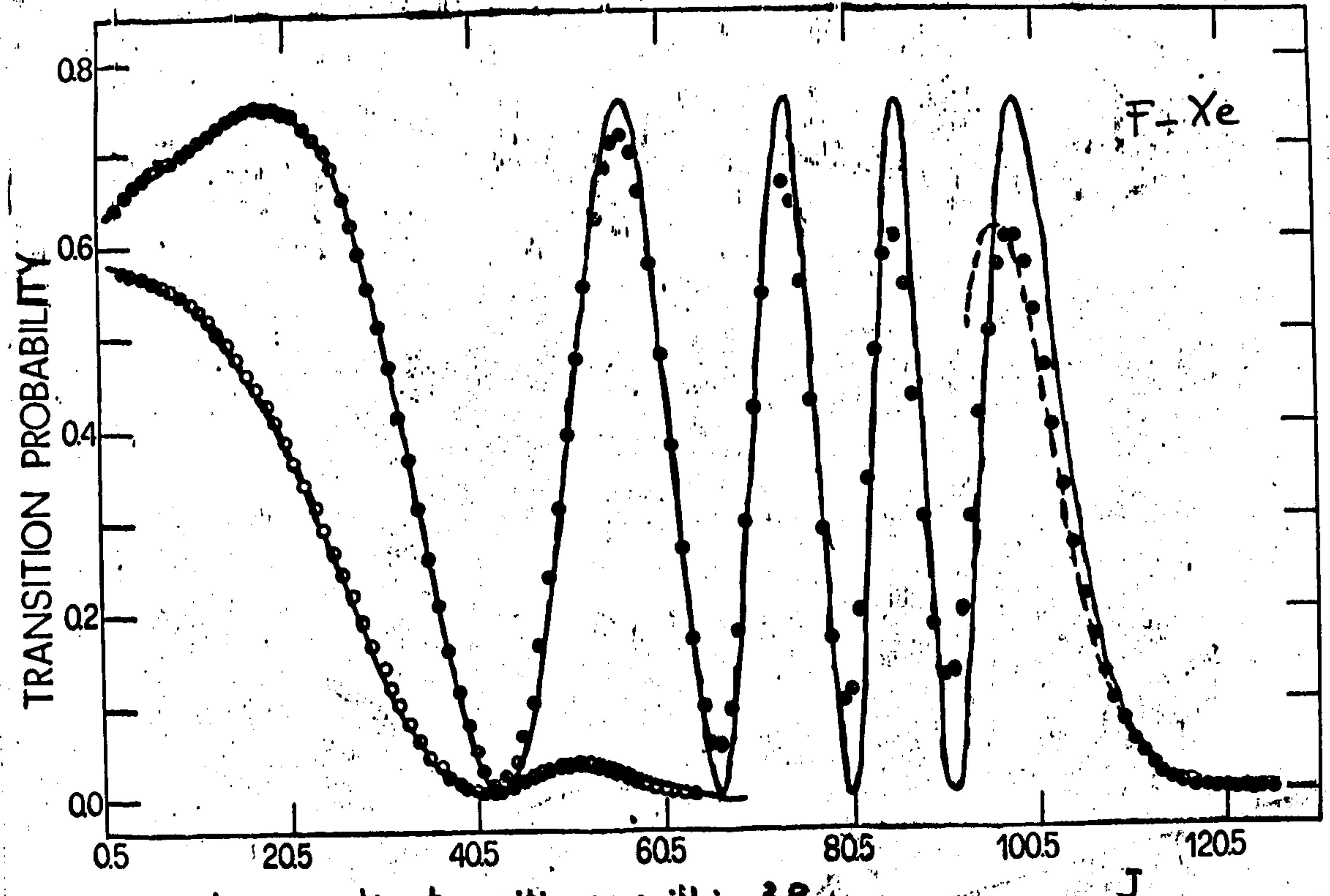
$\underset{\sim}{\ell}^2$ " $\ell(\ell+1)$ " $\vec{\ell} = \vec{J} - \vec{j}$

$\underset{\sim}{V}$ " v^s_Λ " Λ = projection of $\vec{L}$ on $\vec{R}$

case	represent'n	$\underset{\sim}{\mathcal{E}}$	$\underset{\sim}{\ell}^2$	$\underset{\sim}{V}$
e)	$\lvert j\ell\rangle$	diag.	diag.	not diag.
c)	$\lvert j\Omega\rangle$	diag.	diag.	block diag.
a)	$\lvert \Omega\Lambda\Sigma\rangle$	block diag.	not diag.	diag.
b)	$\lvert K\Lambda\rangle$	block diag.	block diag.	diag.
d)	$\lvert \ell K\rangle$	not diag.	block diag.	block diag.

Angular momenta J (total), L (electronic orbital), S (electronic spin) are conserved during the collision

$$\vec{j} = \vec{L} + \vec{S}$$
$$\vec{\ell} = \vec{J} - \vec{j}$$
$$\vec{K} = \vec{J} - \vec{S} = \vec{\ell} + \vec{L}$$



●●● Exact magnetic transitions within $^2P_{3/2}$
○○○ Exact $^2P_{3/2} \leftrightarrow {}^2P_{1/2}$ transitions
—— Ω conserving approximations ---- j conserving approximation

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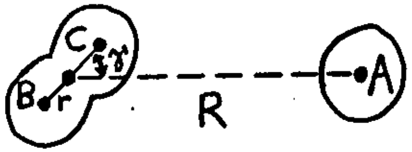
ATOM – DIATOM INTERACTION



$V(R,\gamma)$

$$V(R,\gamma) = V_0(R) + V_1(R)\cdot P_1(\cos\gamma) + V_2(R)\cdot P_2(\cos\gamma) + \dots$$

$$= \varepsilon(\gamma)\cdot f(x) \qquad , \quad x = \frac{R}{R_m(\gamma)}$$

where :

$$\varepsilon(\gamma) = \bar{\varepsilon}\,[\,1 + A_1\cdot P_1(\cos\gamma) + \underline{A_2\cdot P_2(\cos\gamma)} + \dots]$$

$$R_m(\gamma) = \bar{R}_m[\,1 + B_1\cdot P_1(\cos\gamma) + \underline{B_2\cdot P_2(\cos\gamma)} + \dots]$$

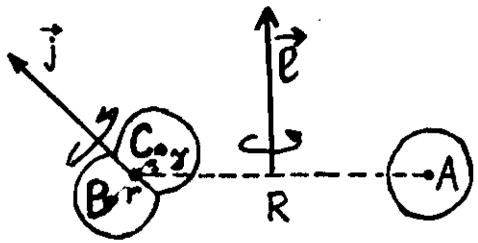
ANISOTROPY
- Inelastic cross sections
- Total (elastic + inelastic) differential cross sections

SPHERICAL
- Total diff. cross sections
- Total integral cross sections
- Second virial coefficient
- Viscosity coefficient
- Diffusion . coefficient

Approximate schemes of analysis

ATOM – DIATOM INTERACTION (A+BC)

$$\left[-\left(\frac{\hbar^2}{2\mu}\right)\underset{\sim}{1}\frac{d^2}{dR^2} + \underset{\sim}{U}^J(R)\right]\vec{\psi} = E\,\underset{\sim}{1}\,\vec{\psi}$$



$$\underset{\sim}{U}(R) = \underbrace{\frac{\hbar^2}{2\mu_{BC}r^2}\underset{\sim}{j}^2}_{\text{rotational term}} + \underbrace{\frac{\hbar^2}{2\mu R^2}\underset{\sim}{\ell}^2}_{\text{centrifugal term}} + \underbrace{\underset{\sim}{V}(\vec{R},\gamma)}_{\text{electrostatic term}}$$

Usual approximations

CENTRIFUGAL SUDDEN (CS) $\quad \ell(\ell+1) \simeq \bar{\ell}(\bar{\ell}+1)$

ENERGY SUDDEN (ES) $\quad j(j+1) \simeq \bar{j}(\bar{j}+1)$

INFINITE ORDER SUDDEN (IOS) $\quad$ IOS = CS + ES

ADIABATIC (within CS) $\quad$ (Aquilanti, Beneventi, Grossi, Vecchiocattivi, J.C.P. 89, 751 (1988))

Near separability

Atom-atom, internuclear distance R, other distances $\{r\} = r_{12}, r_{13}, \dots$

$$\Big(-\frac{1}{2\mu}\Delta^{(3)} \underbrace{-\frac{1}{2m_i}\sum_i \Delta_i^{(3)} + V(R,r)}_{H_{el}(R,r)} - E\Big)\Psi = 0$$

$$H_{el}\,\varphi_i^a(R,r) = \varepsilon_i^a(R)\,\varphi_i^a(R,r)$$

$\left.\begin{array}{l}\varphi_i^a \text{ eigenf.} \\ \varepsilon_i^a \text{ curves}\end{array}\right\}$ adiabatic, parametrically depending on R

$$\Psi = \sum \varphi_i^a(r,R)\,F_i^a(R)$$

$$\Big(-\frac{1}{2\mu}\Big(\frac{d}{dR} + \underline{P}(R)\Big)^2 + \underline{\varepsilon}(R) - E\Big)\,\underline{F}^a(R) = 0$$

$$P_{ij}(R) = \Big\langle \varphi_i^a, \frac{d}{dR}\varphi_j^a \Big\rangle = \frac{1}{\varepsilon_i - \varepsilon_j}\Big\langle \varphi_i^a \frac{dV}{dR}\varphi_j^a \Big\rangle,$$

$$= -P_{ji}(R) \quad \text{(Hellmann - Feynman)}$$

Elimination of first derivatives

$$\underline{F}^a = \underline{C}\,\underline{F}^d \qquad \underline{C}^{-1}\underline{C}' = \underline{P}$$

$$\Big[-\frac{1}{2\mu}\frac{d^2}{dR^2} + \underline{V}^d - E\Big]\underline{F}^d(R) = 0 \qquad \underline{V}^d = \underline{C}\,\varepsilon\,\underline{C}^{-1}$$

diabatic representation, -
not unique

-nelastic problem: solve first in $r, \theta_i, \dots$ parametrically in R, obtaining $\varepsilon_{iv}^J(R)$, $\Phi_{iv}^J(R,r$

Integrate coupled equations in R.

Rearrangement problem: brute force: coordinates changes during the integration.

Does it exist a near-separable coordinate for rearrangement scattering or in general for any many-body problem, even when one cannot use a manifest difference in masses, as in Born-Oppenheimer separation?

Helium-like atom  $M \approx m \approx m_e$

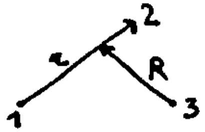
Fano, Macek, Klar: $\boxed{\rho = (r_1^2 + r_2^2)^{1/2}}$

hyperradius of a 6-d sphere

For generalization to any masses, parametrization of angular coordinates, and hyperspherical expansion of the potential energy function, see
V. Aquilanti, G. Grossi and A. Laganà,
J. Chem. Phys. $\underline{76}$, 1587 (1982)

For three particles, $V = V(r_{12}, r_{13}, r_{23})$
(9 coord. − 3 c.m. coord ⇒ 6 coord.)

Jacobi $\quad m = \dfrac{m_1 m_2}{m_1 + m_2}$; $\quad M = \dfrac{m_3(m_1 + m_2)}{m_1 + m_2 + m_3}$



$$\left\{-\frac{1}{2M}\nabla^{(3)}_{\vec{R}} - \frac{1}{2m}\nabla^{(3)}_{\vec{r}} + V - E\right\}\psi = 0$$

$$\vec{R} = (R, \theta_1, \varphi_1) \qquad \vec{r} = (r, \theta_2, \varphi_2)$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

(orbital) $Y_{\ell m_\ell}(\theta_1 \varphi_1)$ $\qquad$ $Y_{j m_j}(\theta_2 \varphi_2)$ (rotat'l.)

Conservation of the total angular momentum
$$\vec{J} = \vec{j} + \vec{\ell}$$

bipolar harmonic $\mathcal{Y}^{JM}_{j\ell}(\theta_1 \varphi_1 \theta_2 \varphi_2) =$
$$= \sum_{m_j m_\ell} \langle \ell m_\ell\, j\, m_j | JM \rangle Y_{\ell m_\ell} Y_{j m_j}$$

Expanding ψ in series of $\mathcal{Y}$

$$\left\{-\frac{1}{2M}\frac{\partial^2}{\partial R^2} - \frac{1}{2m}\frac{\partial^2}{\partial r^2} + \frac{\ell(\ell+1)}{2MR^2} + \frac{j(j+1)}{2mr^2} - E\right\} F^J_{j\ell} = \sum_{j'\ell'} V^J_{j\ell j'\ell'} F^J_{j'\ell'}$$

$$V^J_{j\ell j'\ell'}(r, R) = \langle \mathcal{Y}^{JM}_{j\ell}\; V \;\mathcal{Y}^{JM}_{j'\ell'} \rangle$$ M-independent (Wigner-Eckart)

$$V(\vec{r}, \vec{R}) = \sum_{j\ell} V_{j\ell}(r, R)\, \mathcal{Y}^{JM}_{j\ell}(\theta_1 \varphi_1 \theta_2 \varphi_2)$$

(This expansion of the potential in harmonics allo analytical evaluation of matrix elements (Racah))

Dynamics on Molecular Potential Energy Surfaces

or

how quantum mechanics avoids classical chaos and catastrophes

the Perugia view

"... to my mind, the goal of atomic and molecular collision physics is the elucidation of elementary physico-chemical processes in quantum mechanical terms ..."

