

Quantum reactive scattering: the time - independent approach

I. Principles and early developments

Ralph Jaquet

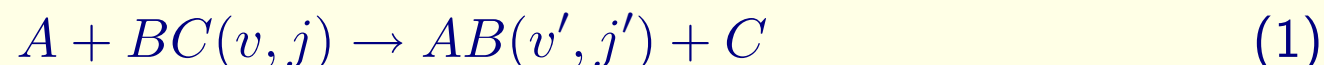
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I.1 Introduction

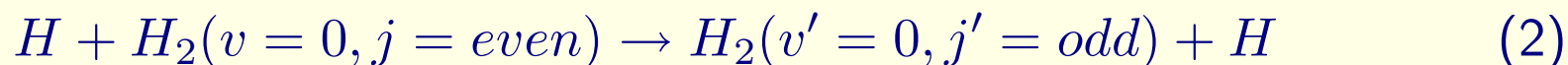
Reactive scattering events are those in which the "chemical identity" of at least some of the particles changes. Included in this would be chemical exchange reactions, dissociation, ionisation, charge transfer, and electronic excitations, or a combination of these. Since the "chemical identity" of the species in a scattering process is a persistent asymptotic property, the theory of such processes must include all relevant asymptotic states which may occur or be measured.

Remarks to quantum reactive scattering

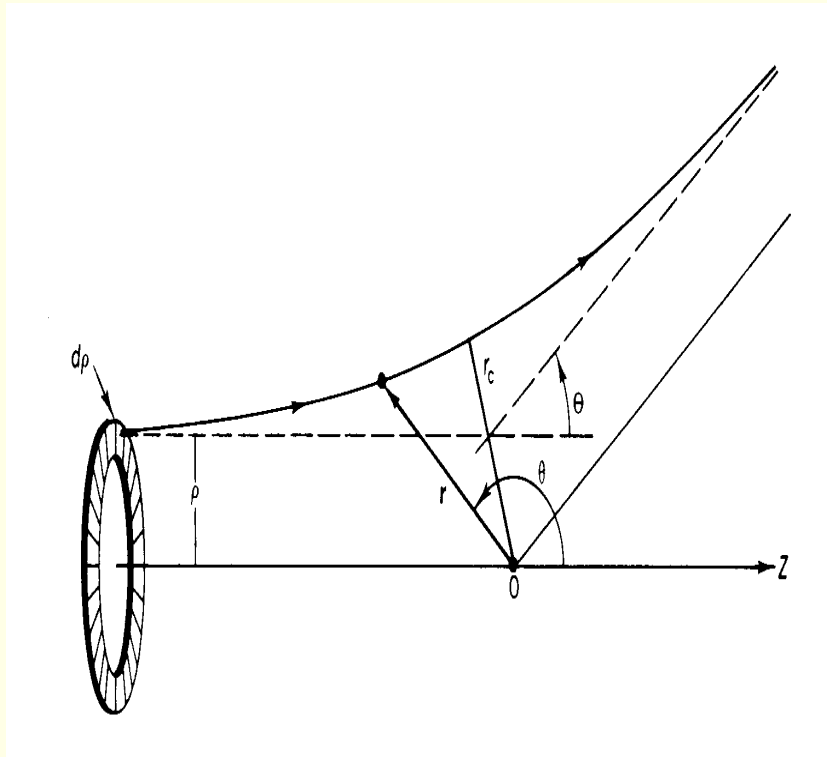
- detailed study of the dynamics of simple chemical reactions in the gas phase and on solid surfaces is a major area of modern physical chemistry
- "complete" picture of the state-to-state dynamics of atom-diatom reactions such as



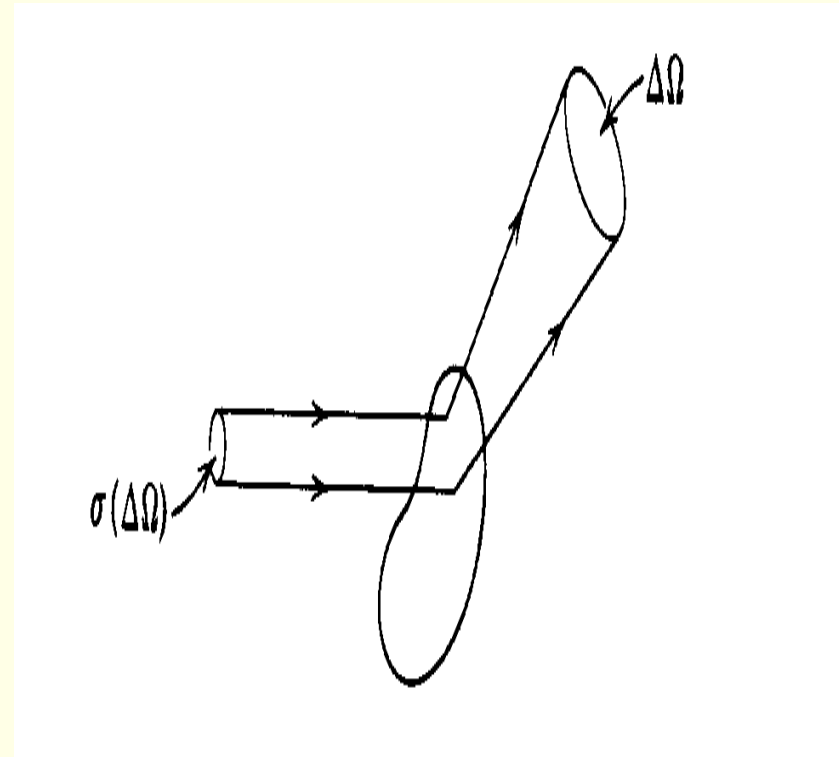
- accurate quantum mechanical calculations up to 1986



- classical trajectory calculations: possible on a wide range of reactions, including those involving polyatomic molecules
- since 1986 remarkable progress in QM 3D chemical reactions



(a)



(b)

Figure 1: (a) A classical trajectory of a particle in a central force field: r, θ are the instantaneous coordinates of the particle, ρ is the impact parameter, r_c is the distance of closest approach, and Θ is the scattering angle, (b) The cross section $\sigma(\Delta\Omega)$ is the area of that part of the target which scatters into $\Delta\Omega$.

most detailed quantity: differential cross section (Fig. 1)

$$\frac{d\sigma_{v,j \rightarrow v',j'}(\theta, E)}{d\Omega} \quad (3)$$

probability of producing the product state (v', j') from the reactant state (v, j) with a solid scattering angle $\Omega = (\theta, \phi)$ and fixed collision energy E

- crossed molecular beam experiments: DCS resolved with respect to θ
- averaging over the scattering angle: integral cross sections

$$\sigma_{v,j \rightarrow v',j'}(E) = 2\pi \int_0^\pi \frac{d\sigma_{v,j \rightarrow v',j'}(\theta, E)}{d\Omega} \sin \theta d\theta \quad (4)$$

- in principle be measured in less sophisticated bulk experiments

thermal rate constants $k(T)$:

Boltzmann averaging these integral cross sections over the initial rovibrational state (v, j) and collision energy E and summed over all possible product states (v', j')

Theory of chemical reaction dynamics:

- provides a crucial link between the results obtained in detailed state selective molecular beam experiments and thermally averaged bulb measurements

exact quantum mechanical methods:

- well established for solving inelastic scattering (energy transfer) problems
- 3D QM reactive scattering problem has begun to become "routine"
slow progress??
- coordinates which most conveniently describe the reactants of a chemical reaction are not particularly convenient for describing the products, and vice versa
- quantum mechanical calculations must, by virtue of the Uncertainty Principle describe *all* regions of the available coordinate space at once
- classical trajectories: no coordinate problem

- four main categories (see Fig. 2): computer modelling, many-channel theories, many-body theories and trajectory theories
- time-independent coupled-channels approach: linear algebraic variational methods and propagation methods

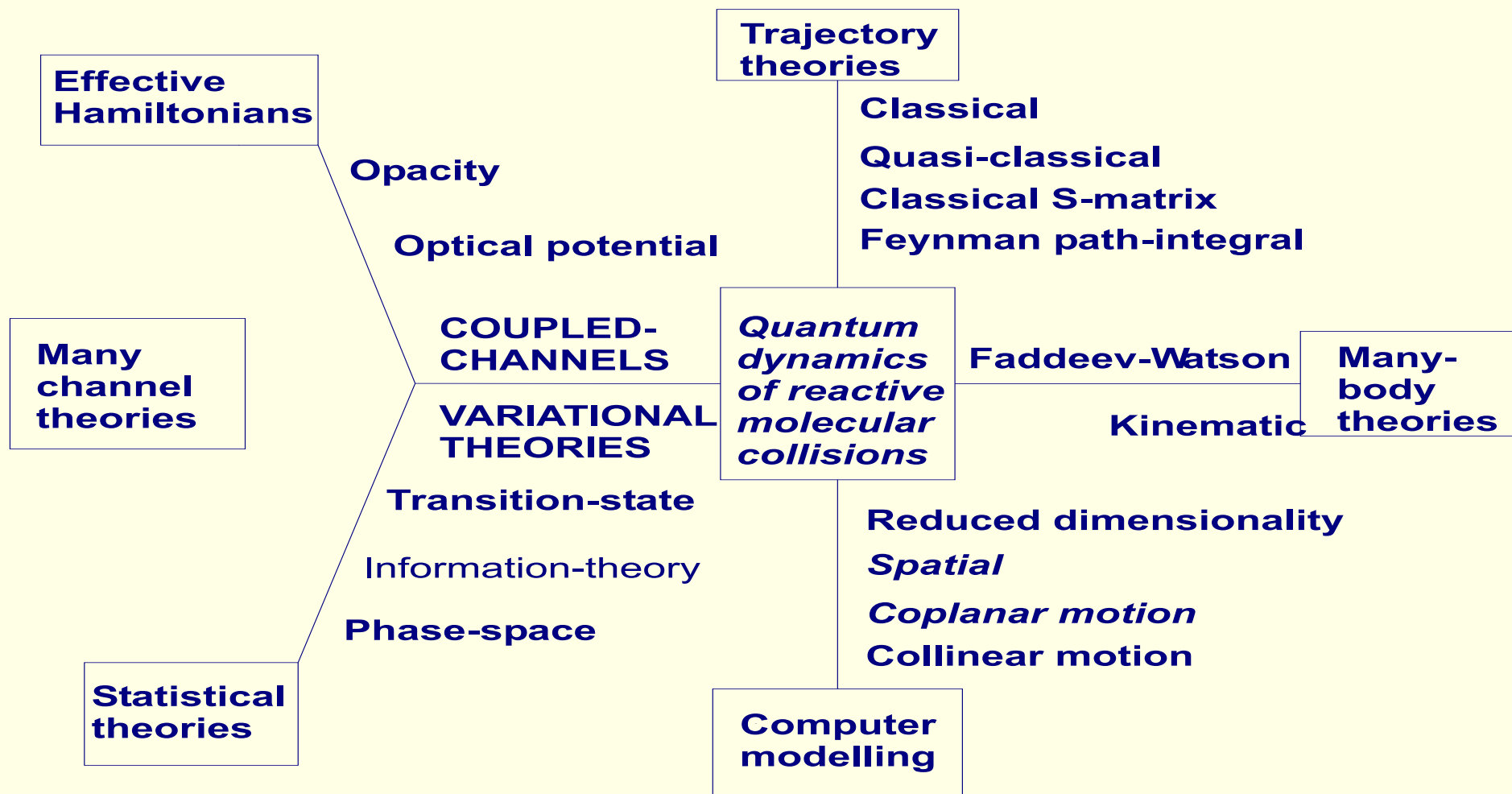


Figure 2: Different theoretical approaches for reactive molecular collisions [20]

Overview of quantum reactive methods and remarks to the coupled equations problem

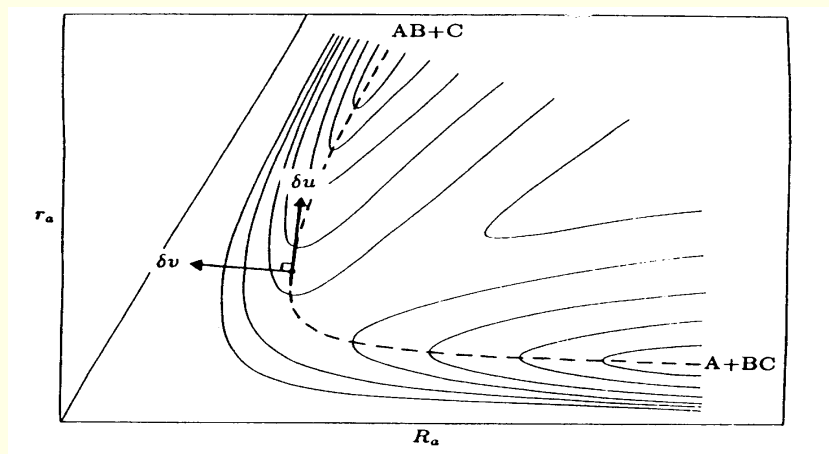
two formal approaches have become important in the quantum theory of atom-diatom reactive scattering:

the *traditional ordinary SE* approach:

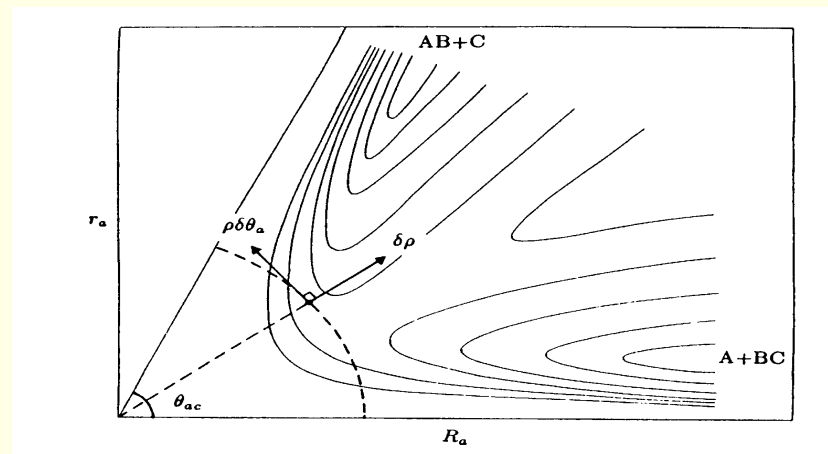
the difference between reagents and products is accounted for essentially by appropriate design of coordinate system, i.e., on the '*kinematical level*' of description

the *generalised SE* approach: approach offered by the arrangement channel quantum mechanics (Kouri and Baer (1986))

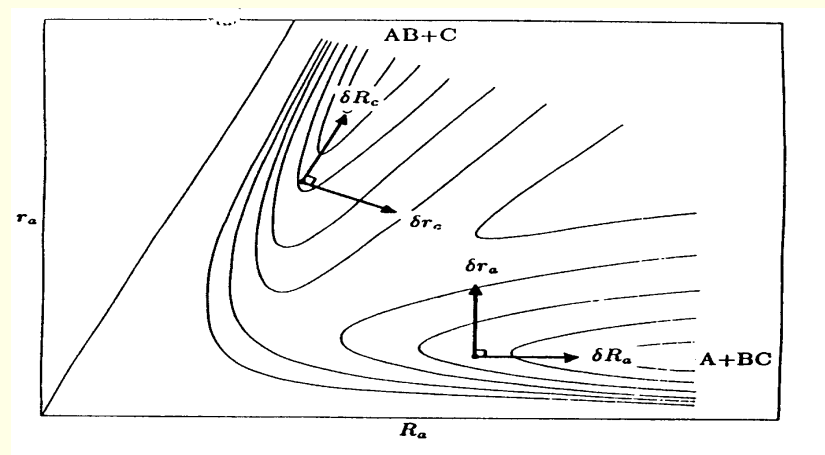
the problem of existence of different asymptotic in reactive collisions is resolved on the '*dynamical level*', by intervening into the structure of the equation of motion



(a) Jacobi coordinates



(b) Hyperspherical coordinates



(c) Natural coordinates

- most of the coordinate systems (see Fig. 3) which have been especially 'designed or adapted' to description of atom-diatom reactive scattering fall into the category of *natural reaction coordinates* (Marcus 1966 , Light 1971) or into the category of *hyperspherical coordinates* (Smith 1960, Johnson 1980)
- essential difference between these categories concerns construction of the so-called *scattering coordinate*: a coordinate which measures the progress the collision system has made from (or to) the condensation stage to (or from) the fragmentation stage
- three different atom-diatom fragmentations -arrangement channels - possible in a triatomic system and the three-atom dissociation channel which is usually excluded from consideration

natural reaction coordinate systems:

the scattering coordinate is defined separately for every atom-diatom arrangement channel, usually as an arc length along some reference curve in the space of relative configurations of the three atomic nuclei which is placed possibly close to the path of minimum electronic energy within a respective arrangement channel region ('tube') of this space

hyperspherical coordinate systems:

the scattering coordinate-the hyperradius-is defined to describe simultaneously all the fragmentation channels possible in a collision system. There is no need for troublesome matching of solutions arising in the strong interaction region. The hyperspherical coordinates become inadequate, however, in describing the system at the fragmentation stage, with atom and diatom fragments infinitely separated. This causes some complications in asymptotic analysis of solutions of the SE

generalised SE approach:

- a decomposition of the total wavefunction into pieces - each describing only one atom-diatom arrangement channel - is made which corresponds, in a sense, to the division of the configuration space into the separate arrangement channel regions in the natural reaction coordinate-ordinary SE approach.
- the matching of the total wave function generated in the different arrangement channel regions is replaced with a coupling of the different arrangement channel components of the total wavefunction which is introduced explicitly into the generalised SE, usually in the form of potential-like terms.
- the choice of coordinate representation is not as essential for overall adequacy of description of reactive collision as in the case of the ordinary SE but it still matters a lot when the generalised equation is to be practically solved.
- of some importance is the fact that each component of the total wavefunction

may be represented in its own coordinate system, most suitable for describing a given atom-diatom arrangement.

- all the channel coordinate systems may have a common scattering coordinate or three different channel scattering coordinates may be employed.

practical approaches: ordinary or generalised SE

- close-coupling methods and variational methods
- variational principle connected with the quantum-mechanical equations of motion
- differences: lies in assumed form of trial solutions of these equations, the 'best' of which is sought for by any individual method

close-coupling methods:

- trial wavefunctions or their arrangement channel components are in the form of expansions in some basis functions which span the parts of the entire configuration space available to the collision system on surfaces with fixed values of the scattering coordinate or the parts of the particular arrangement channel regions on surfaces with fixed values of respective channel scattering coordinates
- the basis functions may be modified, stepwise or continuously, with changing the parameters of the surfaces and the expansion coefficients have to be, of course, functions of the scattering coordinate(s)
- coefficient functions which correspond to the actual (approximate) solution of the ordinary or of the generalised SE, sets of coupled equations-differential or integro -differential in cases with multiple scattering coordinates-are obtained
- the number of equations in a set is made finite by retaining only the most

closely coupled ones-the close-coupling approximation

- the strength of coupling depends on the shape of the potential surface, on properties of the basis functions and on the coordinate system employed
- for usefulness of the close-coupling methods, it is important that a kind of (quasi-)separability exists in the collision system between motion along the scattering coordinate and motions along the remaining coordinates in the coordinate system chosen which allows truncation of the coupled equations to a small set

variational methods:

- trial solutions are expanded in basis functions which describe all degrees of freedom of the collision system
- from the condition of stationarity of the functional employed, sets of algebraic equations are obtained for the expansion coefficients

- since the choice of coordinates and of basis functions is not limited by any quasi-separability requirement these direct variational (algebraic) methods are potentially more flexible than the close-coupling methods in describing collision systems at the condensation stage and therefore are particularly suitable for reactive systems
- methods have been developed using various versions of the Kohn principle, for the scattering S-matrix (Zhang and Miller 1987, 1989), for the log-derivative matrix (Manolopoulos et al 1989), and for the Wigner R matrix (Linderberg et al 1989)
- these methods can be exploited to carry out calculations within the generalised as well as within the ordinary SE approaches
- a parallel (actually an earlier) trend in the search for efficient algebraic methods for molecular reactive scattering calculations has been concerned with the generalised Lippmann-Schwinger equations rather than with the SEs and

has resulted in developing methods which use the Schwinger or Schwinger-like expressions for the reactance matrix (Schwenke et al 1988, Zhang et al 1988) and the methods based on the Newton variational principle (Schwenke et al 1988, 1989) and on the scattering wave variational principle (Sun et al 1990)

close-coupling methods (CC):

- being undoubtedly the most powerful and convenient methods of investigating non- reactive molecular scattering processes (see Lester (1976)
- have played the leading role in advancing the description of reactive atom-diatom collisions from the stage of collinear models to the present level of rigorous quantum-mechanical treatment in full dimensionality
- CC- method seems to be the most natural choice within the ordinary SE approach.

- numerous formulations of the coupled equations for atom-diatom reactive scattering have appeared in the literature
- representative of the class of formulations using natural reaction coordinates and involving matching procedures are those by Elkowitz and Wyatt (1975), by Schatz and Kuppermann (1976) and by Walker et al (1976)
- formulations using hyperspherical coordinates were proposed by Kuppermann et al (1980), Römelt and Manz (1980), Pack and Parker (1987), etc.

I.2 Some aspects to quantum molecular scattering in chemical dynamics

Chemical dynamics:

- link between the potential energy surface (or surfaces) and physically observable chemical phenomena
- the *potential surface* comes in principle from an ab initio quantum chemistry calculation (within the Born-Oppenheimer approximation) or often constructed by some more approximate model, e.g., semiempirical quantum chemistry or totally empirical "force field" models

Elastic Scattering

- study of elastic scattering: in 1960's an important project for developing the tools to be used to study more interesting processes

- elastic scattering of the rare gas atoms, e.g. Y.T.Lee's (1986 Nobel Prize with M. Polanyi and D. Herschbach)
- measurements of the differential scattering cross sections allowed the definitive determination of the intermolecular potential energy function $V(r)$ of essentially all the rare gas atoms with each other

fully rigorous quantum mechanical elastic differential cross section;

$$\sigma_E(\theta) = \left| \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) (e^{2i\eta_l(E)} - 1) \right|^2 \quad (5)$$

phase shift $\eta_l(E)$, orbital angular momentum l , energy E :

determined from the asymptotic form of the regular solution of the radial SE

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - E \right) f_{lE}(r) = 0 \quad (6)$$

asymptotic boundary condition:

$$\lim_{r \rightarrow \infty} f_{lE}(r) \propto \sin\left(kr - \frac{\pi l}{2} + \eta_l(E)\right) \quad (7)$$

- given $V(r)$ and E : solve SE, obtain $\eta_l(E)$ and compute σ_E

hundreds (or thousands) of values of l 's may be needed

- Elastic scattering: theoretical workhorse in earlier years for developing many approximate theoretical methods

semi-classical approximation to quantum mechanics:

1959 Ford and Wheeler: approximations by which the rigorous quantum cross section of eqn. (5-7) degenerates to the completely classical cross section

$$\sigma_E(\theta) = \sum_k \frac{bk}{\sin \theta |\Theta(b_k)|} \quad (8)$$

$b_k \equiv b_k(\theta)$: impact parameters, classically scatter at angle θ

$$|\Theta(b)| = \theta \quad (9)$$

$\Theta(b)$: *classical* deflection angle as a function of b (r_0 : classical turning point)

$$\Theta(b) = \pi - \int_{r_0}^{\infty} dr \frac{2b}{r^2} \left(1 - \frac{V(r)}{E} - \frac{b^2}{r^2} \right)^{-\frac{1}{2}} \quad (10)$$

- *WKB approximation* for the phase shift and the Legendre polynomial, to replace the sum over l by an integral, evaluate the integral by the stationary phase approximation

$$\sigma_E(\theta) = \left| \sum_k \left(\frac{bk}{\sin \theta |\Theta(b_k)|} \right)^{\frac{1}{2}} e^{i\phi_k/\hbar} \right|^2 \quad (11)$$

$\{b_k\}$: the same as in the classical cross section

- l ($l \equiv kb, k = \sqrt{2mE/\hbar^2}$) for which the phase in the integral over l is stationary, makes the dominate contribution to the sum/integral
- phases $\{\phi_k\}$ are the classical action for the k^{th} trajectory that classically scatters at angle θ
- eqn. (5, 8), and (11) show the generic structure relating quantum, classical,

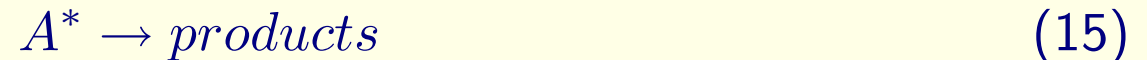
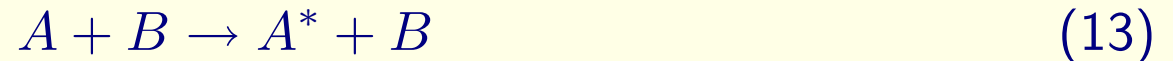
and the semiclassical correction in scattering cross sections:

$$\sigma_{SC}(\theta) = \sigma_{CL}(\theta) + \text{interference terms}, \quad (12)$$

interference: between the different classical contributions to the cross section
(most fundamental effect of quantum mechanics)

Inelastic Scattering

- excitation or relaxation of rotational and vibrational degrees of freedom and also of electronic states
- rovibrational inelasticity: understanding classical transport phenomena in gases, vibrational relaxation of highly excited molecules in unimolecular reactions (Lindeman mechanism)



- understanding vibrational de-activation of highly excited vibrational states

- electronically inelastic collisions: important in many gas laser systems, in the upper atmosphere, and in plasmas; involve ions as collision partners

quantum mechanical description of an inelastic scattering process:

(leaving aside details involving angular momentum)

$$\Psi_i(r, \xi) = \sum_j \phi_j(\xi) f_{j \leftarrow i}(r) \quad (16)$$

$\{\phi_j(\xi)\}$: bound-state eigenfunctions for the internal (rotational, vibrational, and electronic) degrees of freedom (ξ : collectively denoting the appropriate coordinates) of the colliding molecules, r : the radial (translational) coordinate

- radial function (matrix) $f_{j \leftarrow i}(r)$: determined by the coupled-channel SE:

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} - E_j \right) f_{j \leftarrow i}(r) + \sum_{j'} V_{j,j'}(r) f_{j' \leftarrow i}(r) = 0 \quad (17)$$

$V_{j,j'}(r)$: interaction potential $V(\xi, r)$ with respect to the basis of internal states

$$V_{j,j'}(r) = \int d\xi \phi_j(\xi) V(\xi, r) \phi_{j'}(\xi) \quad (18)$$

$E_j = E - \epsilon_j$, E : total energy, ϵ_j : energy eigenvalue, (ϕ_j)

- boundary conditions: radial functions: regular for $r \rightarrow 0$, for large r incoming

radial wave in initial channel i and outgoing waves in all open channels

$$\lim_{r \rightarrow \infty} f_{j \leftarrow i}(r) \sim -\frac{e^{-ik_i r}}{v_i^{\frac{1}{2}}} \delta_{j,i} + \frac{e^{ik_j r}}{v_j^{\frac{1}{2}}} S_{j,i}(E) \quad (19)$$

$v_j = \sqrt{2E_j/\mu}$: translational velocity for channels j , $S_{j,i}$: S-matrix (scattering cross sections)

- full wavefunction at large r :

$$\Psi_i(r, \xi) \sim -\phi_i(\xi) \frac{e^{-ik_i r}}{v_i^{\frac{1}{2}}} \delta_{j,i} + \sum_j \phi_j(\xi) \frac{e^{ik_j r}}{v_j^{\frac{1}{2}}} S_{j,i}(E) \quad (20)$$

initial channel i has an incoming radial wave, all channels have outgoing (scattered) waves

- S-matrix: unitary, interpretation as the probability amplitude for the $i \rightarrow j$ transition

$$P_{j \leftarrow i} = |S_{j,i}|^2 \quad (21)$$

total angular momentum J is conserved: orbital angular momentum of relative motion plus any angular momentum from the internal degrees of freedom (because of the isotropy of space)

diagonal label of the S-matrix, $S_{j,i}^J(E)$

- state-to-state differential cross section: most detailed possible scattering observable

$$\sigma_{j \leftarrow i}(\theta) = \left| \frac{1}{2ik_i} \sum_{J=0}^{\infty} (2J+1) d_{m_j, m_i}^J(\theta) (S_{j,i}^J(E) - \delta_{j,i}) \right|^2 \quad (22)$$

$d_{m_j, m_i}^J(\theta)$: Wigner rotation function, m_i, m_j : projections of the total angular

momentum onto the initial and final relative velocity vectors

– eq. (22) is the generalisation of (5) for the elastic scattering of two structureless particles: $J \rightarrow l$ (the orbital angular momentum l is the total angular momentum), m_j and $m_i \rightarrow 0$, $d_{00}^J = P_l(\cos\theta)$:

$$S_{j,i}^J(E) \rightarrow e^{2i\eta_l(E)} \quad (23)$$

– theoretical task: solve (17) with the boundary conditions of (19) to obtain the S-matrix

number of channels can be large: > 1000

number of rovibr. states of a diatomic molecule with energy $< E$:

$$N(E) = \sum_{v=0} \sum_{j=0} (2j+1) h(E - \epsilon_{vj}) \quad (24)$$

rigid rotor-harmonic oscillator approximation:

$$\epsilon_{vj} \approx \hbar\omega\left(v + \frac{1}{2}\right) + Bj(j+1) \quad (25)$$

ω : vibrational frequency, B : rotation constant

$$N(E) \approx \frac{E^2}{2\hbar\omega B} \quad (26)$$

$E = 0.14$ eV, $\hbar\omega = 2000$ cm⁻¹, $B = 1$ cm⁻¹ (O₂, N₂, CO): $N \sim 160$
I₂ ($\hbar\omega = 215$ cm⁻¹, $B = 0.037$ cm⁻¹): $N \approx 40,000$!
collision of two diatomics at energy E :

$$N(E) \approx \frac{E^4}{4!\hbar\omega_1\hbar\omega_2B_1B_2} \approx \frac{1}{6}N_1N_2 \quad (27)$$

N_1, N_2 : number of channels for molecules 1 and 2

- the more channels strongly coupled: the better is to approximate the dynamics by classical mechanics (more channels for heavier the particles)
- classical trajectory simulations: equations of motion to be solved (Hamiltonian's equations) grows linearly with the number of particles
- coupled-channel: numbers of coupled channels in the coupled-channel SE grows exponentially with this number

variety of approximate quantum mechanical and semiclassical theories:

some of the degrees of freedom can be treated as slow or fast compared to others, leading to sudden or adiabatic approximations, and in some cases the coupling between translational and internal motion can make perturbation theory a useful approximation

Classical S-matrix theory: "rigorous" semiclassical theory

- incorporates the full classical mechanics for all degrees of freedom without approximation
- generalisation of the Ford and Wheeler semiclassical description of elastic scattering

inelastic transition probability:

$$P_{j \leftarrow i}^{SC} = |\sum_k P_{j,i}^{(k)\frac{1}{2}} e^{i\phi_{j,i}^{(k)}/\hbar}|^2 \quad (28)$$

$P_{j,i}^{(k)}$: classical contribution to the $i \rightarrow j$ transition from the k^{th} trajectory

- complete classical transition probability:

$$P_{j \leftarrow i}^{CL} = \sum_k P_{j,i}^{(k)} \quad (29)$$

$\phi_{i,j}$: classical action integral along the corresponding trajectory

- semiclassical transition probability:

$$P_{j \leftarrow i}^{SC} = P_{j \leftarrow i}^{CL} + \text{interference} \quad (30)$$

- Interference between the different classical trajectories:

"rainbows" in the product distribution of internal states

analogous effects in the angular distribution of the DCS in elastic scattering

Reactive Scattering

- Quantum mechanical reactive scattering:
 - provides the fundamental, rigorous and the most complete description of a chemical reaction allowed by the basic laws of nature
 - most complicated to deal with because of the lack of one physically appropriate set of coordinates for "translation" and "internal" degrees of freedom
 - natural coordinates for describing translational and internal degrees of freedom for the reactant molecules are not the natural ones for describing those of the products

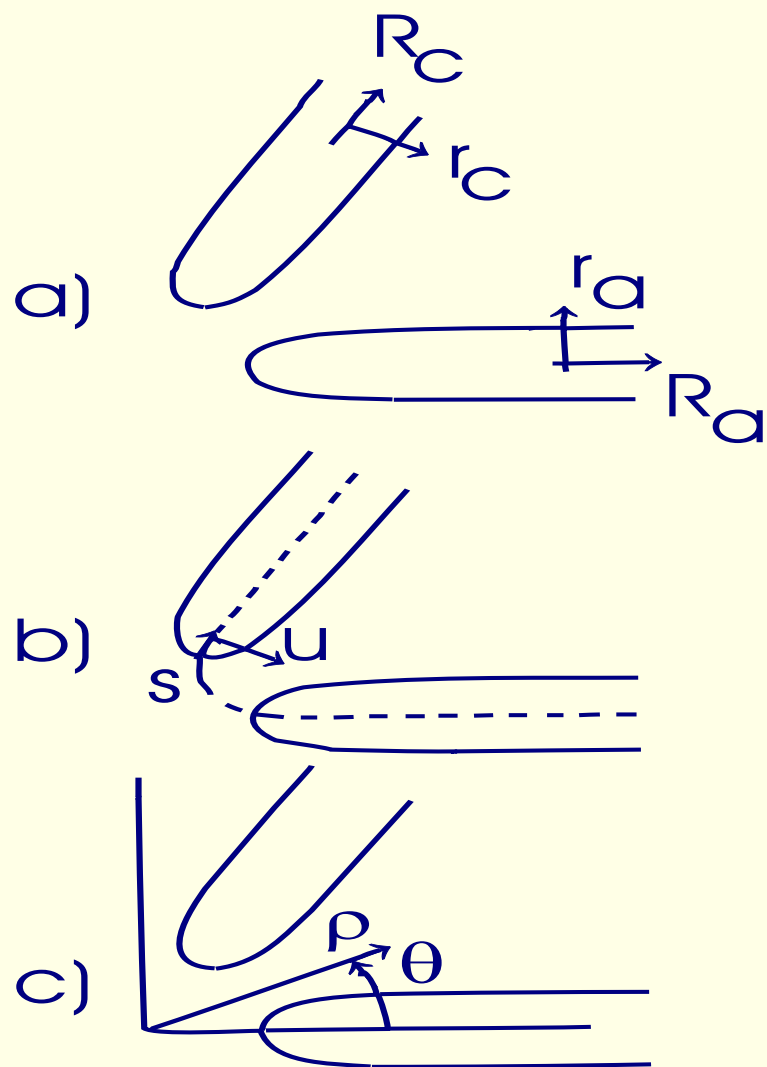
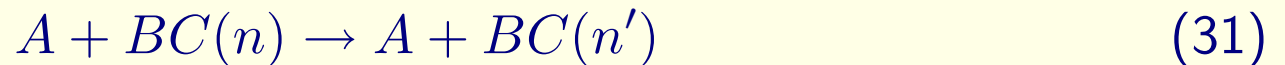


Figure 4: Schematic depiction of a collinear $A + BC \rightarrow AB + C$ potential energy surface and different ways of choosing coordinates. (a) Jacobi coordinates for arrangement a ($A + BC$) and c ($AB + C$), (b) reaction path ('natural coordinates') coordinates, (c) hyperspherical (here simply polar) coordinates.

Why a basis set variational approach to reactive scattering?

- theory of reactive scattering: more complicated than that for elastic and inelastic scattering
- different coordinates and different formulations of reactive scattering
 - inelastic scattering process (i.e. vibrational excitation)



- standard Jacobi coordinates (r_a, R_a) are the natural choice
- coupled-channel expansion of the wavefunction:

$$\psi_{n_1} = \sum_n \phi_n(r_a) f_{n \leftarrow n_1}(R_a) \quad (32)$$

$\{\phi_n\}$: vibrational eigenfunctions for BC, n_1 : initial vibrational state

standard coupled-channel equations:

$$0 = \left(-\frac{h^2}{2\mu} \frac{d^2}{dR_a^2} - E_n\right) f_{n \leftarrow n_1}(R_a) + \sum_{n'} V_{n,n'}(R_a) f_{n' \leftarrow n_1}(R_a), \quad (33)$$

$$V_{n,n'}(R_a) = \int dr_a \phi_n(r_a) (V - v) \phi_{n'}(r_a) \quad (34)$$

$$E_n = E - \epsilon_n, \quad n, E, \epsilon_n, V, v$$

- "coordinate problem": (r_a, R_a) are natural for A+BC and not appropriate for describing AB+C.
- formulation by Miller (1969): Jacobi coordinates for the various "arrangements" (i.e. A+BC, AB+C, AC+B) are all used simultaneously

- collinear case: expansion for the wavefunction

$$\Psi_{\gamma_1 n_1} = \sum_n \phi_n^a(r_a) f_{an \leftarrow \gamma_1 n_1}(R_a) + \sum_n \phi_n^c(r_c) f_{cn \leftarrow \gamma_1 n_1}(R_c) \quad (35)$$

$\gamma = a(A+BC)$, $b(B+AC)$, or $c(C+AB)$, $\{\phi_n^a\}$ and $\{\phi_n^c\}$

- two independent coordinates (degrees of freedom) for the collinear case, r_a and R_a are functions of r_c and R_c

- philosophy of this approach: similar to LCAO

$$\chi(r) = \sum_i a_i \phi_i^a(r_a) + \sum_i b_i \phi_i^b(r_b) \quad (36)$$

r_a, r_b : electron-coord. with respect to nuclei a and b

- eq. (35) is thus a natural and efficient way to represent a reactive scattering wavefunction, but it introduces the complexity that the coupling between terms corresponding to different arrangements are nonlocal, exchange type interactions

$$\begin{aligned} & \left(-\frac{\hbar^2}{2\mu_a} \frac{d^2}{dR_a^2} - E_n^a\right) f_{an \leftarrow \gamma_1 n_1}(R_a) + \sum_{n'} V_{an, an'}(R_a) f_{an' \leftarrow \gamma_1 n_1}(R_a) \\ & - \sum_{\gamma \neq a} \sum_{n'} \int dR_\gamma V_{an, \gamma n'}(R_a, R_\gamma) f_{\gamma n' \leftarrow \gamma_1 n_1}(R_\gamma) = 0 \end{aligned} \quad (37)$$

- exchange interaction: couples states of different arrangements, analogous to electron exchange interactions in quantum chemistry
- analogous to the Hartree-Fock equations of electronic structure theory, cannot be solved by finite difference algorithms

- the most satisfactory way of dealing with exchange is analogous to what quantum chemists do in the Hartree-Fock problem, namely to expand the unknown wavefunctions in a basis set and determine the expansion coefficients via a variational principle
- simplest variational method - the Kohn variational principle- is essentially the Rayleigh-Ritz variational principle for eigenvalues modified to incorporate scattering boundary conditions, it is free of anomalous singularities if it is formulated with S-matrix type boundary conditions rather than standing wave boundary conditions as had been typically used previously
- variational expression for the S-matrix:

$$S [\Psi_f, \Psi_i] = S_{fi}^{(0)} + \frac{i}{\hbar} \langle \Psi_f | H - E | \Psi_i \rangle \quad (38)$$

Ψ_f and Ψ_i : variational ("trial") wavefunctions, have to satisfy the correct

boundary conditions:

$$\Psi_l(\xi, r) \sim -\frac{e^{-ik_l r}}{v_l^{\frac{1}{2}}} \phi_l(\xi) + \sum_j \frac{e^{ik_j r}}{v_j^{\frac{1}{2}}} \phi_j(\xi) S_{j,l}^{(0)} \quad (39)$$

– Ansatz for trial function:

$$\Psi_l(\xi, r) = \Phi_l(\xi, r) + \sum_j \Phi_j(\xi, r)^* C_{j,l} + \sum_k \chi_k(\xi, r) C_{k,l} \quad (40)$$

$\Phi_l(\xi, r)$: asymptotically incoming radial wave in channel l

$$\Phi_l(\xi, r) \sim \frac{e^{-ik_l r}}{v_l^{\frac{1}{2}}} \phi_l(\xi) \quad (41)$$

Φ_l^* : outgoing wave, $\{\chi_k\}$: L^2 basis for the interaction (small r) region, $\{C_{j,l}\}$ and $\{C_{k,l}\}$: variational parameters, S-matrix has to be extremized

– variational condition:

$$0 = \frac{\partial}{\partial C_\lambda} S(\{C_{j,f}\}, \{C_{l,f}\}, \{C_{j,i}\}, \{C_{l,i}\}) \quad (42)$$

– leads to linear equations for the coefficients which are solved by matrix inversion
– using the coefficients in the expression for the S-matrix: variationally optimum result

$$S_{f,i} = \frac{i}{\hbar} (M_{f,i} - \mathbf{M}_f^T \mathbf{M}^{-1} \mathbf{M}_i) \quad (43)$$

$$M_{f,i} = \langle \Phi_f | H - E | \Phi_i \rangle \quad (44)$$

$$\mathbf{M}_1 = \begin{Bmatrix} \langle \Phi_j^* | H - E | \Phi_l \rangle \\ \langle \chi_k | H - E | \Phi_l \rangle \end{Bmatrix} \quad (45)$$

for $l = i$ and f and

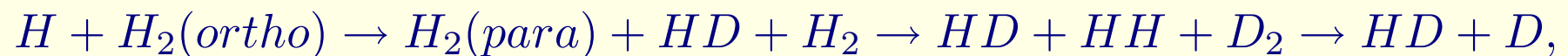
$$\mathbf{M} = \begin{Bmatrix} \langle \Phi_{j'}^* | H - E | \Phi_j \rangle, \langle \Phi_{j'}^* | H - E | \chi_k \rangle \\ \langle \chi_{k'} | H - E | \Phi_j \rangle, \langle \chi_{k'} | H - E | \chi_k \rangle \end{Bmatrix} \quad (46)$$

- scattering problem: has been cast in the form of a standard quantum mechanical calculation, i.e., computing matrix elements of the Hamiltonian with respect to a set of basic functions and then performing a linear algebra calculation
- power of this variational result: applies also for reactive scattering provided if one includes an arrangement label: $A + BC (vjm) \rightarrow AB (v'j'm') + C$
initial channel index $i \equiv (avjm)$, arrangement a and quantum state (vjm) , final channel label $f = (cv'j'm')$

- coordinates appropriate for asymptotic channel l may be different for different channels

$$\Phi_l \sim -\frac{e^{-ik_l r_l}}{v_l^{\frac{1}{2}}} \phi_l(\xi_l) \quad (47)$$

- many of the recent accurate quantum reactive scattering calculations have utilised the above approach
- methods using hyperspherical coordinates have been the primary alternative
- first complete state-to-state differential cross section calculations: $H+H_2$ reaction (isotopic variants), $F+H_2 \rightarrow HF + H$ reaction (mostly for $J = 0$ only)



– cumulative reaction probability (CRP) for a reaction: without having to solve for the individual state-to-state S-matrix elements

thermally averaged rate constant for a reaction can be expressed as the Boltzmann average of the CRP $N(E)$:

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE e^{-E/kT} N(E) \quad (48)$$

CRP: sum of reactive probabilities, squares of S-matrix elements, over all open reactant and product channels

$$N(E) = \sum_{n_r, n_p} |S_{n_p, n_r}(E)|^2 \quad (49)$$

$n_r(n_p)$: asymptotic channel states of the reactant (product)

CRP can also be expressed as

$$N(E) = \frac{1}{2}(2\pi\hbar)^2 \text{tr}[\hat{F}\delta(E - \hat{H})\hat{F}\delta(E - \hat{H})] \quad (50)$$

\hat{H} : Hamiltonian operator, \hat{F} : flux operator, independent of individual reactant and product states, $\delta(E - \hat{H})$: the microcanonical density operator

– inelastic and reactive collision processes may also involve changes in the electronic state:

requires only the addition of the electronic state index to the channel label in the coupled-channel equations or basis functions

in practice, requires that one knows the non-adiabatic coupling and the different potential energy surfaces

I.3A General remarks: Quantum scattering, scattering matrix, Møller operators, etc.

- Time evolution: Schrödinger equation ($\hbar = 1$)

$$i\frac{d}{dt}|\psi_t\rangle = H|\psi_t\rangle \quad (51)$$

conservative systems: Hamiltonian H is independent of t

- general solution:

$$|\psi_t\rangle = U(t)|\psi\rangle = e^{-iHt}|\psi\rangle \quad (52)$$

- basic theorem on linear operators: H is selfadjoint, the evolution operator $U(t)$ is unitary

- evolution operator maps the state vector for time zero ($|\psi\rangle$) onto the corresponding vector for time t

The description of quantum scattering closely parallels the classical formalism:

- classical orbit $x(t)$ is satisfying Newton's equation

- state vector $|\psi_t\rangle$ satisfying the TDSE

- $|\psi_t\rangle$: any vector in the appropriate Hilbert space \mathcal{H}

- $U(t)|\psi\rangle$: no longer an orbit in real space R^3

every orbit $U(t)|\psi\rangle$ can be uniquely identified by the fixed vector $|\psi\rangle$, which is just the state vector at the instant $t = 0$

- fixed local potential: suppose that the orbit $U(t)|\psi\rangle$ describes the evolution of some scattering experiment

– when followed back to a time well before the collision $U(t)|\psi\rangle$ represents a wave packet that is localized far away from the scattering center and behaves like a *free* wave packet

motion of a free particle is given by the free evolution operator:

$$U^0(t) = e^{-iH^0t} \quad (53)$$

and as $t \rightarrow -\infty$,

$$U(t)|\psi\rangle \xrightarrow{t \rightarrow -\infty} U^0(t)|\psi_{in}\rangle \quad (54)$$

for some vector $|\psi_{in}\rangle$

the limit means that the difference of the two vectors tends to zero

- the actual state $U(t)|\psi\rangle$ becomes experimentally indistinguishable from the freely evolving state $U^0(t)|\psi_{in}\rangle$
- after the collision the particle moves away again and we expect that

$$U(t)|\psi\rangle \xrightarrow{t \rightarrow +\infty} U^0(t)|\psi_{out}\rangle \quad (55)$$

for some $|\psi_{out}\rangle$

- these two limits are analogous to the classical limits as seen in Fig. 5a
- analogy with the classical terminology the asymptotic free orbits of eqn. (54) and (55) are called the in and out asymptotes of the actual orbit $U(t)|\psi\rangle$
- quantum asymptotes (54) and (55) are labeled by the fixed vectors $|\psi_{in}\rangle$ and $|\psi_{out}\rangle$

- not every orbit $U(t)|\psi\rangle$ will have asymptotes
- there will be certain scattering orbits that do have asymptotes
- scattering states together with the bound states will span the space \mathcal{H} of *all* states
- every vector in \mathcal{H} (labelled $|\psi_{in}\rangle$ or $|\psi_{out}\rangle$) represents the asymptote of some actual orbit
- for every vector $|\psi_{in}\rangle$ in \mathcal{H} there is a solution $U(t)|\psi\rangle$ of the SE that is asymptotic to the free orbit $U^0(t)|\psi_{in}\rangle$ as $t \rightarrow -\infty$;

and for every $|\psi_{out}\rangle$ as $t \rightarrow +\infty$

– This result is known as the asymptotic condition:

If $V(r)$ falls off fast enough (for $r \rightarrow \infty$), then for every $|\psi_{in}\rangle$ in \mathcal{H} there is a

$|\psi\rangle$ such that

$$U(t)|\psi\rangle - U^0(t)|\psi_{in}\rangle \xrightarrow{t \rightarrow -\infty} 0 \quad (56)$$

and

likewise for every $|\psi_{out}\rangle$ in \mathcal{H} as $t \rightarrow +\infty$

– The asymptotic condition guarantees:

- any $|\psi_{in}\rangle$ in \mathcal{H} is in fact the in asymptote of some actual orbit $U(t)|\psi\rangle$
- the actual state $|\psi\rangle$ of the system at $t = 0$ is linearly related to the in asymptote $|\psi_{in}\rangle$

$$|\psi\rangle = \lim_{t \rightarrow -\infty} U(t)^\dagger U^0(t) |\psi_{in}\rangle \equiv \Omega_+ |\psi_{in}\rangle. \quad (57)$$

the actual state $|\psi\rangle$ at $t = 0$ that will evolve into the out asymptote labelled by $|\psi_{out}\rangle$ is

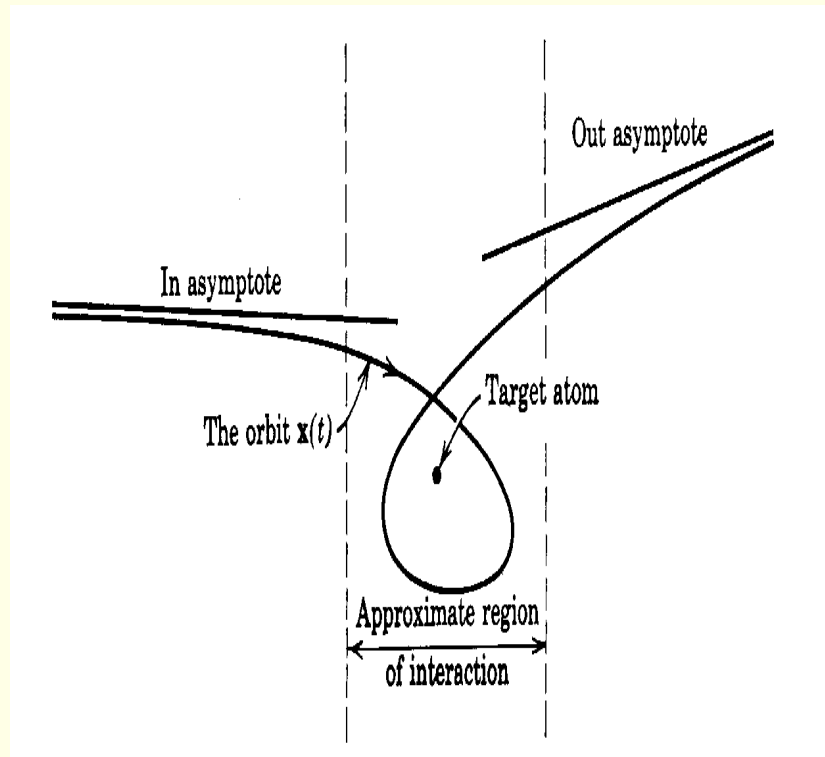
$$|\psi\rangle = \lim_{t \rightarrow +\infty} U(t)^\dagger U^0(t) |\psi_{out}\rangle \equiv \Omega_- |\psi_{out}\rangle \quad (58)$$

The two operators Ω_\pm , defined as the limits

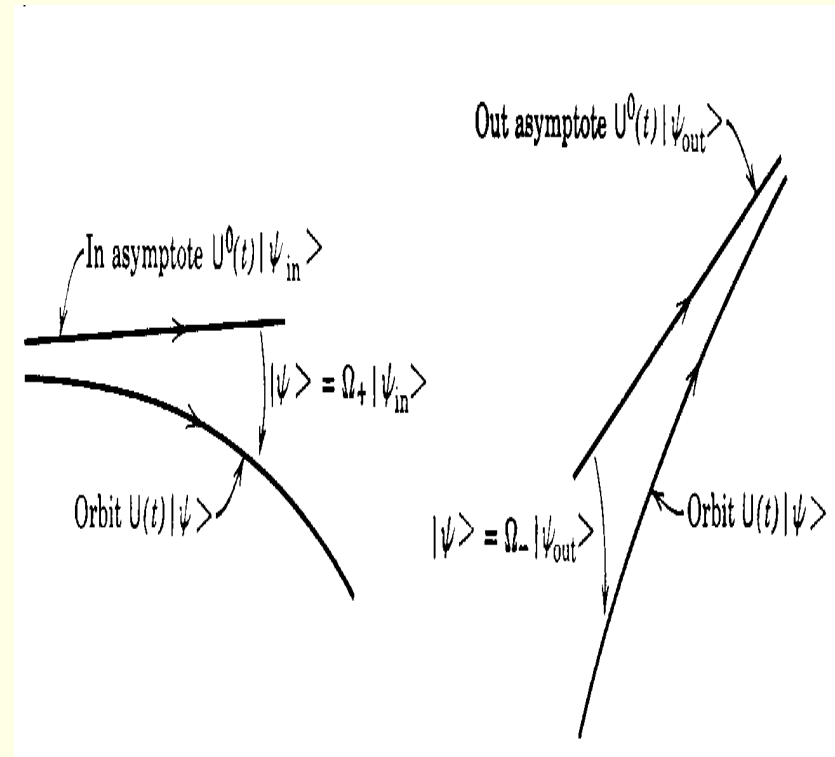
$$\Omega_\pm = \lim_{t \rightarrow \mp\infty} U(t)^\dagger U^0(t) \quad (59)$$

are called the **Møller wave operators** (limits of a unitary operator and so are isometric).

- acting on any vector in \mathcal{H} , they give the actual state at $t = 0$ that would evolve from (or to) the asymptote represented by that vector (Fig. 5b)



(a)



(b)

Figure 5: (a) Typical scattering orbit, (b) Classical representation of the roles of the Møller operators

additional notation:

$$\Omega_+|\phi >\equiv |\phi^+ > \quad [\text{any}|\phi >] \quad (60)$$

$$\Omega_-|\chi >\equiv |\chi^- > \quad [\text{any}|\chi >] \quad (61)$$

$|\phi^+ >$: represents the actual state of the system at $t = 0$, if the in asymptote was $|\psi_{in} > = |\phi >$

$|\chi^- >$: represents the actual state at $t = 0$, if the out asymptote were going to be $|\psi_{out} > = |\chi >$

various notations can be summarised:

$$\begin{array}{ccccc}
 \text{in asymptote} & \xrightarrow{\Omega_+} & \left\{ \begin{array}{c} \text{actual state} \\ \text{at } t=0 \end{array} \right\} & \xleftarrow{\Omega_-} & \text{out asymptote} \\
 |\psi_{in} > & \rightarrow & |\psi > & \leftarrow & |\psi_{out} > \\
 |\phi > & \rightarrow & |\phi^+ > & & \\
 & & |\chi^- > & \leftarrow & |\chi >
 \end{array} \tag{62}$$

every $|\psi_{in} >$ (or $|\psi_{out} >$) in \mathcal{H} labels the in (or out) asymptote of a unique orbit $U(t)|\psi_{out} >$

the Møller operators Ω_{\pm} map each $|\psi_{in} >$ (or $|\psi_{out} >$) in \mathcal{H} onto the corresponding scattering state $|\psi >$ in \mathcal{R} (Fig. 6)

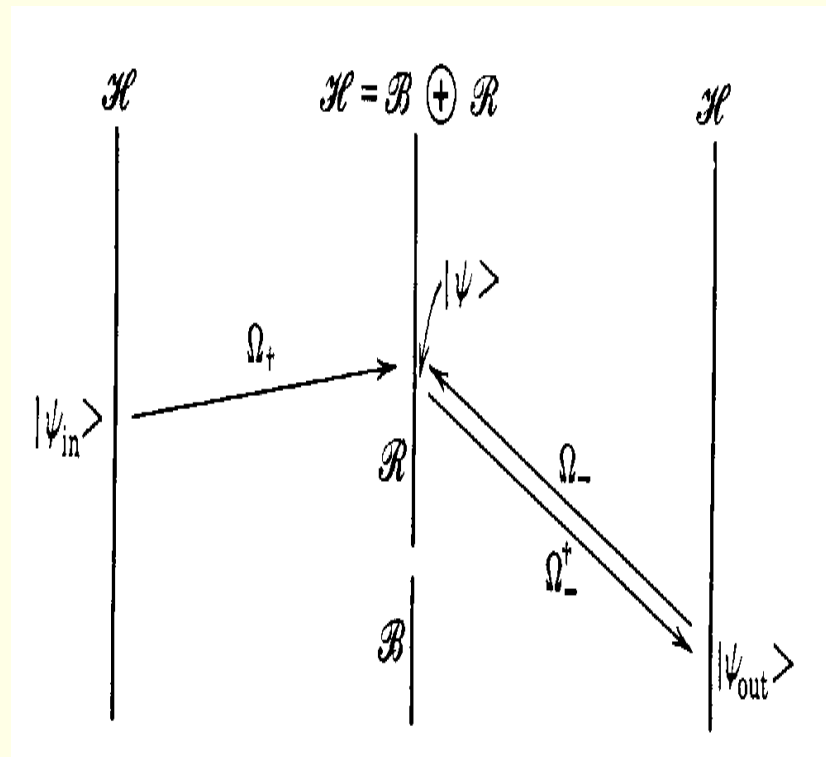


Figure 6: The Møller operators Ω_{\pm} map the in and out asymptotes, represented by $|\psi_{in}\rangle$ and $|\psi_{out}\rangle$, onto the actual orbit labelled by ψ .

The Scattering Operator:

so far: the actual scattering state at $t = 0$ expressed in terms of either of its two asymptotes

- ultimate goal:
- express the out asymptote in terms of the in asymptote without reference to the experimentally uninteresting actual orbit
- because Ω_- is isometric, the relation $|\psi\rangle = \Omega_- |\psi_{out}\rangle$ can be inverted
- since $\Omega_-^\dagger \Omega_- = 1$, we simply multiply on the left by Ω_-^\dagger to give

$$|\psi_{out}\rangle = \Omega_-^\dagger |\psi\rangle = \Omega_-^\dagger \Omega_+ |\psi_{in}\rangle \quad (63)$$

- definition of the scattering operator:

$$S = \Omega_-^\dagger \Omega_+ \quad (64)$$

$$|\psi_{out} \rangle = S |\psi_{in} \rangle \quad (65)$$

- S gives $|\psi_{out} \rangle$ directly in terms of $|\psi_{in} \rangle$
- if a particle enters the collision with in asymptote $|\psi_{in} \rangle$, then it leaves with out asymptote $|\psi_{out} \rangle = S |\psi_{in} \rangle$
- only the asymptotic free motion is observable in practice, the single operator S contains all information of experimental interest
- if we know how to calculate S , then the scattering problem is solved

- experimentally relevant scattering probabilities:
- the quantity of interest is the probability that a particle that entered the collision with in asymptote $|\phi\rangle$ will be observed to emerge with out asymptote $|\chi\rangle$
- the actual state at $t = 0$, which will evolve from the in asymptote $|\phi\rangle$ is $|\phi^+\rangle = \Omega_+|\phi\rangle$, while the actual state at $t = 0$, which would evolve into the out asymptote $|\chi\rangle$ is $|\chi^-\rangle = \Omega_-|\chi\rangle$
- the required probability amplitude is just the scalar product of the actual states at any given time:

$$P(\chi \leftarrow \phi) = |\langle \chi^- | \phi^+ \rangle|^2 \quad (66)$$

$$= |\langle \chi \Omega_-^\dagger \Omega_+ \phi \rangle|^2 \quad (67)$$

$$= |\langle \chi | S | \phi \rangle|^2 \quad (68)$$

- the probability amplitude for the process $(\chi \leftarrow \phi)$ is just the S -matrix element $\langle \chi | S | \phi \rangle$
- $P(\chi \leftarrow \phi)$ is not directly observable
- one cannot actually produce or identify uniquely defined wave packets $|\phi \rangle$ and $|\chi \rangle$
- experimentally observable quantity: the differential cross-section (DCS)
- DCS can be expressed directly in terms of the matrix elements of S

I.3B General formalism: time-dependent and time-independent Schrödinger equation

time-dependent Schrödinger equation (**TDSE**) \Longleftrightarrow time independent Schrödinger equation (**TISE**)

why treat a partial differential equation (PDE) with one additional variable in it if it can be avoided?

if the potential is independent of time (conserve forces), then the variable is separable

(1) TDSE:

$$i\hbar \frac{\partial \chi}{\partial t} = H\chi \quad (69)$$

time-independent Hamiltonian H

$$H = H_0 + V \quad (70)$$

V : perturbation causing scattering among the states of H_0 , this is an initial value problem, generally simpler to solve than boundary value problems

(2) Provided the Hamiltonian is self-adjoint (Hermitian), solutions to the TDSE are L^2 , provided the initial wavepacket is L^2

solutions for scattering of the TISE are not L^2 , the Hamiltonian H has a continuous spectrum and improper eigenstates, which reflect the fact that there is a nonzero (relative) probability of finding the projectile infinitely far from the target

Ansatz: seprable variables

$$\chi = e^{-iEt/\hbar} \chi(E) \quad (71)$$

$$(E - H)\psi(E) = 0 \quad (72)$$

determining $\psi(E)$: TISE

perturbation V causing scattering will be defined as

$$V = H - H_0 \quad (73)$$

$$H_0 = \lim_{\text{large separation of projectile and target}} H \quad (74)$$

$$\lim_{\text{large separation of projectile and target}} V \equiv 0 \quad (75)$$

scattering solution of the TISE:

$$(E - H_0)\psi(E) = V\psi(E) \quad (76)$$

solving this: "causal **Green's operator**" (or **resolvent**)

$$\psi_p^+(E) = \frac{1}{(E - H_0 + i\epsilon)} V \psi_P^+(E) \quad (77)$$

"+" denotes the causal boundary condition of outgoing scattered waves

$\psi_p^+(E)$ is a particular solution of 76 (inhomogeneous equation)

$$(E - H_0)\psi(E) = \mathcal{I}(E) \quad (78)$$

a solution of the homogeneous equation

$$(E - H_0)\phi(E) = 0 \quad (79)$$

complete "solution": **Lippmann-Schwinger**

$$\psi^+(E) = \phi(E) + \frac{1}{E - H_0 + i\epsilon} V \psi^+(E) \quad (80)$$

$+i\epsilon$: selects a unique inverse of $(E - H_0)$, so that $(E - H_0 + i\epsilon)^{-1}$ generates purely outgoing scattering waves at large separations

$\phi(E)$ for a structureless projectile scattering off an infinitely massive center of force satisfies

$$(E + \frac{\hbar^2}{2m} \nabla^2) \phi(E) = 0 \quad (81)$$

plane wave solutions:

$$\phi(E|\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \quad (82)$$

$$\frac{\hbar^2 k^2}{2m} = E \quad (83)$$

$(E - H_0 + i\epsilon)^{-1}$: satisfies outgoing radiation boundary conditions , solves the inhomogeneous TISE

$$(E - H_o)G = I \quad (84)$$

I is the unit operator

$G^+(E) \equiv (E - H_o + i\epsilon)^{-1}$ in the coordinate representation:

$$\langle \mathbf{r} | G^+(E) | \mathbf{r}' \rangle = \langle \mathbf{r} | \frac{1}{(E - H_o + i\epsilon)} | \mathbf{r}' \rangle \quad (85)$$

$$G^+(E | \mathbf{r}, \mathbf{r}') = -\frac{m}{2\pi\hbar^2} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \quad (86)$$

eq. (84) in the coordinate representation:

$$(E + \frac{\hbar^2}{2m} \nabla^2) G^+(E | \mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (87)$$

labeling of ϕ : by a complete set of "good quantum numbers" (not just the

energy), e.g. $\hbar k$ or k , so that

$$\phi_{\mathbf{k}}(E|\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \quad (88)$$

labeling of the scattering state $\psi_{\mathbf{k}}^+(E|\mathbf{r})$: LSE with causal boundary conditions

$$\psi_{\mathbf{k}}^+(E|\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} - \frac{m}{2\pi\hbar^2} \int d\mathbf{r}' \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}) \psi_{\mathbf{k}}^+(E|\mathbf{r}') \quad (89)$$

labelling by different sets of eigenvalues for different commuting operators, e.g. linear momentum and the asymptotic Hamiltonian or angular momentum, its projection onto the z -axis, the magnitude of the linear momentum, and the asymptotic Hamiltonian

- leads to the "partial wave expansion":

$$\phi(E) = Y_{lm}(\hat{\mathbf{r}})j_l(kr) \quad (90)$$

satisfies eq. (81)

Y_{lm} : spherical harmonic normalized Legendre polynomial $P_l(\cos\theta)$ times periodic function $\exp(im\varphi)/\sqrt{2\pi}$

$\hat{\mathbf{r}}$: polar angle (θ, φ)

$j_l(kr)$: regular spherical Bessel function

$$\lim_{r \rightarrow \infty} j_l(kr) = \frac{\sin(kr - l\pi/2)}{kr} \quad (91)$$

partial wave expanded Green's function:

$$G^+(E|\mathbf{r}, \mathbf{r}') = \frac{2mk}{\hbar} \sum_{l=0}^{\infty} \sum_{\mu=-l}^l Y_{l\mu}(\hat{\mathbf{r}}) Y_{l\mu}^*(\hat{\mathbf{r}}') h_l^+(kr_>) j_l(kr_<) \quad (92)$$

$h_l^+(kr)$: spherical outgoing wave Hankel function

$$\lim_{r \rightarrow \infty} h_l^+(kr) = \frac{e^{i(kr - l\pi/2)}}{kr} \quad (93)$$

analogous partial wave expansion:

$$\psi_{\mathbf{k}}^+(E|\mathbf{r}) = 4\pi \sum_{l,l'} \sum_{\mu,\mu'} i^{l'} Y_{l'\mu'}(\hat{\mathbf{r}}) Y_{l\mu}^*(\hat{\mathbf{r}}') g^+(l'\mu' l\mu | r) \quad (94)$$

radial function $g^+(l'\mu'l\mu|r)$ satisfies:

$$g^+(l'\mu'l\mu|r) = \delta_{ll'}\delta_{\mu\mu'}j_l(kr) - \frac{2mk}{\hbar^2} \sum_{l''} \sum_{\mu''} i^{l''-l'} \int d\mathbf{r} Y_{l'\mu'}(\hat{\mathbf{r}}') h_l^+(kr_>) j_l(kr_<) V(\mathbf{r}) Y_{l''\mu''}(\hat{\mathbf{r}}') g^+(l''\mu''l\mu|r') \quad (95)$$

potential is spherically symmetric: ("central potential")

$$g^+(l'\mu'l\mu|r) = \delta_{ll'}\delta_{\mu\mu'} g_l^+(r) \quad (96)$$

$$g_l^+(r) = j_l(kr) - \frac{2mk}{\hbar^2} \int dr' r'^2 h_l^+(kr_>) j_l(kr_<) V(r') g_l^+(r') \quad (97)$$

- what quantities contain the physically significant information?

consider both the TDSE (69) and its complex conjugate:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\chi^* = -i\hbar\frac{\partial\chi^*}{\partial t} \quad (98)$$

V : real potential

Multiplying eq. (69) by χ^* and (98) by χ , and subtract:

$$-\frac{\hbar^2}{2m}[\chi^*\nabla^2\chi - \chi\nabla^2\chi^*] = i\hbar[\chi^*\frac{\partial\chi}{\partial t} + \chi\frac{\partial\chi^*}{\partial t}] \quad (99)$$

identities:

$$\chi^*\nabla^2\chi - \chi\nabla^2\chi^* = \vec{\nabla}[\chi^*\vec{\nabla}\chi - \chi\vec{\nabla}\chi^*] \quad (100)$$

$$\chi^* \frac{\partial \chi}{\partial t} + \chi \frac{\partial \chi^*}{\partial t} = \frac{\partial}{\partial t} [\chi^* \chi] \quad (101)$$

write eq. (99) as "continuity equation"

$$\vec{\nabla} \cdot \vec{j} = -\frac{\partial \rho}{\partial t} \quad (102)$$

$$\rho = \chi^* \chi \quad (103)$$

"flux vector" \vec{j} :

$$\vec{j} = \frac{-i\hbar}{2m} [\chi^* \vec{\nabla} \chi - \chi \vec{\nabla} \chi^*] \quad (104)$$

\vec{j} : the flux vector for the probability density ρ . (This identification can be made sharper by integrating (102) over an arbitrary volume). Now we note that for solutions to the TDSE of the form (71), ρ is independent of time and \vec{j} becomes a zero divergence vector.

the flux associated with the plane wave unperturbed state $\psi_{\mathbf{k}}(E|\mathbf{r})$:

$$\begin{aligned}\vec{j} &= \frac{-i\hbar}{2m} [e^{-i\mathbf{k}\mathbf{r}}(i\mathbf{k})e^{i\mathbf{k}\mathbf{r}} - e^{i\mathbf{k}\mathbf{r}}(-i\mathbf{k})e^{-i\mathbf{k}\mathbf{r}}] \\ &= \hbar\mathbf{k}/m = \mathbf{p}/m\end{aligned}\tag{105}$$

\vec{j} : equal to the velocity of the particle, plane wave normalized to a constant probability density of 1

particle-in-a-box normalisation:

$$\phi_{\mathbf{k}}(E|\mathbf{r}) = \frac{1}{L^{\frac{3}{2}}} e^{i\mathbf{k}\mathbf{r}} \quad (106)$$

$L^{\frac{3}{2}}$: volume

flux:

$$\vec{j} = \frac{\mathbf{p}}{L^3 m} = \text{density} * \text{velocity} \quad (107)$$

flux of an incompressible fluid

- experiment: incident flux, one measures the probability that the projectile is scattered into a detector

- detector: characterised by a solid angle of acceptance, one observes the rate at which projectiles are scattered into a given solid angle $d\Omega$
- one measures the probability per second of a projectile being scattered into the solid angle $\sin\theta d\theta d\varphi = d\Omega$

define a scattered flux \vec{j}_{scatt} : $\hat{\mathbf{n}}$ is a unit vector pointing in the direction of the detector

$$\hat{\mathbf{n}} \vec{j}_{scatt} = \text{probability flux of scattering into } d\Omega \quad (108)$$

- incident and scattered flux have units of probability/unit area*sec
- at the detector: area $r^2 d\Omega$, the unit vector pointing in the direction of observation is $\hat{\mathbf{r}}$

- the probability per sec of the projectile being scattered into the detector equals $\vec{j}_{scatt} \hat{\mathbf{r}} r^2 d\Omega$
- this is proportional to the magnitude of the incident flux (single collisions)

$$j_{incid} d\sigma = \frac{\text{probability of scattering into the detector}}{\text{sec}} \quad (109)$$

$d\sigma$: constant of proportionality, in units of area

$$j_{incid} d\sigma = (\hat{\mathbf{r}} \vec{j}_{scatt}) r^2 \sin \theta d\theta d\varphi \quad (110)$$

$$d\sigma = \frac{(\hat{\mathbf{r}} \vec{j}_{scatt}) r^2 \sin \theta d\theta d\varphi}{j_{incid}} \quad (111)$$

incident flux (105b) for the incident plane wave scattered wavefunction: see eq. (89)

$$\psi_{\mathbf{k}}^+(E|\mathbf{r}) = \psi_{incid} + \psi_{scatt} \quad (112)$$

$$\psi_{\mathbf{k},scatt}^+(E|\mathbf{r}) = -\frac{m}{2\pi\hbar^2} \int d\mathbf{r}' \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}) \psi_{\mathbf{k}}^+(E|\mathbf{r}') \quad (113)$$

- detector: typically located far from the target, we need $\psi_{\mathbf{k},scatt}^+(E|\mathbf{r})$ at large \mathbf{r} ("far field scattered wave"), perform Taylor expansions of $|\mathbf{r}-\mathbf{r}'|$ in the exponent and denominator in the integral in (113)
- $d\sigma$: contains a factor r^2 so that any contribution \vec{j}_{scatt} that decays faster than $1/r^2$ can be made arbitrarily small by positioning the detector a large enough r

calculating the scattered flux:

$$\vec{\nabla} = \hat{\mathbf{r}} \frac{\partial}{\partial r} + \frac{1}{r} O(\theta, \varphi) \quad (114)$$

leading term of $\psi_{\mathbf{k},scatt}^+(E|\mathbf{r})$: $1/r$ due to the $1/|\mathbf{r} - \mathbf{r}'|$ factor

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r|\hat{\mathbf{r}} - \mathbf{r}'/r|} \quad (115)$$

- role of the potential is to bound the largest r' contributing significantly to the integral over $d\mathbf{r}$ in (113); then large r means large with respect to the largest r' contributing to the integral
- Taylor expansion of the phase of the Green's function, $ik|\mathbf{r} - \mathbf{r}'|$ must include one higher term than the expansion of $1/|\mathbf{r} - \mathbf{r}'|$

- far field scattered wave:

$$\psi_{\mathbf{k},scatt}^+(E|\mathbf{r}) \rightarrow \frac{e^{ikr}}{r} f(\theta, \varphi) \quad (116)$$

θ and φ : angles of observation

$$f(\theta, \varphi) = -\frac{m}{2\pi\hbar^2} \int d\mathbf{r}' e^{ik\hat{\mathbf{r}}\mathbf{r}'} V(\mathbf{r}) \psi_{\mathbf{k}}^+(E|\mathbf{r}') \quad (117)$$

$\chi^* \vec{\nabla} \chi$ and $\chi \vec{\nabla} \chi^*$: will fall off at least as fast as $1/r^3$ so far as contributions from the $\mathcal{O}(\theta, \varphi)/r$ portion of $\vec{\nabla}$ is concerned

these terms will be negligible at the detector

- *only* term which survives the large r -limit: comes from the $\hat{\mathbf{r}} \frac{\partial}{\partial r}$ piece of $\vec{\nabla}$

$$\begin{aligned} \vec{j}_{scatt} = & -\frac{i\hbar}{2m} \hat{\mathbf{r}} \left[\frac{e^{-ikr}}{r} f^*(\hat{\mathbf{r}}) \frac{ik}{r} e^{ikr} f(\hat{\mathbf{r}}) - \right. \\ & \left. \frac{e^{ikr}}{r} f(\hat{\mathbf{r}}) \frac{(-ik)}{r} e^{ikr} f^*(\hat{\mathbf{r}}) \right] = \hat{\mathbf{r}} \frac{\hbar k}{mr^2} |f(\hat{\mathbf{r}})|^2 \end{aligned} \quad (118)$$

$\hat{\mathbf{r}} \vec{j}_{scatt}$ is trivially calculated:

$$d\sigma = \frac{(\hbar k/mr^2)}{(\hbar k/m)} |f(\hat{\mathbf{r}})|^2 r^2 \sin \theta d\theta d\varphi \quad (119)$$

$$\frac{d\sigma}{d\Omega} = |f(\theta, \varphi)|^2 = |f(\hat{\mathbf{r}})|^2 \quad (120)$$

$\frac{d\sigma}{d\Omega}$: "differential scattering cross section" determined by $f(\theta, \varphi)$

- it is the size that the target presents to the projectile which causes it to be scattered into the solid angle $d\Omega$
- "sums" over all solid angles: total size σ , presented by the target that causes scattering of the projectile:

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} \quad (121)$$

- important point: although the analysis of the cross sections (and standard experimental geometries) involves the far field behavior of $\psi_{\mathbf{k}}^+(E|\mathbf{r})$, one does *not* have to carry out calculations all the way to the far field region in order to obtain $f(\hat{\mathbf{r}})$, rather one needs only know $\psi_{\mathbf{k}}^+(E|\mathbf{r})$ in the region where the potential is significantly different from zero (since $f(\hat{\mathbf{r}})$ is determined by the integral (117))

Computational methods based on differential equation solvers

comments on methods that solve the equations as coupled ordinary differential equations:

general scattering problems, including those involving rearrangements and breakup

- one must use coordinates that are able, with a single distance variable, to describe all possible arrangements, e.g. hyperspherical coordinates
- how are the solutions generated that satisfy the boundary conditions?

consider the scattering of a projectile in $3D$ by a nonspherical scatterer: potential $V(\mathbf{r})$ depends on r θ and φ

TISE:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi = E\psi \quad (122)$$

expand ψ in a truncated basis of spherical harmonics:

$$\psi(\mathbf{r}) = \sum_{l'}^{l_{\max}} \sum_{m'} Y_{l'm'}(\hat{\mathbf{r}}) U_{l'm'}(r)/r \quad (123)$$

substitute eq. (123) into (122) and project with a particular basis function $Y_{lm}(\hat{\mathbf{r}})$:

$$\begin{aligned} \left(E + \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{\hbar^2 l(l+1)}{2mr^2} \right) U_{lm}(r) = \\ \sum_{l'} \sum_{m'} V(lm l' m' | r) U_{l'm'}(r) \end{aligned} \quad (124)$$

– with a total of N -basis functions in the expansion, eq. (124) will have $2N$ linearly independent solutions

- only N of these can be made to be regular at $r = 0$, and these are the physically relevant ones, it is therefore convenient to add a label to U_{lm} , to signify the linearly independent solution:

$$\begin{aligned} & \left(E + \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{\hbar^2 l(l+1)}{2mr^2}\right) U(lm l_0 m_0 | r) \\ &= \sum_{l'} \sum_{m'} V(lm l' m' | r) U(l' m' l_0 m_0 | r) \end{aligned} \quad (125)$$

matrix notation:

$$(E\bar{1} - \bar{K}) * \bar{U}(r) = \bar{V} * \bar{U}(r) \quad (126)$$

$\bar{1}$ and \bar{K} are diagonal matrices, one interpretes the lm indices of $U(lm l_0 m_0 | r)$ as "final state" indices and $l_0 m_0$ as "initial state" indices

- regularity condition at $r = 0$ (which for typical potentials in atom-diatom scattering becomes the condition that $U(lm l_0 m_0 | 0) = 0$)

- we want to impose the asymptotic condition

$$\lim_{r \rightarrow \infty} U(lm l_0 m_0 | r) = \delta_{ll_0} \delta_{mm_0} j_l(kr) + h_l^+(kr) T(lm l_0 m_0) \quad (127)$$

- "two point" boundary condition problem: $T(lm l_0 m_0)$, this is equivalent to saying that although we know that $U(lm l_0 m_0 | 0) = 0$, we do *not* know what the correct value is for the derivatives $dU(lm l_0 m_0 | r)/dr$ at $r = 0$.