Ugo Fano

quoted in Europhysics News August '86

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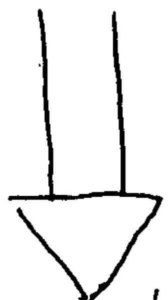
kinetic energy $\qquad\qquad$ Potential energy

classical $\qquad\qquad$ empirical

semiclassical $\qquad\qquad$ semiempirical

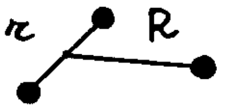
quantum $\qquad\qquad$ ab initio

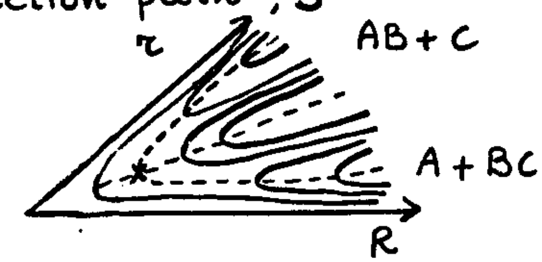


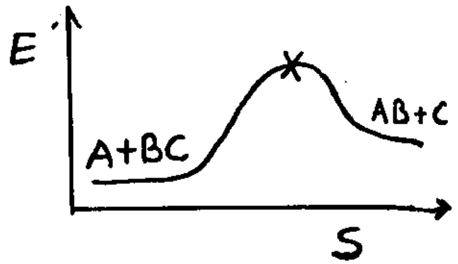
chemical kinetics

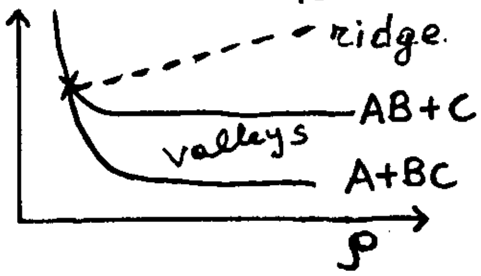
Kinetic radius, ρ

- (hyper) radius of $3(n-1)$ dim. sphere
  - proportional to the n-body moment of inertia
  - adiabatically separable variable (except ridges where nonadiabatic transitions are localized)
  - alternative to reaction path, S





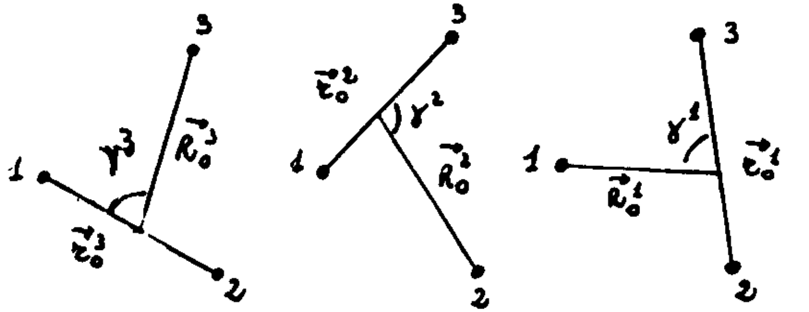




choice of ρ allows to treat

- large curvature (small m transferred)
- reaction $A+BC \to AB+C$, $A+BC \to AC+B$ bifurcation; $A+BC \to A+B+C$ dissociation
- quantization on hypersphere and continuum discretization

HYPERSPHERICAL COORDINATES



Alternative Jacobi vectors

$$\underline{T} = -\frac{\hbar^2}{2\mu_{k,je}}\Delta_{\vec R_0^k} - \frac{\hbar^2}{2\mu_{je}}\Delta_{\vec r_0^k}$$

$$\mu_{k,je} = \frac{m_k(m_j+m_e)}{m_k+m_j+m_e} \qquad \mu_{je} = \frac{m_j m_e}{m_j+m_e}$$

$$\vec R^k = a_k \vec R_0^k \qquad \vec r^k = a_k^{-1}\vec r_0^k$$

$$a_k = (\mu_{k,je}/\mu_{je})^{1/4}$$

3-body reduced mass

$$\underline{T} = -\frac{\hbar^2}{2\mu}\left(\Delta_{\vec R^k} + \Delta_{\vec r^k}\right) \qquad \mu = \left(\frac{m_j m_k m_e}{m_j+m_k+m_e}\right)^{1/2}$$

$$R^k = \rho \sin\chi^k \qquad r^k = \rho\cos\chi^k$$

$$\Longrightarrow \underbrace{\rho^2 = (R^k)^2 + (r^k)^2}_{\text{hyperradius}} \qquad \underbrace{\chi^k = \arctan\left(\frac{R^k}{r^k}\right)}_{\text{hyperangle}}$$

$$\underline{T} = -\frac{\hbar^2}{2\mu}\left[\rho^{-5}\frac{\partial}{\partial\rho}\left(\rho^5\frac{\partial}{\partial\rho}\right) + \rho^{-2}\Delta(\Omega_5)\right] =$$

$$= -\frac{\hbar^2}{2\mu}\Delta(\rho,\Omega_5)$$

6-space Laplacian

HYPERSPHERICAL ADIABATIC REPRESENTATIONS

Chem. Phys Lett 93 174 (1982)

N-dimensional problem: a radial variable ρ (hyperradius of the N-1 hypersphere) and N-1 angles Ω.

Adiabatic expansion

$$\vec{\Psi}(\rho,\Omega) = \underline{F}(\rho)\,\vec{\Phi}(\rho,\Omega)$$

where $\vec{\Phi}(\rho,\Omega)$ solves a N-1 dimensional problem with eigenenergies $\underline{\varepsilon}(\rho)$ parametrically dependent on ρ.

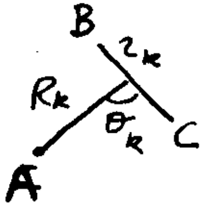
$$-\frac{\hbar^2}{2\mu}\left[\underline{1}\frac{d}{d\rho} + \underline{P}(\rho)\right]^2 \vec{F}(\rho) = \left[\underline{\varepsilon}(\rho) - \underline{1}E\right]\vec{F}(\rho)$$

$\underline{\varepsilon}(\rho)$ matrix of adiabatic potential energy curves (diagonal)

$$P_{ij}(\rho) = -P_{ji}(\rho) = \langle \Phi_i | \frac{d}{d\rho}\Phi_j \rangle = \frac{1}{\varepsilon_i-\varepsilon_j}\langle \Phi_i \frac{\partial V}{\partial R}\Phi_j$$

↳ NON-ADIABATIC COUPLING, exhibiting maxima at avoided crossings, changes in coupling schemes, ridges between modes

Alternative parametrization of hyperangles



$$\rho^2 = R_k^2 + r_k^2$$

$$\tan\chi_k = R_k/r_k$$

mass scaled!

$k = ABC, ACB, \ldots$

Kuppermann mapping $\rho, \theta_k, 2\chi_k$

Felix Smith symmetric parametrization

$$\sin 2\chi_k \cos\theta_k = \cos 2\Theta \sin 2\Phi_k$$
$$\sin 2\chi_k \sin\theta_k = \sin 2\Theta$$
$$\cos 2\chi_k = \cos 2\Theta \cos 2\Phi_k$$

Φ_k = kinematic rotation

Θ = reduced area ($\sin\Theta = A/4\rho^2$)

[$\Theta = 0$, collinearity, $\Theta = \frac{\pi}{4}$ equilateral triangle]

References:

- coordinates, J. Chem. Phys. 85 (1986) 1355
- kinetic energy and alternative coupling schemes, J. Chem. Phys. 76 (1982) 1587; 81 (1984) 3355; 85 (1986) 1362

A GUIDE TO OUR PUBLISHED WORK ON THEORY OF HYPERSPHERICAL AND RELATED APPROACH.

- COORDINATES
  JCP 85 (1986) 1355
- KINETIC ENERGY and ALTERNATIVE COUPLING SCHEMES
  JCP 85 (1986) 1362 ; CPL 93 (1982) 174
  JCP 76 (1982) 1587 ; JCP 81 (1984) 3355

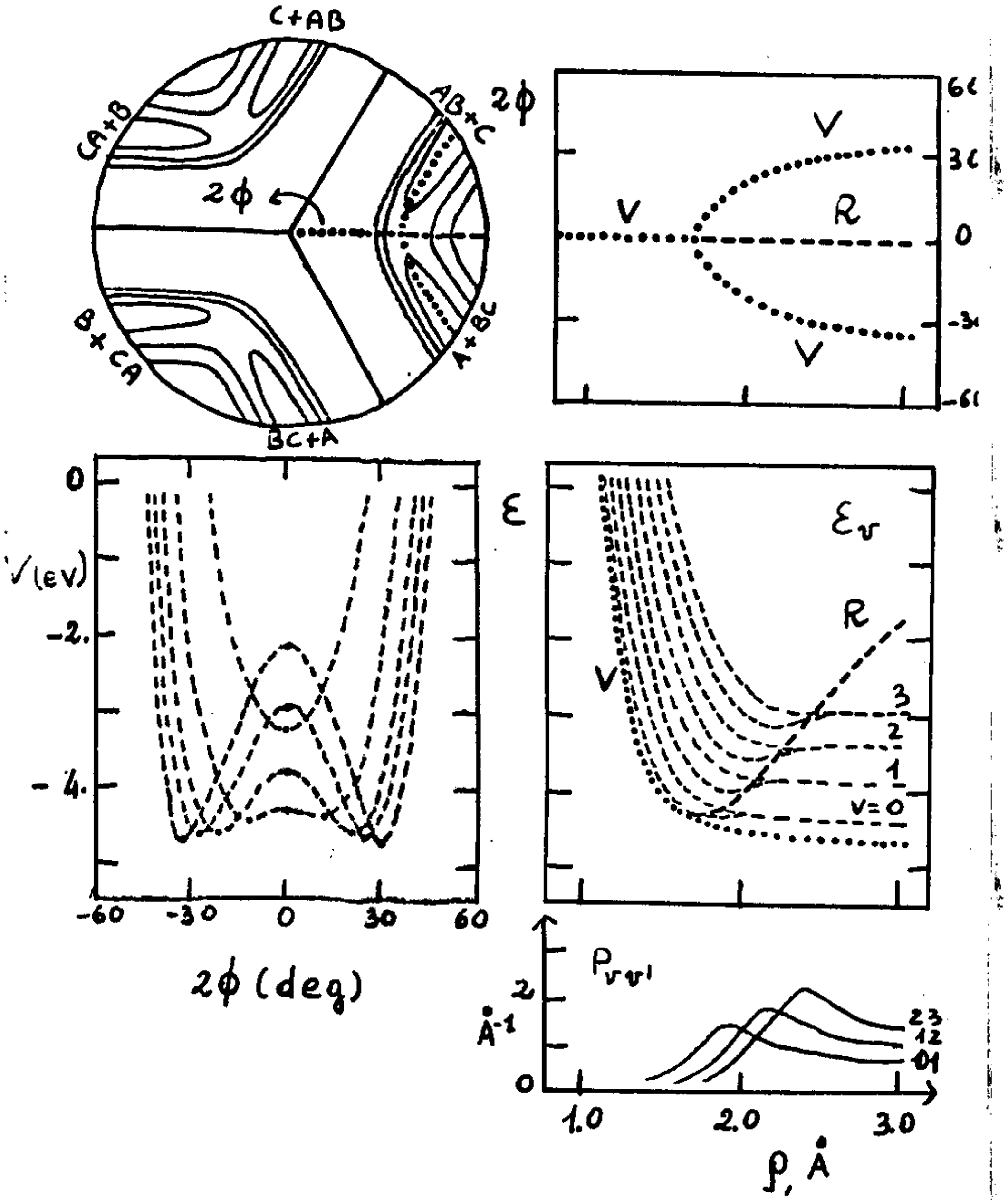
- INTERFERENCES and RESONANCES IN COLLINEAR REACTIONS.
  in : " THE THEORY OF CHEMICAL REACTION DYNAMICS" Reidel 1986, p. 383 ; CPL 93 (1982) 179 ;
  J. MOL. STRUCT. THEOCHEM 93 (1983) 319 and 107 (1984) 95

- TRANSITION BETWEEN MODES OF COUPLED OSCILLATORS (ridge effect)
  in " CHAOTIC BEHAVIOR IN QUANTUM SYSTEMS" Plenum 1985 p. 233 ; CPL 110 (1984) 43 ;
  THEOR. CHIM. ACTA in press .