- the usual way to circumvent this difficulty: convert the problem into a *pseudo – initial value problem*

the initial conditions typically are:

$$(a) \quad U(lm l_0 m_0 | 0) = 0 \quad (128)$$

$$(b) \quad \frac{d}{dr} U(lm l_0 m_0 | r) |_{r=0} = \delta_{ll_0} \delta_{mm_0} \quad (129)$$

- these initial conditions will *not*, in general produce the correct large- r behavior
- however, knowing the N -linearly independent solutions allows one to take linear combinations that possess the correct asymptotic behavior
- requires solving a system of linear algebraic equations that yields the scattering amplitudes
- practical difficulty that makes additional computational effort necessary: different l -values lead to different classical turning points at a given total energy E
- the pieces of the solution matrix grow at different rates in their nonclassical regions

- the most rapidly growing component can become dominant in several (or even all) of the solution vectors, causing them to be multiples of one another; i.e., they become linearly dependent
- if this occurs, it is no longer possible to construct the physical solution
- this is manifested by the relevant algebraic equations becoming ill-conditioned
- various techniques are employed to avoid this difficulty, but they all essentially amount to periodically scrambling the column solutions (before they become linearly dependent) so as to maintain explicitly linearly independent solutions, many methods are used to solve the coupled equations (125), including varieties of the Numerov method, the so-called log- derivative method (which essentially calculates $\bar{U}^{-1} * d\bar{U}/dr$), etc.
- computational effort: scales with problem size

- some methods may be very efficient for small problems but rapidly become impractical as the complexity increases
- some methods may not be so efficient for smaller problems, but have slow scaling with problem size
- all of the methods involve either matrix-matrix multiplications or solutions of linear algebraic equations
- both procedures scale as the cube of the matrix dimensions
- the number of matrix multiplications, the number of times the linear equations must be solved, and the dimensions of the relevant matrices can be quite different for the various methods
- the non-iterative Volterra equation propagation method, and the propagation methods which solve coupled differential equations both must generate N -linearly

independent solutions, the size of the matrices is the same for both these types of approaches (it equals the number of internal states, including those associated with any angular momentum in the system)

- these types of approaches involve of the order of N^3 multiplications at each step in propagating from $r = 0$ out beyond the range of the potential
- if P steps are required, on the order of $N^3 P$ multiplications must be performed, this work must be repeated at every desired energy
- there are methods in which the number of internal states changes as the propagation moves further out and the potential becomes weaker, these scale more slowly
- the algebraic variational methods involve expansion in f_n -basis functions for each internal quantum state, n (f_n can differ for different quantum states), the

total number of unknowns, U , is then the sum over n of the f_n

$$U = \sum_{n=1}^N f_n \quad (130)$$

- the computational effort then scales as U^3
- some of the work is independent of the energy of interest, but in general, a substantial amount of work must be repeated at each new energy

if one introduces an "average" number of basis functions, $\langle f_n \rangle$:

$$U = N \langle f_n \rangle \quad (131)$$

then the computational effort scales as $N^3 \langle f_n \rangle^3$

- clearly, if $\langle f_n \rangle^3$ is larger than P , the variational method will not be as efficient as the propagation methods for a given energy
- it is also possible to solve the variational equations for a restricted set of initial states (rather than for all N initial states)
- if one can construct reasonable starting "guesses" for the solution vectors, then iterative methods can be used to solve the algebraic equations; in this case, the effort scales more slowly than U^3 , and this can lead to a very efficient computational approach

I.4 Coordinate systems: collinear, planar, 3D, reduced degrees of freedom

Introduction

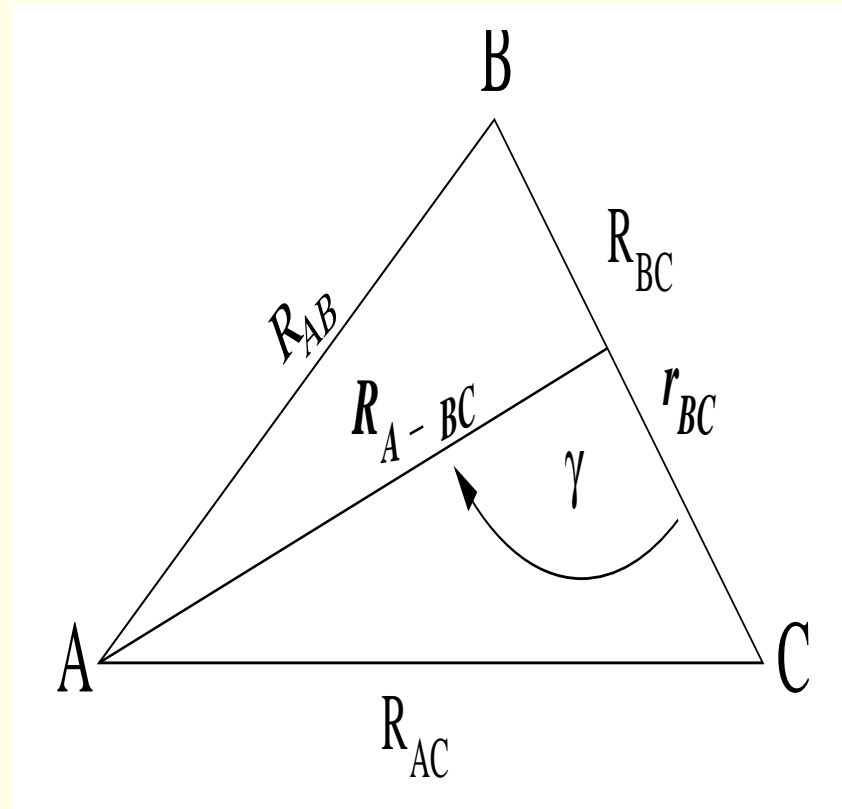
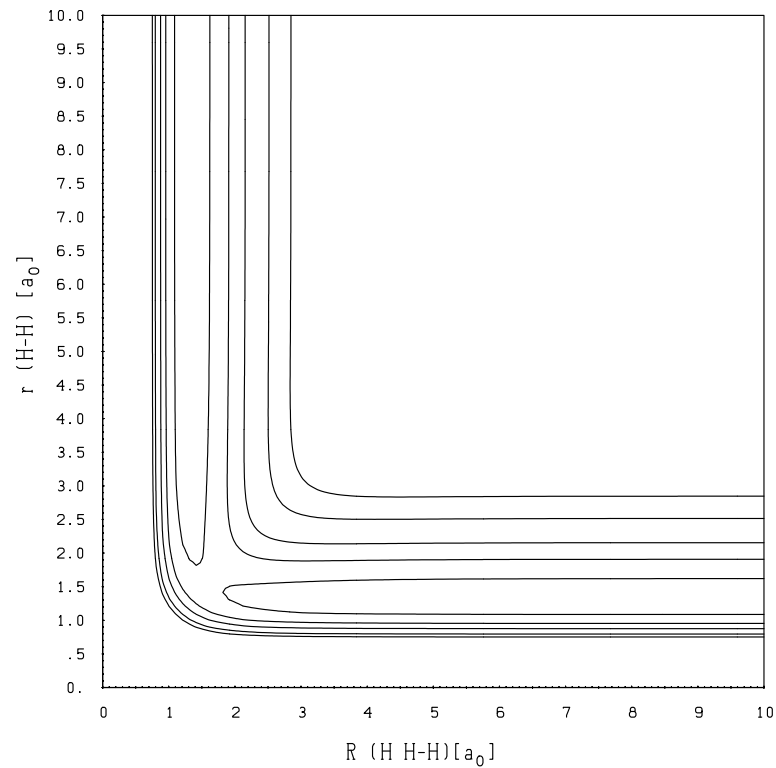
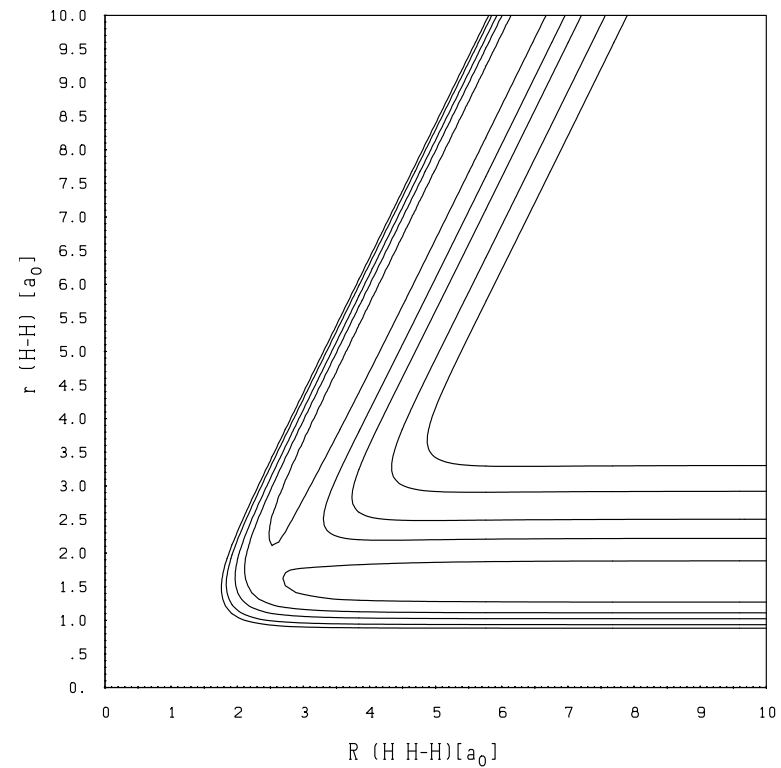


Figure 7: Atomic distances R_{A-B} , R_{A-C} , R_{B-C} and Jacobi coordinates R_{A-BC} , r_{BC} , γ of the triatomic system ABC. R_{A-BC} is the distance between the atom A and the center-of-mass of the molecule BC.

- description of the nuclear dynamics: all coordinate systems are physically equivalent
- typical picture of the potential in the different coordinate systems can look differently
- triatomic molecule ABC: three internal coordinates (R_{A-B} , R_{A-C} and R_{B-C}) (Fig. 7) and the three Euler angles potential energy depends on the internal coordinates: $V = V(R_{A-B}, R_{A-C}, R_{B-C})$.
- collinear configuration: V depends only on R_{A-BC} (or R_{A-B}) and R_{B-C} (Fig. 8a)
- reactive scattering: need coordinates, which are convenient in describing reactant and product arrangements simultaneously, which have the correct asymptotic behaviour
- But: no such a unique coordinate system \implies compromise between practicability, numerical efficiency and physical insight and interpretation of the reaction dynamics



(a)



(b)

Figure 8: Contour lines (0.35- 3.0 [eV]) for the H+H₂ Porter-Karplus potential. a) internal coordinates (R_{AB} , R_{BC}), b) mass-weighted Jacobi coordinates (R_{A-BC} , r_{BC})

Which coordinate system for which quantum reactive procedure?

Jacobi coordinates

collinear configuration: coordinates, so that the kinetic energy operator becomes "simpler" (Jacobi-coordinates or mass-scaled Jacobi-coordinates)

$$R_{A-BC} = R_{AB} + [m_C/(m_B + m_C)]R_{BC}, \quad r_{BC} = \sqrt{\frac{m_{BC}}{m}}R_{BC} \quad (132)$$

$$m = \frac{m_A(m_B + m_C)}{(m_A + m_B + m_C)}, \quad m_{BC} = \frac{m_B m_C}{(m_B + m_C)} \quad (133)$$

$$T = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial R_{A-BC}^2} + \frac{\partial^2}{\partial r_{BC}^2} \right) \quad (134)$$

for V : see Fig. 8b, with skewing angle φ_α :

$$\varphi_\alpha = \arctan[m_B(m_A + m_B + m_C)/(m_A m_B)]^{1/2} \quad (135)$$

- skewing angle is large: $m_B \gg m_A, m_C$
- skewing angle is small: $m_B \ll m_A, m_C$
- equal masses: skewing angle is 60°
- effect of changing translational energy of the reactants into vibrational energy for the products: explained with the pictures of PESs potential energy surface in skewed coordinates
- skewing angle very small: calculations can become problematic
- for FHD: see Fig. 9

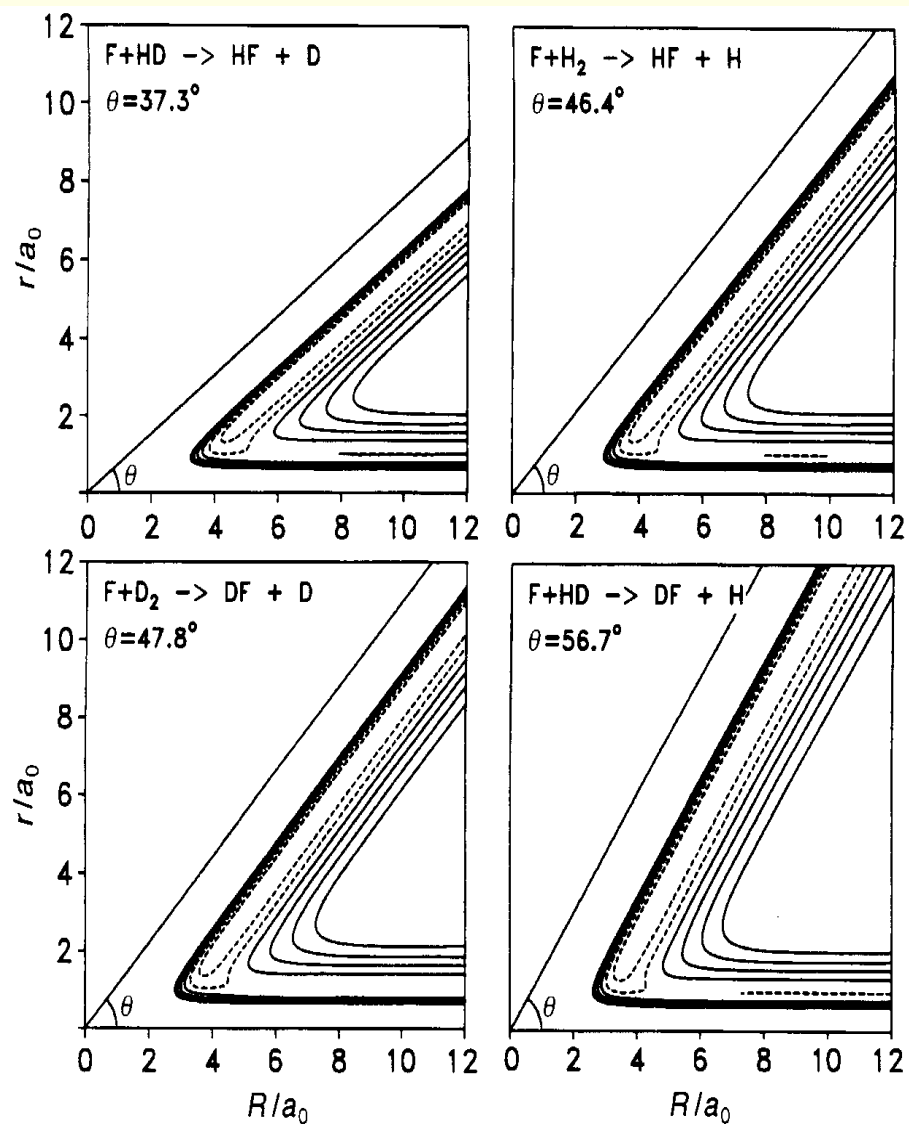


Figure 9: Collinear potential-energy contours and kinematic skewing angles for the four deuterium-substituted isotopomers of the $F + H_2$ reactions. (J. F. Castillo, D. E. Manolopolous, Faraday Discuss. **110** (1998) 119.

Reactant and product coordinates

3D: three independent sets of Jacobi-coordinates:

$A + BC$ (R_α, r_α), $AB + C$ (R_β, r_β) and $AC + B$ (R_γ, r_γ)

\mathbf{x}_i, m_i ($i=1,2,3$ or A,B,C): pos. and masses of three particles, X : center of mass

$$\mathbf{X} = \sum_{i=1}^3 m_i \mathbf{x}_i / M \quad (136)$$

three types of mass norm. Jacobi coord. $((i, j, k)$ is a cyclic permut. $(1, 2, 3))$:

$$\mathbf{r}^k = (\mathbf{x}_j - \mathbf{x}_i) / d_k, \quad \mathbf{R}^k = d_k [\mathbf{x}_k - \frac{m_i \mathbf{x}_i + m_j \mathbf{x}_j}{m_i + m_j}] \quad (137)$$

$$M = \sum_{i=1}^3 m_i, \quad d_k^2 = (1 - m_k / M) m_k / \mu \quad (138)$$

$$\mu = \sqrt{m_1 m_2 m_3 / M} \quad (139)$$

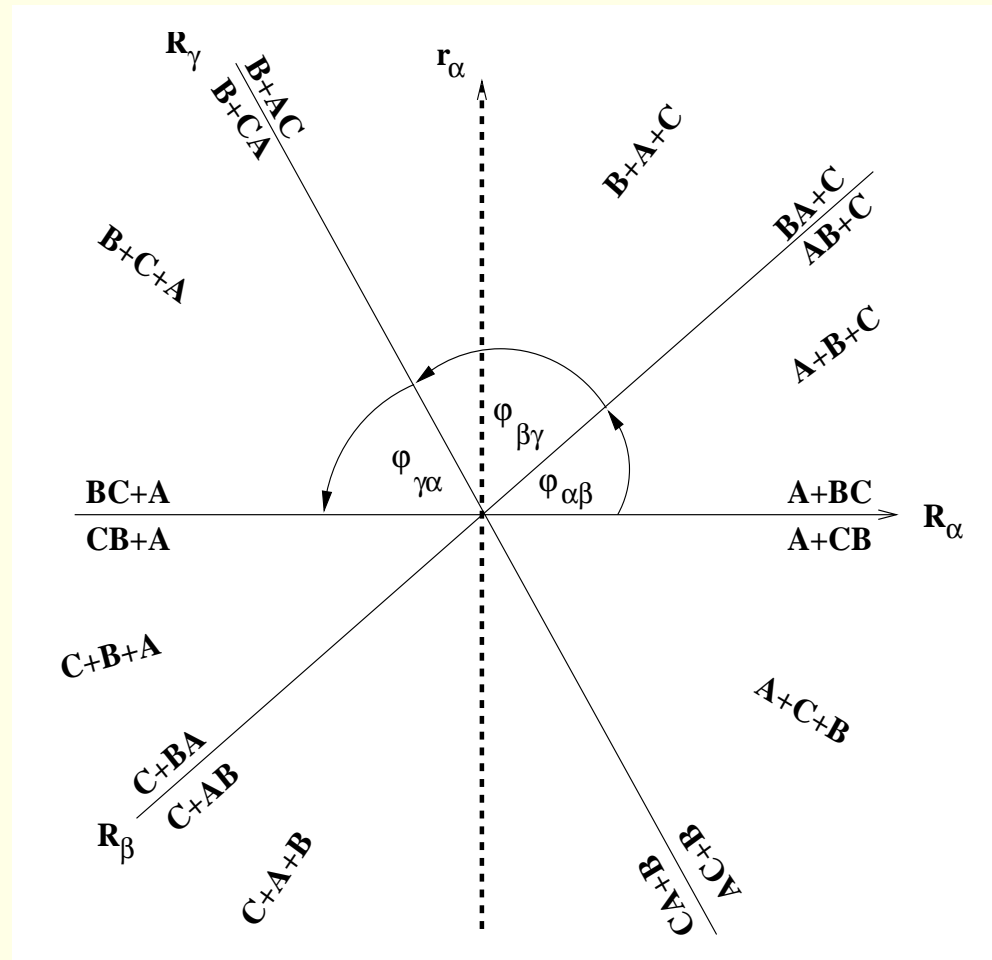


Figure 10: Configuration space of a triatomic system ABC with the arrangements α, β, γ [16]

- transformation between the mass-weighted coordinates in configuration α (reactant coordinate) and configuration β (product coordinate):

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{m_A m_C}{(m_A+m_B)(m_C+m_B)}} - \sqrt{\frac{m_B(m_A+m_B+m_C)}{(m_A+m_B)(m_C+m_B)}} \\ \sqrt{\frac{m_B(m_A+m_B+m_C)}{(m_A+m_B)(m_C+m_B)}} - \sqrt{\frac{m_A m_C}{(m_A+m_B)(m_C+m_B)}} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix} \quad (140)$$

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} \cos \phi_{\alpha\beta} & -\sin \phi_{\alpha\beta} \\ \sin \phi_{\alpha\beta} & \cos \phi_{\alpha\beta} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix} \quad (141)$$

$\phi_{\alpha\beta}$ lies between π and $3\pi/2$

Hyperspherical coordinates

- many different ways of defining hyperspherical coordinates
- collinear atom-diatom reaction: polar coordinates
- collinear Delves coordinates: in terms of the mass-scaled Jacobi vectors ($a(A + BC)$)

$$\rho = \sqrt{R_a^2 + r_a^2} \quad (142)$$

$$\theta_a = \tan^{-1}(r_a/R_a) \quad (143)$$

hyperradius ρ in eq. (142) is universal

Delves hyperangle θ_a : a function of the arrangement

reactant and product hyperangle θ_a , θ_c are related: $\theta_a + \theta_c = \theta_{ac}$ (Fig. 3b)

$$\theta_{ac} = \tan^{-1}(m_B/\mu), \quad \mu = \left(\frac{m_C m_B m_C}{m_a + m_B + m_C}\right)^{1/2} \quad (144)$$

solution of the SE in hyperspherical coordinates in two distinct steps:

- bound θ_α motion is solved first: at the centres of a number of different 'sectors' in the hyperradial coordinate ρ
- a set of 'surface' eigenfunctions and eigenvalues within each sector, substituted back into the SE to leave a system of coupled second order linear differential equations in ρ
- 'close-coupled' equations have exactly the same form as those encountered in inelastic scattering
- surface eigenfunctions and eigenvalues are often quite difficult to obtain
- fundamental reason for this: the reactant and product arrangement channels

are confined to smaller and smaller regions of the available hyperangular (θ_a) space as ρ increases

- this unavoidable feature of hyperspherical coordinates (exacerbated in 3D) makes it difficult to devise numerical methods for solving the surface eigenproblem that work equally well for all required values of ρ
- progress has been made in this direction in recent years

final comments:

- the solution of the surface eigenvalue problem is completely independent of the scattering energy E

- once this eigenvalue problem has been solved all that remains is to call a standard close-coupled equation solver at each energy required
- since this is comparatively straightforward, calculations can be performed on a tight energy grid, which greatly facilitates the analysis of narrow scattering resonances due to short-lived meta-stable states (b)
- the hyperspherical coordinates may well be the only practical approach to certain physical regimes (heavy-light-heavy reactions: small skewing angle θ_{ac})
- collinear Delves hyperspherical coordinates are essentially unique, several different possibilities arise when one moves to 3D for triatomics

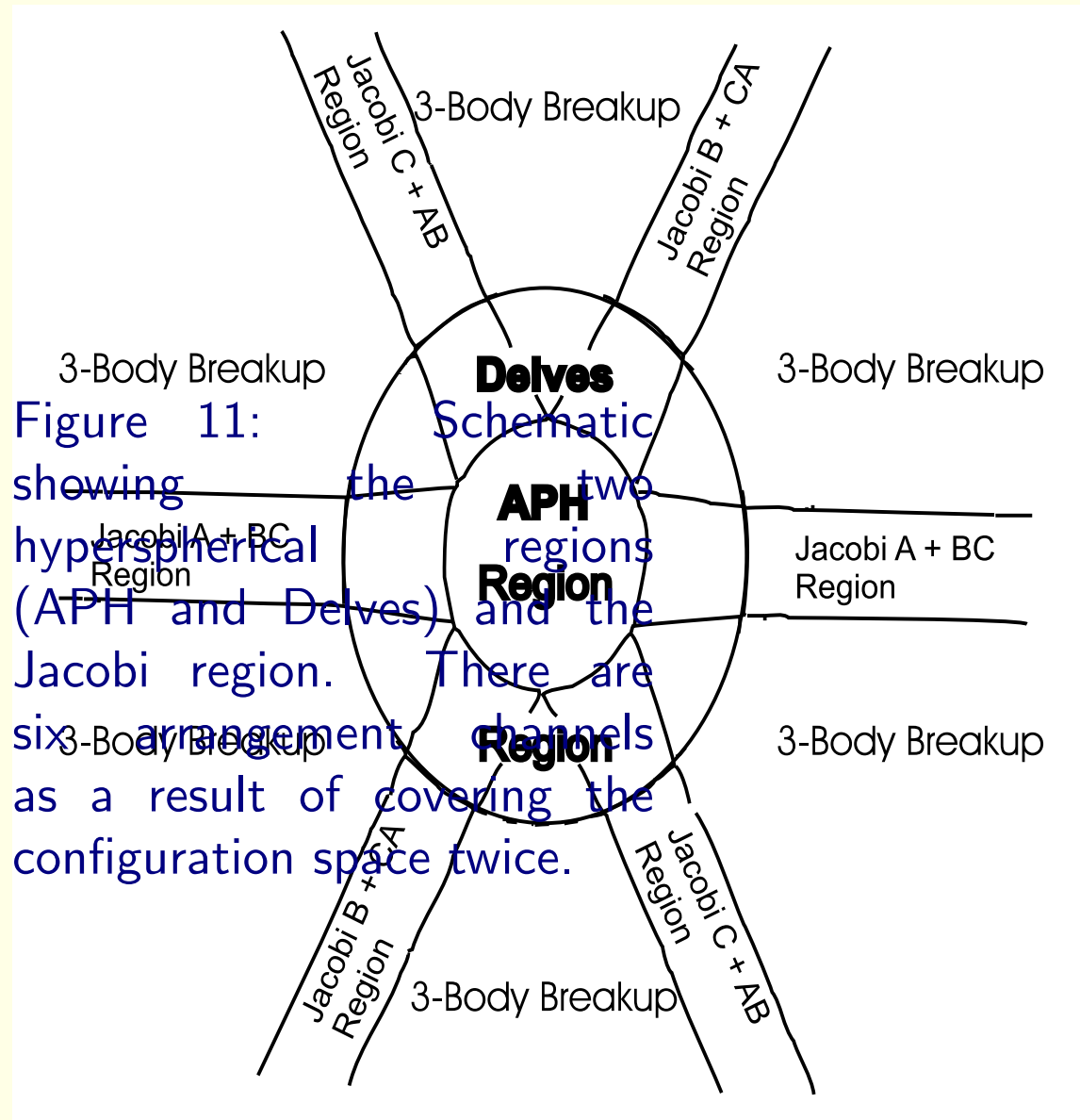
see the work of Pack and Parker (1987)

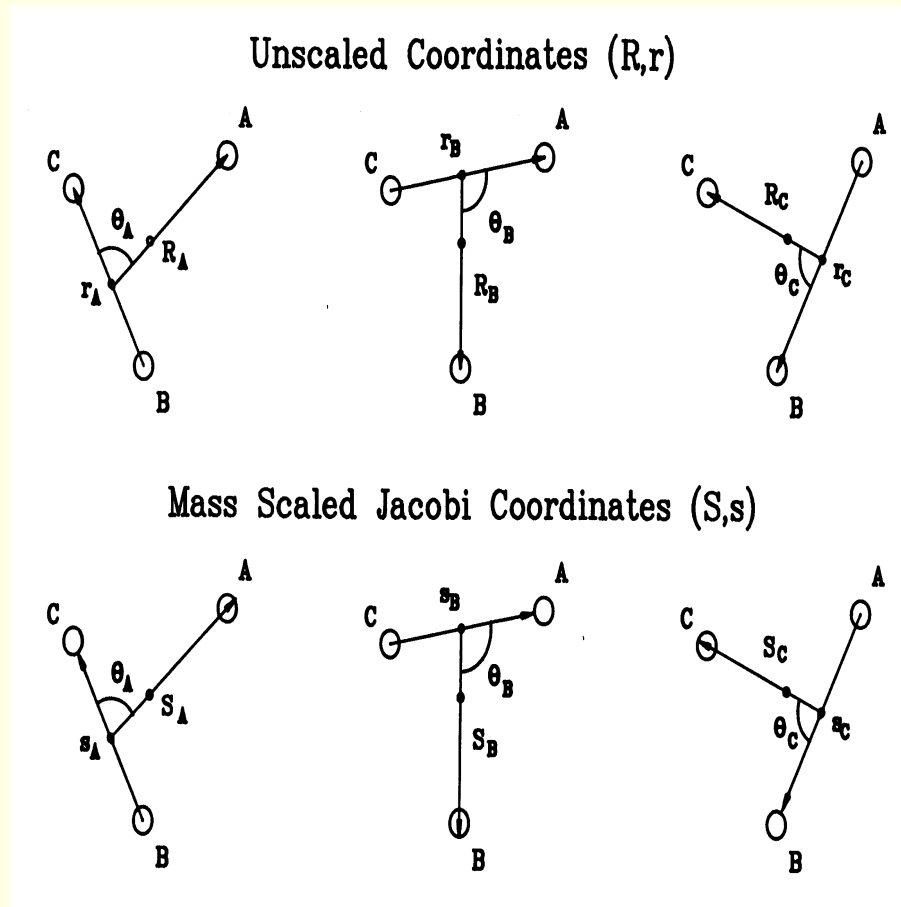
reactive scattering:

Johnson, Pack, Linderberg and Hinze and Wolniewicz have chosen so-called "democratic" hyperspherical coordinates

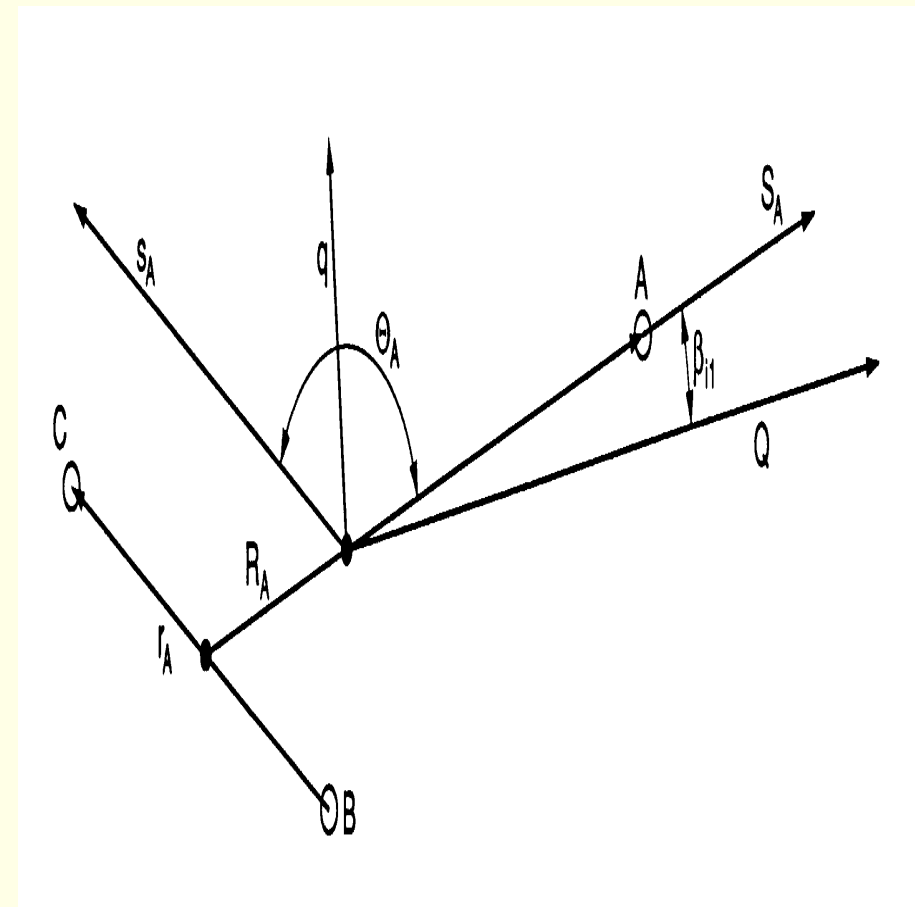
other coordinates: Fock, Launay and LePetit; all channels cannot be treated equally

Kupperman: coordinates that are not so optimal for treating the Pauli-principle for identical nuclei (Manolopolous, Clary, 1989)





(a) Unscaled and scaled Jacobi coordinates



(b) Scaled Jacobi vectors are plotted from the center of mass. BF_A z axis is along \mathbf{R}_A and \mathbf{S}_A , BF_Q z axis is along \mathbf{Q} and the BF_Q x axis is along \mathbf{q} .

Figure 12:

hyperspherical coordinates are chosen such that Euler angles α, β and γ define the orientation of the body-fixed frame, with the z -axis pointing in the direction of the vector product

$$\mathbf{A} = \frac{1}{2}(\mathbf{r} \times \mathbf{R}) \quad (145)$$

remaining internal coordinates ρ, θ and ϕ :

$$\rho^2 = |\mathbf{r}|^2 + |\mathbf{R}|^2, \quad \cos \theta = 4|\mathbf{A}|/\rho^2, \quad \cos \phi^k = 2(\mathbf{r}^k \cdot \mathbf{R}^k)/(\rho^2 \sin \theta) \quad (146)$$

only ϕ depends on the index k of the particular set of Jacobi coordinates

the different sets of Jacobi coordinates are connected via kinematic rotations, i.e. different origins for the angle ϕ

distance between the particles:

$$|\mathbf{x}_j - \mathbf{x}_i| = d_k \rho [1 + \sin \theta \sin \phi_k]^{\frac{1}{2}},$$
$$d_k^2 = (1 - m_k/M) m_k / \mu \quad (147)$$

$$\mu = m_1 m_2 m_3 / M, \quad M = m_1 + m_2 + m_3 \quad (148)$$

volume element:

$$d^6 v = \frac{1}{8} \rho^5 d\rho \sin \theta \cos \theta d\theta d\phi d\omega \quad (149)$$

$$d\omega = d\alpha \sin \beta d\beta d\gamma \quad (150)$$

range of the coordinates:

$$\begin{aligned} 0 \leq \rho \leq \infty, 0 \leq \theta \leq \frac{\pi}{2}, 0 \leq \phi \leq 4\pi, \\ 0 \leq \alpha \leq 2\pi, 0 \leq \beta \leq \pi, 0 \leq \gamma \leq 2\pi \end{aligned} \quad (151)$$

Pack, Parker and coworkers use a combination of different coordinates for different interaction regions:

- (a) adiabatically adjusting principal-axis hyperspherical (APH) coordinates for the strong interaction region
- (b) Delves hyperspherical coordinates outside the APH-region, where there is strong coupling within each arrangement channel, but negligible coupling between the arrangement channel
- (c) just beyond the Delves region one has the Jacobi region, where the coupling within each arrangement channel varies from moderate to zero

definitions by Pack, Parker and coworkers:

- six mass scaled Jacobi coordinates $(S_\tau, \hat{S}_\tau, s_\tau, \hat{s}_\tau)$ are the space-fixed (SF) Jacobi coordinates whereas the coordinates $(S_\tau, s_\tau, \Theta_\tau, \alpha_\tau, \beta_\tau, \gamma_\tau)$ are the body-fixed (BF) Jacobi coordinates
- the angles \hat{S}_τ and \hat{s}_τ are the two sets of polar and azimuthal angles associated with the vectors S_τ and s_τ respectively, and the angle between these vectors is

$$\Theta_\tau = \cos^{-1} \left[\frac{\mathbf{S}_\tau \cdot \mathbf{s}_\tau}{S_\tau s_\tau} \right] \quad (152)$$

- the three Euler angles $(\alpha_\tau, \beta_\tau, \gamma_\tau)$ of the BF system are usually chosen to orient the body-fixed z -axis along \mathbf{S}_τ or \mathbf{s}_τ depending on the relative masses of the

particles involved Delves hyperspherical coordinates for arrangement τ :

$$\rho = (S_\tau^2 + s_\tau^2)^{\frac{1}{2}}, \quad \theta_{D\tau} = \tan^{-1}\left(\frac{s_\tau}{S_\tau}\right) \quad (153)$$

in addition: four SF or four BF angles of

APH coordinates:

$$\rho = (S_\tau^2 + s_\tau^2)^{\frac{1}{2}} \quad (154)$$

$$\tan \theta = \frac{[(S_\tau^2 - s_\tau^2)^2 + (2\mathbf{S}_\tau \cdot \mathbf{s}_\tau)^2]^{\frac{1}{2}}}{2S_\tau s_\tau \sin \Theta_\tau} \quad (155)$$

$$\sin(2\chi_\tau) = \frac{2\mathbf{S}_\tau \cdot \mathbf{s}_\tau}{[(S_\tau^2 - s_\tau^2)^2 + (2\mathbf{S}_\tau \cdot \mathbf{s}_\tau)^2]^{\frac{1}{2}}} \quad (156)$$

$$\cos(2\chi_\tau) = \frac{(S_\tau^2 - s_\tau^2)^2}{[(S_\tau^2 - s_\tau^2)^2 + (2\mathbf{S}_\tau \cdot \mathbf{s}_\tau)^2]^{\frac{1}{2}}} \quad (157)$$

and Euler angles $(\alpha_\tau, \beta_\tau, \gamma_\tau)$ to orient the body-fixed z -axis along the smallest principal moment of inertia

- these coordinates minimize the Coriolis coupling for reactions that are collinearly

dominated A contour plot for the H_3 potential energy surface and the lowest surface function eigenvalues in hyperspherical coordinates are given in Fig. 13, 14 and perspective plots of the first 7 surface eigenfunctions for H_3 are presented in Fig. 15, 16.

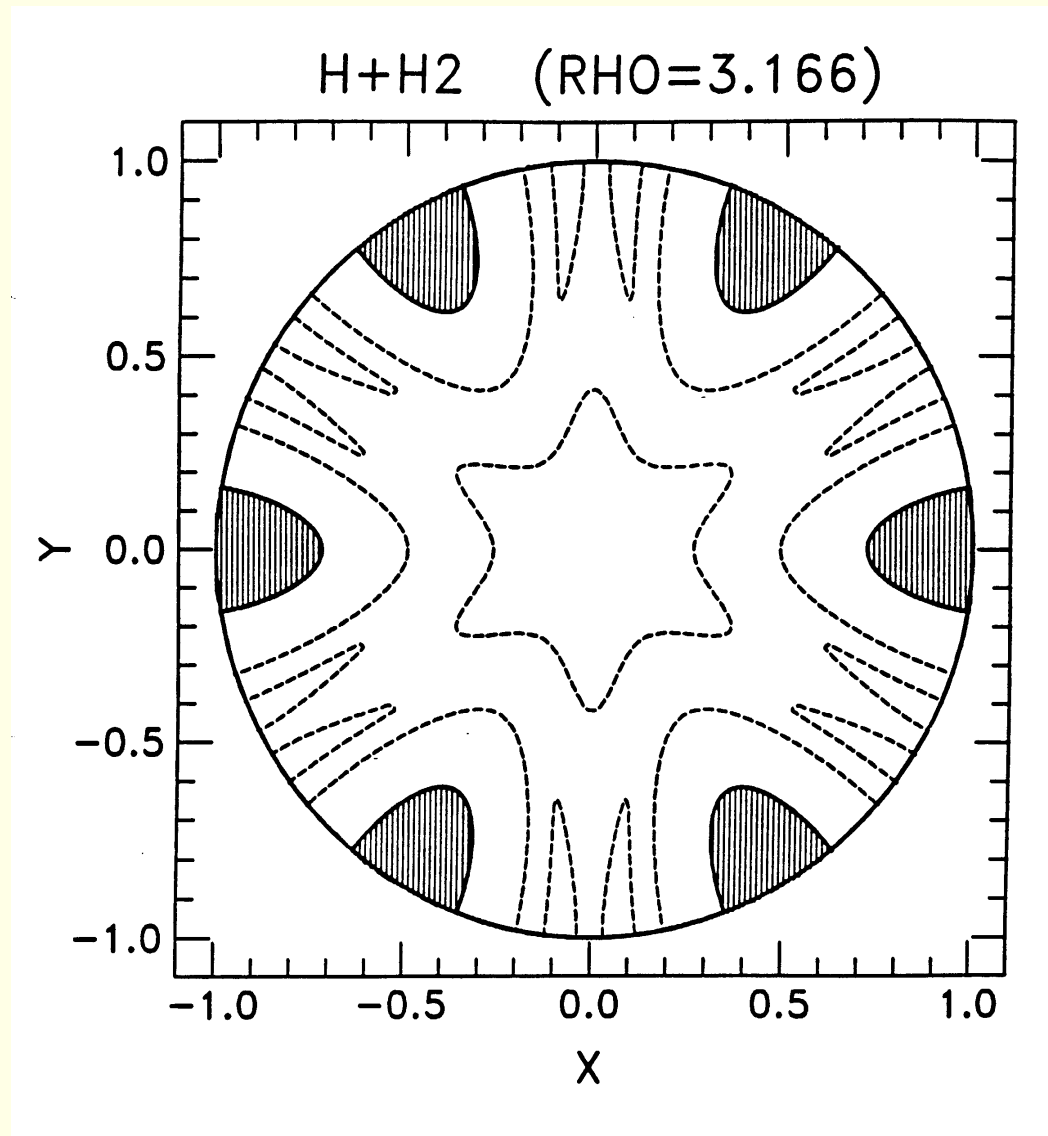


Figure 13: Stereographic projection of a contour plot of the H_3 PES at $\rho=3.166 a_0$

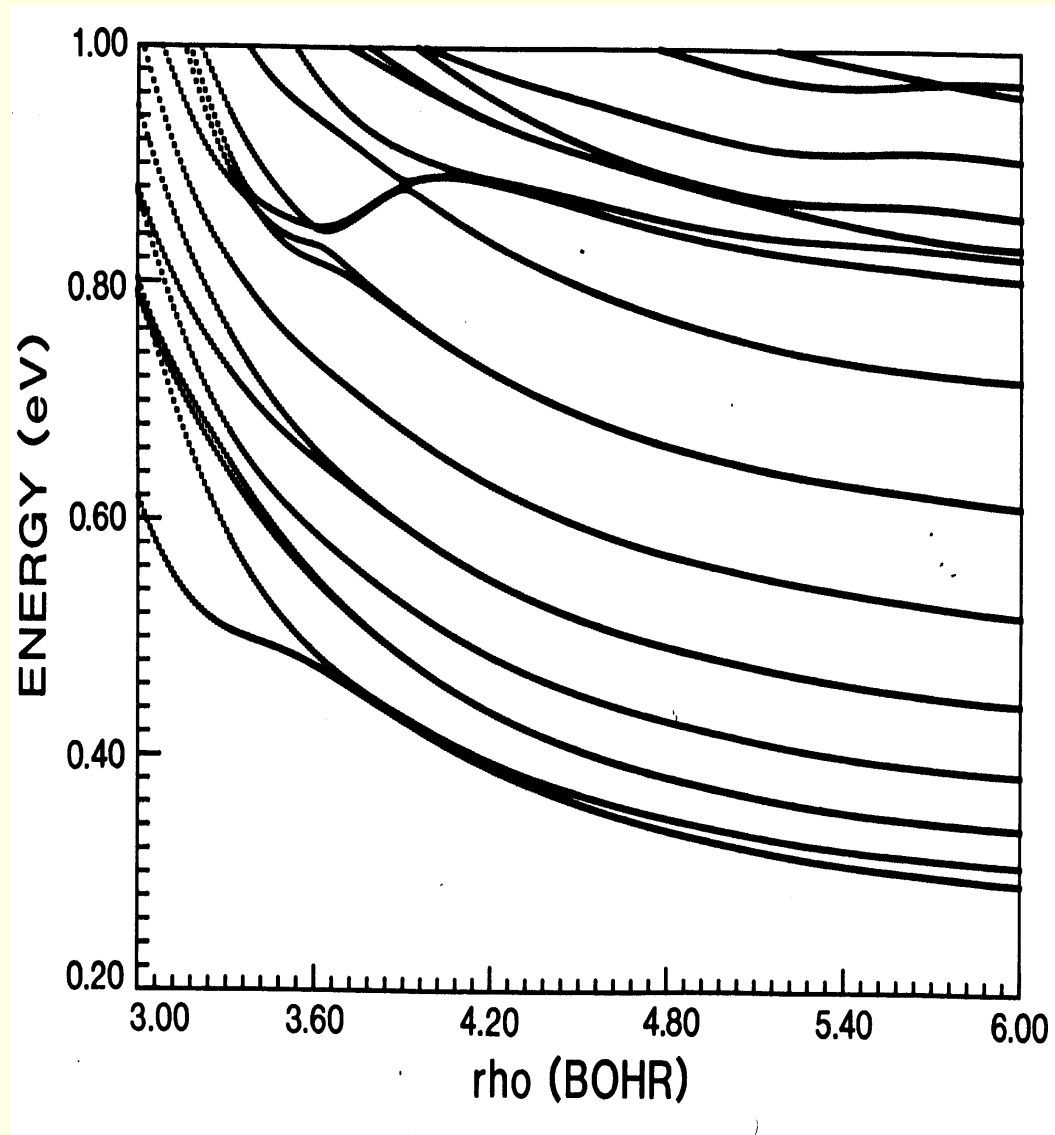


Figure 14: Surface function eigenvalues vs ρ for H_3 for $J = \Lambda = p = 0$ and even j_i . Pack, R.T., Parker, G.A.: J. Chem. Phys. **87** (1987) 3888.

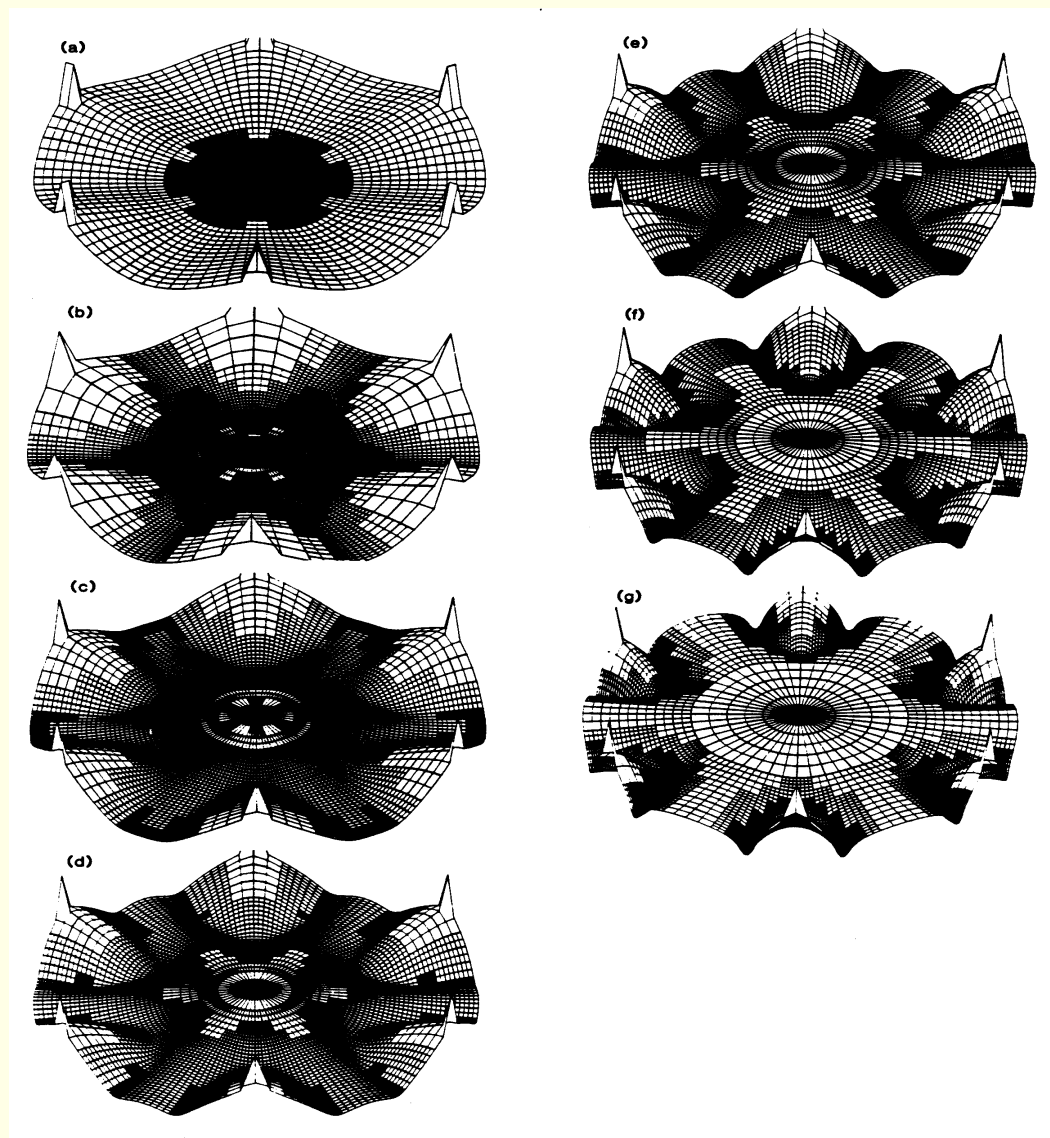


Figure 15: Perspective plots of the PK2 H₃ PES as a function of θ and ξ_i for ρ at 2.0, 2.5, 3.166, 3.6, 4.0, 5.0 and 6.0 a₀.

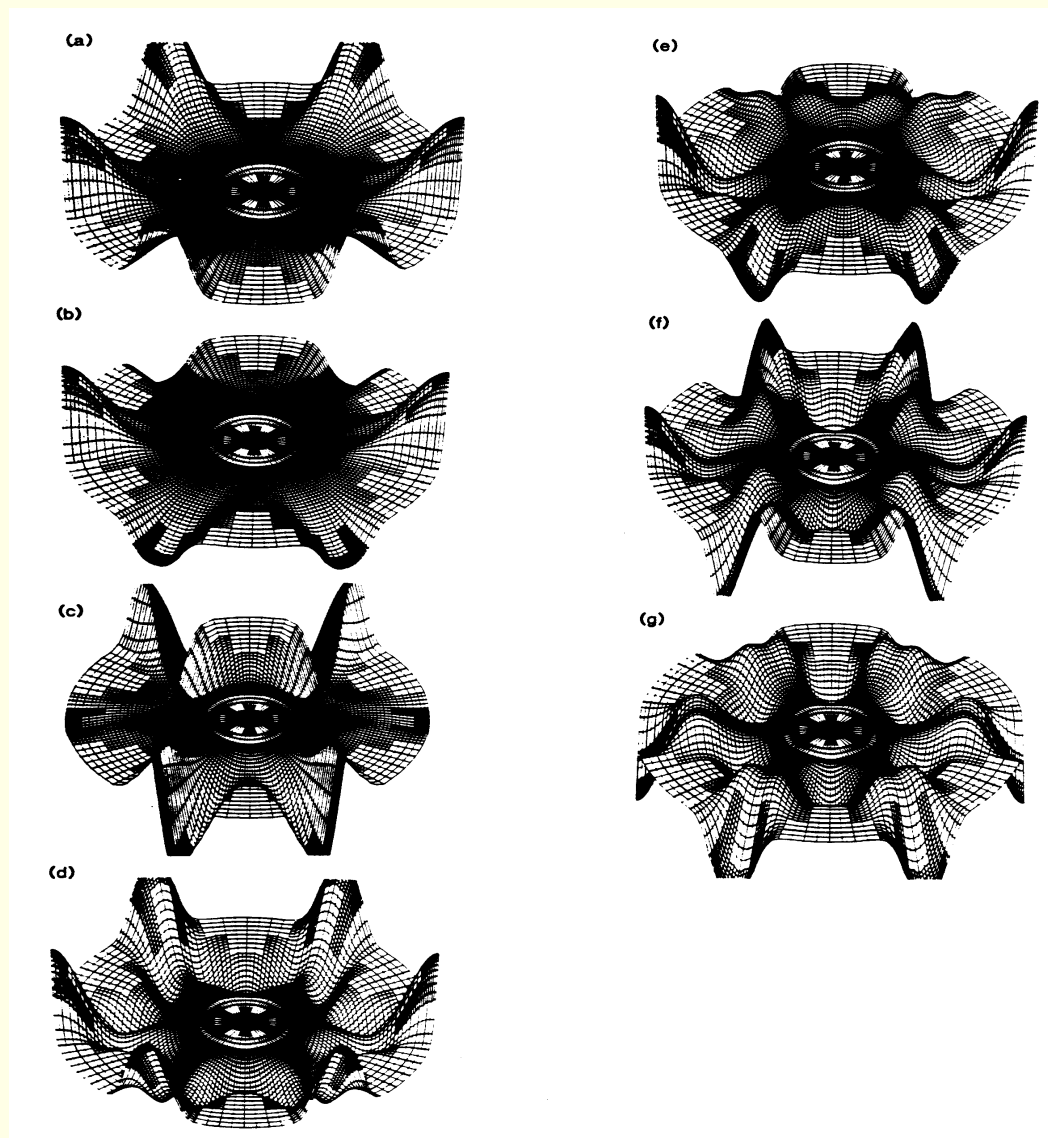


Figure 16: Perspective plots of the first 7 surface eigenfunctions Φ_{t0}^{00} at $\rho=3.166 a_0$ for H_3 . Pack, R.T., Parker, G.A.: J. Chem. Phys. **87** (1987) 3888.

Natural coordinates

earliest "exact" 3D quantum reactive scattering calculations for $\text{H} + \text{H}_2$:

Kuppermann and Schatz, Elkowitz and Wyatt and Walker, Stechel and Light used extensions of the 'natural collision coordinates' introduced by Marcus

- collinear atom-diatom reaction: natural collision coordinates swung smoothly from the reactants, $\text{A} + \text{BC}$, to the products, $\text{AB} + \text{C}$ (Fig. 3a)
- δu : increment of the 'translational' coordinate u which asymptotically describes a mass-scaled separation between the atom A or C and the diatom BC or AB; along this coordinate, from minus infinity to plus infinity the reaction actually proceeds
- δv : increment of the 'vibrational' coordinate v which asymptotically describes a mass-scaled separation of the two atoms in the diatomic BC or AB

- vibrational transitions that occur during the course of the reaction are easily rationalized in terms of coupling between the nuclear motions along u and v
- easy physical interpretation of natural collision coordinates, combined with the fact that the translational motion along the reaction path can be solved using essentially standard inelastic scattering techniques, led to the success of the early $\text{H} + \text{p-H}_2 \rightarrow \text{o-H}_2 + \text{H}$ calculations and appeared to bode well for future applications of the approach
- attempts to generalize methods based on these coordinates beyond the simplest 3D reaction soon ran into technical difficulties which seemed impossible to overcome
- difficulties are not immediately apparent in the collinear model of Fig. 3a

two observations (about difficulties) should give the general idea:

- (a) for an $A + BC$ atom-diatom reaction in 3D, at each value of the conserved total angular momentum quantum number J , the vibrational coordinate v in Fig. 3a becomes a 2D (rovibrational) surface in the 3D internal coordinate space which specifies the size and shape of the three-atom triangle
- this surface typically has quite complicated metric properties, which in turn lead to lengthy algebra in the development of any new numerical approach
- (b) in general a third ($B + CA$) arrangement must also be considered in 3D and this makes the idea of a translational 'reaction coordinate' somewhat more difficult to grasp
- in practice one can avoid the problem by introducing 'matching surfaces' between the three arrangements, but this is a great deal easier to do for the symmetric $H + H_2$ reaction than it is for anything else
- Light and coworkers had these tremendous technical difficulties finally been

overcome

- Webster and Light describe in their papers complete and general 3D atom-diatom reactive scattering methodology

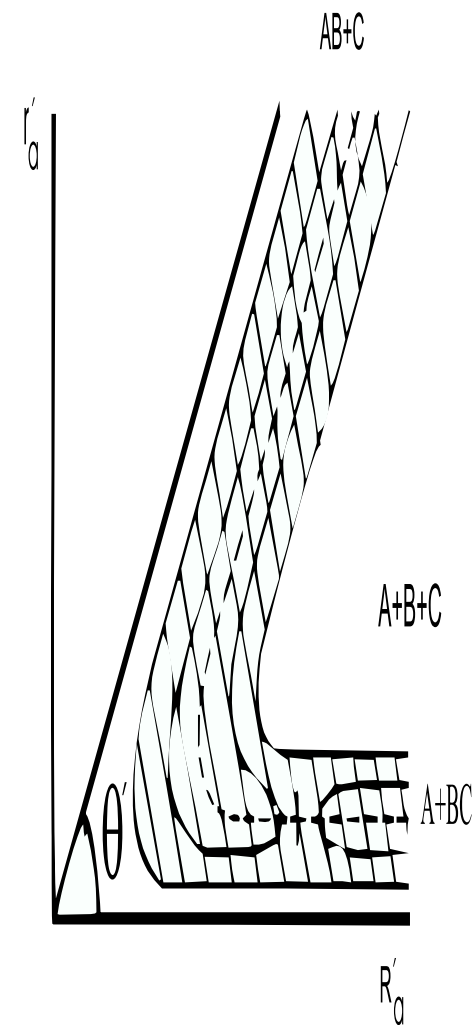
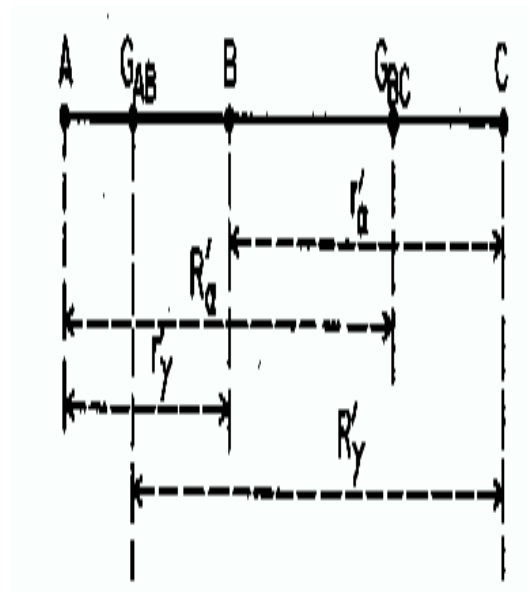
result: use more convenient coordinate schemes

Coordinates used in the 'early' $\text{H} + \text{H}_2$ calculations

Collinear triatomic reaction coordinates

Figure 17: (a) Coordinates for collinear triatomic systems, (b) Potential energy surface V for a collinear triatomic system ABC in the distance coordinates of (a). The solid curves are lines of constant V . The dashed line is the minimum energy path. The angle θ' is given by eq. 158

– Ralph Jaquet, University Siegen –



angle θ' : range $\pi/4$ to $\pi/2$

$$\theta' = \tan^{-1}[1 + m_B/m_C] \quad (158)$$

nuclear motion Hamiltonian:

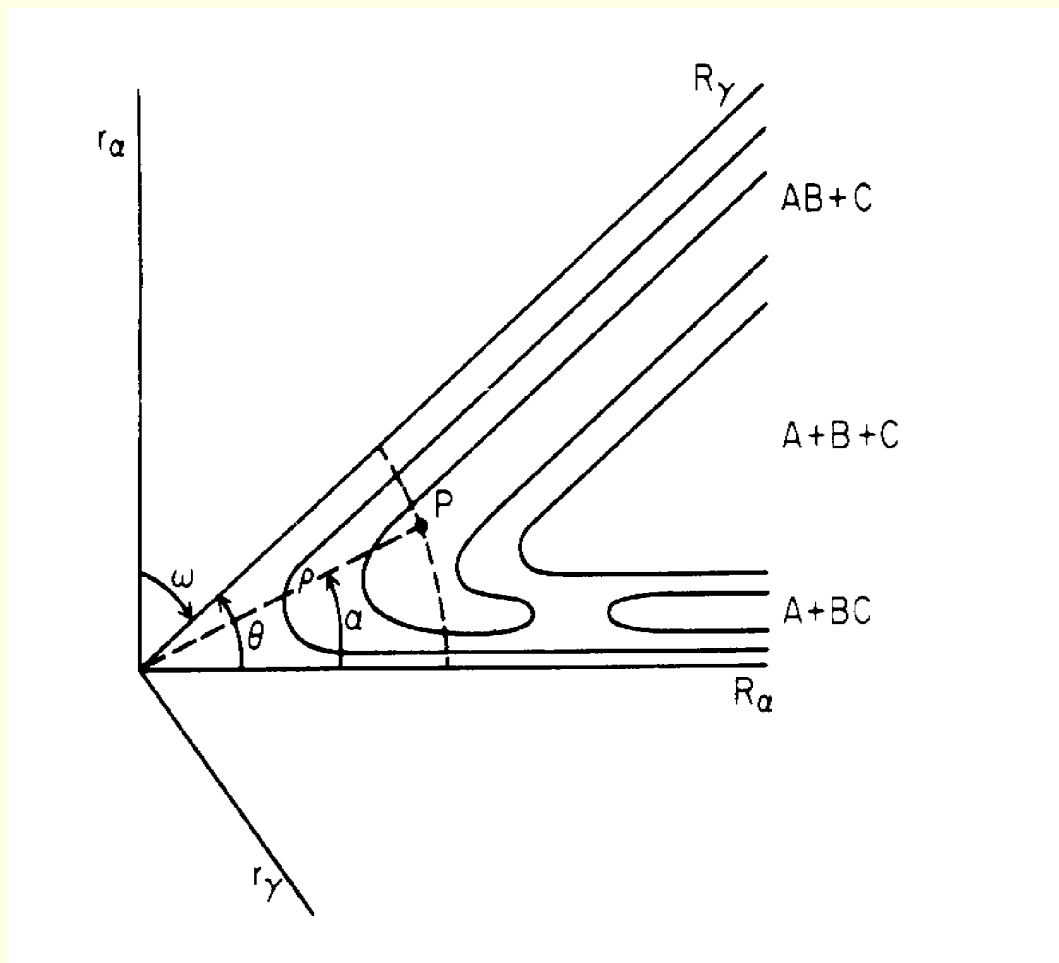
$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu_{A,BC}} \frac{\partial^2}{\partial R'_\alpha{}^2} - \frac{\hbar^2}{2\mu_{BC}} \frac{\partial^2}{\partial r'_\alpha{}^2} + V_\alpha(R'_\alpha, r'_\alpha) \\ &= -\frac{\hbar^2}{2\mu_{C,BA}} \frac{\partial^2}{\partial R'_\gamma{}^2} - \frac{\hbar^2}{2\mu_{BA}} \frac{\partial^2}{\partial r'_\gamma{}^2} + V_\gamma(R'_\gamma, r'_\gamma) \end{aligned} \quad (159)$$

$$\mu_{A,BC} = \frac{m_A(m_B+m_C)}{m_A+m_B+m_C}, \quad \mu_{BC} = \frac{m_B m_C}{m_B+m_C} \quad (160)$$

Scaled coordinates in 2D

convenient conceptual and computational simplification: scaling transformations

Figure 18: Potential energy surface for a collinear triatomic system ABC in the scaled coordinates (R_α, r_α) and (R_γ, r_γ) . The circular polar coordinates (ρ, α) are considered in the next section. Both sets of axes (R_α, r_α) and (R_γ, r_γ) are in the same plane. Kuppermann, A. in: *Theoretical Chemistry and Perspectives*, **6A**, Henderson, D. (Ed.) (Academic, NY, 1981), p. 79.



$$\begin{aligned}
R_\alpha &= a_\alpha R'_\alpha, \quad r_\alpha = (a_\alpha)^{-1} r'_\alpha, \quad a_\alpha = (\mu_{A,BC}/\mu_{BC})^{1/4} \\
R_\gamma &= a_\gamma R'_\gamma, \quad r_\gamma = (a_\gamma)^{-1} r'_\gamma, \quad a_\gamma = (\mu_{C,BA}/\mu_{BA})^{1/4}
\end{aligned} \tag{161}$$

(Delves, 1959,1960)

nuclear motion Hamiltonian:

$$\begin{aligned}
H &= -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_\alpha^2} + \frac{\partial^2}{\partial r_\alpha^2} \right) + V_\alpha(R_\alpha, r_\alpha) \\
&= -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_\gamma^2} + \frac{\partial^2}{\partial r_\gamma^2} \right) + V_\gamma(R_\gamma, r_\gamma)
\end{aligned} \tag{162}$$

μ : independent of α or γ

$$\mu = [(m_A m_B m_C)/M]^{1/2}, \quad M = m_A + m_B + m_C \tag{163}$$

$(R_\alpha, r_\alpha) \rightarrow (r_\gamma, R_\gamma)$ transformation: 2-MD coordinate-axis rotation in the scaled configuration space:

$$\begin{pmatrix} r_\gamma \\ R_\gamma \end{pmatrix} = \begin{pmatrix} \cos \omega & -\sin \omega \\ \sin \omega & \cos \omega \end{pmatrix} \begin{pmatrix} R_\alpha \\ r_\alpha \end{pmatrix} \quad (164)$$

clockwise rotation angle ω : $0 - \pi/2$ range

$$\omega = \tan^{-1}[(m_A m_C)/(m_B M)]^{1/2} \quad (165)$$

- (R_α, r_α) and (r_γ, R_γ) systems of axes are both orthogonal
- interchange of the R and r is a peculiarity of the collinear world.
- important: under the $\alpha \rightarrow \gamma$ transformation in the scaled configuration space, the equipotential surface does not change shape; this is not the case for the unscaled (R'_α, r'_α) configuration space

- consequence of these properties: nuclear motion of the ABC triatomic system on a laboratory-fixed straight line is completely isomorphic with that of a single particle of mass μ moving in the 2-MD scaled configuration space and subject to the potential V

skew angle θ between the R_α and R_γ axes: dynamic significance

$$\theta = \tan^{-1}[(m_B M)/(m_A m_C)]^{1/2} \quad (166)$$

3D scaled coordinates

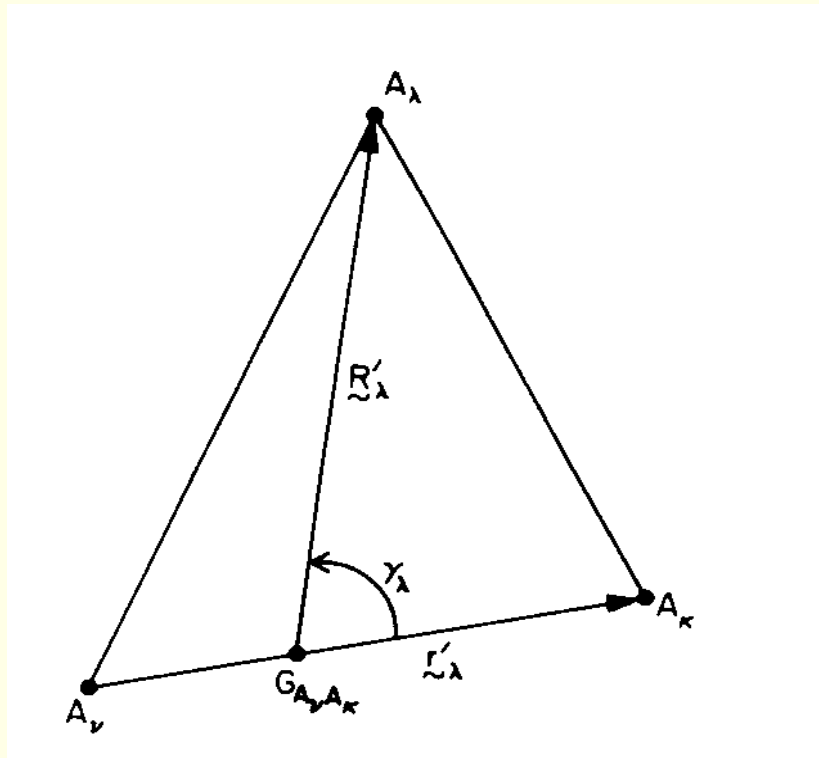


Figure 19: Relative position vectors for triatomic system in three physical dimension (3-PD).