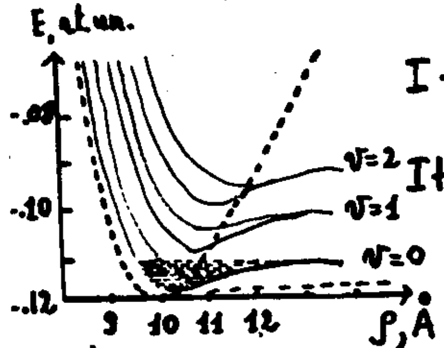
- UNIMOLECULAR DECAY
  CPL 133 (1987) 533 ; CPL 133 (1987) 538

" Supercomputers for reactivity, dynamics and kinetics..." A. Laganà, Editor, Reidel 1989.

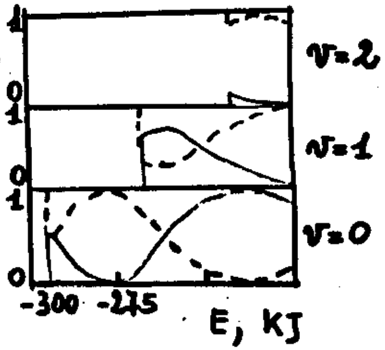
$H + H_2$ (nearly collinear)



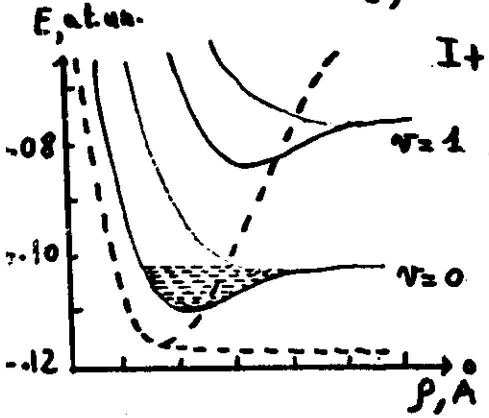
Collinear IHI - IMuI

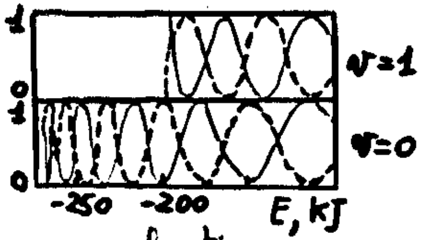


I + HI(v) → IH(v) + I



I + MuI(v) → IMu(v) + I





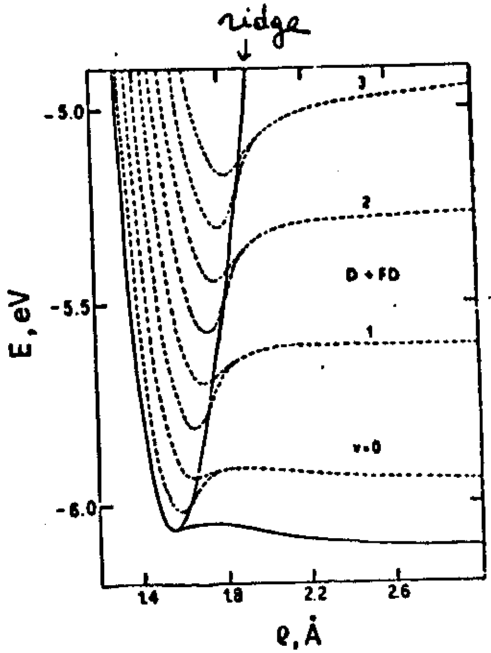
--- elastic

--- reactive

probabilities

COLLINEAR D+FD light-heavy-light

skewing angle 84.5 deg.



adiabatic curves

Interferences : Chem. Phys. Lett. 93 179 (1982)
(and Resonances)
Three-body bound states on a purely repulsive potential energy surface (4 for IHI, 18 for IMuI): Hyperfine Interactions, 17/19 739 (1984)

Adiabatic decoupling, semiclassical approach. Heavy-light-heavy, small skewing angle.

non adiabatic coupling

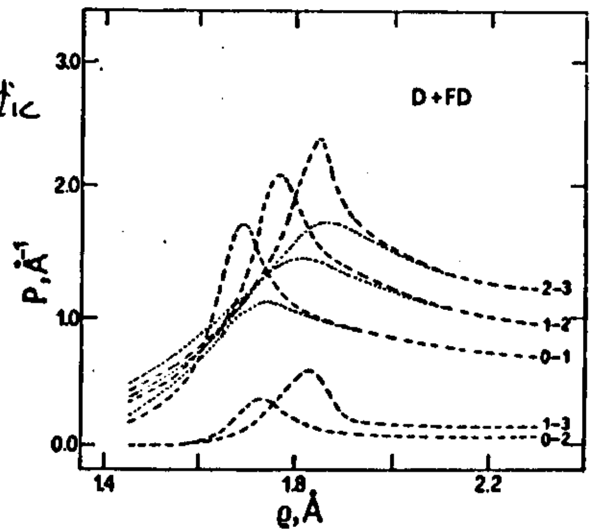
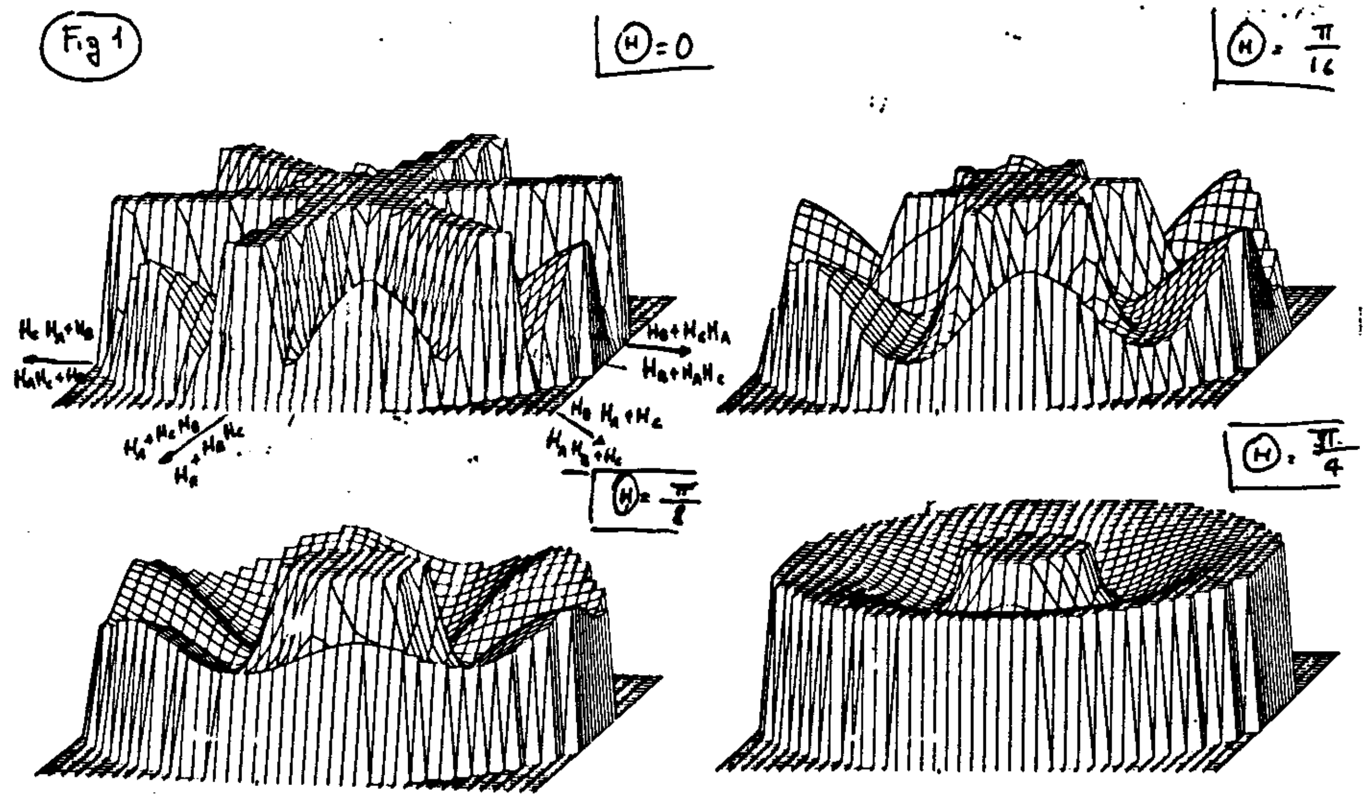


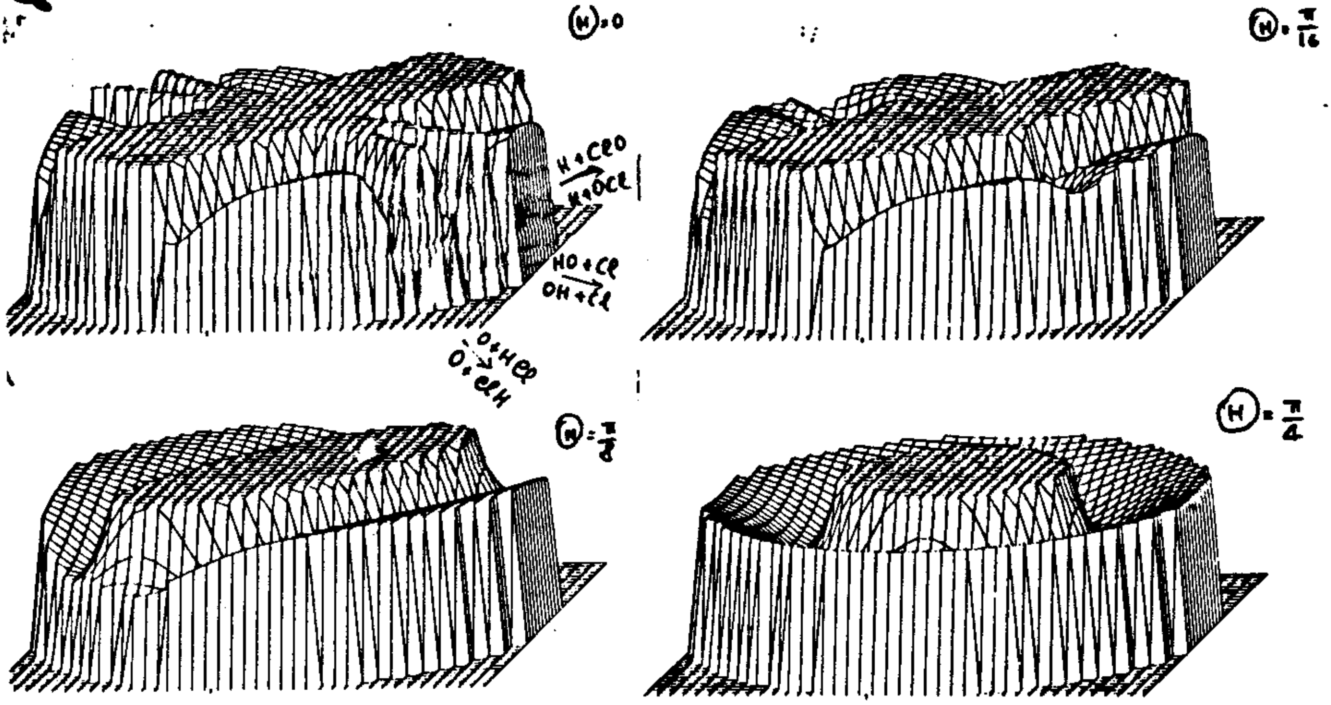
Fig 1



V. Aquilanti, A. Laganá, R.D. Levine

An all channels representation of PES in press

29



V. Aquilanti, A. Laganá, R.D. Levine
in press

Angular momentum barriers: quantum

Write the PES

$$V(\rho,\Omega_5) = V_0(\rho) + \bar{V}(\rho,\Omega_5)$$

where $V_0(\rho)$ valley bottom

and $\bar{V}(\rho,\Omega_5) \geq 0$

Adiabatic energy curves $\varepsilon_n^J(\rho)$ are solutions of

$$\left\{\frac{\hbar^2}{2\mu\rho^2}\left(\Lambda^2 + \frac{15}{4}\right) + V(\rho,\Omega_5) - \varepsilon_n^J(\rho)\right\}\psi_n^J(\rho,\Omega_5) = 0$$

where Λ^2 is the grand angular momentum operator, acting in S^5. Expanding in hyperspherical harmonics $Y_{\lambda,j,\ell}^{JM}(\Omega_5)$

$$\psi_n^J(\rho,\Omega_5) = \sum_{\lambda,j,\ell} \phi_{n\lambda}^{j\ell}(\rho)\, Y_{\lambda,j,\ell}^{JM}(\Omega_5)$$

where $Y_{\lambda,j\ell}^{JM}(\Omega_5)$ solve

$$\Lambda^2\, Y_{\lambda j\ell}^{JM}(\Omega_5) = \lambda(\lambda+4)\, Y_{\lambda j\ell}^{JM}$$

Now

$$Y_{\lambda j\ell}^{JM}(\Omega_5) = Y_{\lambda j\ell}(\chi) \sum_{m_j m_\ell} \langle j\,\ell\, m_j\, m_\ell | JM\rangle\, Y_{\ell m_\ell}(\vartheta_1,\varphi_1)\, Y_{j m_j}(\vartheta_2,\varphi_2)$$

where (V. Aquilanti et al. JCP 85, 1362 (1986)):

$$\lambda \geq j+\ell \qquad \text{but also} \qquad J \leq j+\ell$$

thus

$$\lambda \geq J$$

Therefore

$$\varepsilon_n^J(\rho) \geq V_0(\rho) + \frac{J(J+4) + 15/4}{2\mu\rho^2}$$

This result is similar to, but stronger, than Pollak, Schlier, Child,..., who do not exploit hyperspherical coordinates and use classical mechanics.

Angular momentum barriers:
classical stability analysis.

Much sharper results can be obtained by classical mechanics. In Smith's coordinates (see e.g. Johnson, JCP 79, 1906 (1983)) we obtain for the Hamiltonian

$$H = \frac{1}{2\mu}\left[P_\rho^2 + \frac{4}{\rho^2} L^2(\Theta,\phi)\right] + \frac{P_\gamma(P_\gamma + 4P_\phi \sin 2\Theta)}{2\mu\rho^2\cos^2 2\Theta} +$$

$$+ \frac{(J^2 - P_\gamma^2)}{\mu\rho^2 \sin^2 2\Theta}\left[1 + \cos 2\Theta \cos 2\gamma\right] + V(\rho,\Theta,\phi)$$

containing internal coordinates ρ, Θ, ϕ and only one Euler's angle γ.
Stability analysis requires we look for critical points for the effective potential ($\nabla V = 0$)

$$V_{eff} = V(\rho,\Theta,\phi) + \frac{J^2}{\mu\rho^2} f(\Theta,\gamma)$$

The condition $\frac{\partial V_{eff}}{\partial \gamma} = 0 \rightarrow \cos 2\gamma = -1$

($\gamma = \pm\frac{\pi}{2}$) for $0 \le \Theta < \frac{\pi}{4}$ gives:

$$V_{centrifugal} \geqslant \frac{J^2}{\mu\rho^2}\left(\frac{1}{1+\cos 2\Theta}\right)$$

The further conditions

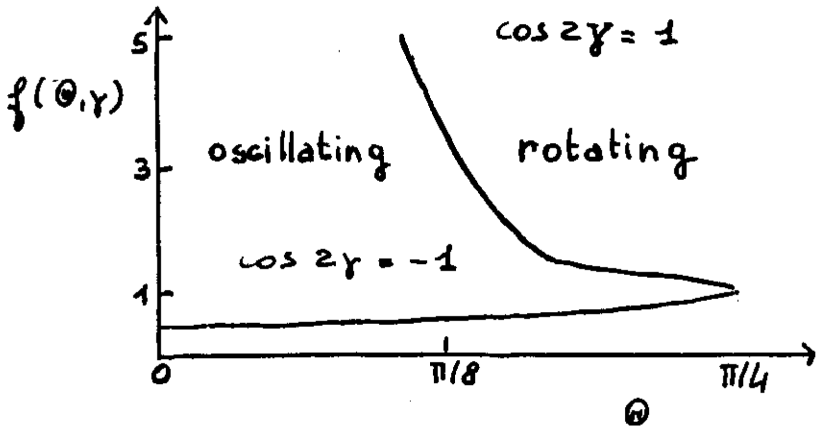
$$\frac{\partial V_{eff}}{\partial \Theta} = 0 \quad , \quad \frac{\partial V_{eff}}{\partial \phi} = 0$$

fix valley bottom line and ridge line as a function of ρ.

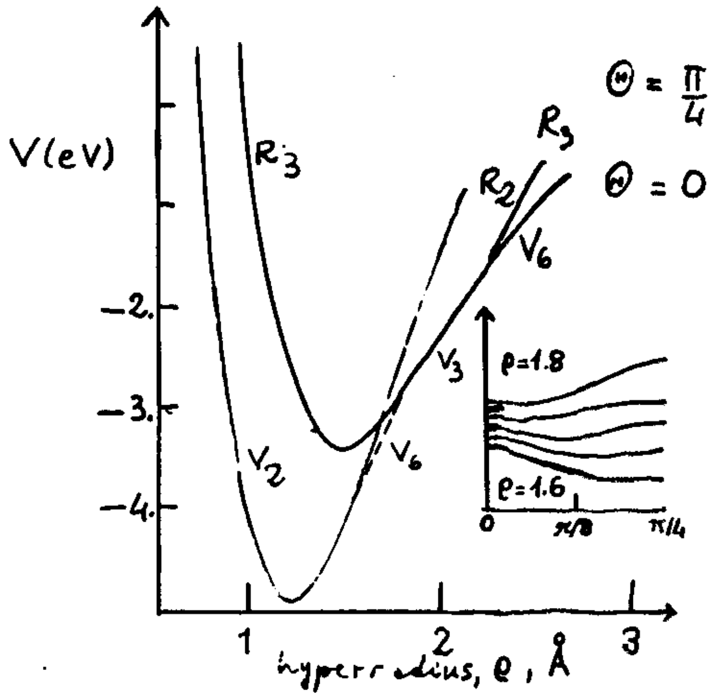
[the further condition $\frac{\partial V}{\partial \rho} = 0$ gives overall minima and saddles of the whole surface].

$$f(\Theta,\gamma) = \frac{1+\cos 2\Theta \cos 2\gamma}{\sin^2 2\Theta}$$ Angular part of V_{centr}

Pendulum like modes



Valley bottoms and ridges for H_3^+ (Tully-Preston's DIM surface) as an example of transition between triangular and collinear configuration.

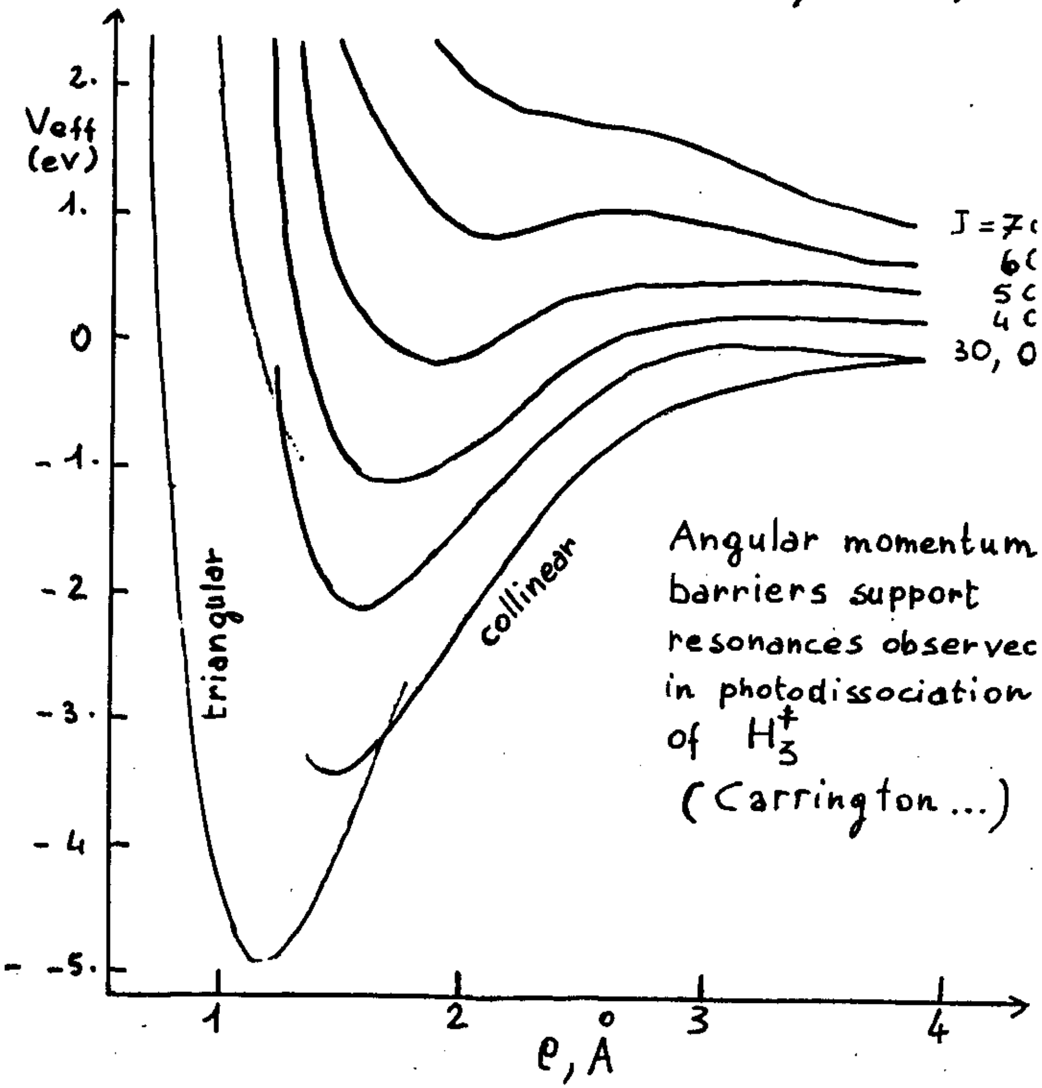


CPL, 141 (1987) 309

At short ρ, Θ = π/4 is a minimum and there are three saddles at Θ = 0 (elliptic umbilic catastrophe, cf. Hénon-Heiles potential (Aquilanti et al. in Chaotic Behavior..., Plenum 1985; CPL 110, 43 (1984)). At larger ρ, Θ = π/4 is a saddle and three saddles at Θ = 0 are now minima corresponding as before to the cusp catastrophe typical of collinear reactions.

Angular momentum favours collinear configurations..

CPL, 141 (1987) 309



Angular momentum barriers support resonances observed in photodissociation of H_3^+ (Carrington...)

The search for extrema in PES as a function of ρ is basic to dynamic studies

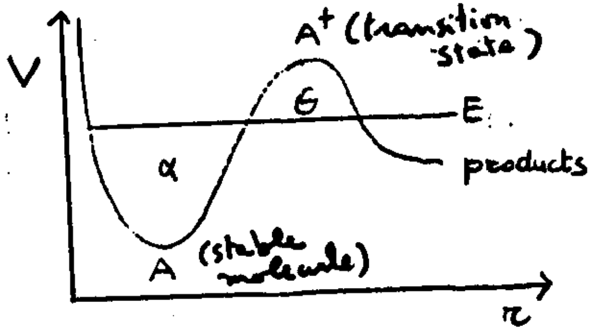
QUANTUM RESONANCE LIFETIMES AND UNIMOLECULAR RATE CONSTANTS.

$E = E_R - \frac{i}{2}\Gamma$ poles of $\underline{S}$ matrix.

$\exp[-iEt/\hbar] = \exp[iE_R t/\hbar]\exp[-\Gamma t/2\hbar]$ time evolution

lifetime $\tau = \hbar/\Gamma$ $\qquad k = \tau^{-1} = \Gamma/\hbar$ microcanonical rate constant

<u>monodimensional case</u>.

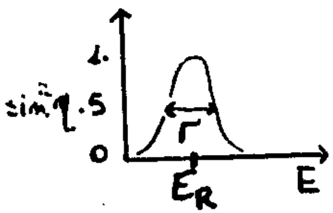


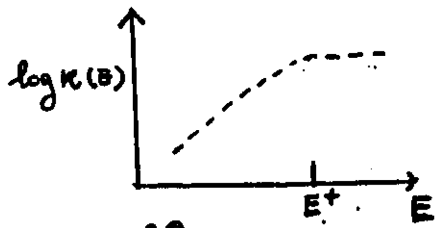
$S = e^{2i\eta}$.