- labeling: $A = A_\alpha$, $B = A_\beta$, and $C = A_\gamma$
- $\lambda\nu\kappa$ be a cyclic permutation of the indices $\alpha\beta\gamma$ - λ coordinates ($\lambda = \alpha, \beta, \gamma$):
 \mathbf{r}'_λ : internuclear vector - from A_ν to A_κ ; \mathbf{R}'_λ : position vector of A_λ with respect to the center of mass $G_{A_\nu A_\kappa}$ of the $A_\nu A_\kappa$ diatom
- γ_λ : angle in the $0-\pi$ range between \mathbf{r}'_λ and \mathbf{R}'_λ

nuclear motion Hamiltonian:

$$H = -\frac{\hbar^2}{2\mu_{\lambda,\nu k}}\nabla_{\mathbf{R}'_\lambda}^2 - \frac{\hbar^2}{2\mu_{\nu k}}\nabla_{\mathbf{r}'_\lambda}^2 + V_\lambda(R'_\lambda, r'_\lambda, \gamma'_\lambda) \quad (167)$$

potential energy function: $V_\lambda(R'_\lambda, r'_\lambda, \gamma'_\lambda)$

scaled position vector coordinates $\mathbf{R}_\lambda, \mathbf{r}_\lambda$:

$$\begin{aligned} \mathbf{R}_\lambda &= a_\lambda \mathbf{R}'_\lambda, \quad \mathbf{r}_\lambda = (a_\lambda)^{-1} \mathbf{r}'_\lambda, \\ a_\lambda &= (\mu_{\lambda,\nu k}/\mu_{\nu k})^{1/4}, \quad \lambda = \alpha, \beta, \gamma. \end{aligned} \quad (168)$$

$$H = -(\hbar^2/2\mu)(\nabla_{\mathbf{R}_\lambda}^2 + \nabla_{\mathbf{r}_\lambda}^2) + V_\lambda(R_\lambda, r_\lambda, \gamma_\lambda). \quad (169)$$

transformation from λ coordinates to ν coordinates:

$$\begin{pmatrix} \mathbf{r}_\nu \\ \mathbf{R}_\nu \end{pmatrix} = \begin{pmatrix} \cos \alpha_{\nu\lambda} & -\sin \alpha_{\nu\lambda} \\ \sin \alpha_{\nu\lambda} & \cos \alpha_{\nu\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\lambda \\ \mathbf{r}_\lambda \end{pmatrix} \quad (170)$$

$$\begin{aligned} \cos \alpha_{\nu\lambda} &= -\{m_\lambda m_\nu / [(m_\lambda + m_k)(m_\nu + m_k)]\}^{1/2}, \\ \sin \alpha_{\nu\lambda} &= \{m_k M / [(m_\lambda + m_k)(m_\nu + m_k)]\}^{1/2} \end{aligned} \quad (171)$$

Eqn. (170) and (171) represent a rigid rotation in the six-mathematical dimensional (6-MD) configuration space spanned by \mathbf{R}_λ and \mathbf{r}_λ , not the case for the transformation of the unscaled coordinates

Laplacian operators:

$$\nabla_{\mathbf{R}_\alpha}^2 + \nabla_{\mathbf{r}_\alpha}^2 = \nabla_{\mathbf{R}_\beta}^2 + \nabla_{\mathbf{r}_\beta}^2 = \nabla_{\mathbf{R}_\gamma}^2 + \nabla_{\mathbf{r}_\gamma}^2 = \nabla^2 \quad (172)$$

$$H = -(\hbar^2/2\mu)\nabla^2 + V \quad (173)$$

- Hamiltonian describes the motion of a single particle P of mass μ in the 6-MD scaled configuration space subject to the potential V
- motion of the three-particle ABC system in 3-PD space is isomorphic to the motion of P in this 6-MD space

Potential energy surface mapping in symmetrized hyperspherical coordinates

Visualization of the spacial characteristics of the potential energy surface $V_\lambda(R_\lambda, r_\lambda, \gamma_\lambda)$:

- collinear case: $\gamma_\lambda = \pi$ or 0 , contour lines of constant V in the 2-MD scaled configuration space R_α, r_α
- 3-PD: configuration space is six dimensional, V is a function of three variables only
- attempt: to display surfaces of constant V for every configuration which correspond one and one only point Q (Fig. 20)
- spherical polar coordinates: ρ, η_λ and γ_λ

$$\rho = (R_\lambda^2 + r_\lambda^2)^{1/2}, \quad \eta_\lambda = \tan^{-1}(r_\lambda/R_\lambda), \quad 0 \leq \eta_\lambda \leq \pi/2 \quad (174)$$

ρ is invariant with respect to a $\lambda \rightarrow \nu$ transformation, cylindrical and spherical polar coordinates (Fig. 20)

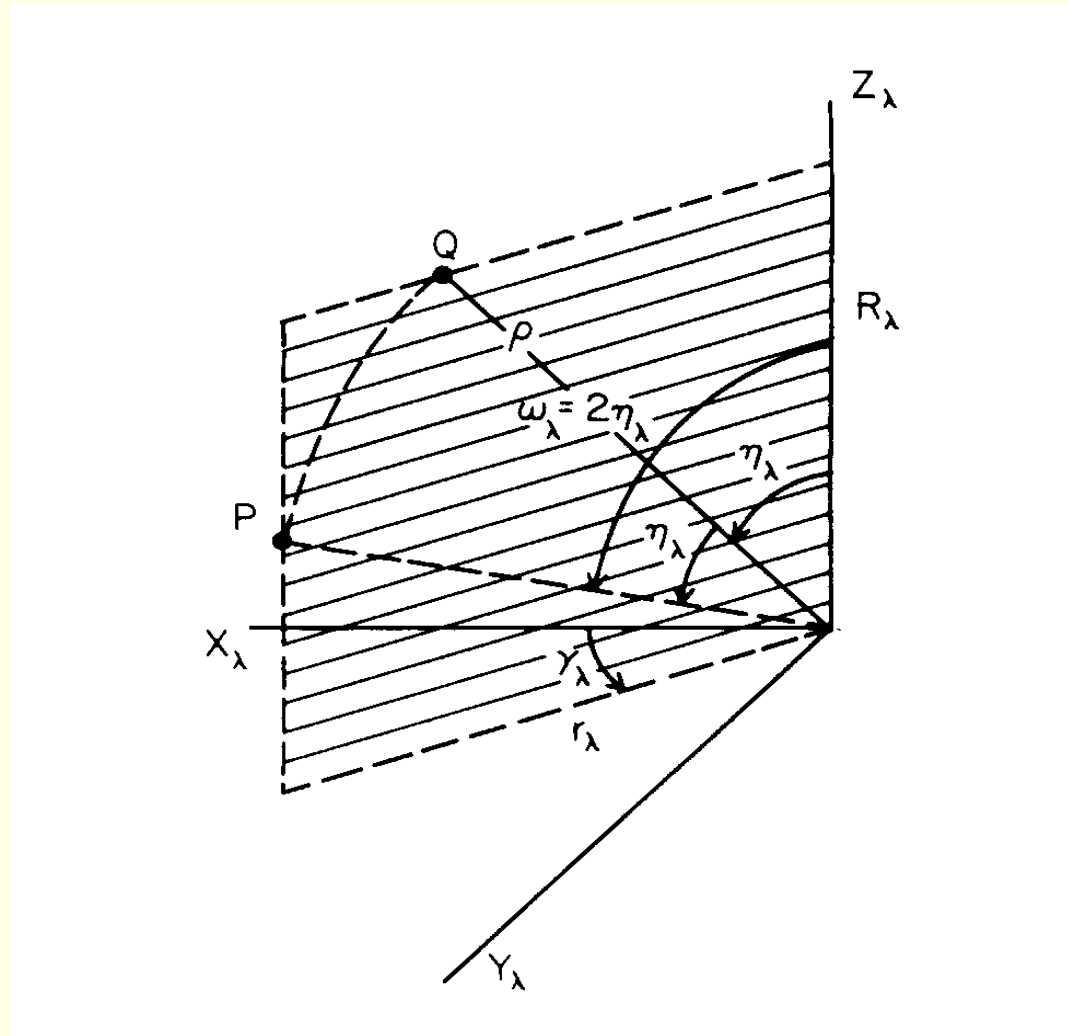


Figure 20: Cylindrical and spherical polar coordinates for mapping potential energy function for noncollinear triatomic system.

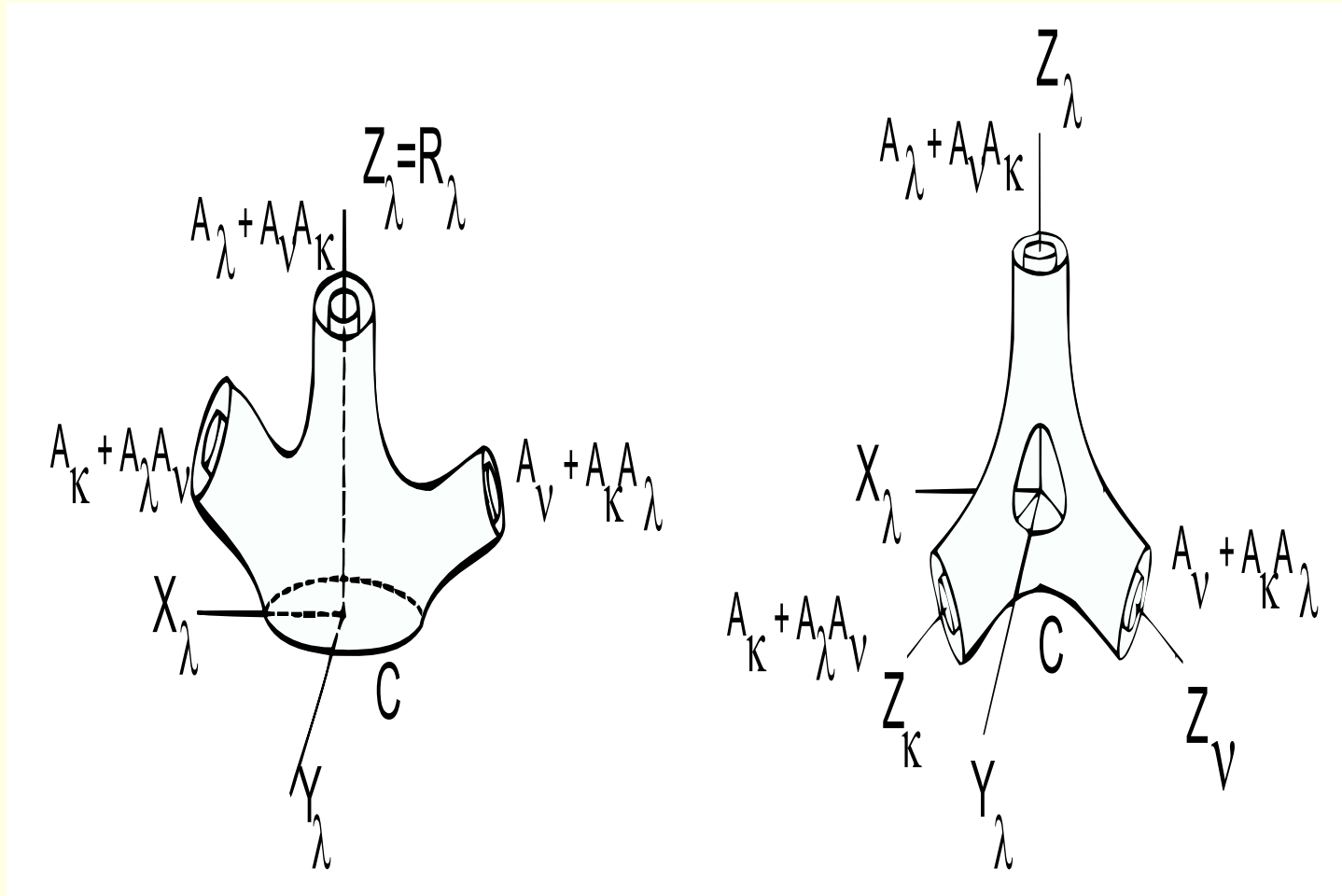


Figure 21: Equipotential surface for noncollinear $A_\lambda A_\nu A_\kappa$ triatomic system in spherical polar coordinates. a) $\rho = (R_\lambda^2 + r_\lambda^2)^{1/2}$, $\eta_\lambda = \tan^{-1}(r_\lambda/R_\lambda)$ and γ_λ , b) $\rho = (R_\lambda^2 + r_\lambda^2)^{1/2}$, $\omega_\lambda = 2 \tan^{-1}(r_\lambda/R_\lambda)$ and γ_λ . Kuppermann, A. (1981)

- typical equipotential surface is displayed in Fig. 21a

this mapping suffers from two crucial defects:

one does not have the basic one-to-one correspondence property between configurations and points Q

equipotentials of V in this map do not have the symmetry one would desire with respect to the interchange of identical atoms

- better: choose for the spherical polar coordinates the quantities $\rho, \omega_k = 2\eta_k$ and γ_k as indicated in Fig. 20 by point P

– this "umbrella opening" transformation on $\rho, \eta_\lambda, \gamma_\lambda$ collapses the circles C of Fig. 20 into a single point located on the negative half of the Z_λ axis (see Fig. 21b)

- in this same $\rho, \omega_\lambda, \gamma_\lambda$ system of polar coordinates the equipotential surfaces are also symmetric with respect to the interchange of identical atoms
- for the H_3 system: C_{3v} -symmetry
- the hole around the origin is due to the strong repulsion occurring at configurations for which all three atoms are close together
- $\lambda \rightarrow \nu$ coordinate transformation in the 3-MD $X_\lambda Y_\lambda Z_\lambda$ internal configuration subspace of Fig. 21b is a rigid rotation around the Y_λ axis
- this means that this transformation is equivalent to moving the Z_λ axis to the Z_ν position (Fig. 20) while otherwise not changing the shape of the equipotentials
- shape invariance with respect to coordinate transformations: $\rho, \omega_\lambda, \gamma_\lambda$ are called **symmetrized hyperspherical coordinates**
- the dynamical details of nonreactive or reactive collisions depend on the internal

topology of the equipotentials, i.e. the nature of the passageways between the different arrangement channel regions (Fig. 21b)

further visualization: cuts of the equipotentials of V by the $X_\alpha Z_\alpha (Y_\alpha = 0, \pi)$ and $Y_\alpha Z_\alpha (\gamma_\alpha = \pi/2, -\pi/2)$ planes for the Porter and Karplus (1964) H_3 potential energy surfacea (Fig. 22)

- the mapping gives an intuitive feeling for the dynamic properties of the corresponding system

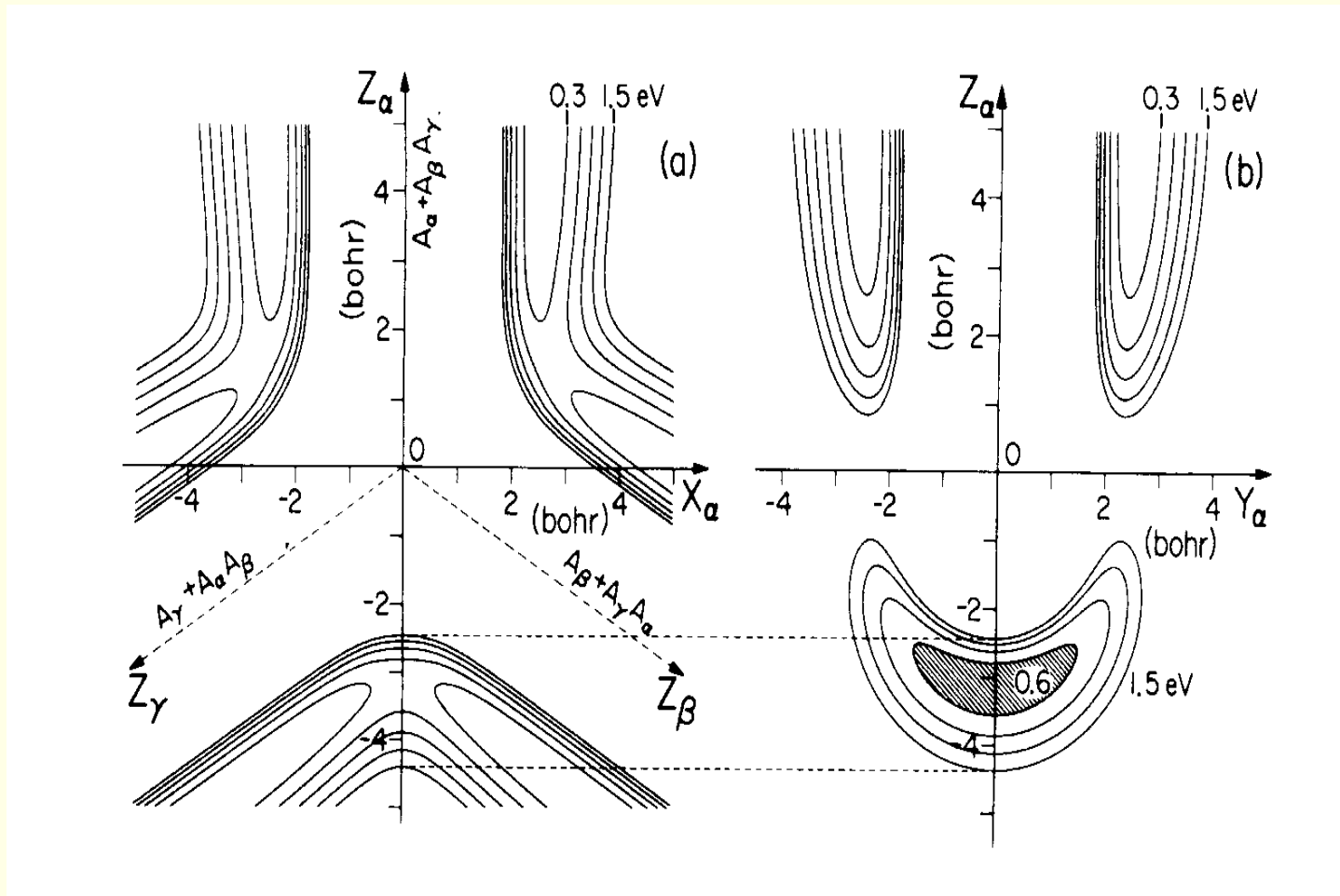


Figure 22: Cuts of equipotential surfaces for H_3 (a) Cut through $X_\alpha Z_\alpha$ plane. (b) Cut through $Y_\alpha Z_\alpha$ plane. The origin of measurement of the energy is the minimum of the isolated H_2 diatomic potential energy curve. The curves are intersections of the equipotentials with these planes. Their energies range from 0.3 to 1.5 eV in steps of 0.3 eV, as indicated on top of figure.

I.5 Quantum reactive scattering in the nineteen seventies: $\text{H} + \text{H}_2$. The matching procedures

- about 1975: first accurate calculations of the differential and integral cross sections of a simple chemical reaction: $\text{H} + \text{H}_2$
- Porter-Karplus surface is approximate, the dynamical calculations performed on them were accurate

The Quantum Dynamics of Reactive Collinear Triatomic Reactions

- triatomic exchange reactions of the type $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$ with A, B, and C representing atoms confined to move on a laboratory-fixed straight line, constitute the simplest reactive systems that display a basic characteristic of many chemical reactions: the dissolution of a chemical bond and the formation of a new one
- low math. dimensionality of the theory permits a presentation unencumbered by the math. complexities of molecular rotations, allowing thereby a fairly direct analysis of the effects of transl. and vibrat. degrees of freedom
- we consider the case of electronically adiabatic exchange reactions

Reactive scattering formalism

nuclear motion SE:

$$H\psi = E\psi \quad (175)$$

asymptotic conditions: for A + BC collisions

$$\psi^{\alpha n'_\alpha} \begin{cases} \sim_{R'_\alpha \rightarrow \infty} e^{-ik'_{\alpha n'_\alpha} R'_\alpha} \phi_{\alpha n'_\alpha}(r') + \sum_{n_\alpha} f'^{\alpha n'_\alpha}_{\alpha n_\alpha} e^{ik'_{\alpha n_\alpha} R'_\alpha} \phi_{\alpha n_\alpha}(r'_\alpha) \\ \sim_{R'_\gamma \rightarrow \infty} \sum_{n_\gamma} f'^{\alpha n'_\alpha}_{\gamma n_\gamma} e^{ik'_{\gamma n_\gamma} R'_\gamma} \phi_{\gamma n_\gamma}(r'_\gamma) \end{cases} \quad (176)$$

$$R'_\alpha \rightarrow \infty : \phi_{\alpha n'_\alpha} \quad n'_\alpha \quad k'_{\alpha n'_\alpha} \quad k'_{\alpha n_\alpha},$$

$$R'_\gamma \rightarrow \infty : \phi_{\gamma n_\gamma} \quad k'_{\gamma n_\gamma}$$

conservation of energy:

$$\frac{\hbar^2 k_{\alpha n'_\alpha}'^2}{2\mu_{A,BC}} + E_{\alpha n'_\alpha} = \frac{\hbar^2 k_{\alpha n_\alpha}'^2}{2\mu_{A,BC}} + E_{\alpha n_\alpha} = \frac{\hbar^2 k_{\gamma n_\gamma}'^2}{2\mu_{C,AB}} + E_{\gamma n_\gamma} = E \quad (177)$$

explanations:

- $E_{\lambda n_\lambda} (\lambda = \alpha, \gamma)$: vibrational energies associated with $\phi_{\lambda n_\lambda}(r'_\lambda)$
- $E_{\lambda n_\lambda}$ are quantized, the $k'_{\lambda n_\lambda}$ are not, and neither is E
- E is assumed known: we can prepare reagents in known internal states moving with respect to one another with known relative kinetic energy $E_{\lambda n_\lambda} > E$, eq. (177) furnishes $k'^2_{\lambda n_\lambda} < 0$
 - corresponding terms in eq. (176) are said to be associated with closed channels, and are needed for the mathematical completeness of the expansions on the right-hand side
 - values of $k'_{\lambda n_\lambda}$ for such channels are pure positive imaginary, and the corresp. exponentials are real negative, decaying with increasing R'_α or R'_γ
 - complex coefficient $f'^{\alpha n'_\alpha}_{\lambda n_\lambda} (\lambda = \alpha, \gamma)$: scattering amplitude from initial state $\alpha n'_\alpha$ to final state λn_λ
 - if the latter is open, the flux associated with the corresponding term is

$$v'_{\lambda n_\lambda} |f'_{\lambda n_\lambda}{}^{\alpha n'_\alpha}|^2$$

– flux associated with the initial collision term is $v'_{\alpha n'_\alpha}$

collision cross section: for (1-PD) world (or (2-MD) world) the $\alpha n'_\alpha \rightarrow \lambda n_\lambda$ processes is dimensionless

probability (see eq. (200)):

$$P_\lambda^{\alpha n'_\alpha} n_\lambda = (v'_\lambda n_\lambda / v'_{\alpha n'_\alpha}) |f'_{\lambda n_\lambda}{}^{\alpha n'_\alpha}|^2 \quad (178)$$

C + BA collisions: eq. (176) can be rewritten as

$$\psi^{\lambda' n'_{\lambda'}} \sim \sum_{\lambda n_\lambda} [\delta_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} \exp(-ik'_{\lambda n_\lambda} R'_\lambda) + f_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} \exp(ik'_{\lambda n_\lambda} R'_\lambda)] \phi_{\lambda n_\lambda}(r'_\lambda) \quad (179)$$

$\lambda'n'_{\lambda'}$: the initial state of the reagents (which are $A + BC$ for $\lambda' = \alpha$ and $C + BA$ for $\lambda' = \gamma$, where B is always the central atom), the \sim sign indicates that we are considering asymptotically the regions of configuration space in which either $R'_\alpha \rightarrow \infty$ with r'_α finite or $R'_\gamma \rightarrow \infty$ with r'_γ finite, and $\delta_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}$ is the Kronecker symbol, which is unity if $\lambda' = \lambda$ and $n'_{\lambda'} = n_\lambda$, and vanishes otherwise

– probability of $\lambda'n'_{\lambda'} \rightarrow \lambda n_\lambda$ process ($\lambda'n'_{\lambda'}, \lambda n_\lambda$: open channels):

$$P_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} = (v'_{\lambda n_\lambda} / v'_{\lambda' n'_{\lambda'}}) |f_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}|^2 \quad (180)$$

Scattering and reactance matrices and boundary conditions

- definition of the scattering matrix **S** and the reactance matrix **R**: permits us to decouple the problem of obtaining arbitrary solutions of the Schrödinger equation from the problem of imposing asymptotic conditions appropriate for collision processes on these solutions
 - λ arrangement channel region: expand the eigenfunction $\psi^{\lambda' n'_{\lambda'}}$ in the basis set $\phi_{\lambda n_{\lambda}}(r_{\lambda})$, forced to be complete and discrete by setting the diatomic potential $v_{\lambda}(r_{\lambda}) = V(R_{\lambda} \rightarrow \infty, r_{\lambda})$ in that channel equal to zero at and beyond a value

$r_{\lambda_{max}}$ of r_λ

$$\psi^{\lambda'n'_{\lambda'}} \sim \sum_{\lambda n_\lambda} g^{\lambda'n'_{\lambda'}}_{\lambda n_\lambda}(R_\lambda) \phi_{\lambda n_\lambda}(r_\lambda) \quad (181)$$

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \phi_{\lambda n_\lambda}}{dr_\lambda^2} + v_\lambda(r_\lambda) \phi_{\lambda n_\lambda} = E_{\lambda n_\lambda} \phi_{\lambda n_\lambda} \quad (182)$$

$$\phi_{\lambda n_\lambda}(0) = \phi_{\lambda n_\lambda}(r_{\lambda_{max}}) = 0 \quad (183)$$

replacement of eq. (181) into eq. (175) with H given by eq. (162), multiplication of both sides by $\phi_{\bar{\lambda}\bar{n}_\lambda}^*(r_{\bar{\lambda}})$ integration over $r_{\bar{\lambda}}$ and, in the end, replacement of $\bar{\lambda}$ by λ leads to the set of asymptotic uncoupled differential equations:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 g^{\lambda'n'_{\lambda'}}_{\lambda n_\lambda}}{dR_\lambda^2} \sim (E - E_{\lambda n_\lambda}) g^{\lambda'n'_{\lambda'}}_{\lambda n_\lambda} \quad (184)$$

solutions:

$$g_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} \sim_{R_\lambda \rightarrow \infty} v_{\lambda n_\lambda}^{-1/2} [\mathcal{I}_\lambda(R_\lambda) A_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} - \mathcal{O}_{\lambda n_\lambda}(R_\lambda) B_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}] \quad (185)$$

$A_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}$, $B_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}$: integration constants, $v_{\lambda n_\lambda}$: the channel velocity $\hbar|k_{\lambda n_\lambda}|/\mu$,
 $k_{\lambda n_\lambda}$: channel wave number:

$$k_{\lambda n_\lambda} = \hbar^{-1} [2\mu(E - E_{\lambda n_\lambda})]^{1/2} \quad (186)$$

- $\mathcal{I}_{\lambda n_\lambda}$, $\mathcal{O}_{\lambda n_\lambda}$ are the incoming and outgoing waves

$$\mathcal{I}_{\lambda n_\lambda}(R_\lambda) = \begin{cases} e^{-ik_{\lambda n_\lambda} R_\lambda} & \text{for open channels} \\ e^{|k_{\lambda n_\lambda}| R_\lambda} & \text{for closed channels} \end{cases} \quad (187)$$

$$\mathcal{O}_{\lambda n_\lambda}(R_\lambda) = \begin{cases} e^{ik_{\lambda n_\lambda} R_\lambda} & \text{for open channels} \\ e^{-|k_{\lambda n_\lambda}| R_\lambda} & \text{for closed channels} \end{cases} \quad (188)$$

eq. (185) can be put in the matrix form

$$\mathbf{g} \sim \mathbf{v}^{-1/2} [\mathcal{I} \mathbf{A} - \mathcal{O} \mathbf{B}] \quad (189)$$

$$\mathbf{g}, \mathbf{A}, \mathbf{B}: g_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}, A_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}, B_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}$$

$\mathbf{v}, \mathcal{I}, \mathcal{O}$: diagonal matrices $v_{\lambda n_\lambda}, \mathcal{I}_{\lambda n_\lambda}, \mathcal{O}_{\lambda n_\lambda}$

• scattering matrix \mathbf{S} :

$$\mathbf{B} = \mathbf{S} \mathbf{A} \quad (190)$$

– if we know what the state and flux of the reagents coming into a collision is, the scattering matrix permits us to obtain the states and fluxes of the outgoing products

(1) \mathbf{S} is unique: independent of the choice of \mathbf{A} , if we arbitrarily pick two coefficient matrices \mathbf{A}_1 , and \mathbf{A}_2 that are non-singular, the SE forces the corresponding \mathbf{B}_1 , and \mathbf{B}_2 to satisfy the relation $\mathbf{B}_1\mathbf{A}^{-1} = \mathbf{B}_2\mathbf{A}^{-2}$. \mathbf{S} does, however, depend on the total energy E of the system

(2) \mathbf{S} is symmetric, this leads to the quantum mechanical principle of microscopic reversibility or detailed balancing

(3) the open part \mathbf{S}° of \mathbf{S} , formed from its open channel rows and columns, is unitary, this results in conservation of particle flux

eq. (189) can also be put in the equivalent form

$$\mathbf{g} \sim \mathbf{v}^{-1/2}[\mathcal{S}\mathbf{C} + \mathcal{C}\mathbf{D}] \quad (191)$$

\mathbf{C} and \mathbf{D} : new integration constant matrices, \mathcal{S} and \mathcal{C} are diagonal sine and cosine stationary wave matrices

$$\mathcal{S}_{\lambda n_\lambda}(R_\lambda) = \begin{cases} \sin(k_{\lambda n_\lambda} R_\lambda) & \text{for open channels} \\ e^{|k_{\lambda n_\lambda}| R_\lambda} & \text{for closed channels} \end{cases} \quad (192)$$

$$\mathcal{C}_{\lambda n_\lambda}(R_\lambda) = \begin{cases} \cos(k_{\lambda n_\lambda} R_\lambda) & \text{for open channels} \\ e^{-|k_{\lambda n_\lambda}| R_\lambda} & \text{for closed channels} \end{cases} \quad (193)$$

- reactance matrix \mathbf{R} (sometimes called the \mathbf{K} matrix):

$$\mathbf{D} = \mathbf{R}\mathbf{C} \quad (194)$$

- (1) \mathbf{R} is unique
 - (2) \mathbf{R} is real
 - (3) the open part \mathbf{R}° of \mathbf{R} is symmetric
- from eqn. (189 - 194):

$$\mathbf{S}^\circ = (\mathbf{I} + i\mathbf{R}^\circ)(\mathbf{I} - i\mathbf{R}^\circ)^{-1} \quad (195)$$

\mathbf{I} : identity matrix, spanned by indices λn_λ and $\lambda' n'_{\lambda'}$.

- sine and cosine standing waves associated with \mathbf{R} do not carry flux
- advantage of \mathbf{R} : being real, calculable using real quantities only

- complex \mathbf{S}° matrix:

$$\begin{aligned}\mathbf{S}^\circ &= \text{Re}\mathbf{S}^\circ + \mathbf{i}\text{Im}\mathbf{S}^\circ \\ \text{Re}\mathbf{S}^\circ &= (\mathbf{I} - \mathbf{R}^{\circ 2})(\mathbf{I} + \mathbf{R}^{\circ 2})^{-1}, \\ \text{Im}\mathbf{S}^\circ &= 2\mathbf{R}^\circ(\mathbf{I} + \mathbf{R}^{\circ 2})^{-1}\end{aligned}\tag{196}$$

- scaled configuration-space scattering amplitude $f_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}$:

$$f_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} = (v_{\lambda' n'_{\lambda'}}/v_{\lambda n_\lambda})^{1/2} \mathbf{S}_{\lambda n_\lambda}^{\circ \lambda' n'_{\lambda'}}\tag{197}$$

$v_{\lambda n_\lambda}$: scaled channel velocities (185) probabilities $P_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}$: in terms of scaled

channel quantities (180):

$$P_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} = (v_{\lambda n_\lambda}/v_\lambda) |f_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}|^2, \quad P_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} = |S_{\lambda n_\lambda}^{\circ \lambda' n'_{\lambda'}}|^2 \quad (198)$$

- once the open part of the scattering matrix is known, so are all the reaction probabilities at the same total energy
- from the symmetry of **S**: principle of microscopic reversibility

$$P_{\lambda' n'_{\lambda'}}^{\lambda n_\lambda} = P_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} \quad (199)$$

- from unitarity of **S**^o (sum over open channels):

$$\sum_{\lambda n_\lambda} P_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} = 1 \quad (200)$$

eq. (200) constitutes the property of flux conservation, and justifies the use of the term probability for the quantities $P_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}$

Computation methodology

- to determine the transition probabilities $P_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}$, including include reactive ($\lambda \neq \lambda'$) as well as the nonreactive ($\lambda = \lambda'$) ones, it suffices to obtain the reactance matrix **R**
- one needs a sufficiently large number of linearly independent solutions of the SE and putting the associated **g** matrix form of eq. (191)
- from this, the square coefficient matrices **C** and **D** can be obtained, and **R** calculated from eq. (194) as long as care has been taken to ascertain that **C** is nonsingular
- different approaches: to obtain such linearly independent solutions of the SE: Mortensen and Pitzer, Mortensen, Diestler and McKoy, Truhlar and Kuppermann, and Truhlar et al used finite different methods and Cartesian coordinates

- finite difference methods: computationally very inefficient and inappropriate for extension to problems of higher dimensionality
 - other approaches: solve the integral equation equivalent to eq. (175): Sams and Kouri
 - variational approach: Mortensen and Gucwa
 - finite element approach: Askar et al
 - most widely used approach: the coupled-channel (i.e., close-coupling - CC) method
-
- basic method: choose a set of two convenient variables x and y to describe the configuration of the system; the variables may be different in different regions of configuration space, but satisfy the central property that for x , equal to a constant \bar{x} , the potential energy function $V(\bar{x}, \bar{y})$ assumes very large values for small and for large y
 - the wave function $\psi(x, y)$ is expanded in eigenfunctions of a one-mathematical-

dimensional Hamiltonian in y containing $V(\bar{x}, \bar{y})$, the resulting coupled ordinary differential equations in the x -dependent coefficients are solved

- variations of this approach: Rankin and Light, Miller and Light, Kuppermann, Diestler, Johnson, and Light and Walker

- Kuppermann method: the scaled configuration space is divided into three regions (denoted by I, II, and III in Fig. 23) and called, respectively, the reagent, the strong interaction, and the product regions

- in each of these regions different coordinates and different basis sets for expanding the wave function are used

- along the line P_1P_2 : the asymptotic behavior $v_\alpha(r_\alpha)$

- along P_6P_7 : equals $v_\gamma(r_\gamma)$

- P_0 : inside the dissociated plateau

- wave function: vanish along the line $P_1P_0P_7$, and along the line $P_2P_4P_6$

- to integrate the SE: Cartesian coordinates (R_α, r_α) and (R_γ, r_γ) in regions I and III, in region II the circular polar coordinates (ρ, ψ) with origin P_0

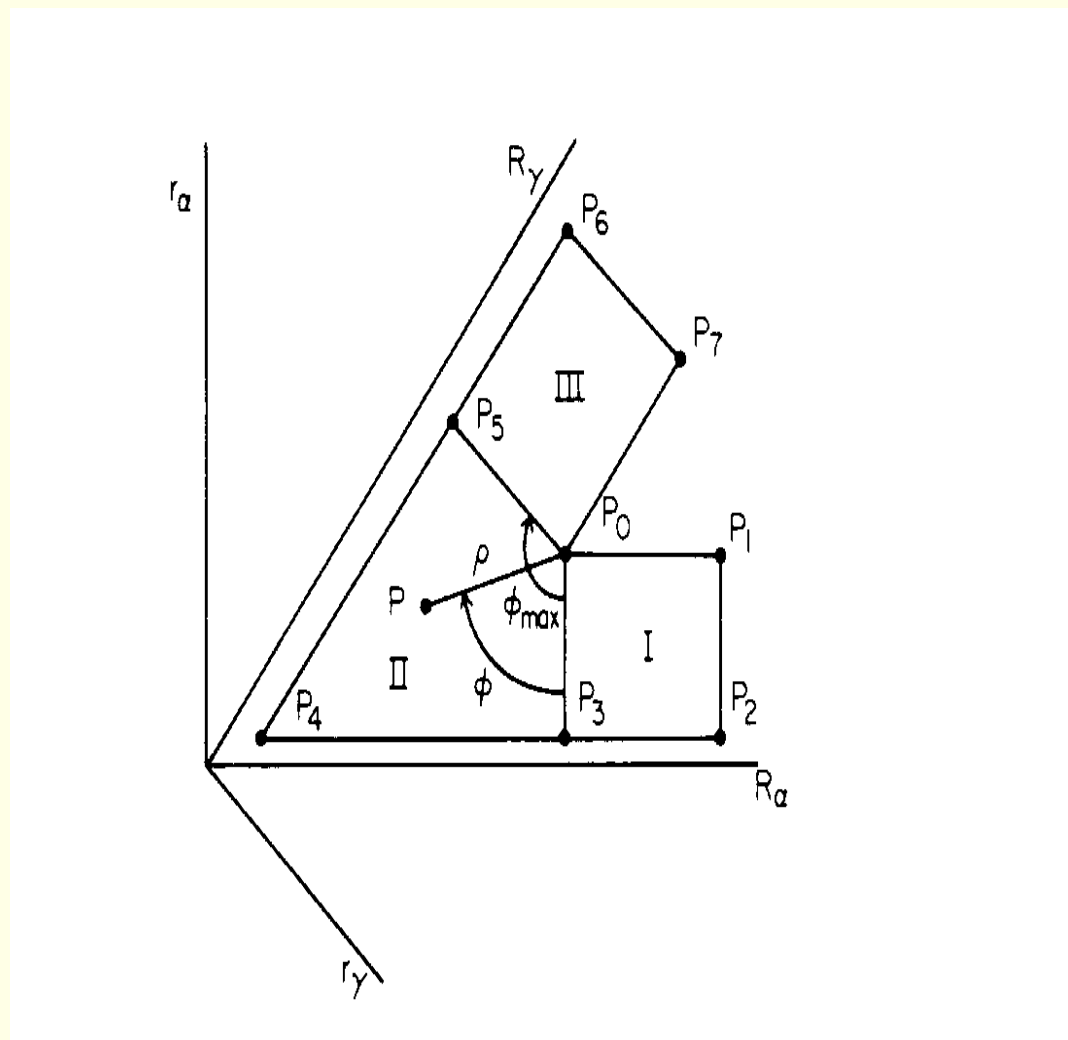


Figure 23: Coordinates and regions of scaled configuration space for integrating the Schrödinger equation for collinear triatomic reactions.