α, θ = well and tunnel phase integral.

$$\eta = \arctan\left\{\frac{[(e^{2\theta}+1)^{1/2}-1]}{[(e^{2\theta}+1)^{1/2}+1]}\tan\alpha\right\}$$

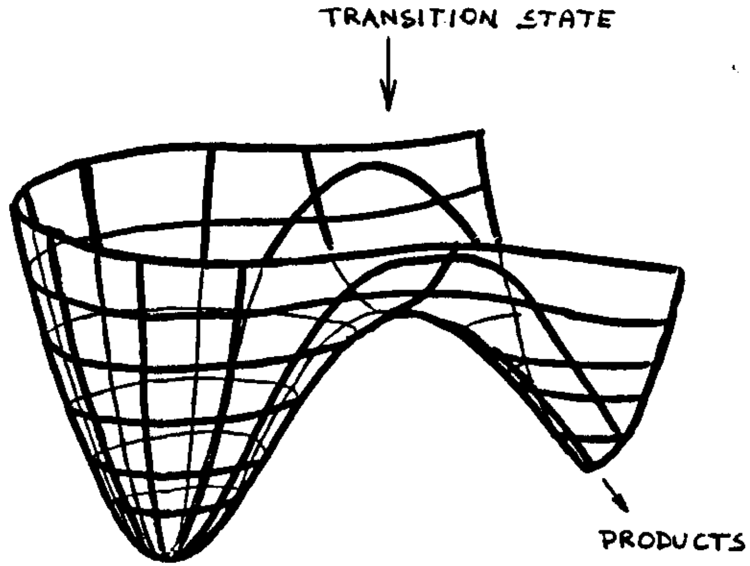
scattering phase shif

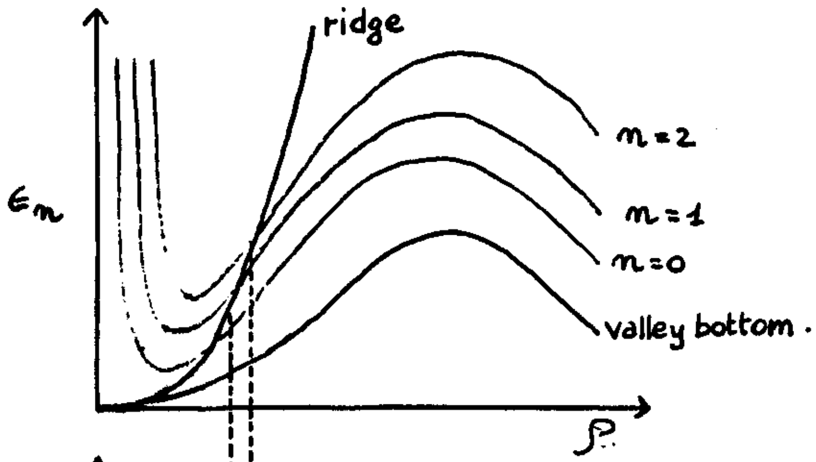


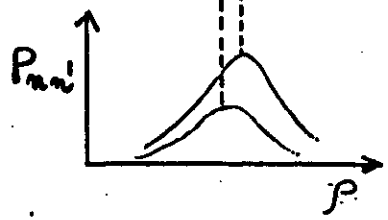


Gamow: $k = \Gamma/\hbar = \frac{\omega}{2\pi}e^{-2\theta}$ (cf. Bohr → RRK nuclear fission

α decay

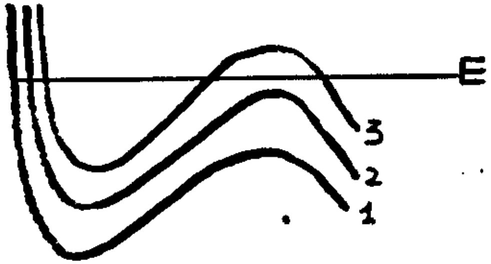




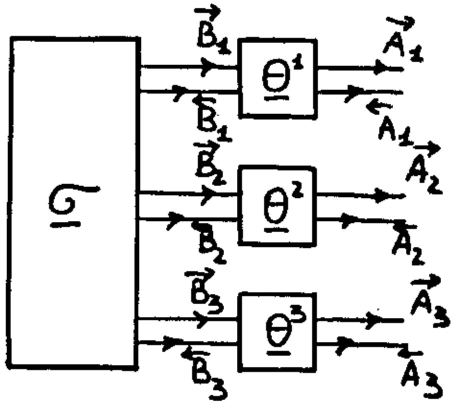


nonadiabatic coupling.

MULTICHANNEL SCATTERING MATRIX



κ^{-2} tunnel probability



$$\begin{pmatrix}\vec{B}_i\\ \overleftarrow{B}_i\end{pmatrix} = \underline{\Theta}^{(i)}\begin{pmatrix}\vec{A}_i\\ \overleftarrow{A}_i\end{pmatrix}$$

$$\underline{\Theta}^{(i)} = \begin{pmatrix}(1+k_i^2)^{1/2} & i k_i\\ -i k_i & (1+k_i^2)^{1/2}\end{pmatrix},$$

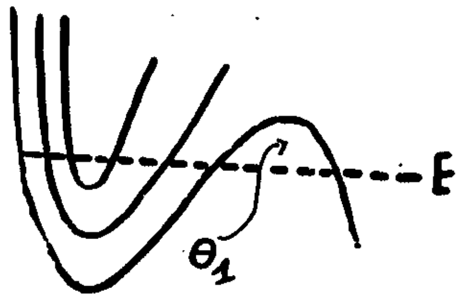
$$\vec{\underline{B}} = \underline{\sigma}\,\overleftarrow{\underline{B}}$$

$$\begin{pmatrix}\vec{A}_1\\ \vec{A}_2\\ \vdots\\ \vec{A}_n\end{pmatrix} = \underbrace{\left[(\underline{1}+\underline{k}^2)^{1/2}+i\underline{\sigma}\,\underline{k}\right]^{-1}\left[-i\underline{k}+\underline{\sigma}(\underline{1}+\underline{k}^2)^{1/2}\right]}_{\underline{S}}\begin{pmatrix}\overleftarrow{A}_1\\ \overleftarrow{A}_2\\ \vdots\\ \overleftarrow{A}_n\end{pmatrix}$$

$$\det\left[(\underline{1}+\underline{k}^2)^{1/2}+i\underline{\sigma}\right] = 0$$

$E = E_R - i\Gamma/2 \qquad \tau = \hbar/\Gamma \qquad k = \tau^{-1}$

ONE EXIT CHANNEL.



eigenphase analysis of the intramolecular motion.

$\underline{\Sigma} = \underline{T}\, e^{i\underline{\delta}}\,\tilde{\underline{T}}$ $\qquad \underline{\delta}$ eigenphases..

$\underline{T} \in SO(n)$

$$H = \arctan\left\{\frac{(1+e^{2\Theta_1})^{1/2}-1}{(1+e^{2\Theta_1})^{1/2}+1}\tan\Delta\right\}$$

scattering phase

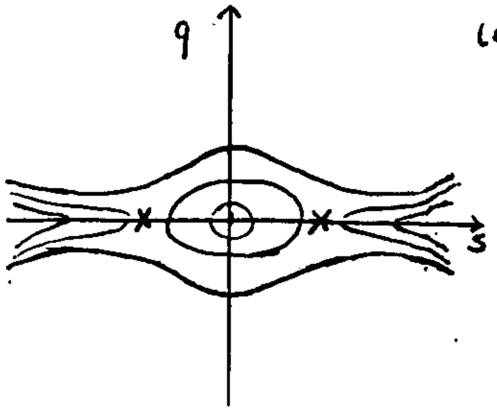
$\tan\Delta = \sum_{j=1}^{n} t_{j1}^2 \tan(\delta_j+\pi/4) \qquad t_{j1}$ one row of $\underline{T}$

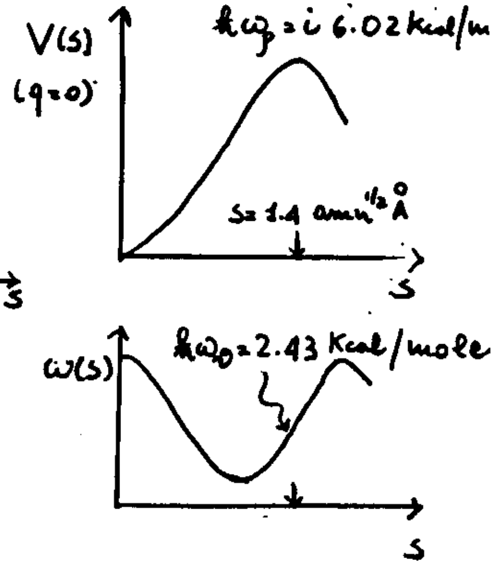
Limits:

1. <u>adiabatic</u> $\quad t_{j1} = \delta_{j1}$
2. <u>statistical</u> $\quad t_{j1} = 1/n$
3. <u>sudden RZ</u> $\quad t_{j1} = 2^{-j/2}$

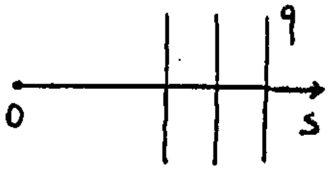
FORMALDEHYDE $CH_2O \longrightarrow CO + H_2$

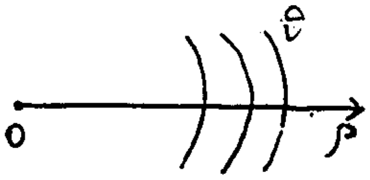
(Miller '83)





for $s \gg 0$, along the reaction path, $q \simeq 0$





in the neighborhood of the saddle

$$V(s,q) = V_s(s) + \tfrac{1}{2}\,\omega(s)\,q^2 \approx V(\rho,\vartheta) = V_s(\rho) + \tfrac{1}{2}\,\omega^2(\rho)\,\rho^2 \cdot$$

$$- \tfrac{1}{2}\,\omega^2(\rho)\,\rho^2 \cos 2\vartheta = V_0(\rho) - V_2(\rho)\cos 2\vartheta\ .$$

$V_0 - V_2 = V_s$ valleybottom

$V_0 + V_2 = V_s + \omega^2(\rho)\,\rho^2$ ridge

SEMICLASSICAL LIMIT: ASYMPTOTICS IN $\hbar$

$$\left(\frac{d^2}{d\tau^2} + \frac{p^2(\tau)}{\hbar^2}\right)\psi(\tau) = 0$$

where: $p^2(\tau) = 2m\,[E - V(\tau)]$

Assume: $\psi(\tau) = \exp[i\,S(\tau)/\hbar]$

(1) $i\hbar \dfrac{d^2}{d\tau^2} S(\tau) - \left[\dfrac{d}{d\tau} S(\tau)\right]^2 + p^2(\tau) = 0$ Riccati equation

Neglecting $\hbar$ → Hamilton-Jacobi equation

→ $S'(\tau) = \pm\, p(\tau)$

WKB expansion

$$S(\tau) = S_0(\tau) + \hbar\, S_1(\tau) + \cancel{\hbar^2 S_2(\tau)} + \dots$$

in (1) gives the semiclassical wavefunctions

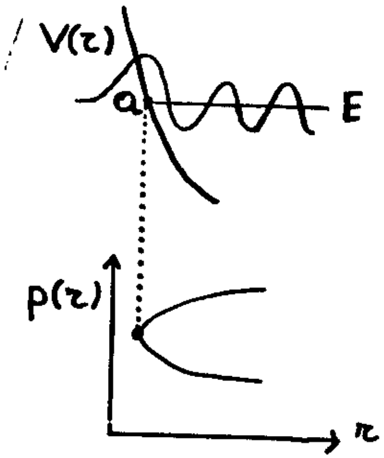
$$\psi(\tau) = C\exp[i(S_0 + \hbar S_1)] =$$

$$= C\left[\frac{p(\tau)}{\hbar}\right]^{1/2} \exp\left[\pm i \int [\,p(\tau)/\hbar\,]^{1/2}\, d\tau\right]$$

to be amended whenever $p(\tau) = 0$ or

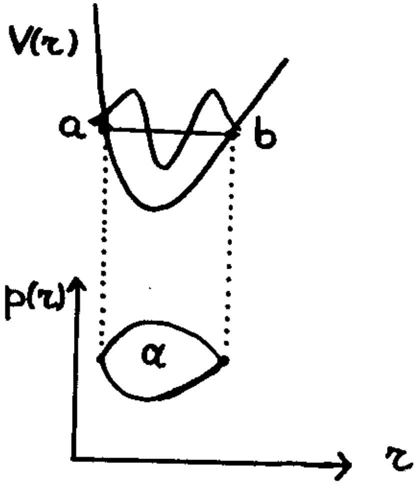
$E = V(\tau)$ (turning points)

Semiclassical phaseshifts, bound states, resonance



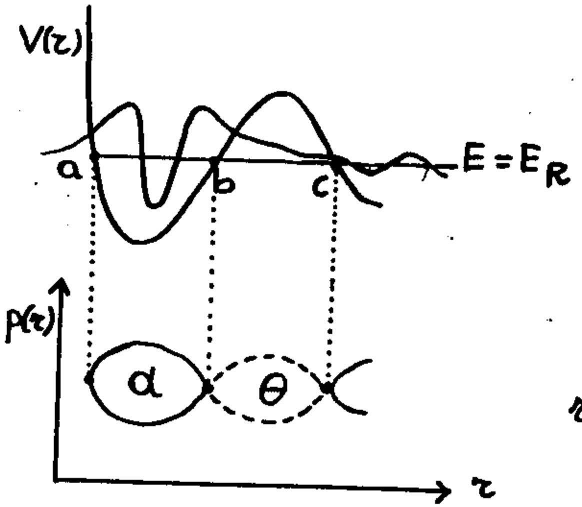
$$\delta = \lim_{r\to\infty}\left[\int_0^r \frac{p(r)}{\hbar} + \frac{p_0}{\hbar} r + \frac{\pi}{4}\right]$$