- the nuclear motion Hamiltonian: in terms of (R_α, r_α) and (R_γ, r_γ) (see eq. (162), in the (ρ, ψ) coordinates:

$$H = -\frac{\hbar^2}{2\mu} \left[\frac{1}{\rho^{1/2}} \frac{\partial^2}{\partial \rho^2} \rho^{1/2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right] + V(\rho, \phi) - \frac{\hbar^2}{8\mu\rho^2} \quad (201)$$

- subdivide region I into n_I subregions separated by lines of constant R_α at $R_\alpha = R_\alpha^0, R_\alpha^1, \dots, R_\alpha^{n_I}$, where $R_\alpha^0 = R_{\alpha 1}$ and $R_\alpha^{n_I} = R_{\alpha 0}$ are the R_α coordinate of points P_1 , and P_0
- range of the i th subregion is $R_\alpha^{i-1} < R_\alpha < R_\alpha^i$
- expanding the wave function: choose as basis functions the eigenfunctions $\phi_{\alpha n_\alpha}(r_{\alpha i}; R_\alpha^{i0})$ of the reference potential $V_{ref}^{\alpha 1}(r_\alpha; R_\alpha^{i0}) = V(R_\alpha^{i0}, r_\alpha)$

- ϕ satisfies:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR_\alpha^2} + V_{ref}^\alpha(r_\alpha; R_\alpha^{i0})\right] \phi_{\alpha n_\alpha}(r_\alpha; R_\alpha^{i0}) = E_{\alpha n_\alpha}(R_\alpha^{i0}) \phi_{\alpha n_\alpha}$$

$$\phi_{\alpha n_\alpha}(r_{\alpha 1}; R_\alpha^{i0}) = \phi_{\alpha n_\alpha}(r_{\alpha 2}; R_\alpha^{i0}) = 0 \quad (202)$$

$r_{\alpha 1}$, $r_{\alpha 2}$: r_α coordinates of points P_1 and P_2

$E_{\alpha n_\alpha}(R_\alpha^{i0})$: energy levels of the local transverse vibration at $R_\alpha = R_\alpha^{i0}$

– basis set $\phi_{\alpha n_\alpha}(r_\alpha : R_\alpha^{i0})$ furnishes a better representation of the scattering wave functions than do the diatom eigenfunctions $\phi_{\alpha n_\alpha}(r_\alpha; R_\alpha \rightarrow \infty)$:

$$\psi^{\lambda' n'_{\lambda'}} = \sum_{n_\alpha} g_{\alpha n_\alpha}^{\lambda' n'_{\lambda'}}(R_\alpha; R_\alpha^{i0}) \phi_{\alpha n_\alpha}(r_\alpha; R_\alpha^{i0}) \quad (203)$$

– substitute into eq. (175) with H given by the first part of eq. (162), multiply both sides by $\phi_{\alpha\bar{n}_\alpha}^*(r_\alpha; R_\alpha^{i0})$, integrate over r_α from $r_{\alpha2}$ to $r_{\alpha1} \implies$ coupled equations:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \mathbf{g}^I}{d\mathbf{R}_\alpha^2} + \mathbf{V}^I(R_\alpha; R_\alpha^{i0}) \mathbf{g}^I = \mathbf{E}^I(R_\alpha^{i0}) \mathbf{g}^I \quad (204)$$

matrices dimension: $N=n_\alpha$

– expansion should be infinite; it is truncated at a finite N , which is greater than the number of open channels at the energy being considered, convergence with respect to increasing N is determined numerically

$\mathbf{g}^I : g_{\alpha n_\alpha}^{\lambda' n_{\lambda'}}$, \mathbf{E}^I : diagonal matrix $E - E_{\alpha n_\alpha}(R_\alpha^{i0})$

\mathbf{V}^I : interaction potential matrix

$$V_{n_\alpha}^{In'_\alpha}(R_\alpha; R_\alpha^{i0}) = \langle \phi_{\alpha n_\alpha}(r_\alpha; R_\alpha^{i0}) | V_\alpha(R_\alpha, r_\alpha) - V_\alpha(R_\alpha^{i0}, r_\alpha) | \phi_{\alpha n'_\alpha}(r_\alpha; R_\alpha^{i0}) \rangle \quad (205)$$

- SE is integrated in region **I** for N independent solutions by choosing $\mathbf{g}^I(R_{\alpha 1}; R_{\alpha}^{i0}) = d\mathbf{g}_0^I$ and $d\mathbf{g}^I(R_{\alpha 1}; R_{\alpha}^{i0})/dR_{\alpha} = \mathbf{g}_0^I$ arbitrarily, but not simultaneously zero. One such choice is to make the first equal to the identity matrix and the second equal to the null matrix
- this corresponds to a choice of initial conditions at the start. value $R_{\alpha 1}$ of R_{α}
- one integrates the coupled equations through subregion I, change to the basis set for subregion II at the boundary between these subregions, continue in this manner until one reaches the end of region I
- change in vibrational basis sets at the boundary between subregions i and $i + 1$ is accomplished by imposing the condition that the wave function $\psi^{\lambda' n'_{\lambda'}}$ and its derivative with respect to R_{α} be continuous at that boundary

- this results in the relations:

$$\mathbf{g}^I(R_\alpha^i; R_\alpha^{i+1,o}) = \mathbf{S}_i^I \mathbf{g}^I(R_\alpha^i, R_\alpha^{io}), \frac{d\mathbf{g}^I(R_\alpha^i; R_\alpha^{i+1,o})}{dR_\alpha} = \mathbf{S}_i^I \frac{d\mathbf{g}^I(R_\alpha^i; R_\alpha^{io})}{dR_\alpha}, \quad (206)$$

\mathbf{S}_i^I : overlap matrix between the basis functions for subregions i and $i + 1$

$$S_{in_\alpha}^{In'_\alpha} = \langle \phi_{\alpha n_\alpha}(r_\alpha; R_\alpha^{i+1,o}) | \phi_{\alpha n'_\alpha}(r_\alpha; R_\alpha^{io}) \rangle. \quad (207)$$

- proceeding to region II: also subdivided into subregions by lines of constant ϕ at $\phi = \phi^0, \phi^1, \dots, \phi^{nII}$, where $\phi^0 = 0$ and $\phi^{nII} = \phi_{max}$ are the ϕ coordinate of points P_3 and P_5
- range of the i th subregion is $\phi^{i-1} < \phi < \phi^i$
- potential energy functions $V(\rho, \phi)$: along lines of constant ϕ have the shape of diatomic molecule potential energy functions

- choose as basis functions for the i th subregion the eigenfunctions $\psi_{II}(\rho; \phi^{io})$ of the reference potential $V_{ref}^{II}(\rho; \phi^{io}) = V(\rho, \phi^{io})$, where ϕ^{io} is a value of ϕ in that subregion

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho^2} + V_{ref}^{II}(\rho; \phi^{io})\right] \phi_{||n}(\rho; \phi^{io}) = E_{||n}(\phi^{io}) \phi_{||n} \quad (208)$$

- boundary conditions:

$$\phi_{||n}(\rho_{max}^i; \phi^{io}) = \phi_{||n}(\rho = 0; \phi^{io}) = 0, \quad (209)$$

ρ_{max}^i : value of ρ for the intersection point between the $\phi = \phi^{i0}$ line and the line $P_3P_4P_5$

- $\phi_{||n}$ and $E_{||}$ are local transverse vibrational eigenfunctions and eigenvalues that lead to a much more rapidly converging expansion of the scattering wave

function in subregion II than would the eigenfunctions of the isolated diatom reagent or product

expansion of the wave function:

$$\psi^{\lambda' n'} = \rho^{-1/2} \sum_n g_{\text{II}n}^{\lambda' n'}(\phi; \phi^{io}) \phi_{\text{II}n}(\rho; \phi^{io}). \quad (210)$$

substituting this expression into eq. (175) with H given by eq. (201):

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \mathbf{g}^{\text{II}}}{d\phi^2} + \rho^2(\phi^{io}) \mathbf{V}^{\text{II}}(\phi; \phi^{io}) \mathbf{g}^{\text{II}} = \rho^2 \mathbf{E}^{\text{II}}(\phi^{io}) \mathbf{g}^{\text{II}}. \quad (211)$$

$\mathbf{g}^{\text{II}}: \mathbf{g}_{\parallel n}^{\lambda' n'_{\lambda'}}; ; \rho^2, \mathbf{V}^{\text{II}}$ and $\mathbf{E}^{\text{II}} :$

$$\rho_n^{2n'}(\phi^{io}) = \langle \phi_{\parallel n}(\rho; \phi^{io}) | \rho^2 | \phi_{\parallel n'}(\rho; \phi^{io}) \rangle$$

$$V_n^{\parallel n'}(\phi; \phi^{io}) = \langle \phi_{\parallel n}(\rho; \phi^{io}) | V(\rho, \phi) - V(\rho, \phi^{io}) - \frac{\hbar^2}{8\mu\rho^2} | \phi_{\parallel n'}(\rho; \phi^{io}) \rangle$$

$$E_n^{\parallel n'}(\phi^{io}) = \delta_n^{n'} [E - E_{\parallel n}(\phi^{io})]. \quad (212)$$

– condition: at the boundary between regions I and II $\psi^{\lambda' n'_{\lambda'}}$ and its derivative with respect to R_α are continuous, this leads to the following relations between

the initial values of g^{II} or its ϕ derivative and the final values of g^I or its R_α derivative:

$$\mathbf{g}^{II}(\phi = 0; \phi^{1o}) = \rho^{1/2} \mathbf{g}^I(R_{\alpha 0}; R_\alpha^{n|o}) \quad (213)$$

$$d\mathbf{g}^{II}(\phi = 0; \phi^{io})/d\phi = -\rho^{3/2}[d\mathbf{g}^I(R_{\alpha 0}; R_\alpha^{n|o})/dR_\alpha],$$

$$\rho_n^{bn'} = (\phi_{||n}(\rho; \phi^{io})|\rho^b|\phi_{||n'}(r_{\alpha 1} - \rho; R_\alpha^{n|o})), \quad b = \frac{1}{2}, \frac{3}{2}. \quad (214)$$

– change in vibrational basis set at the boundary between subregions IIi and $IIi + 1$ is: analogous to eqn. (206) and (207)

- using them and eq. (213) one can integrate eq. (211) from the beginning through the end of region II
- region III: analogous to eqn. (202 - 207) with I and α replaced by III and γ respectively
- boundary between regions II and III: analogous to eq. (213) with a plus rather than a minus sign in the right-hand side of the second of these equations to indicate that both ϕ and R_γ increase in the direction of integration
- procedure: integrate the SE from the beginning of region I to the end of III
 - CC solvers commonly used: Gordon, Magnus, and Light and Walker
 - due to the necessary inclusion of closed channels in the expansion of $\psi^{\lambda' n'_{\lambda'}}$ the columns of the g matrices tend to become linearly dependent as the integration proceeds, thereby destroying the needed linear independence of the $\psi^{\lambda' n'_{\lambda'}}$
 - this can be avoided by reorthogonalization procedures, one of which involves

right multiplying \mathbf{g} and \mathbf{g}' by \mathbf{g}^{-1} , which means continuing the integration with $\mathbf{g}_{new} = I$ and $\mathbf{g}'_{new} = \mathbf{g}^I \mathbf{g}^{-1}$

- this corresponds to obtaining n solutions with the modified initial conditions $\mathbf{g}_{0_{new}}^I = \mathbf{g}_0^I \mathbf{g}^{-1}$ and $\mathbf{g}_{new}^{I'} = \mathbf{g}_0^{I'} \mathbf{g}^{-1}$
- each time a reorthogonalization procedure is performed anywhere in regions I, II, or III, the initial conditions of region I must be modified accordingly
- R-matrix method developed by Light and Walker (1976) has elegantly bypassed this complication

\mathbf{g}_f^{III} : the final \mathbf{g}^{III} matrix at the end of region III

\mathbf{g}_0^I : initial \mathbf{g}^I matrix at the beginning of region I, equivalent notation for the derivatives with respect to R_γ and R_α

- perform integrations of the SE starting at the beginning of region III and

terminating at the end of region I

\mathbf{g}_o^{III} and \mathbf{g}_f^I : initial and final matrices, with a similar notation for their derivatives

- with the help of these several matrices we can determine the \mathbf{R} matrix
- define the global \mathbf{g} and \mathbf{g}' matrices:

$$\mathbf{g} = \begin{pmatrix} \mathbf{g}_o^I & \mathbf{g}_f^I \\ \mathbf{g}_f^{III} & \mathbf{g}_o^{III} \end{pmatrix}, \quad \mathbf{g}' = \begin{pmatrix} \mathbf{g}_o^{I'} & \mathbf{g}_f^{I'} \\ \mathbf{g}_f^{III'} & \mathbf{g}_o^{III'} \end{pmatrix} \quad (215)$$

\mathbf{g} must have assumed the form given by eq. (191):

$$\mathbf{g} = v^{-1/2}[\mathcal{S}\mathbf{C} + \mathcal{C}\mathbf{D}], \quad \mathbf{g}' = v^{-1/2}[\mathcal{S}'\mathbf{C} + \mathcal{C}'\mathbf{D}] \quad (216)$$

\mathcal{S}' and \mathcal{C}' : diagonal matrices, whose diagonal elements are the derivatives with respect to R_λ of eqn. (192) and (193)

eq. (216): all matrices except \mathbf{C} and \mathbf{D} are now known

- from these equations we can therefore obtain these unknowns and from them \mathbf{R} by using eq. (194)
 - from the open part \mathbf{R}° of \mathbf{R} we obtain \mathbf{S}° from either eqn. (195) or (196)
 - transition probabilities $P_{\lambda n_\lambda}^{\lambda' n_{\lambda'}}$: use eq. (198).

Electronically nonadiabatic exchange reactions

- chemical reaction: involves change in the electronic state of the triatomic system:
 - extension of theoretical formulation of exchange reaction (eqn. (176) and (179))
 - family of electronically diabatic potential energy surfaces as well as a family of coupling potential energy surfaces
 - the lowest two of these surfaces interact and the others are at energies that are high compared to the collision energy being considered: use the two-state

approximation

$$\begin{aligned} \left(-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial R_\alpha^2} + \frac{\partial^2}{\partial r_\alpha^2}\right) + V_1(R_\alpha, r_\alpha) - E\right)\psi_1(R_\alpha, r_\alpha) &= -V_{12}(R_\alpha, r_\alpha)\psi_2(R_\alpha, r_\alpha) \\ \left(-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial R_\alpha^2} + \frac{\partial^2}{\partial r_\alpha^2}\right) + V_2(R_\alpha, r_\alpha) - E\right)\psi_2(R_\alpha, r_\alpha) &= -V_{21}(R_\alpha, r_\alpha)\psi_1(R_\alpha, r_\alpha) \end{aligned} \tag{217}$$

V_1 and V_2 : electronically diabatic surfaces

V_{12} : coupling potential energy surface

– asymptotic conditions:

$$\begin{aligned}\psi^{i\lambda'n'_{\lambda'}} &\sim \sum_{\lambda n_{\lambda}} [e^{(-ik_{i\lambda n_{\lambda}} R_{\lambda})} \delta_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}} + e^{ik_{i\lambda n_{\lambda}} R_{\lambda}} f_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}] \phi_{i\lambda n_{\lambda}}(r_{\lambda}), \quad i = 1, 2 \\ \psi^{j\lambda'n'_{\lambda'}} &\sim \sum_{\lambda n_{\lambda}} f_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}} e^{ik_{j\lambda n_{\lambda}} R_{\lambda}} \phi_{j\lambda n_{\lambda}}(R_{\lambda}), \quad j \neq i, \quad j = 1, 2\end{aligned}\quad (218)$$

The Quantum Dynamics of Three-Dimensional Reactive Triatomic Systems

- generalization of the description of the electronically adiabatic reactive scattering of collinear triatomic systems to three physical dimensions (3-PD)
- appropriate spherical scattered waves replace the corresponding collinear plane waves
- additional difference: two reactive product arrangement channels ($AB + C$ and $AC + B$), bifurcation" problem

Reactive-scattering formalism

- choose a system of coordinates that spans the 6-MD configuration space
- $Oxyz$ be a system of coordinates whose origin 0 is the center of mass of the system and whose axes are parallel to a system of laboratory-fixed axes (LAB = laboratory-fixed system)
- spherical polar coordinates of the scaled \mathbf{R}_λ in this system are $R_\lambda, \theta_\lambda, \phi_\lambda$
- body-fixed (BF) coordinate system $OX_\lambda Y_\lambda Z_\lambda$ obtained by rotating the $Oxyz$ axis by the Euler angles $\phi_\lambda, \theta_\lambda, 0$ (see Fig. 24)
- resulting OZ_λ axis points along the $\mathbf{R}_\lambda, \mathbf{r}_\lambda$
- spherical polar coordinates in the space-fixed (SF) system are $\mathbf{r}_\lambda^{sf} = (r_\lambda, \theta_{r\lambda}, \phi_{r\lambda})$ and in body-fixed system are $r_\lambda^{bf}(r_\lambda, \gamma_\lambda, \psi_\lambda)$
- γ_λ : the angle between \mathbf{R}_λ and \mathbf{r}_λ ; ψ_λ : tumbling a. around (\mathbf{R}_λ, Oz) plane
- BF coordinates: leads to simpler final expressions for the cross sections and to a simpler solution to the bifurcation problem
- SF coordinates can also be used

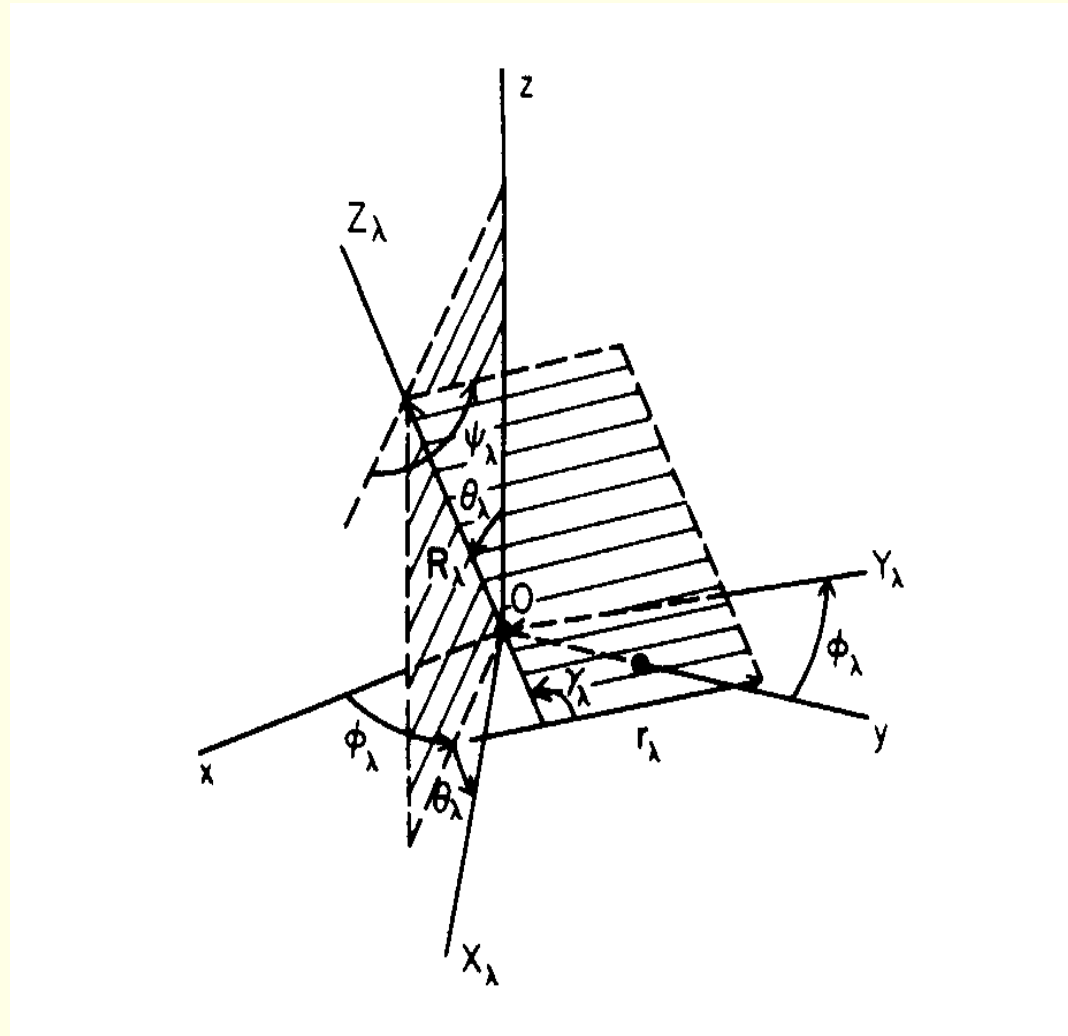


Figure 24: Body-fixed (BF) and space-fixed (SF) coordinates for triatomic system in three physical dimensions.

- BF coordinates: SE equation

$$H\psi^{\lambda'n'_{\lambda'}} = E\psi^{\lambda'n'_{\lambda'}} \quad (219)$$

- asymptotic condition for large $R_\lambda(\lambda = \alpha, \beta, \gamma)$:

$$\begin{aligned} \psi^{\lambda'n'_{\lambda'}} &\sim \exp(ik_{\lambda'c'_{\lambda'}j'_{\lambda'}}R_{\lambda'_z})\Phi_{\lambda'n'_{\lambda'}}(\mathbf{r}_{\lambda'}^{sf}) + \\ &\sum_{\lambda n_\lambda} f_{\lambda n_\lambda}^{\lambda'n'_{\lambda'}}(\theta_\lambda, \phi_\lambda)(R_\lambda)^{-1} \exp(ik_{\lambda c_\lambda j_\lambda}R_\lambda)\phi_{\lambda n_\lambda}(\mathbf{r}_\lambda^{bf}) \end{aligned} \quad (220)$$

λ and λ' : designate the final and initial arrangement channels

n_λ : set of quantum numbers $c_\lambda, j_\lambda, m_{j_\lambda}$ of the $A_\nu A_k$ isolated diatom

c_λ : vibrational quantum number, j_λ : its rotational angular momentum quantum number

m_{j_λ} : quantum number associated with the projection of the diatom's rotational angular momentum along the direction of the final relative wave-number vector $\mathbf{k}_{\lambda c_\lambda j_\lambda}$ (i.e., the helicity polarization quantum number) which, as $R_\lambda \sim \infty$, lies in the $\theta_\lambda, \phi_\lambda$ direction

$n'_{\lambda'}$: represents the corresponding quantum numbers $c'_{\lambda'} j'_{\lambda'} m'_{j'_{\lambda'}}$ of the initial diatomic reagent $A_{\nu'} A_{k'}$ where the axis of quantization for $m'_{j'_{\lambda'}}$ is the direction of the initial relative wave-number vector $\mathbf{k}_{\lambda' c'_{\lambda'} j'_{\lambda'}}$ that has been chosen to lie along the laboratory-fixed Oz axis

$R_{\lambda'_z}$: component of $\mathbf{R}_{\lambda'}$ along that axis, for $R_{\lambda'} \sim \infty$ $\mathbf{R}_{\lambda'}$ lies in the $-\mathbf{k}_{\lambda' c'_{\lambda'} j'_{\lambda'}}$ direction in the negative Oz direction

helicity representation: axis of quantization for the reagent and product diatoms:
initial and final relative wave-number vectors

- this particular choice of representation greatly simplifies the expression for the scattering amplitude given by eq. (238)
- $\phi_{\lambda n_{\lambda}}(\mathbf{r}_{\lambda}^{bf})$ and $\phi_{\lambda' n'_{\lambda'}}(\mathbf{r}_{\lambda'}^{sf})$ in eq. (220): diatomic product and reagent rovibrational eigenfunctions in scaled coordinates and in the helicity representation
- $(R_{\lambda})^{-1} \exp(ik_{\lambda c_{\lambda} j_{\lambda}})$: a spherical radial scattered wave
- $\exp(ik_{\lambda' c'_{\lambda'} j'_{\lambda'}} R_{\lambda' z'})$: plane wave representing the initial relative motion of the atom A_{λ} with respect to the diatomic molecule $A_{\nu'} A_{k'}$ in scaled coordinates
- $f_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}(\theta_{\lambda}, \phi_{\lambda})$: scattering amplitude from initial state $\lambda' n'_{\lambda'}$ of the reagent to final state λn_{λ} of the product, for initial and final relative atom-diatom

wave-number vectors $\mathbf{k}_{\lambda'c'_{\lambda'}j'_{\lambda'}}$ and $\mathbf{k}_{\lambda c_{\lambda}j_{\lambda}}$

- $\theta_{\lambda}\phi_{\lambda}$: polar angles in the $Oxyz$ system whose Oz axis lies along $\mathbf{k}_{\lambda'c'_{\lambda'}j'_{\lambda'}}$
- energy conservation relation:

$$(\hbar^2 k_{\lambda'c'_{\lambda'}j'_{\lambda'}}^2/2\mu) + E_{\lambda'c'_{\lambda'}j'_{\lambda'}} = (\hbar^2 k_{\lambda c_{\lambda}j_{\lambda}}^2/2\mu) + E_{\lambda c_{\lambda}j_{\lambda}} = E, \quad \lambda = \alpha, \beta, \gamma \quad (221)$$

$E_{\lambda'c'_{\lambda'}j'_{\lambda'}}$, $E_{\lambda c_{\lambda}j_{\lambda}}$: rovibrational energy of the initial and final diatoms; E: total energy

- unscaled coordinate scattering amplitude $f_{\lambda n_{\lambda}}^{\lambda'n'_{\lambda'}}(\theta_{\lambda}, \phi_{\lambda})$ is related to the scaled one by:

$$f_{\lambda n_{\lambda}}^{\lambda'n'_{\lambda'}}(\theta_{\lambda}, \phi_{\lambda}) = (a_{\lambda})^{-1}(a_{\lambda}/a_{\lambda'})^{1/2} f_{\lambda n_{\lambda}}^{\lambda'n'_{\lambda'}}(\theta_{\lambda}, \phi_{\lambda}) \quad (222)$$

- a_λ : eq. (168) differential cross section for the $\lambda'n'_{\lambda'} \rightarrow \lambda n_\lambda$ process:

$$\sigma_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}(\theta_\lambda, \phi_\lambda) = (v'_{\lambda n_\lambda}/v'_{\lambda' n'_{\lambda'}})|f_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}}(\theta_\lambda, \phi_\lambda)|^2 \quad (223)$$

$v'_{\lambda n_\lambda}$ and $v'_{\lambda' n'_{\lambda'}}$: final and initial unscaled coordinate velocities

- sum in the right-hand side of eq. (220) includes the closed-channel terms, for which $E_{\lambda c_\lambda j_\lambda} > E$
- present formulation: A_α , A_β , and A_γ (distinguishable atoms)
- when they are not, the scattering wave function must be made to satisfy the Pauli principle
- this can be achieved a posteriori, after solving the SE and ignoring this principle

Scattering and reactance matrices and boundary conditions

- define: surface functions $\phi_{\lambda b_\lambda}^{JM_J}(\hat{\mathbf{R}}_\lambda, \mathbf{r}_\lambda^{\text{bf}})$: $\hat{\mathbf{R}}_\lambda$ is the unit vector in the \mathbf{R}_λ direction(laboratory-fixed polar angles $\theta_\lambda, \phi_\lambda$)

- function of five scalar variables $\theta_\lambda, \phi_\lambda, \gamma_\lambda, \psi_\lambda$, defined as a simultaneous eigenfunction of the following five operators:

- (1) the square of the triatomic system total angular momentum J_{op}^2

- (2) the Oz laboratory-fixed component of that angular momentum $J_{z_{op}}$

- (3) the energy of the isolated A_ν A_k diatom $h_{\lambda_{op}}$

- (4) the square of the rotat. ang. momentum of that isolated diatom $j_{\lambda_{op}}^2$

- (5) the component of that angular momentum along the body-fixed OZ_λ (i.e., \mathbf{R}_λ) axis $j_{z_{\lambda_{op}}}$

quantum numbers: $J, M_J, c_\lambda, j_\lambda$ and Ω_λ respectively, and b_λ designates the $c_\lambda, j_\lambda, \Omega_\lambda$ subset

Ω_λ : ass. with tumbling motion around R_λ ; tumbling angle ψ_λ

$$\phi_{\lambda b_\lambda}^{JM_J}(\hat{\mathbf{R}}_\lambda, \mathbf{r}_\lambda^{\text{bf}}) = [(2J+1)/4\pi]^{1/2} D_{M_J \Omega_\lambda}^J(\phi_\lambda \theta_\lambda) \Phi_{\lambda c_\lambda j_\lambda \Omega_\lambda}(\mathbf{r}_\lambda^{\text{bf}}) \quad (224)$$

$D_{M_J \Omega_\lambda}^J$: Wigner rotation function, $\Phi_{\lambda c_\lambda j_\lambda \Omega_\lambda}(\mathbf{r}_\lambda^{\text{bf}})$: simultaneous eigenfunction of the $h_{\lambda_{op}}$ (Hamiltonian), $j_{\lambda_{op}}^2$ and $j_{z_{\lambda_{op}}}$: operators of the isolated $A_\nu A_k$ diatom in the scaled coordinates $OX_\lambda Y_\lambda Z_\lambda$ body-fixed system of axis for a molecule in a Σ state:

$$\Phi_{\lambda c_\lambda j_\lambda \Omega_\lambda}(\mathbf{r}_\lambda^{\text{bf}}) = (r)^{-1} \phi_{\lambda c_\lambda j_\lambda \Omega_\lambda}(r_\lambda) Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \quad (225)$$

$Y_{j_\lambda \Omega_\lambda}$: spherical harmonic

$\phi_{\lambda c_\lambda j_\lambda}(r_\lambda)$ satisfies radial SE:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr_\lambda^2} + v_\lambda(r_\lambda) + \frac{j_\lambda(j_\lambda + 1)\hbar^2}{2\mu r_\lambda^2} \right] \phi_{\lambda c_\lambda j_\lambda}(r_\lambda) = E_{\lambda c_\lambda j_\lambda} \phi_{\lambda c_\lambda j_\lambda}(r_\lambda) \quad (226)$$

$v_\lambda(r_\lambda)$: interatomic potential of the isolated $A_\nu A_k$

– let $\psi^{JM_J \lambda' b'_{\lambda'}}$ be a simultaneous eigenfunction of H , J_{op}^2 and $J_{z_{op}}$:
for large R_λ : expansion in surface functions

$$\psi^{JM_J \lambda' b'_{\lambda'}} \sim \sum_{\lambda b_\lambda} (R)^{-1} (g^{JM_J})_{\lambda b_\lambda}^{\lambda' b'_{\lambda'}}(R) \phi_{\lambda b_\lambda}^{JM_J}(\hat{\mathbf{R}}_\lambda, \mathbf{r}_\lambda^{\text{bf}}) \quad (227)$$

$$(g^{JM_J})_{\lambda b_\lambda}^{\lambda' b'_\lambda}(R_\lambda) R'_\alpha \xrightarrow{\sim} \infty v_{\lambda c_\lambda j_\lambda}^{-1/2} [\mathcal{I}_{\lambda c_\lambda j_\lambda}^J(R_\lambda) (A^{JM_J})_{\lambda b_\lambda}^{\lambda' b'_\lambda} - \mathcal{O}_{\lambda c_\lambda j_\lambda}^J(R_\lambda) B^{JM_J}_{\lambda b_\lambda}^{\lambda' b'_\lambda}] \quad (228)$$

\mathcal{I} and \mathcal{O} : incoming and outgoing waves

$$\begin{aligned} \mathcal{I}_{\lambda c_\lambda j_\lambda}^J(R_\lambda) &= \begin{cases} e^{-i[k_{\lambda c_\lambda j_\lambda} R_\lambda - \frac{1}{2}(J+j_\lambda)\pi]} & \text{for open channels} \\ e^{-|k_{\lambda c_\lambda j_\lambda}| R_\lambda} & \text{for closed channels} \end{cases} \\ \mathcal{O}_{\lambda c_\lambda j_\lambda}^J(R_\lambda) &= \begin{cases} e^{i[k_{\lambda c_\lambda j_\lambda} R_\lambda - \frac{1}{2}(J+j_\lambda)\pi]} & \text{for open channels} \\ e^{|k_{\lambda c_\lambda j_\lambda}| R_\lambda} & \text{for closed channels} \end{cases} \end{aligned} \quad (229)$$

phase $\frac{1}{2}(J + j_\lambda)\pi$ is introduced for convenience

rewrite eq. (228):

$$\mathbf{g}^{JM_J} \sim \mathbf{v}^{-1/2} [\mathcal{I}^J \mathbf{A}^{JM_J} - \mathcal{O}^J \mathbf{B}^{JM_J}] \quad (230)$$

intermediate scattering matrix $\bar{\mathbf{S}}^J$:

$$\mathbf{B}^{JM_J} = \bar{\mathbf{S}}^J \mathbf{A}^{JM_J} \quad (231)$$

body-fixed helicity scattering matrix \bar{S}^J :

$$(\mathbf{S}^J)_{\lambda c_\lambda j_\lambda m_{j_\lambda}}^{\lambda' c'_{\lambda'} j'_{\lambda'} m'_{j_{\lambda'}}} = (\bar{\mathbf{S}}^J)_{\lambda c_\lambda j_\lambda, \Omega_{j_\lambda} = m_{j_\lambda}}^{\lambda' c'_{\lambda'} j'_{\lambda'}, \Omega'_{j_{\lambda'}} = -m'_{j_{\lambda'}}} \quad (232)$$

negative sign in the column label of this expression is introduced because as $R_{\lambda'} \sim \infty$, $\mathbf{R}_{\lambda'}$ and $\mathbf{k}_{\lambda' c'_{\lambda'} j'_{\lambda'}}$ become antiparallel

(1) \mathbf{S}^J is unique: independent of \mathbf{A}^{JM_J} and of M_J ; depends on E and J

(2) open part \mathbf{S}_o^J of \mathbf{S}^J is symmetric, this property leads to the principle of microscopic reversibility

(3) \mathbf{S}_o^J is unitary

– this results in the conservation of particle flux

eq. (230) can also be written as:

$$\mathbf{g}^{JM_J} \sim \mathbf{v}^{-1/2} [\mathcal{S}^J \mathbf{C}^{JM_J} + \mathcal{C}^J \mathbf{D}^{JM_J}] \quad (233)$$

$$\mathcal{S}_{\lambda b_\lambda}^J(R_\lambda) = \begin{cases} \sin[k_{\lambda c_\lambda j_\lambda} R_\lambda - \frac{1}{2}(J + j_\lambda)\pi] & \text{for open channels} \\ e^{|k_{\lambda c_\lambda j_\lambda} R_\lambda|} & \text{for closed channels} \end{cases} \quad (234)$$

$$\mathcal{C}_{\lambda b_\lambda}^J(R_\lambda) = \begin{cases} \cos[k_{\lambda c_\lambda j_\lambda} R_\lambda - \frac{1}{2}(J + j_\lambda)\pi] & \text{for open channels} \\ e^{-|k_{\lambda c_\lambda j_\lambda} R_\lambda|} & \text{for closed channels} \end{cases} \quad (235)$$

reactance matrices:

$$\mathbf{D}^{\mathbf{JM}_J} = \mathbf{R}^J \mathbf{C}^{\mathbf{JM}_J},$$

$$(\mathbf{R}^J)_{\lambda c_\lambda j_\lambda m_{j_\lambda}}^{\lambda' c'_\lambda j'_\lambda m'_{j_{\lambda'}}} = (\bar{\mathbf{R}}^J)_{\lambda c_\lambda j_\lambda, \Omega_{j_\lambda} = m_{j_\lambda}}^{\lambda' c'_\lambda j'_\lambda, \Omega'_{j_{\lambda'}} = -m'_{j_{\lambda'}}} \quad (236)$$

body-fixed helicity reactance matrix \mathbf{R}^J : important properties

(1) \mathbf{R}^J is unique

(2) \mathbf{R}^J is real

(3) the open part \mathbf{R}_o^J of \mathbf{R}^J is symmetric

$$\mathbf{S}_o^J = (\mathbf{I} + \mathbf{iR}_o^J)(\mathbf{I} - \mathbf{iR}_o^J)^{-1} \quad (237)$$

Distinguishable atom scattering amplitudes and cross sections

- scaled coordinate distinguishable-atom scattering amplitude for the $\lambda'n'_{\lambda'} \rightarrow \lambda n_{\lambda}$ transition in the body-fixed helicity representation :

$$f_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}(\theta_{\lambda}, \phi_{\lambda}) = \left(\frac{v_{\lambda' c'_{\lambda'} j'_{\lambda'}}}{v_{\lambda, c_{\lambda} j_{\lambda}}} \right)^{1/2} \frac{\exp(im_{j_{\lambda}} \phi_{\lambda})}{2k_{\lambda' c'_{\lambda'} j'_{\lambda'}}} i^{j'_{\lambda'} - j_{\lambda} + 1} \sum_{J=0}^{\infty} (2J+1) d_{m'_{j'_{\lambda'}} m_{j_{\lambda}}}^J(\theta_{\lambda}) (\mathbf{T}_0^J)_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}} \quad (238)$$

transition matrix \mathbf{T}_o^J :

$$\mathbf{T}_o^J = \mathbf{I} - \mathbf{S}_o^J \quad (239)$$

$\lambda'n'_{\lambda'} \rightarrow \lambda n_{\lambda}$ distinguishable-atom differential cross section :

$$\sigma_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}(\theta_{\lambda}) = (4k_{\lambda' c'_{\lambda'} j'_{\lambda'}}^2)^{-1} \left| \sum_{J=0}^{\infty} (2J+1) d_{m'_{j'_{\lambda'}} m_{j_{\lambda}}}^J(\theta_{\lambda}) (\mathbf{T}_0^J)_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}} \right|^2 \quad (240)$$

k' : initial wave number in unscaled coordinates

- dependence of σ on θ_{λ} :
- $d_{m'_{j'_{\lambda'}} m_{j_{\lambda}}}^J$: are real and display an oscillatory dependence on θ_{λ} , the higher the value of J , the faster is the rate of oscillation
- for direct reactions such as the distinguishable atom $\text{H} + \text{H}_2$ exchange reaction: the variation of σ with θ_{λ} is monotonic
- phases and amplitudes of the \mathbf{T}_o^J matrix elements bear a relationship to each other that leads, for such reactions, to the disappearance of the oscillations in σ
- although the scattering amplitudes depend on θ , the differential cross sections

do not, because the initial probability density is cylindrically symmetrical around the quantization axis, and therefore so must the final one be, in the absence of external fields

- $d_{m'm}^J(0) = \delta_{m'm}$ and $d_{m'm}^J(\pi) = (-1)^{J+m} \delta_{m'-m}$:
- from eq. (240): for $m'_{j_{\lambda'}} \neq m_{j_{\lambda}}$: $\sigma_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}(\pi)$ vanishes
- from $m'_{j_{\lambda'}} \neq -m_{j_{\lambda}}$: $\sigma_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}(\pi)$ vanishes
- integral cross section $Q_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}$:

$$Q_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}} = \frac{\pi}{k_{\lambda' c'_{\lambda'} j'_{\lambda'}}^2} \sum_{J=0}^{\infty} (2J+1) |(\mathbf{T}_0^J)_{\lambda n_{\lambda}}^{\lambda' n'_{\lambda'}}|^2 \quad (241)$$