↑
phaseshift



Bohr-Sommerfeld quantization rule

$$\alpha = \int_a^b \frac{p(r)}{\hbar}\, dr = (n+\tfrac{1}{2})\pi$$



$$E_R \simeq (n+\tfrac{1}{2})\hbar\omega$$

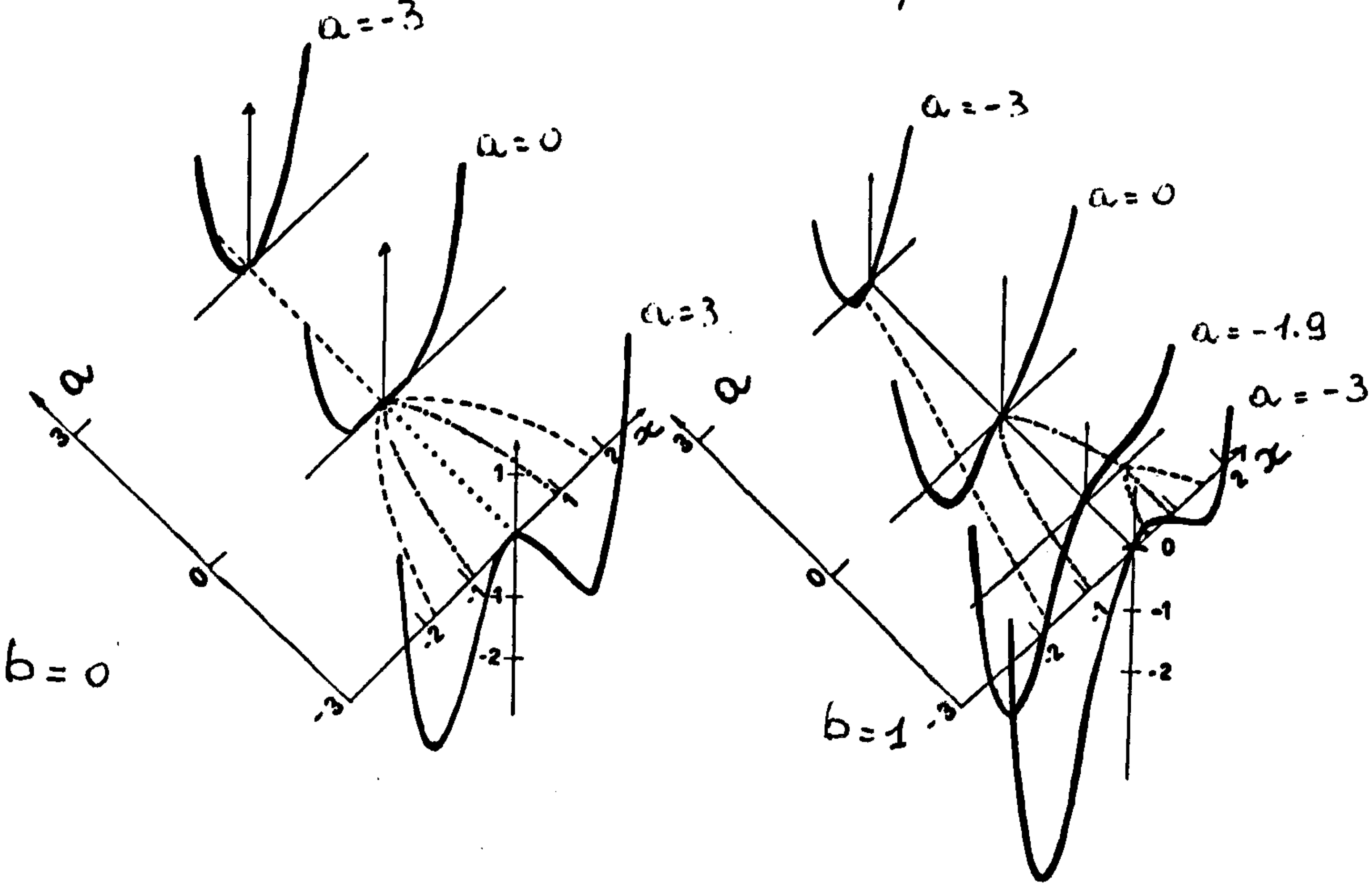
$$\Gamma \simeq \frac{\hbar\omega}{2\pi} e^{-2\theta}$$

↑
resonance width

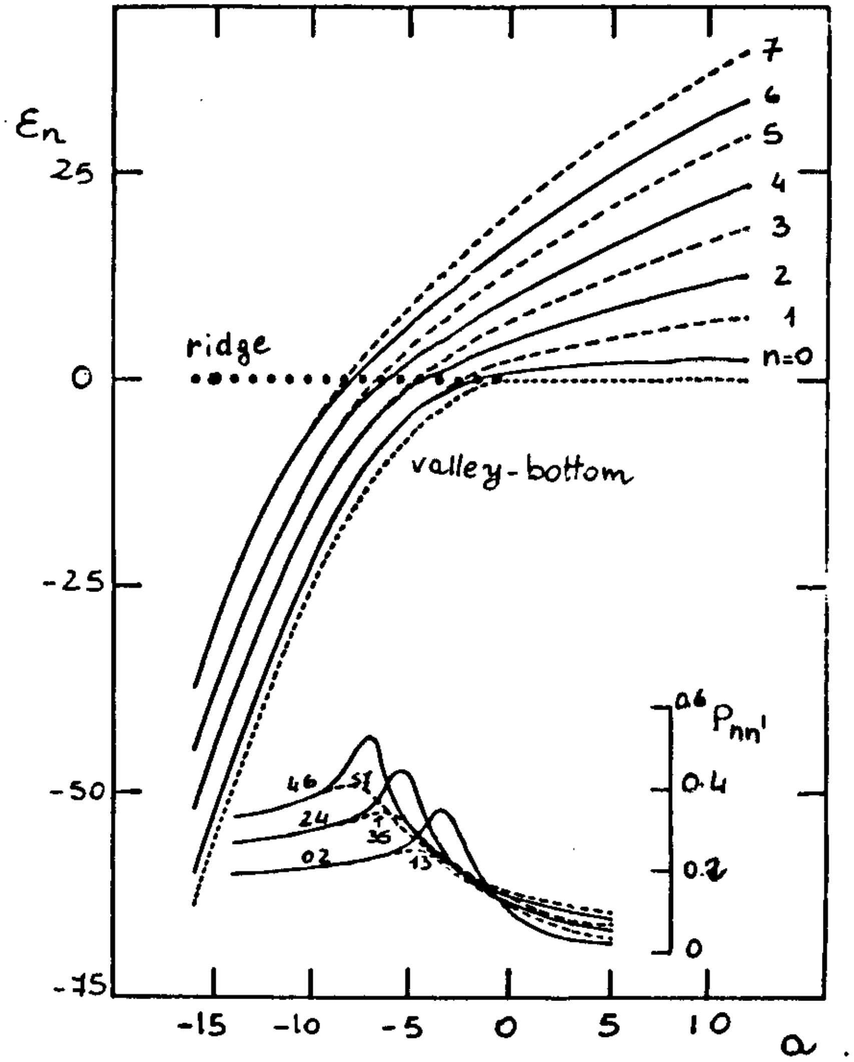
Canonical form	Comparison Eq.^n	Examples
… one-dimensional …		
x	Airy	JWKB phaseshifts
$\frac{1}{2}x^2 - \varepsilon$	Weber-Hermite	Bohr Sommerfeld quantization. Tunneling
$\frac{1}{3}x^3 + ax - \varepsilon$	Fold Catastrophe	Resonances
$\frac{1}{4}x^4 + \frac{1}{2}ax^2 + bx - \varepsilon$	Cusp catastrophe	Near collinear reaction
… two-dimensional …		
$\frac{1}{2}(x^2+y^2) + \lambda(xy^2 - \frac{x^3}{3})$ or $\frac{1}{2}\rho^2 - \lambda\rho^3\cos\frac{3\phi}{3}$	Elliptic Umbilic Catastrophe.	Stretching and Decomposition o Bent Molecules; Hénon-Heiles coupled oscillato (onset of chaos)
… periodic boundary conditions …		
$q\cos\phi - \varepsilon$	Mathieu	Quantum pendulum. Fixed ρ Hénon-Heiles.

See notes on mathematical background.

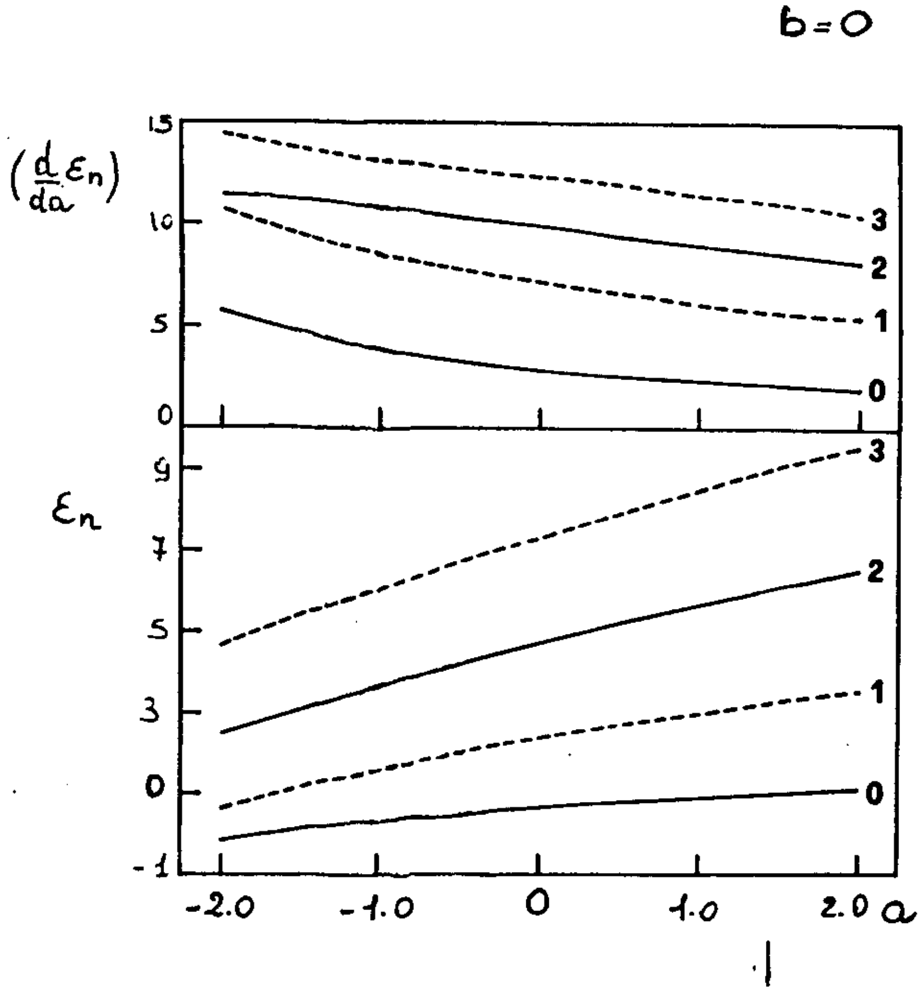
the cusp catastrophe



$$\frac{1}{4}x^4 + \frac{1}{2}ax^2 + bx$$

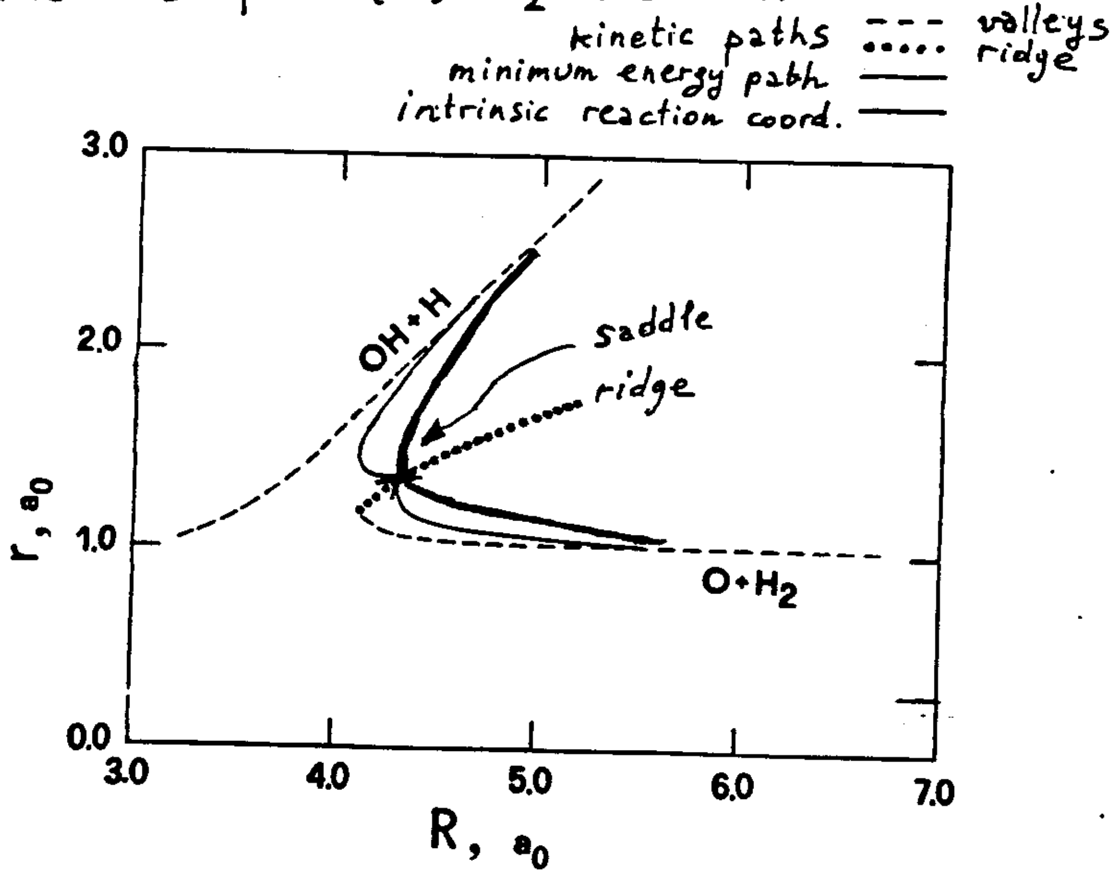


$\mathcal{E}_n$
25
0
-25
-50
-75
-15 -10 -5 0 5 10
a
7
6
5
4
3
2
1
n=0
ridge
valley-bottom
$\rho_{nn'}$
0.6
0.4
0.2
0
46
57
24
35
02
13