- no need for accurate phases of the transition matrix to obtain accurate integral cross sections; integral cross sections are easier to calculate

$\lambda'n'_{\lambda'} \rightarrow \lambda n_{\lambda}$ J partial wave reaction probability:

$$P_{\lambda n_{\lambda}}^{J\lambda'n'_{\lambda'}} = |(\mathbf{S}_0^J)_{\lambda n_{\lambda}}^{\lambda'n'_{\lambda'}}|^2 \quad (242)$$

$\lambda'n'_{\lambda'} \rightarrow \lambda n_{\lambda}$ integral cross section:

$$Q_{\lambda n_{\lambda}}^{\lambda'n'_{\lambda'}} = \frac{\pi}{k_{\lambda'c'_{\lambda'}j'_{\lambda'}}^2} \sum_{J=0} (2J+1) P_{\lambda n_{\lambda}}^{J\lambda'n'_{\lambda'}}, \quad \lambda n_{\lambda} \neq \lambda'n'_{\lambda'} \quad (243)$$

$\sigma_{\lambda n_{\lambda}}^{\lambda'n'_{\lambda'}}$ and $Q_{\lambda n_{\lambda}}^{\lambda'n'_{\lambda'}}$ may be averaged over the initial $m'_{j'_{\lambda'}}$ and summed over the final $m_{j_{\lambda}}$ to give the degeneracy-averaged quantities $\sigma_{\lambda c_{\lambda} j_{\lambda}}^{\lambda' c'_{\lambda'} j'_{\lambda'}}$ and $Q_{\lambda c_{\lambda} j_{\lambda}}^{\lambda' c'_{\lambda'} j'_{\lambda'}}$

- for inelastic or reactive transitions:

$$Q_{\lambda c_{\lambda} j_{\lambda}}^{\lambda' c'_{\lambda'} j'_{\lambda'}} = \frac{\pi}{k_{\lambda' c'_{\lambda'} j'_{\lambda'}}'^2} \sum_{J=0}^{\infty} (2J+1) P_{\lambda c_{\lambda} j_{\lambda}}^{J \lambda' c'_{\lambda'} j'_{\lambda'}}, \quad \lambda c_{\lambda} j_{\lambda} \neq \lambda' c'_{\lambda'} j'_{\lambda'} \quad (244)$$

opacity function $P_{\lambda c_{\lambda} j_{\lambda}}^{J \lambda' c'_{\lambda'} j'_{\lambda'}}$:

$$P_{\lambda c_{\lambda} j_{\lambda}}^{J \lambda' c'_{\lambda'} j'_{\lambda'}} = (2j'_{\lambda'} + 1)^{-1} \sum_{m_{j_{\lambda}} m'_{j'_{\lambda'}}} P_{\lambda n_{\lambda}}^{J \lambda' n'_{\lambda'}} \quad (245)$$

- from the unitarity of the scattering matrix:

(1) Conservation of flux for body-fixed helicity transition probabilities

$$\sum_{\lambda n_\lambda} P_{\lambda n_\lambda}^{J \lambda' n'_{\lambda'}} = 1 \quad (246)$$

(2) Conservation of opacity

$$\sum_{\lambda c_\lambda j_\lambda} P_{\lambda c_\lambda j_\lambda}^{J \lambda' c'_{\lambda'} j'_{\lambda'}} = 1 \quad (247)$$

- from the symmetry of \mathbf{S}_o^J we obtain:

(3) Microscopic reversibility for body-fixed helicity transition probabilities

$$P_{\lambda n_\lambda}^{J^{\lambda' n'_{\lambda'}}} = P_{\lambda' n'_{\lambda'}}^{J^{\lambda n_\lambda}} \quad (248)$$

(4) Microscopic reversibility for opacity functions

$$(2j'_{\lambda'} + 1) P_{\lambda c_{\lambda} j_\lambda}^{J^{\lambda' c'_{\lambda'} j'_{\lambda'}}} = (2j_\lambda + 1) P_{\lambda' c'_{\lambda'} j'_{\lambda'}}^{J^{\lambda c_{\lambda} j_\lambda}} \quad (249)$$

(5) Microscopic reversibility for body-fixed integral helicity cross sections

$$k'^2_{\lambda' c'_{\lambda'} j'_{\lambda'}} Q_{\lambda n_\lambda}^{\lambda' n'_{\lambda'}} = k'^2_{\lambda c_{\lambda} j_\lambda} Q_{\lambda' n'_{\lambda'}}^{\lambda n_\lambda} \quad (250)$$

(6) Microscopic reversibility for degeneracy-averaged integral cross sections

$$(2j'_{\lambda'} + 1)k'^2_{\lambda'c'_{\lambda'}j'_{\lambda'}} Q^{\lambda'c'_{\lambda'}j'_{\lambda'}}_{\lambda c_{\lambda}j_{\lambda}} = (2j_{\lambda} + 1)k'^2_{\lambda c_{\lambda}j_{\lambda}} Q^{\lambda c_{\lambda}j_{\lambda}}_{\lambda'c'_{\lambda'}j'_{\lambda'}} \quad (251)$$

(7) Microscopic reversibility for body-fixed helicity differential cross sections

$$k'^2_{\lambda'c'_{\lambda'}j'_{\lambda'}} \sigma^{\lambda'n'_{\lambda'}}_{\lambda n_{\lambda}}(\theta_{\lambda}) = k'^2_{\lambda c_{\lambda}j_{\lambda}} \sigma^{\lambda n_{\lambda}}_{\lambda' n'_{\lambda'}}(\theta_{\lambda'} = \theta_{\lambda}) \quad (252)$$

– eqn. (246 - 252) relate properties of forward ($\lambda' \rightarrow \lambda$) and backward ($\lambda \rightarrow \lambda'$) processes occurring at the same total energy E

Cross sections for systems containing identical atoms

for undistinguishable atoms:

include the effects of the Pauli principle on the reactive scattering problem

- interaction energies between the nuclear spin and the orbital motions: in general several orders of magnitude smaller than the Born-Oppenheimer interaction potential
- neglect those spin-orbit interactions in the present considerations
- Pauli principle may be introduced: the techniques of post-antisymmetrization (for identical fermions) or post-symmetrization (for identical bosons)
- H_3 system: two independent sets of distinguishable scattering amplitudes: reactive (or exchange) f'^R and nonreactive (or direct) f'^N

- appropriately antisymmetrized scattering wave functions can be obtained by taking linear combinations of those of the distinguishable atom (Kuppermann et al, 1976)
- correct antisymmetrized differential cross sections can be expressed in terms of the f'^R and f'^N :

(1) para \rightarrow para(j' , j even)

$$\sigma_{pn}^{pn'} = \frac{v'_{cj}}{v'_{c'j'}} |f'_n{}^{Nn'} - f'_n{}^{Rn'}|^2 \quad (253)$$

(2) para \rightarrow ortho (j' even j odd)

$$\sigma_{on}^{pn'} = 3 \frac{v'_{cj}}{v'_{c'j'}} |f'_n{}^{Rn'}|^2 \quad (254)$$

(3) ortho \rightarrow para (j' odd, j even)

$$\sigma_{pn}^{on'} = \frac{v'_{cj}}{v'_{c'j'}} |f_n'^{Rn'}|^2 \quad (255)$$

(4) ortho \rightarrow ortho (j', j odd)

$$\sigma_{on}^{on'} = \frac{v'_{cj}}{v'_{c'j'}} (|f_n'^{Nn'} + f_n'^{Rn'}|^2 + 2|f_n'^{Rn'}|^2) \quad (256)$$

– in eqn. (253) and (256): interference effects between the $f'^N \pm f'^R$ terms

Computational methodology

- about 1976, only three coupled-channel methods have been used in cross section calculations for 3-PD systems
 - Elkowitz and Wyatt (EW): natural collision coordinates (NCC) and local hindered asymmetric-top-vibrator basis sets
 - Kuppermann and Schatz (KS): uses asymptotic free rotor local vibrator basis sets, and different coordinates in different regions of configuration space
 - advantage of EW-approach: their basis functions furnish an efficient representation of the local motion; contain very useful interpretive information in the form of asymmetric top-rotational energy correlation diagrams
 - but NCC are more cumbersome to use in the representation of the potential energy function and in the calculation of the matrix elements that appear in the coupled-channel equations

- Walker et al: has elements in common with both the Elkowitz and Wyatt and the Kuppermann and Schatz approaches

- Schatz and Kuppermann:

define the complete discrete orthonormal body-fixed basis set:

$$\mathcal{Y}_{j_\lambda \Omega_\lambda}^{JM_J}(\theta_\lambda, \phi_\lambda, \gamma_\lambda, \psi_\lambda) = \left(\frac{2J+1}{4\pi}\right)^{1/2} D_{M_J \Omega_\lambda}^J(\phi_\lambda, \theta_\lambda, 0) Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \quad (257)$$

- simultaneous eigenfunctions of the operators J_{op}^2 , $J_{z_{op}}$ and $j_{\lambda_{op}}^2$; span the 4-MD subspace $\theta_\lambda, \phi_\lambda, \gamma_\lambda, \psi_\lambda$
- $\psi_\lambda^{JM_J}$: simultaneous eigenfunctions of H , J_{op}^2 and $J_{z_{op}}$ expressed in λ arrangement channel coordinates $\mathbf{R}_\lambda, \mathbf{r}_\lambda^{bf}$

$$\psi_\lambda^{JM_J}(\mathbf{R}_\lambda, \mathbf{r}_\lambda^{bf}) = \sum_{\Omega_\lambda=-J}^J \sum_{j_\Omega=|\Omega_\lambda|}^{\infty} (R_\lambda r_\lambda)^{-1} F_{\lambda j_\lambda \Omega_\lambda}^J(R_\lambda, r_\lambda) \mathcal{Y}_{j_\lambda \Omega_\lambda}^{JM_J}(\theta_\lambda, \phi_\lambda, \gamma_\lambda, \psi_\lambda) \quad (258)$$

coupled-channel partial differential equations for the functions $F_{\lambda j_\lambda, \Omega_\lambda}^J$:

$$t_{\Omega_\lambda, \Omega_{\lambda-1}}^{J\lambda j_\lambda} F_{\lambda j_\lambda, \Omega_{\lambda-1}}^J + t_{\Omega_\lambda, \Omega_\lambda}^{J\lambda j_\lambda} F_{\lambda j_\lambda, \Omega_\lambda}^J + t_{\Omega_\lambda, \Omega_{\lambda+1}}^{J\lambda j_\lambda} F_{\lambda j_\lambda, \Omega_{\lambda+1}}^J + \sum_{j'\lambda} V_{j_\lambda j'_\lambda}^{\lambda\Omega_\lambda} F_{\lambda j_\lambda, \Omega_\lambda}^J = E F_{\lambda j_\lambda, \Omega_\lambda}^J$$

kinetic energy operators:

$$t_{\Omega_\lambda, \Omega_\lambda}^{J\lambda j_\lambda}(R_\lambda, r_\lambda) = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_\lambda^2} + \frac{\partial^2}{\partial r_\lambda^2} \right) + \frac{j_\lambda(j_\lambda + 1)\hbar^2}{2\mu r_\lambda^2} +$$

$$\frac{\hbar^2}{2\mu R_\lambda^2} [J(J+1) - 2\Omega_\lambda^2 + j_\lambda(j_\lambda + 1)] t_{\Omega_\lambda, \Omega_{\lambda\pm 1}}^{J\lambda j_\lambda}(R_\lambda) = -\frac{\hbar^2}{2\mu R_\lambda^2} \xi_\pm(J, \Omega_\lambda) \xi_\pm(j_\lambda, \Omega_\lambda)$$

$$\xi_\pm(j, m) = [j(j+1) - m(m \pm 1)^{1/2}], \quad |m| \leq j \quad (260)$$

potential energy function:

$$V_{j_\lambda j'_\lambda}^{\lambda \Omega_\lambda}(R_\lambda, r_\lambda) = (j_\lambda \Omega_\lambda | V_\lambda(R_\lambda, r_\lambda, \gamma_\lambda) | j'_\lambda \Omega_\lambda) \quad (261)$$

- eq. (259): $t_{\Omega_\lambda, \Omega_{\lambda \pm 1}}^{J \lambda j_\lambda}$ terms are centrifugal coupling terms that are independent of V and couple $F_{\lambda j_\lambda, \Omega_\lambda}^J$ with $F_{\lambda j_\lambda, \Omega_{\lambda \pm 1}}^J$, they depend only on R_λ and the quantum numbers $J, j_\lambda, \Omega_\lambda$
- for reactive systems: the range of total angular momentum quantum numbers J that contribute appreciably to the reactive cross sections is usually much smaller than that which contributes to nonreactive inelastic cross sections, and in many instances these $t_{\Omega_\lambda, \Omega_{\lambda \pm 1}}^{J \lambda j_\lambda}(R_\lambda)$ terms can be neglected
- in this case eq. (259) becomes diagonal in Ω_λ i.e. the $F_{\lambda j_\lambda, \Omega_\lambda}^J$ for different tumbling angular momenta in arrangement channel λ are decoupled, since the $V_{j_\lambda j'_\lambda}^{\lambda \Omega_\lambda}$ do not couple such functions

- this leads to the tumbling decoupling approximation
- for each J : a system of coupled equations scanned by the rotational quantum numbers j_λ and Ω_λ
- the potential energy function couples different j_λ
- angular-momentum tumbling centrifugal terms couple different Ω_λ
- method of solution of these coupled-channel equations: consider the internal configuration space $R_\lambda, r_\lambda, \gamma_\lambda$ in the symmetrized hyperspherical coordinate mapping (coordinate axes are $X_\lambda Y_\lambda Z_\lambda$)

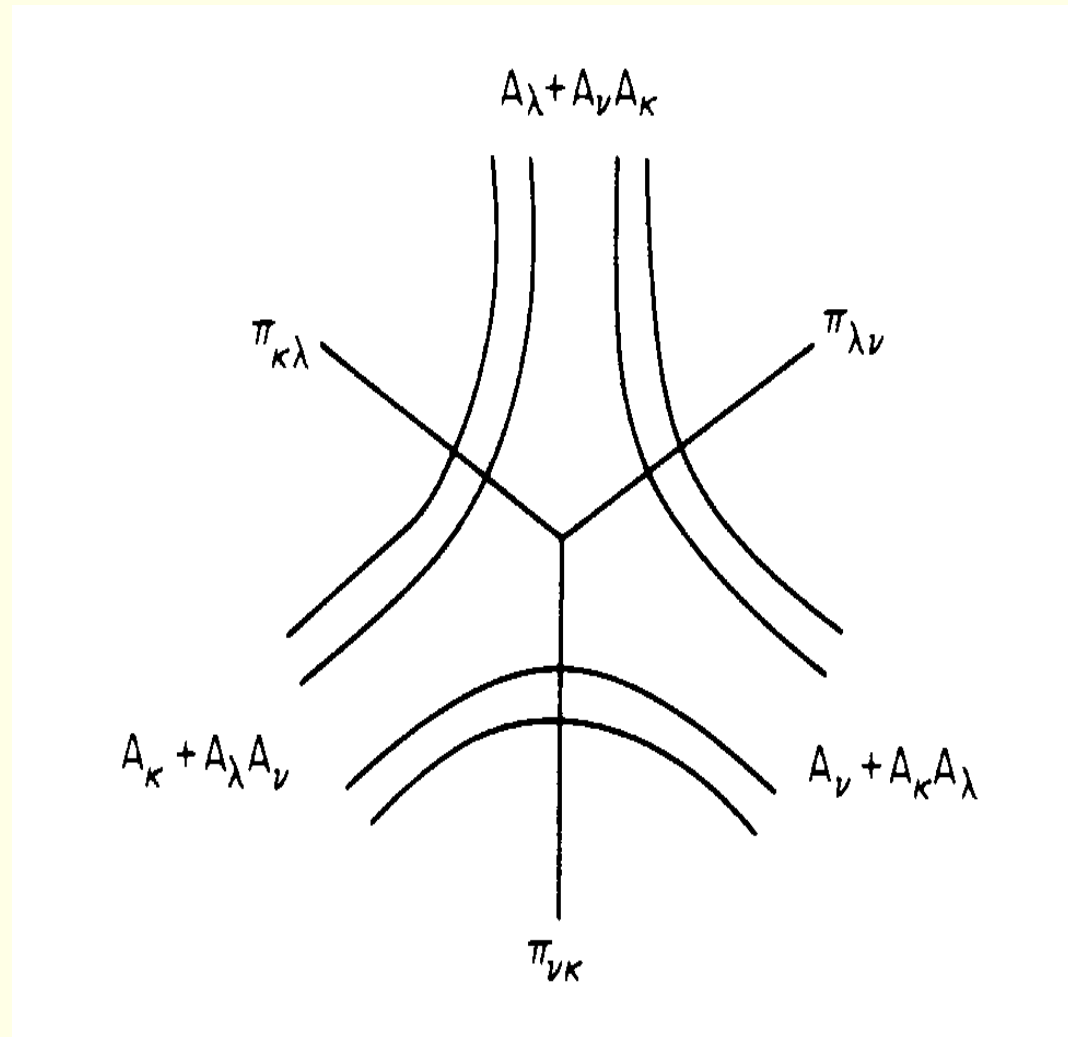


Figure 25: Intersection of matching half-planes $\pi_{\lambda\nu}, \pi_{\nu\kappa}, \pi_{\kappa\lambda}$ with the $X_\lambda Z_\lambda$ plane of Fig. 21b. Curves are intersections of an equipotential surface with that same coordinate plane.

– Ralph Jaquet, University Siegen –

- Fig. 25: outline of a equipotential on the $X_\lambda Z_\lambda$ plane (which coincides with the $X_\nu Z_\nu$ and $X_k Z_k$ planes), and the intersection with that plane of three halfplanes, labeled $\pi_{\lambda\nu}$, $\pi_{\nu k}$, and $\pi_{k\lambda}$ whose common edge is the Y_λ , axis (which coincides with the Y_ν , and Y_k axes), perpendicular to the plane of the figure
- these half-planes divide the internal configuration space into three arrangement-channel subspaces, λ , ν and k
- they define three subspaces of the total configuration space
- method of solution consists of integrating the coupled equations eq. (259) over the range of R_λ, r_λ which, together with γ_λ , spans the λ arrangement-channel subspace
 - integration is performed by dividing the R_λ, r_λ subspace into regions, using appropriate variables and basis sets in each region
 - in each region: a set of coupled ordinary differential equations that can be integrated numerically by the use of an appropriate efficient algorithm
 - this procedure generates a set of linearly independent wave functions

- $\psi_{\lambda b_\lambda}^{JM_J}(\mathbf{R}_\lambda, \mathbf{r}_\lambda^{bf})$ that span the λ arrangement-channel subspace, but do not cover the entire configuration space
- generate wave functions $\psi_{\nu b_\nu}^{JM_J}(\mathbf{R}_\nu, \mathbf{r}_\nu^{bf})$ and $\psi_{kb_k}^{JM_J}(\mathbf{R}_k, \mathbf{r}_k^{bf})$ that span the ν and k arrangement-channel subspaces
 - these λ, ν and k solutions overlap on the $\pi_{\lambda\nu}, \pi_{\nu k}$ and $\pi_{k\lambda}$ half-planes, but have in general different values on those surfaces
 - generate solutions of the SE for a given J and M_J , which are everywhere continuous and smooth, we take linear combinations of the $\psi_{\lambda b_\lambda}^{JM_J}(R_\lambda, r_\lambda^{bf})$ in the λ arrangement-channel subspace, of the $\psi_{\nu b_\nu}^{JM_J}(R_\nu, r_\nu^{bf})$ in the ν subspace and of the $\psi_{kb_k}^{JM_J}(R_k, r_k^{bf})$ in the k subspace
 - impose on these three different sets of linear combinations the conditions that they be continuous on the $\pi_{\lambda\nu}, \pi_{\nu k}$ and $\pi_{k\lambda}$ half-planes and that their derivatives normal to these half-planes also be continuous

Results for $\text{H} + \text{H}_2$

1970ies: only system for which accurate 3-PD quantum mechanical reactive scattering cross-section calculations had been performed was the $\text{H} + \text{H}_2$ system

(a) Kuppermann and Schatz (KS) [104, 241]

(b) Elkowitz and Wyatt (EW) [220, 221]: natural collision coordinate method and rotationally adiabatic basis functions

c) Walker, Light, and Altenberger-Siczek [48]: asymmetric $\text{A} + \text{BC}$ reaction

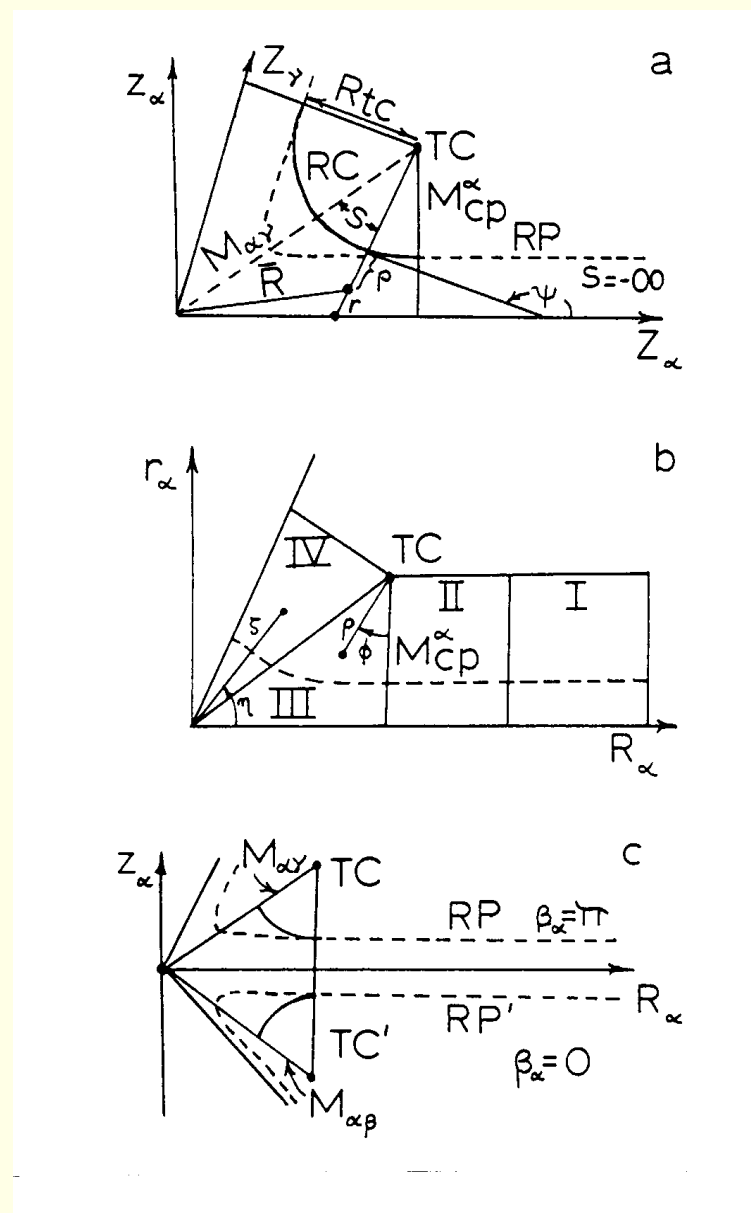


Figure 26: Internal translation-vibration coordinates. (a) Natural coordinates by EW [220, 221], drawn in the first quadrant only. On the match surface $M_{\alpha\gamma}$, $s = 0$, and on the approach to $M_{\alpha\gamma}$ from reactants, s increases toward

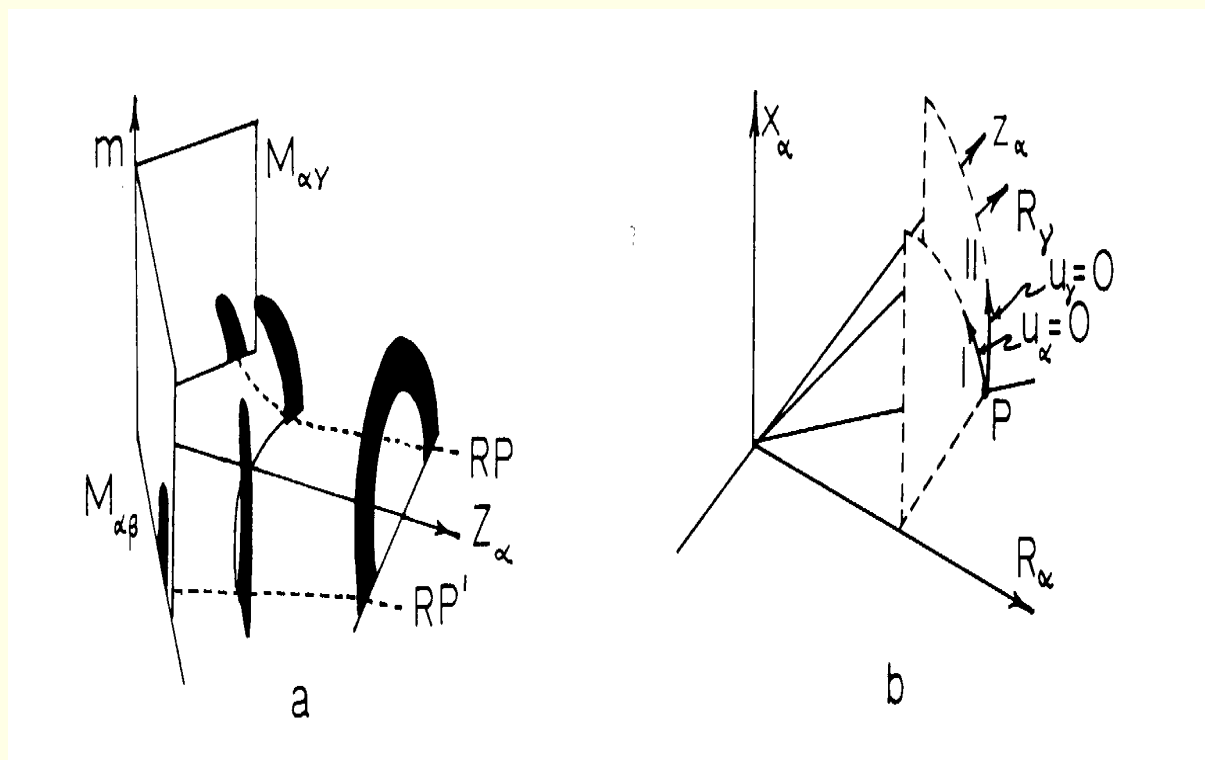


Figure 27: (a) Reactant tube for α arrangement, showing reaction paths RP and RP' , and match surfaces $M_{\alpha\gamma}$ and $M_{\alpha\beta}$. The dark regions locate geometries where $V < 1$ eV, for example, for a reaction passing through two near-linear intermediates. (b) Rotation out of the collinear plane (at P) about the R_α or R_γ (with $u_\alpha = 0$ and $u_\gamma = 0$, respectively) does not define the $\alpha\gamma$ match surface. $(x_\alpha z_\alpha)$ are the components of r_γ on the BF axes.

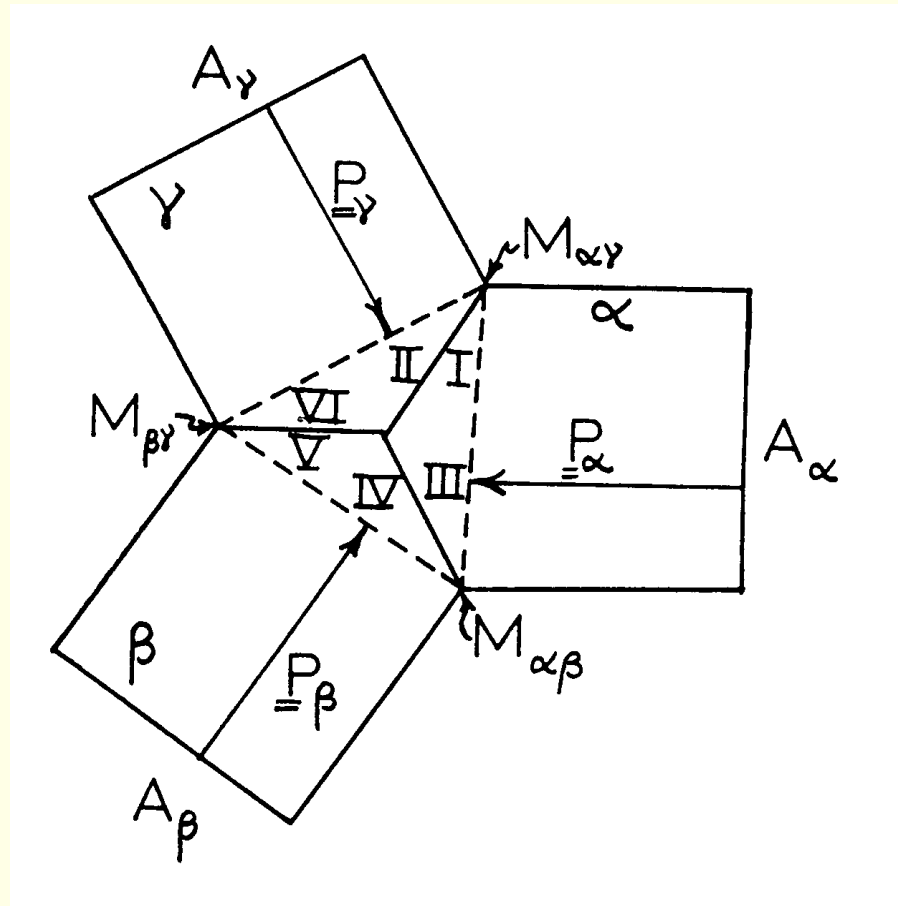


Figure 28: Schematic illustration of three arrangements tubes, with their asymptotic regions (A_λ) and tube propagators (P_λ). The scattering wave functions and normal derivatives are required to be continuous across the three match surfaces ($M_{\alpha\beta}$, $M_{\alpha\gamma}$, $M_{\beta\gamma}$): e.g. $\Psi_{\alpha I} = \Psi_{\alpha II}$ and $\hat{n} * \nabla \Psi_{\alpha I} = \hat{n} * \nabla \Psi_{\alpha II}$

References

- [1] M. Baer, ed., Theory of Chemical Reaction Dynamics, Vols. I-IV, CRC Press, Boca Raton, FL, 1985.
- [2] D. C. Clary, ed., The Theory of Chemical Dynamics, Dordrecht: Reidel 1986.
- [3] W. H. Miller, ed., Dynamics of Molecular Collisions, Parts A and B (Vols. 1 and 2 of Modern theoretical Chemistry), Plenum, NY, 1976.
- [4] J. M. Bowman, ed., Advances in Molecular Vibrations and Collision Dynamics, Vol. 2, JAI Press, Greenwich, CT, 1994.
- [5] R. B. Bernstein, ed., Atom-Molecule Collision Theory: a Guide for the Experimentalist, Plenum, NY, 1979.
- [6] J. Z. H. Zhang and R. E. Wyatt, Eds., Dynamics of molecules and chemical reactions, Dekker (1996)
- [7] Tsipis et al, Eds., New methods in quantum theory, NATO, Series 3, Vol. 8, 1997
- [8] C. Cerjan, Ed., Numerical Grid Methods and their Application to Schrödinger's Equation, NATO ASI Series C 412 (Kluwer, Dordrecht, 1993)
- [9] Supercomputer algorithms for reactivity, dynamics and kinetics of small molecules, Ed. A. Lagana, Kluwer, Dordrecht, 1989.
- [10] W. H. Miller, in NATO book 1995, Ed. Yurtsever
- [11] F. Mrugala, Int. Rev. Phys. Chem., 12 (1993) 1
- [12] D. J. Kouri and D. K. Hoffman, in 'Multiparticle quantum scattering with applications to nuclear, atomic and molecular physics', Eds. D. G. Tuhlar, B. Simon, Springer 1997
- [13] D. E. Manolopoulos and D. C. Clary, Ann. Rep. C Roy. Soc. of Chem. 80, 95 (1989).
- [14] KUPPERMANN, A., 1981, Theoretical Chemistry and Perspectives, 6A, edited by D. Henderson (New York: Academic), p. 79.
- [15] Schatz, G. C., and Kupperman, A. (1976). J. Chem. Phys. 65, 4642-4667.

- [16] J. M. Launay in Dynamical Processes in Molecular Physics (Institute of Physics Publishing Bristol and Philadelphia, ed. G. Delgado-Barrio) (1991) 97
- [17] R. D. Levine, R. B. Bernstein, Molecular Reaction Dynamics, Oxford, 1974.
- [18] D. Secrest, in [5]
- [19] D. Truhlar, Muckerman, in [5]
- [20] D. Micha, Adv. Chem. Phys. **30**, 7, 1975.
- [21] KOURI, D. J., and BAER, M., 1986, The Theory of Chemical Dynamics, edited by D. C. Clary (Dordrecht: Reidel), p. 359.
- [22] MARCUS, R. A., 1966, J. Chem. Phys., 45, 4493, 4500
- [23] LIGHT, J. C., 1971, Methods in Computational Physics, 10, edited by B. Alder, S. Fernbach and M. Rotenberg (New York: Academic), p. 111.
- [24] SMITH, F. T., 1960, Phys. Rev., 118, 349
- [25] SMITH, F. T., 1960, Phys. Rev., 120, 1058; 1969, Ibid., 179, 111.
- [26] JOHNSON, B. R., 1973, J. Comput. Phys., 13, 445; 1978a, J. Chem. Phys., 67, 4086; 1978b, Ibid., 69, 4678; 1980, Ibid., 73, 5051.
- [27] WALKER, R. B., and LIGHT, J. C., 1980, Ann. Rev. Phys. Chem., 31, 401.
- [28] BAER, M., 1982, Adv. Chem. Phys., edited by I. Prigogine and S. A. Rice (New York: Wiley), Vol. 49, p. 191 ; 1989, Phys. Rep., 178, 99.
- [29] BASILEVSKY, M. V., and RYABOY, V. M., 1982, Adv. quant. Chem., edited by P. O. Löwdin (New York: Academic), Vol. 15, p. 1.
- [30] ZHANG, J. Z. H., and MILLER, W. H., 1987, Chem. Phys. Lett., 140, 329.
- [31] ZHANG, J. Z. H., and MILLER, W. H., 1989, J. Chem. Phys., 91, 1528; 1990, Ibid., 92, 1811.
- [32] LINDERBERG, J., PADKJAER, S. B., ÖHRN, Y., and VESSAL, B., 1989, J. Chem. Phys., 90, 6254.
- [33] SCHWENKE, D. W., HAUG, K., ZHAO, M., TRUHLAR, D. G., SUN, Y., and KOURI, D. J., 1988, J. Phys. Chem., 92, 3202.

- [34] ZHANG, J. Z. H., KOURI, D. J., HAUG, K., SCHWENKE, D. W., SHIMA, Y., and TRUHLAR, D. G., 1988, J. Chem. Phys., 88, 2492.
- [35] SCHWENKE, D. W., MLADENOVIC, M., ZHAO, M., TRUHLAR, D. G., SUN, Y., and KOURI, D. J., 1989, Supercomputer Algorithms for Reactivity, Dynamics and Kinetics of Small Molecules, edited by A. Lagana (Dordrecht: Kluwer), p. 131.
- [36] SUN, Y., KOURI, D. J., TRUHLAR, D. G., and SCHWENKE, D. W., 1990, Phys. Rev. A, 41, 4837.
- [37] SUN, Y., KOURI, D. J., and TRUHLAR, D. G., 1990, Nucl. Phys. A, 508, 410.
- [38] LESTER, W. A. JR., 1971, Methods in Computational Physics, 10, edited by B. Adler, S. Fernbach and M. Rotenberg (New York: Academic); 1976, Dynamics of Molecular Collisions, Part, A, edited by W. H. Miller (New York: Plenum), p. 1.
- [39] WYATT, R. E. 3 1979, Atom-Molecule Collision Theory. A Guide for the Experimentalists, edited by R. B. Bernstein (New York: Plenum), p. 477.
- [40] SCHATZ, G. C., 1986, The Theory of Chemical Dynamics, edited by D. C. Clary (Dordrecht: Reidel), p. 1; 1988, Chem. Phys. Lett., 150, 92; 1989, J. Chem. Phys., 90, 3582.
- [41] Pack R T and Parker G A 1987 J. Chem. Phys., 87, 3888 Quantum reactive scattering in three dimensions using hyperspherical coordinates : Theory
- [42] PACK, R. T., and PARKER, G. A., 1989, J. Chem. Phys., 90, 3511.
- [43] PARKER, G. A., PACK, R. T., ARCHER, B. J., and WALKER, R. B., 1987, Chem. Phys. Lett., 137, 564.
- [44] BACIC, Z., KRESS, J. D., PARKER, G. A., and PACK, R. T., 1990, J. Chem. Phys., 92, 2344.
- [45] DARAKJIAN, Z., HAYES, E. F., PARKER, G. A., BUTCHER, E. A., and KRESS, J. D., 1991, J. Chem. Phys., 95, 2516.
- [46] ELKOWITZ, A. B ., and WYATT, R. E., 1975, J. Chem. Phys., 63, 702.
- [47] SCHATZ, G. C., and KUPPERMANN, A., 1976, J. Chem. Phys., 65, 4642.
- [48] WALKER, R. B., LIGHT, J. C., and ALTENBERGER-SICZEK, A., 1976, J. Chem. Phys., 64, 1166.
- [49] LIGHT, J. C., and WALKER, R. B., 1976a, J. Chem. Phys., 63, 1598; 1976b, Ibid., 65, 4272.