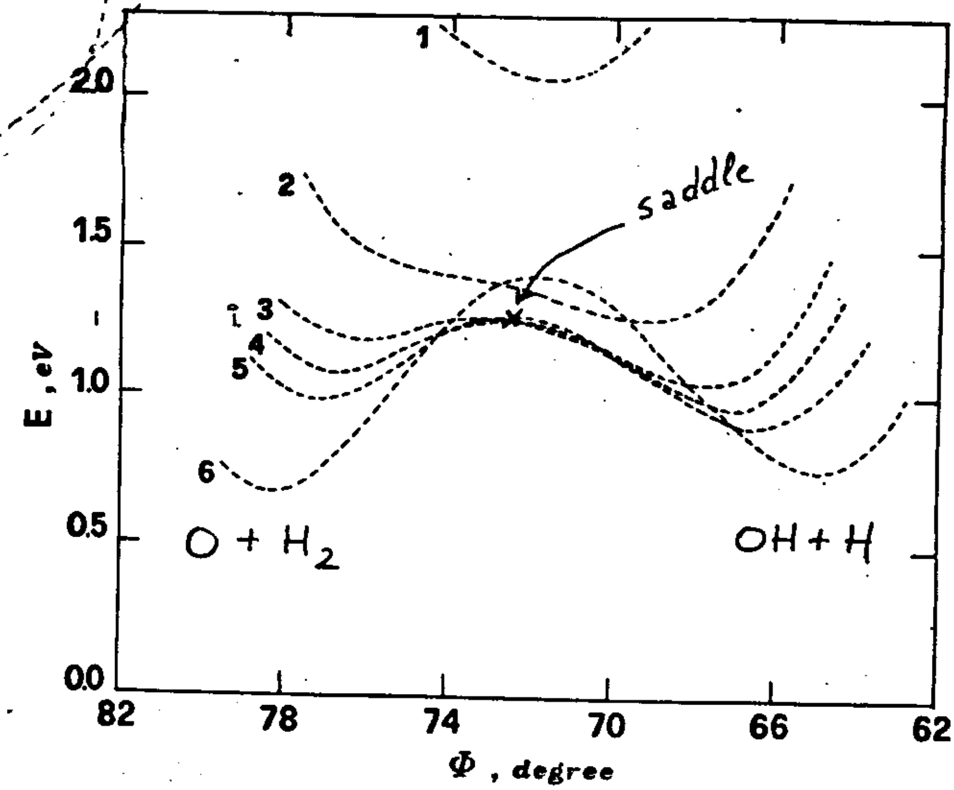
b=0
$\left(\frac{d}{da}\mathcal{E}_n\right)$
15
10
5
0
$\mathcal{E}_n$
9
7
5
3
0
-1
-2.0 -1.0 0 1.0 2.0 a
3
2
1
0

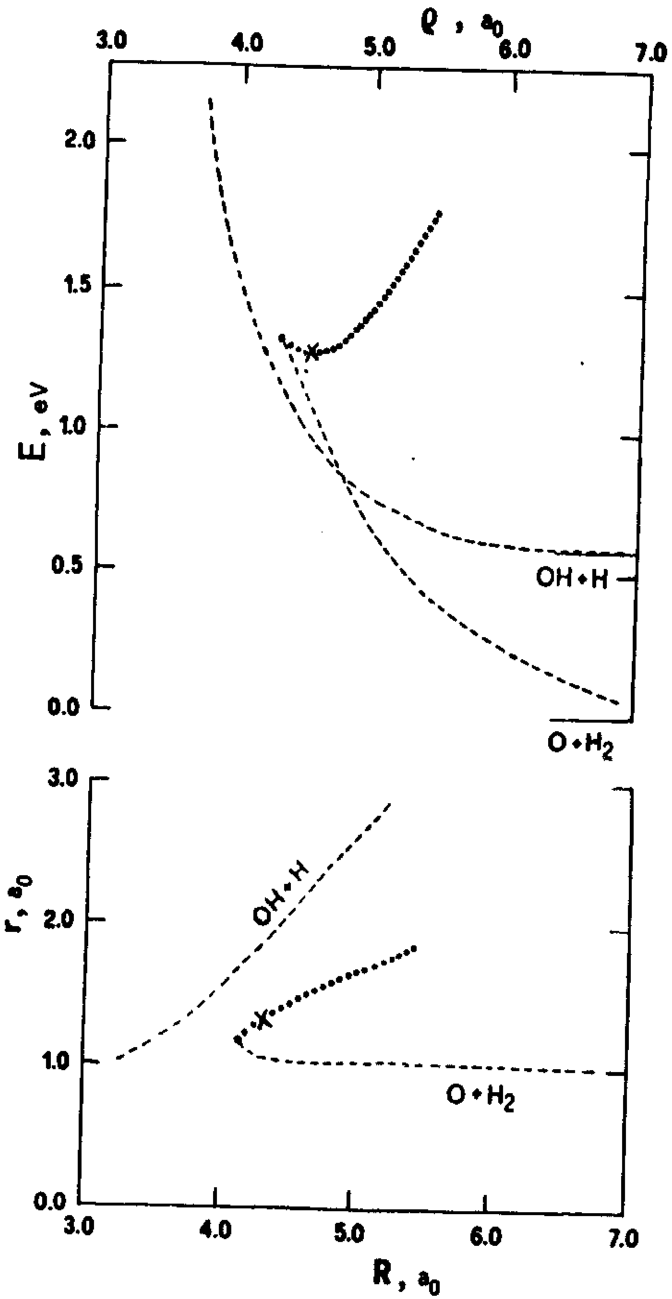
Ab initio PES for $O(^3P) + H_2 \longrightarrow OH + H$



Ab initio PES for $O(^3P) + H_2 \longrightarrow OH + H$ reaction

Cuts of the surface at fixed, progressive values of the hyper-radius in the region around the saddle.





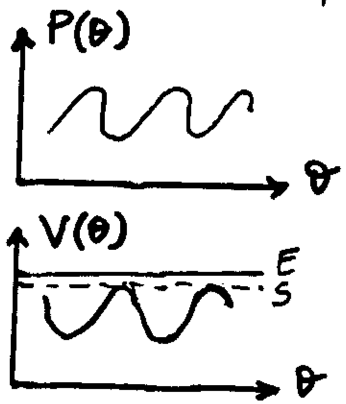
THE CLASSICAL SEMICLASSICAL QUANTUM PENDULUM

AND THE RIDGE EFFECT

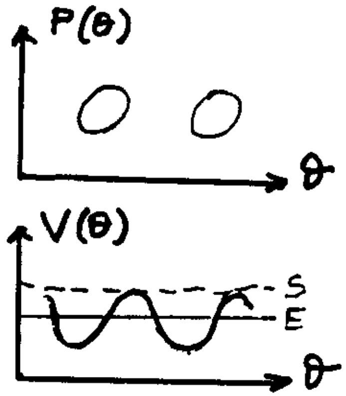
TRANSITIONS between MODES

normal, rotating, precessing, Q_I
intermediate complex

local, vibrating, librating, Q_{II}
reactants & products



regular



irregular

chaotic, non EBK quantizable, N

classical
quantum
semiclassical

PENDULUM

elliptic functions
Mathieu functions
elliptic integrals

RIDGE LOCALIZATION OF ADIABATIC BREAKDOWN

CLASSICAL SEPARATRIX S

Chem. Phys. Letters
110, 43 (1984)

QUANTUM PENDULUM : Mathieu eigenvalues and P-matrix elements

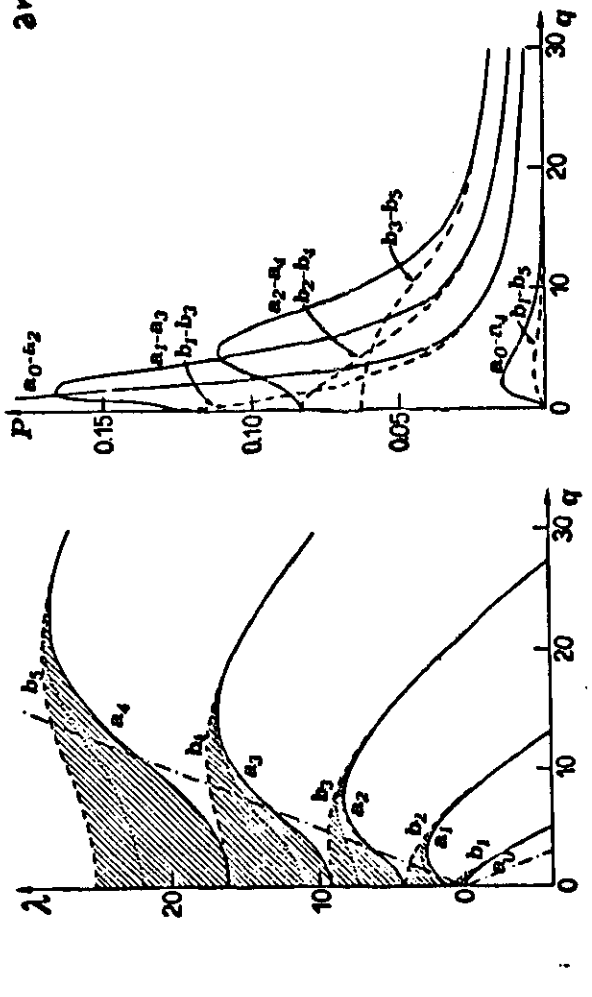


Fig. 2

Chem. Phys. Letters in press

HYPERSPHERICAL ADIABATIC REPRESENTATION

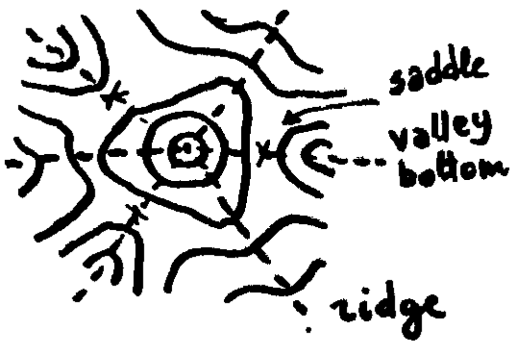
$$\frac{\hbar^2}{2\mu}\left[\underline{1}\frac{d}{d\rho} + \underline{P}(\rho)\right]^2 \vec{F} = [\underline{\varepsilon}(\rho) - E]\,\vec{F}$$

$\underline{\varepsilon}(\rho)$ = adiabatic diagonal matrix

$$P_{ij}(\rho) = -P_{ij}(\rho) = \langle \varphi_i \mid \frac{d}{d\rho}\varphi_j \rangle = \frac{1}{\varepsilon_i - \varepsilon_j}\langle \varphi_i \frac{dV}{dR}\varphi_j \rangle$$

(large at avoided crossings, ridges, ...)

HÉNON - HEILES



$V(x,y) = \frac{1}{2}(x^2+y^2) + \lambda(xy^2 - \frac{x^3}{3})$

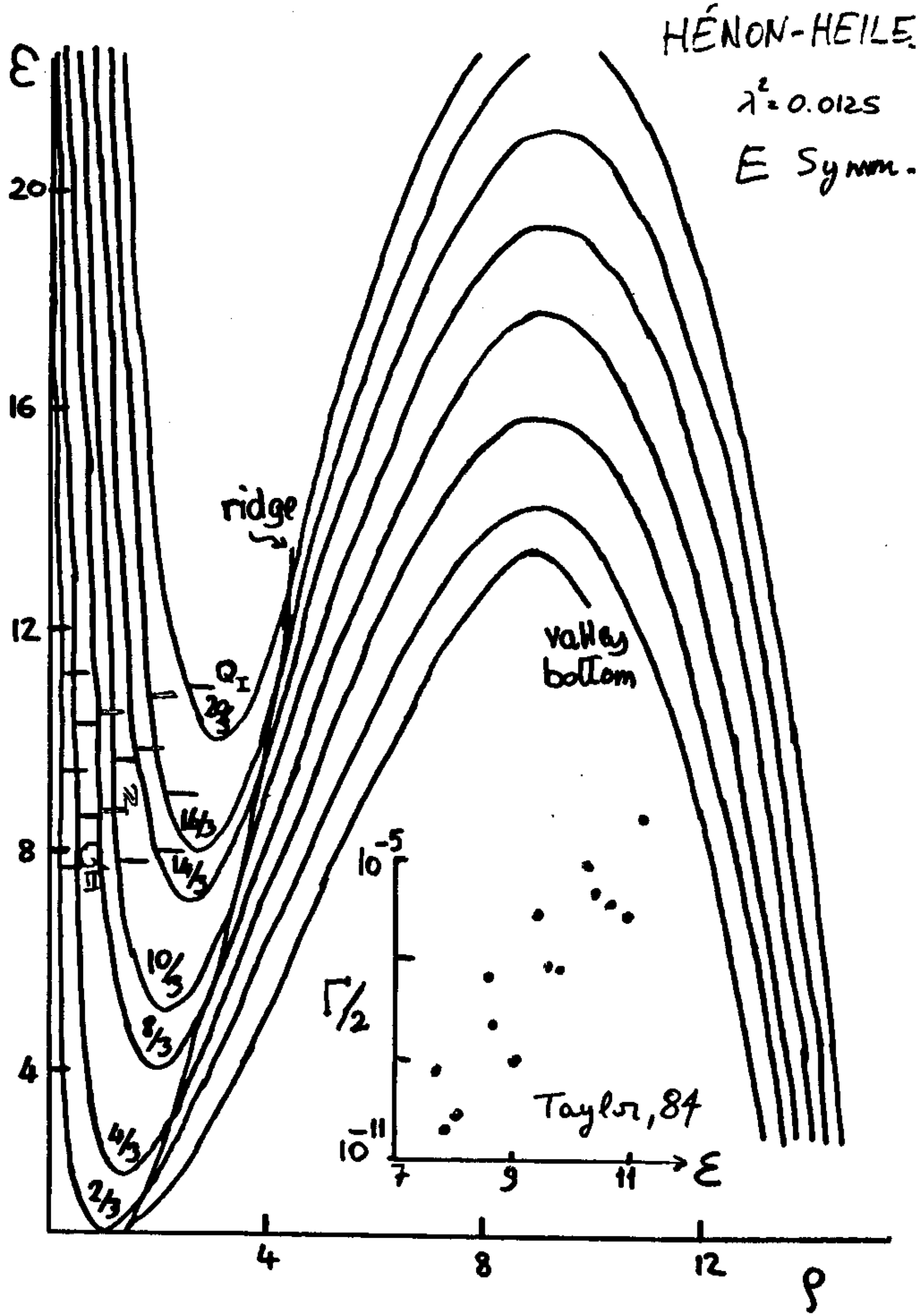
or

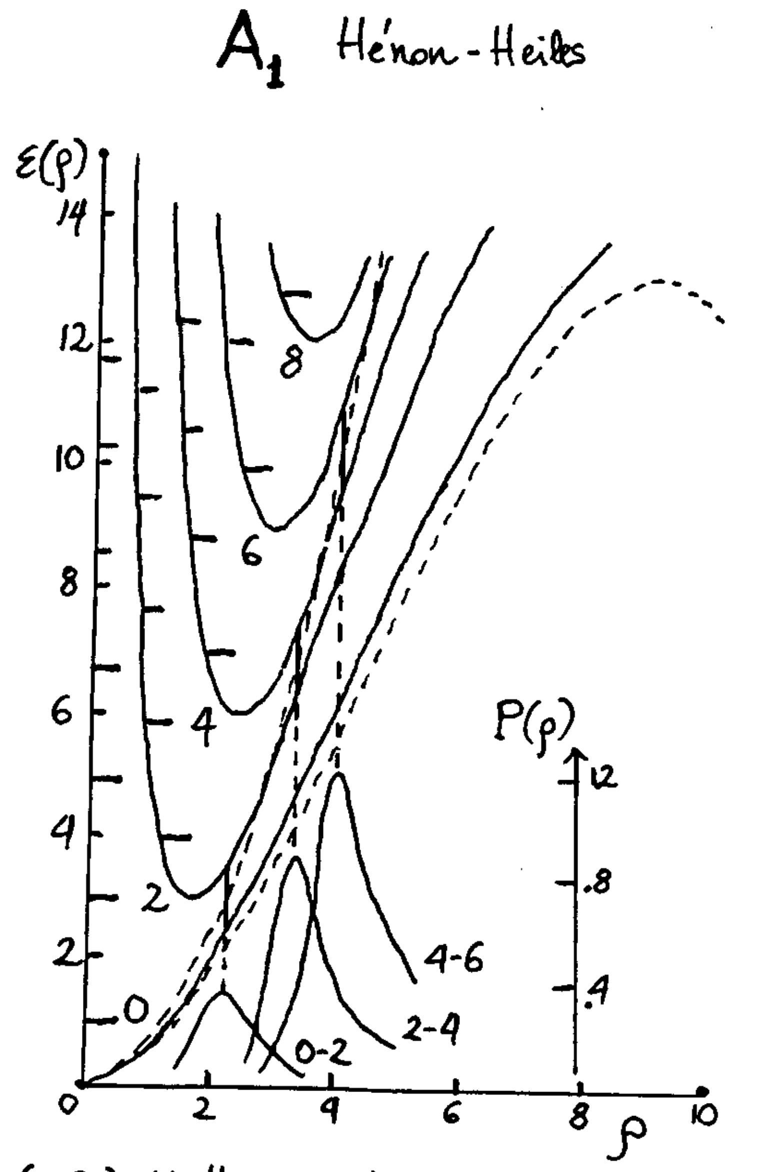
$V(\rho,\theta) = \frac{1}{2}\rho^2 + \frac{\lambda\rho^3}{3}\cos 3\theta$

$\lambda = 80^{-1/2} = .1118$

Adiabatic (fixed ρ) $\longrightarrow$ a quantum pendulum $\longrightarrow$ Mathieu, with $q = \frac{4}{27}\lambda\rho^5$ and C_{3v} symmetry $\longrightarrow$ A_1 A_2 E states.

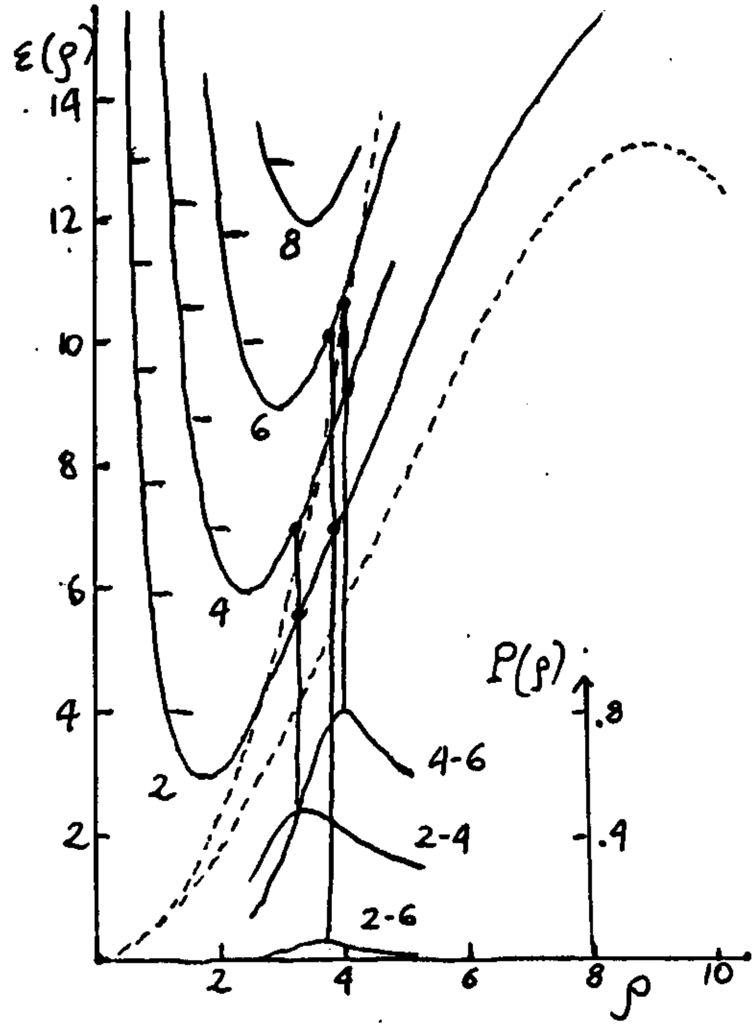
See: V. Aquilanti, S. Cavalli, G. Grossi in "Chaotic Behavior of Quantum Systems" Plenum (1985)





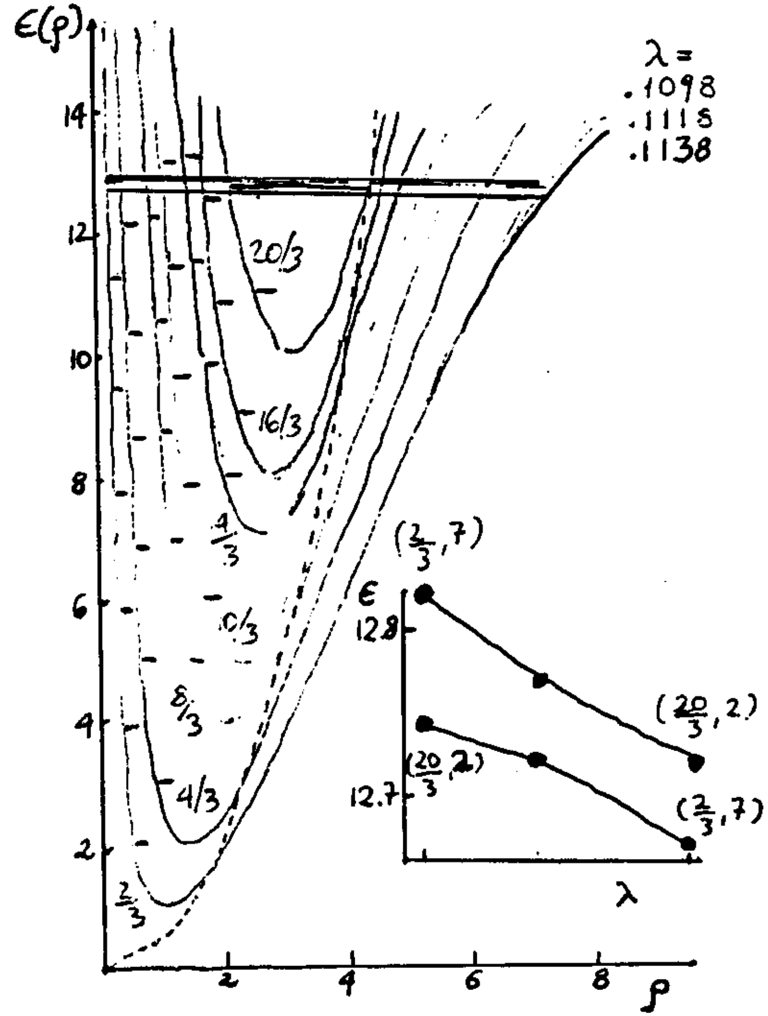
$ce_n(q,\theta)$ Mathieu, with eigenvalues $a_n(q)$

A_2 Hénon-Heiles



$se_n(q,\theta)$ Mathieu, with eigenvalues $b_n(q)$

E Hénon-Heiles



Mathieu functions and eigenvalues of fractional order.

See: V. Aquilanti, S. Cavalli, G. Grossi, in "Fundamental Processes in Atomic Collision Physics" H. Kleinpoppen ed. Pl...... 1985

- differential cross sections — Laura Beneventi, Piero Casavecchia, G. G. Volpi
- integral cross sections for magnetically analyzed atoms — Fernando Pirani, Roberto Candori, Giorgio Liuti, G. G. Volpi
- correlation of van der Waals forces and atomic properties (polarizabilities...) — Fernando Pirani, Giorgio Liuti
- transport properties — Fernando Pirani, Franco Vecchiocattivi
- Ionization by metastable atoms — Bruno Brunetti, Franco Vecchiocattivi, G.G. Volpi
- Angular momentum coupling schemes and discrete representations — Gaia Grossi
- classical, semiclassical, quantum mechanics of elementary chemical reactions (hyperspherical approach) — Simona Cavalli, Gaia Grossi, Antonio Laganà
- chaos and catastrophes in quantum mechanics — Simona Cavalli, Gaia Grossi
- quantum chemistry calculations of potential energy surfaces — Marzio Rosi, Antonio Sgamellotti, Francesco Tarantelli