- [50] KUPPERMANN, A., KAYE, J. A., and DWYER, J. P. , 1980, Chem. Phys. Lett., 74, 257.
- [51] KUPPERMANN, A., and HIPES, P. G., 1986, J. Chem. Phys., 84, 5962.
- [52] CUCCARO, S. A., HIPES, P. G., and KUPPERMANN, A. , 1989, Chem. Phys. Lett., 154, 155.
- [53] HAUKE, G., MANZ, J., and RÖMELT, J., 1980, J. Chem. Phys., 73, 5040.
- [54] RÖMELT, J., 1980, Chem. Phys. Lett., 74, 263; Ibid., 87, 259.
- [55] DIESTLER, D. J. ., 1971, J. Chem. Phys., 54, 4547.
- [56] STECHEL, E. B., SCHMALZ, T. G., and LIGHT, J. C., 1979, J. Chem. Phys., 70, 5640.
- [57] Top, Z. H., and SHAPIRO, M., 1983, J. Chem. Phys., 77, 5009.
- [58] SCHWENKE, D. W., TRUHLAR, D. G., and KOURI, D. J., 1987, J. Chem. Phys., 86, 2772.
- [59] SCHATZ, G. C., 1986, The Theory of Chemical Dynamics, edited by D. C. Clary (Dordrecht: Reidel), p. 1; 1988, Chem. Phys. Lett., 150, 92; 1989, J. Chem. Phys., 90, 3582.
- [60] Y. T. Lee, et al., J. Chem. Phys. 53, 2123 (1970); 53, 3755 (1970); 55, 5762 (1971); 56, 1511 (1972); 56, 5801 (1972); 59, 601 (1973).
- [61] R. B. Bernstein, Adv. Chem. Phys. 10, 75 (1966).
- [62] K. W. Ford and J. A. Wheeler, Ann. Phys. 7, 259, 287 (1959).
- [63] M. V. Berry and K. E. Mount, Rept. Prog. Phys. 35, 315 (1972).
- [64] (a) M. S. Child, Semiclassical Mechanics with Molecular Applications, Oxford U. P., 1991. (b) W. H. Miller, Science 233, 171 (1986).
- [65] (a) P. A. Robinson and R. A. Holbrook, Unimolecular Reactions, Wiley, NY, 1972. (b) W. Forst, Theory of Unimolecular Reactions, Academic Press, NY, 1973. (c) R. G. Gilbert and S. C. Smith, Theory of Unimolecular and Recombination Reactions, Blackwell, Oxford, 1990.
- [66] E. g., see J. Troe, J. Chem. Phys. 97, 288 (1992), and references therein.

- [67] (a) W. A. Lester, ref. [3], p. 1. (b) J. C. Light, ref. [5], p. 239. (c) See, e. g., D. Secrest, in ref. [5], pp. 265, 377.
- [68] (a) R. N. Porter and L. M. Raff, ref. [3], pg. 1. (b) W. H. Hase, ref. [3], p. 121. (c) M. D. Pattengill, ref. [5], p. 359. (d) L. M. Raff and D. L. Thompson, ref. [1], vol. 111, p. 2.
- [69] . E. g., (a) D. A. Micha, ref. [3], p. 81. (b) H. K. Shin, ref. [3], p. 131. (c) R. E. Wyatt, ref. [5], p. 477. (d) J. Jellinek and D. J. Kouri, ref. [1], Vol. II, p. 1.
- [70] W. H. Miller, Adv. Chem. Phys. 25, 69 (1974); 30, 77 (1975).
- [71] W. H. Miller, Ann. Rev. Phys. Chem. 41, 245 (1990).
- [72] W. A. Lester, in [3], p. 1.
- [73] J. C. Light, in [5], p. 239.
- [74] D. Secrest, in [5], pp. 265, 377.
- [75] MILLER, W. H., 1969, J. Chem. Phys., 50, 407.
- [76] Burke Taylor 1966
- [77] Tang Mehre Thompson 1978
- [78] G. Wolken and M. Karplus, J. Chem. Phys. 60, 351 (1974).
Soc. of Chem. 80, 95 (1989).
- [79] A. Kuppermann, in ref. [4], and earlier references therein.
- [80] W. H. Miller and B. M. D. D. Jansen op de Haar, J. Chem. Phys. 86, 6213 (1987).
- [81] J. Z. H. Zhang, S. I. Chu, and W. H. Miller, J. Chem. Phys. 88, 6233 (1988).
- [82] J. Z. H. Zhang and W. H. Miller, J. Chem. Phys. 91, 1528 (1989).
- [83] . (a) D. G. Truhlar and D. J. Kouri, et al., J. Chem. Phys. 91, 1643 (1989). (b) D. G. Truhlar and D. J. Kouri, et al., J. Phys. Chem. 92, 3202 (1988).

- [84] D. E. Manolopoulos and R. E. Wyatt, Chem. Phys. Lett. 152, 23 (1988); 159, 123 (1989); J. Chem. Phys. 91, 6096 (1989); 93, 403 (1990).
- [85] S. L. Mielke, D. G. Truhlar, and D. W. Schwenke, J. Phys. Chem. 98, 1053 (1994).
- [86] J. M. Launay and M. Le Dournef, Chem. Phys. Lett. 169, 473 (1990).
- [87] R. T Pack, E. A. Butcher, and G. A. Parker, J. Chem. Phys. 99, 9310 (1993).
- [88] W. H. Miller, Accts. Chem. Res. 26, 174 (1993).
- [89] (a) W. H. Miller, S. D. Schwartz, and J. W. Tromp, J. Chem. Phys. 79, 4889 (1983). (b) T. Seideman and W. H. Miller, J. Chem. Phys. 96, 4412 (1992); 97, 2499 (1992).
- [90] U. Manthe and W. H. Miller, J. Chem. Phys. 99, 3411 (1993).
- [91] D. Thirumalai, B. C. Garrett, and B. J. Berne, J. Chem. Phys. 83, 2972 (1985).
- [92] V. A. Mandelshtam and H. S. Taylor, J. Chem. Phys. 99, 222 (1993).
- [93] (a) M. Baer and C. Y. Ng, eds., Advances in Chemical Physics, 82, Part 2, 1992. (b) M. S. Child, in ref. [5], p. 427.
- [94] Extensive references and many recent papers describing computational methods for the TDSE can be found in Time-Dependent Quantum Molecular Dynamics, eds. J. Broeckhove and L. Lathouwers, NATO ASI Series B: Physics Vol. 299 (Plenum, New York, 1992) and in the thematic volume of Compute7 Physics Communications, Ed. K. Kulander, Vol. 63 (North-Holland, Amsterdam, 1991).
- [95] R. G. Newton, Scattering Theory of Waves and Particles (Springer-Verlag, New York, 1982).
- [96] J. L. Powell and B. Crasemann, Quantum Mechanics (Addison-Wesley, Reading, MA, 1961) pp. 96-98.
- [97] The amplitude density for non-reactive scattering was introduced by B. R. Johnson and D. Secrest, J. Math Phys. 7, 2187 (1966) and generalized to reactive scattering by D. J. Kouri, J. Chem. Phys. 51, 5204 (1969). The solution method for the amplitude density was introduced by M. Baer and D. J. Kouri; see, e. g., J. Chem. Phys. 56, 1758 (1972).
- [98] D. Secrest, in Atom-Molecule Collision Theory, Ed. R. B. Bernstein (Plenum, New York, 1979) Chp. 8.

- [99] J. C. Polany, *Angew. Chemie*, **99** (1987) 981;
- [100] R. M. J. Dantus and A. H. Zewail, *J. Chem. Phys.*, **89** (1988) 6113
- [101] R. M. J. Dantus and A. H. Zewail, *J. Chem. Phys.*, **89** (1988) 6128
- [102] R. M. J. Dantus and A. H. Zewail, *Science*, **241** (1988) 1200
- [103] A. Kuppermann and G. C. Schatz, *J. Chem. Phys.*, **62** (1975) 2502
- [104] G. C. Schatz and A. Kuppermann, *Phys. Rev. Lett.*, **35** (1975) 1266
- [105] G. C. Schatz and A. Kuppermann, *J. Chem. Phys.*, **65** (1976) 4642, 4668
- [106] R. B. Walker, E. B. Stechel and J. C. Light, *J. Chem. Phys.*, **69** (1978) 2922
- [107] J. C. Light and R. B. Walker, *J. Chem. Phys.*, **65** (1967) 4272
- [108] F. Webster and J. C. Light, *Chem. Phys. Lett.*, **90** (1989) 265, 300
- [109] J. Linderberg, *J. Int. Quant. Chem.*, **35** (1989) 801
- [110] W. Kohn, *Phys. Rev.*, **74** (1948) 1763
- [111] L. Hulthén, *Kgl. Fysiogr. Sällsk. Lund Forh.*, **14** (1944) 21
- [112] L. Hulthén, *Arkiv. Mat. Ast. Fys.*, **35A** (1948) 25
- [113] T. -Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice Hall, Englewood Cliffs, New Jersey, 1962), p. 64
- [114] W. H. Miller, *Comments At. Mol. Phys.*, **22** (1988) 115
- [115] B. R. Johnson, *J. Chem. Phys.*, **79** (1983) 1906, 1916
- [116] C. A. Mead, *Chem. Phys.*, **49** (1980) 23
- [117] R. T. Pack, *Chem. Phys. Lett.*, **108** (1984) 333
- [118] J. M. Launay and B. Lepetit, *Chem. Phys. Lett.*, **144** (1988) 346; **151** (1988) 287
- [119] K. Haug, D. W. Schwenke, Y. Shima, D. G. Truhlar, J. Z. H. Zhang and D. J. Kouri, *J. Phys. Chem.*, **90** (1986) 6757

- [120] K. Haug, D. W. Schwenke, Y. Shima, D. G. Truhlar, J. Z. H. Zhang and D. J. Kouri, J. Phys. Chem., **87** (1987) 1892
- [121] J. Z. H. Zhang, D. J. Kouri, K. Haug, D. W. Schwenke, Y. Shima and D. G. Truhlar, J. Phys. Chem., **88** (1988) 2492
- [122] D. Kosloff and R. Kosloff, J. Chem. Phys., **52** (1983) 35
- [123] D. E. Manolopoulos and R. E. Wyatt, J. Chem. Phys., **92** (1990) 810
- [124] J. Z. H. Zhang, Chem. Phys. Lett., **181** (1991) 63
- [125] J. M. Launay and M. Le Dourneuf, Chem. Phys. Lett., **169** (1990) 437
- [126] G. C. Schatz, Chem. Phys. Lett., **150** (1988) 92
- [127] Q. Sun and J. M. Bowman, J. Chem. Phys., **92** (1990) 5201
- [128] Q. Sun, D. L. Yang, N. S. Wang and J. M. Bowman, J. Chem. Phys., **93** (1990) 4730
- [129] D. Wang and J. M. Bowman, J. Chem. Phys., **96** (1992) 8906
- [130] D. C. Clary, Chem. Phys. Lett., **192** (1991) 34 D. C. Clary, J. Chem. Phys., **95** (1991) 7298 D. C. Clary, J. Chem. Phys., **96** (1992) 3656
- [131] D. H. Zhang and J. Z. H. Zhang, J. Chem. Phys., **99** (1993) 5615 D. H. Zhang and J. Z. H. Zhang, J. Chem. Phys., **100** (1994) 2697
- [132] D. C. Clary and G. C. Schatz, J. Chem. Phys., **99** (1993) 4578
- [133] J. Echave and D. C. Clary, J. Chem. Phys., **100** (1994) 3556
- [134] J. Z. H. Zhang, S. -I. Chu and W. H. Miller, J. Chem. Phys., **88** (1988) 6233
- [135] J. Z. H. Zhang and W. H. Miller, Chem. Phys. Lett., **153** (1988) 465
- [136] G. C. Groenenboom and D. T. Colbert, J. Chem. Phys., **99** (1993) 9681
- [137] J. C. Light, I. P. Hamilton, J. V. Lill, J. Chem. Phys., **84** (1986) 1400
- [138] J. Linderberg and B. Vessal, Int. J. Quant. Chem., **31** (1987) 65

- [139] A. Kuppermann and P. G. Hipes, J. Chem. Phys., **84** (1986) 5962
- [140] P. G. Hipes and A. Kuppermann, Chem. Phys. Let, **133** (1987) 1
- [141] R. T. Pack and G. A. Parker, J. Chem. Phys., **87** (1987) 3888
- [142] J. Linderberg, S. Padkjaer, Y. Öhrn and B. Vessal, J. Chem. Phys., **90** (1989) 6254
- [143] A. Askar, H. Rabitz, J. Chem. Phys., **80** (1984) 3586
- [144] R. Jaquet, Comp. Phys. Com., **58** (1990) 275
- [145] R. Jaquet, Habilitationsschrift (1987), Siegen (Shaker, Aachen, 1992)
- [146] R. Jaquet and U. Schnupf, Chem. Phys., **165** (1992) 287
- [147] R. Jaquet and J. Gribkova, Theoret. Chim. Acta, **89** (1994) 363
- [148] R. N. Porter and M. Karplus, J. Chem. Phys., **40** (1964) 1105
- [149] W. H. Miller, Annu. Rev. Phys. Com., **41** (1990) 245
- [150] G. C. Schatz, J. Chem. Phys., **90** (1988) 1237, 4847
- [151] M. Baer, ed., Theory of Chemical Reaction Dynamics, Vol 1, CRC Press, Boca Raton, FL, 1985
- [152] Aquilanti in [4]
- [153] Clary in [4]
- [154] Kuppermann in [6]
- [155] R. A. Marcus, J. Chem. Phys. , 45 (1966) 4493
- [156] M. S. Child, 'Molecular Collision Theory', Academic Press, London, 1974, chap. 10.
- [157] L. M. Delves, Nucl. Phys., 1959, 9, 391; 1960, 20, 275.
- [158] F. T. Smith, J. Math. Phys., 1962, 3, 735; R. C. Whitten and F. T. Smith, J. Math. Phys., 1968, 9, 1103; R. C. Whitten, I Math. Phys., 1969, 10, 1631.

- [159] A. Kuppermann, Chem. Phys. Lett., 1975, 32, 374.
- [160] C. A. Mead, Chem. Phys., 1980, 49, 23; J. Chem. Phys., 1980, 72, 3839.
- [161] B. R. Johnson, J. Chem. Phys., 1980, 73, 5051; 1983, 79, 1906, 1916.
- [162] G. C. Schatz, Chem. Phys. Lett., 1988, 150, 92.
- [163] W. H. Miller, J. Chem. Phys., 1969, 50, 407.
- [164] M. Baer and D. J. Kouri, Phys. Rev. A, 1971, 4, 1924; J. Chem. Phys., 1972, 56, 4840; J. Math. Phys., 1973, 14, 1637.
- [165] R. Kosloff and D. Kosloff, J. Chem. Phys., 1983, 79, 1823; R. Kosloff, J. Phys. Chem., 1988, 92, 2087.
- [166] J. N. Brooks and D. C. Clary, J. Chem. Phys., 1990, 92, 4178.
- [167] A. Kuppermann and G. C. Schatz, J. Chem. Phys., 1975, 62, 2502; 1976, 65, 4642, 4668.
- [168] (a) A. B. Elkowitz and R. E. Wyatt, J. Chem. Phys. 62, 2504 (1975); 62, 3683 (1975); (b) S. A. Harms and R. E. Wyatt, J. Chem. Phys. 62, 3162 (1975); 62, 3173 (1975).
- [169] Walker et al 1978
- [170] Light Walker 1976, Stechel et al 1978
- [171] J. C. Light, R. B. Walker, E. B. Stechel, and T. G. Schmalz, Comp. Phys. Comm, , 1979, 17, 89; J. V. Lill, T. G. Schmalz, and J. C. Light, J. Chem. Phys., 1983, 78, 4456.
- [172] R. B. Walker and J. C. Light. Ann. Rev. Phys. Chem., 1980, 31, 401.
- [173] E. B. Stechel, F. Webster, and J. C. Light. J. Chem. Phys., 1988, 88, 1824.
- [174] F Webster and J. C. Light, J. Chem. Phys., 1989, 90, 265.
- [175] F. Webster and J. C. Light, J. Chem. Phys., 1989, 90, 300.
- [176] A. Kuppermann in 'Potential Energy Surfaces and Dynamics Calculations', ed. D. G. Truhlar, Plenum Press, New York, 1981, p. 375.
- [177] G. A. Parker, R. T. Pack, B. J. Archer, and R. B. Walker, Chem. Phys. Lett., 1987, 137, 564.

- [178] G. A. Parker, R. T. Pack, A. Lagani, B. J. Archer, J. D. Kress, and Z. Basic in 'Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules', ed. A. Lagana, Kluwer, Dordrecht, 1989, p. 105.
- [179] J. D. Kress, Z. Basic, G. A. Parker, and R. T. Pack, Chem. Phys. Lett., 1989, 157, 484.
- [180] J. C. Light, I. P. Hamilton, and I. V. Lill, J. Chem. Phys., 1985, 82, 1400.
- [181] R. M. Whitnell and J. C. Light, J. Chem. Phys., 1988, 89, 3674.
- [182] J. M. Launay and M. Le Dourneuf, Chem. Phys. Lett., 1989, 163, 178.
- [183] I-C. Nieh and J. J. Valentini, Phys. Rev. Lett., 1988, 60, 519; J. Chem. Phys., 1990, 92, 1083.
- [184] J. Z. H. Zhang and W. H. Miller', Chem. Phys. Lett. , 1988, 153, 465.
- [185] M. Mishra, J. Linderberg, and Y. Ohm, Chem. Phys. Lett., 1984, 111, 4A
- [186] J. Linderberg, Int. J. Quantum Chem. S., 1986, 19, 467.
- [187] J. Linderberg and B. Vessal, Int. J. Quantum Chem., 1987, 31, 65.
- [188] J. Linderberg, S. B. Padkjaer, Y. Öhrn, and B. Vessal, J. Chem. Phys., 1989, 90, 6254.
- [189] A. Kuppermann and P. G. Hipes, J. Chem. Phys., 1986, 94, 5962.
- [190] L. Eisenbud, Ph. D. Thesis, Princeton, 1948; E. P. Wigner, Phys. Rev., 1955, 98, 145.
- [191] F. T. Smith, Phys. Rev., 1960, 118, 349.
- [192] S. A. Cuccaro, P. G. Hipes, and A. Kuppermann, Chem. Phys. Lett., 1989, 154, 155.
- [193] G. C. Schatz, Chem. Phys. Lett., 1988, 151, 409.
- [194] C. Schatz, J. Chem. Phys., 1989, 90, 3582.
- [195] D. W. Schwenke, D. G. Truhlar, and D. J. Kouri, J. Chem. Phys., 1987, 86, 2772.
- [196] Y. Öhrn and J. Linderberg, Mol. Phys., 1983, 49, 53,
- [197] X. Chapuisat, Chem. Phys. Lett., 1987, 136, 153,

- [198] M. Baer, Phys. Rep., 1989, 178, 99.
- [199] R. K. Nesbet, 'Variational Methods in Electron- Atom Scattering Theory' Plenum, New York, 1980, chap. 2.
- [200] W. Kohn, Phys. Rev., 1948, 74, 1763.
- [201] J. Schwinger, Phys. Rev. , 1947, 72, 742.
- [202] R. G. Newton, 'Scattering Theory of Particles and Waves', Springer, New York, 1982, p. 320.
- [203] C. Schwartz, Phys. Rev., 1961, 124, 1468; Ann. Phys. , New York, 1961, 10, 36.
- [204] W. H. Miller and B. M. D. Jansen op de Haar, J. Chem. Phys., 1987, 86, 6213.
- [205] A. Messiah, 'Quantum Mechanics', Wiley, New York, 1962, chap. 19.
- [206] L. F. X. Gaucher and W. H. Miller, Israel J. Chem., 1989, 29, 349.
- [207] R. R. Lucchese, Phys. Rev. A, (1991).
- [208] J. Z. H. Zhang, S-I. Chu, and W. H. Miller, J. Chem. Phys., 1988, 88, 6233; 1988, 89, 4454.
- [209] W. H. Miller, Collect. Czech. Chem. Commun., 1988, 53, 1873.
- [210] W. H. Miller, Comments At. Mol. Phys., 1988, 22, 115.
- [211] J. Z. H. Zhang and W. H. Miller, J. Chem. Phys., 1988, 88, 4549; 1989, 90, 7610.
- [212] J. Z. H. Zhang and W. H. Miller, Chem. Phys. Lett., 1989, 159, 130.
- [213] G. C. Schatz, Ann. Rev. Phys. Chem., 1988, 39, 317.
- [214] W. H. Miller, Ann. Rev. Phys., Chem., (1991)
- [215] Adams, J. T., Smith, R. L., and Hayes, E. F. (1974). J. Chem. Phys. 61, 2193-2199.
- [216] Askar, A., Cakmak, A. S., and Rabitz, H. A. (1978). Chem. Phys. 33, 267-286.
- [217] Davydov, A. S. (1965). "Quantum Mechanics", Chapter VI. Addison Wesley, Reading, Massachusetts.
- [218] Delves, L. M. (1959). Nucl. Phys. 9, 391-399; (1960). Nucl. Phys. 20, 275-308.

- [219] Diestler, D. J., and McKoy, V. (1968). J. Chem. Phys. 48, 2951-2959.
- [220] Elkowitz, A. B., and Wyatt, R. E. (1975). J. Chem. Phys. 62, 2504-2506.
- [221] Elkowitz, A. B., and Wyatt, R. E. (1975). J. Chem. Phys. 63, 702-721.
- [222] Eyring, H. (1935). J. Chem. Phys. 3, 107-115.
- [223] Gordon, R. G. (1969). J. Chem. Phys. 51, 14-25.
- [224] Johnson, B. R. (1972). Chem. Phys. Lett. 13, 172-175.
- [225] Kuppermann, A. (1970). In "Proceedings of the Conference on Potential Energy Surfaces in Chemistry" (W. A. Lester, ed.), pp. 121-124. University of California, Santa Cruz.
- [226] Kuppermann, A. (1972). Proc. Int. Com. Phys. Electron. At. Collisions, 7th, 1971. pp. 3-5.
- [227] Kuppermann, A. (1975). Chem. Phys. Lett. 32, 374-375.
- [228] Kuppermann, A., and Schatz, G. C. (1975). J. Chem. Phys. 62, 2502-2504.
- [229] Kuppermann, A., Schatz, G. C., and Baer, M. (1976). J. Chem. Phys. 65, 4596-4623.
- [230] Lane, A. M., and Thomas, R. G. (1958). Rev. Mod. Phys. 30, 257-353.
- [231] Light, J. C., and Walker, R. B. (1976). J. Chem. Phys. 65, 4272-4282.
- [232] McCullough, E. A., Jr., and Wyatt, R. E. (1969). J. Chem. Phys. 51, 1253-1254.
- [233] McCullough, E. A., Jr., and Wyatt, R. E. (1971). J. Chem. Phys. 54, 3578-3591, 3592-3600.
- [234] Miller, G., and Light, J. C. (1971). J. Chem. Phys. 54, 1635-1642, 1643-1651.
- [235] Mortensen, E. M. (1968). J. Chem. Phys. 48, 4029-4039.
- [236] Mortensen, E. M., and Gucwa, L. D. (1969). J. Chem. Phys. 51, 5695-5702.
- [237] Mortensen, E. M., and Pitzer, K. S. (1962). J. Chem. Soc., Spec. Publ. 16, 57-75.
- [238] Pack, R. T. (1974). J. Chem. Phys. 60, 633-639.

- [239] Rankin, C. C., and Light, J. C. (1969). J. Chem. Phys. 51, 1701-1719.
- [240] Sams, W. M., and Kouri, D. J. (1969). J. Chem. Phys. 51, 4809-4814, 4815-4819.
- [241] Schatz, G. C., and Kuppermann, A. (1976c). J. Chem. Phys. 65, 4668-4692.
- [242] Truhlar, D. G., Kuppermann, A., and Adams, J. T. (1973). J. Chem. Phys. 59, 395-402.
- [243] Truhlar, D. G. and Horowitz, C. G. (1978). J. Chem. Phys. 68, 2466-2476.
- [244] Truhlar, D. G., and Kuppermann, A. (1970). J. Chem. Phys. 52, 3841-3843.
- [245] Truhlar, D. G., and Kuppermann, A. (1972). J. Chem. Phys. 56, 2232-2252.
- [246] Walker, R. B., Stechel, E. B. and Light, J. C. (1978). J. Chem. Phys. 69, 2922-2923.
Theory" (R. B. Bernstein, ed.), Chapter 17. Plenum, New York.
- [247] L. E. Elsgolc, Calculus of Variations (Pergamon Press, 1961)
- [248] J. P. Boyd, Chebyshev and Fourier Spectral Methods (Springer Verlag, New York, 1989)
- [249] W. H. Miller und. B. M. D. D. Jansen op de Haar, J. Chem. Phys., **86** (1987) 6213
- [250] C. W. McCurdy, T. N. Rescigno, B. I. Schneider, Phys. Rev. A **36** (1987) 2061
- [251] C. W. McCurdy, T. N. Rescigno, Phys. Rev. A **37** (1988) 1044
- [252] C. W. McCurdy, T. N. Rescigno, B. I. Schneider, Phys. Rev. Lett. **63** (1989) 248
- [253] J. E. G. Farina, Quantum Theory of Scattering (Pergamon Press, 1973)
- [254] R. K. Nesbet, Variational Methods in Electron-Atom Scattering Theory (Plenum Press, New York 1980)
- [255] H. Feshbach, Ann. Phys. (N. Y.) **5** (1958) 357, **19** (1962) 287
- [256] A. J. F. Siegert, Phys. Rev. **56** (1939) 750
- [257] J. Z. Zhang, W. H. Miller, J. Chem. Phys., **91** (1989) 1528
- [258] J. Tennyson, S. Miller, Comp. Phys. Comm., **55** (1989) 149

- [259] J. Tennyson, J. R Henderson, J. Chem. Phys., **91** (1989) 3815
- [260] B. T. Sutcliffe and J. Tennyson, Mol. Phys., **58** (1986) 1053
- [261] H. R. Schwarz, Methode der finiten Elemente, Teubner, Stuttgart, 1988
- [262] D. H. Norrie and G. de Vries , The Finite Element Methode, Academic Press, New York, 1973
- [263] B. R. Johnson, J. Chem. Phys., **67** (1977) 4086
- [264] B. R. Johnson and D. Secrest, J. Math. Phys., **7** (1966) 2187
- [265] P. Pechuskas and J. C. Light, J. Chem. Phys., **44** (1966) 3897
- [266] M . Abramowitz and I. A. Stegun, Handbook of Mathematical Functions (National Burreau of Standarts, Washington, D. C. 1968)
- [267] M. S. Reeves, M. J. Unekis, D. W. Schwenke, N. M. Harvey, and D. G. Truhlar, RMPROP-Version 2. 1, University of Minnesota, Minneapolis, 1994
- [268] W. Eastes, D. Secrest , J. Chem. Phys., **56** (1972) 641
- [269] D. G. Truhlar and R. E. Wyatt, Ann. Rev. Phys. Chem., **27** (1976) 1
- [270] 1976) H. Eyring and M. Polanyi, Z. Phys. Chem., **B12** (1931) 279 (1977) 45
- [271] R. Jaquet, *Theoret. Chim. Acta*, 1987, **71**, 425.
- [272] R. Jaquet, *Comp. Phys. Comm.* , 1990, **58**, 257.
- [273] J. Z. H. Zhang, S. I. Chu and W. H. Miller, J. Chem. Phys. , 1988, **88**, 6233.
- [274] W. H. Miller, *Comments At. Mol. Phys.* , 1988, **22**, 115.
- [275] J. Z. H. Zhang and W. H. Miller, Chem. Phys. Let, 1987, **140**, 329.
- [276] J. Z. H. Zhang, J. Chem. Phys. , 1991, **94**, 6047.
- [277] D. T. Colbert and W. H. Miller, J. Chem. Phys. , 1992, **96**, 1982.
- [278] A. K. Belyaev, D. T. Colbert, G. C. Groenenboom and W. H. Miller, Chem. Phys. Let, 1993, **209**, 309.

- [279] G. C. Groenenboom and D. T. Colbert, *J. Chem. Phys.* , 1993, **99**, 9681.
- [280] D. H. Zhang and J. Z. H. Zhang, *J. Chem. Phys.* , 1994, **100**, 2697.
- [281] W. H. Miller, in [3], p. 1
- [282] L. Hulthén, *Kgl. Fysiogr. Sallsk. Lund Förh.* , 1944, **14**, 21.
- [283] L. Hulthén, *Arkiv Mat. Astron. Fysik.* , 1948, **35A**, 25.
- [284] W. Kohn, *Phys. Rev.* , 1948, **74**, 1763.
- [285] R. K. Nesbet, *Variational Methods in Electron Atom Scattering Theory*, Plenum, New York, 1980.
- [286] C. J. Joachain, *Quantum collision theory*, Elsevier, Amsterdam, 1983.
- [287] R. N. Porter and M. Karplus, *J. Chem. Phys.* , 1964, **40**, 1105.
- [288] R. Jaquet and J. Gribkova, *Theoret. Chim. Acta*, 1994, **89**, 363.
- [289] J. Tennyson and S. Miller, *Comp. Phys. Comm.* , 1989, **55**, 149.
- [290] J. Tennyson and J. R Henderson, *J. Chem. Phys.* , 1989, **91**, 3815.
- [291] B. T. Sutcliffe and J. Tennyson, *Mol. Phys.* , 1986, **58**, 1053.
- [292] R. Röhse, W. Kutzelnigg, R. Jaquet and W. Klopper *J. Chem. Phys.* , 1994, **101**, 2231.
- [293] J. C. Light, I. P. Hamilton and J. V. Lill. *J. Chem. Phys.* , 1985, **82**, 1400.
- [294] Schatz G C and Kuppermann A 1976 *J. Chem. Phys.* 65 4642-91 Quantum mechanical reactive scattering for three-dimensional atom plus diatom systems
- [295] Elkowitz A B and Wyatt R E 1975 *J. Chem. Phys.* 62 2504-6 Quantum mechanical reaction cross sections for the three-dimensional hydrogen exchange reaction
- [296] Walker R B, Stechel E B and Light J C 1978 *J. Chem. Phys.* 69 2922-3 Accurate H3 dynamics on an accurate potential surface
- [297] Messiah A 1961 *Quantum mechanics Vol. 1*, Amsterdam: North-Holland Publishing

- [298] Arthurs A M and Dalgarno A 1960 Proc. R. Soc. A 256 540-51 The theory of scattering by a rigid rotator
- [299] Johnson B R 1983 J. Chem. Phys. 79 1916-25 The quantum dynamics of three particles in hyperspherical coordinates
- [300] Johnson B R 1973 J. Comp. Phys. 14 445-9 The multichannel log-derivative method for scattering calculations
- [301] Manolopoulos D E 1986 J. Chem. Phys. 85 6425-9 An improved log-derivative method for inelastic scattering
- [302] Fock V 1958 D. Kon. Nors. Vidensk. Selsk. Forh. 31 138-52 On the Schrödinger equation of the helium atom
- [303] Whitten R C and Smith F T 1968 J. Math. Phys. 9 1103- 13 Symmetric representation for three-body problems. 11 : Motion in space
- [304] Kuppermann A 1975 Chem. Phys. Lett. 32 374-5 A useful mapping of triatomic potential energy surfaces
- [305] Johnson B R 1980 J. Chem. Phys. 73 5051-8 On hyperspherical coordinates and mapping the internal configurations of a triatomic system
- [306] Aquilanti V, Grossi G and Lagana A 1982 J. Chem. Phys. 76 1587-8 On hyperspherical mapping and harmonic expansions for potential energy surfaces Introduction to the quantum theory of reactive scattering 119
- [307] Hipes P G and Kuppermann A 1987 Chem. Phys. Letters 133 1-7 Lifetime analysis of high-energy resonances in three-dimensional reactive scattering
- [308] Launay J M and Lepetit B 1988 Chem. Phys. Lett. 144 346-352 Three-dimensional quantum study of the reaction $\text{H} + \text{FH}(\nu, j) \rightarrow \text{HF}(\nu', j) + \text{H}$ in hyperspherical coordinates
- [309] Linderberg J, Padkjaer S, Öhrn Y and Vessal B 1989 J. Chem. Phys. 90 6254-65 Numerical implementation of reactive scattering theory
- [310] Launay J M and Le Dourneuf M 1989 Chem. Phys. Lett. 163 178-88 Hyperspherical close-coupling calculation of integral cross sections for the reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$
- [311] Wu Y S M, Cuccaro S A, Hipes P G and Kuppermann A 1991 Theor. Chim. Acta 79 225-39 Quantum chemical reaction dynamics on a highly parallel supercomputer Wu Y S M, Kuppermann A and Lepetit B 1991 Chem. Phys. Lett. 186 319-28 Theoretical calculation of experimentally observable consequences of the geometric phase on chemical reaction cross sections

- [312] Pack R T and Parker G A 1989 J. Chem. Phys., 90 3511- 9 Quantum reactive scattering in three dimensions using hyperspherical coordinates : III. Small θ behaviour and corrigenda
- [313] Launay J M and Le Dourneuf M 1990 Chem. Phys. Lett. 169 473-83 Quantum mechanical calculations of integral cross sections for the reaction $F + H_2(v=0, j=0) \rightarrow FH(v', j) + H$ by the hyperspherical method
- [314] Launay J M 1991 Theor. Chim. Acta. 79 183-90 Computation of cross sections for the $F + H_2 (v = 0, j = 0) \rightarrow FH(v', j') + H$ by the hyperspherical method
- [315] Launay J M and Padkjaer S B 1991 Chem. Phys. Lett. 181 95-99 Quantum dynamical study of the $Cl + H_2 \rightarrow ClH + H$ reaction
- [316] Lepetit B and Launay J M 1991 J. Chem. Phys. 95 5159- 68 Quantum mechanical study of the reaction $He + H_2^+ \rightarrow HeH^+$ with hyperspherical coordinates
- [317] Ed. J. Bowman, Advances in Molecular Vibrations and Collision Dynamics, JAI Press, 1991
- [318] S. C. Althorpe et al, J. Chem. Soc., Faraday Trans., 93,703 (1997)
- [319] R. Pack in [4]
- [320] R. E. Wyatt in [5]
- [321] D.E. Manolopolous, J. Chem. Soc., Faraday Trans., 93, 673 (1997)
- [322] J. F. Castillo, D. E. Manolopolous, Faraday Discuss. 110, 119, 1998
- [323] A. Kuppermann, in [7]
- [324] G. Herzberg and H. C. Longuet-Higgins, Intersection of potential energy surfaces in polyatomic molecules, Discussion Faraday Soc. 35: 77 (1963).
- [325] H. C. Longuet-Higgins, The intersection of potential energy surfaces in polyatomic molecules, Proc. R. Soc. Lond A 344: 147 (1975).
- [326] H. A. Jahn and E. Teller, Stability of polyatomic molecules in degenerate electronic states. 1: Orbital degeneracy, Proc. R. Soc. A 161: 220 (1937).
- [327] P. G. Carrick, A. J. Merer, and R. F. Curl, $A^2\Pi \leftarrow X^2\Sigma^+$ infrared electronic transition of C_2H , J.Chem. Phys. 78: 3652 (1983).

- [328] W. B. Yan, J. L. Hall, J. W. Stephens, M. L. Richnow, and R. F. Curl, Color center laser spectroscopy of excited C_2H , J.Chem Phys. 86: 1657 (1987).
- [329] C. Petrongolo, G. Hirsch, and R. J. Buenker, Diabatic representation of the $A_2A, 1h_2B$, conical intersection in NH_2 , Mol. Phys. 70: 835 (1990).
- [330] G. Hirsch, R. J. Buenker and C. Petrongolo, Ab initio study of NO ,. II: Non-adiabatic coupling between the two lowest $2 A'$ states and the construction of a diabatic representation, Mol. Phys. 70: 835 (1990).
- [331] D. C. Robie, M. Hunger, J. L. Bates, and H. Reisler, Product state distributions in the photodissociation of expansion-cooled NO_2 near the $NO(X^2n)V = 1$ threshold, Chem. Phys. Lett. 193: 413 (1992).
- [332] S. P. Walch and R. J. Duchovic, Theoretical characterization of the potential-energy surface for $H + O_2 - H_2O^* - OH + O$. 111: Computed points to define a global potential-energy surface, J. Chem. Phys. 94: 7068 (1991).
- [333] B. Kendrick and R. T. Pack, Potential energy surfaces for the low-lying $2A''$ and $'A'$ states of HO_2 : Use of the diatomics in molecules model to fit ab initio data, J. Chem. Phys. 102: 1994 (1995).
- [334] C. A. Mead and D. G. Truhlar, On the determination of Born-Oppenheimer nuclear motion wave functions including complications due to conical intersections and identical nuclei, J. Chem. Phys. 70: 2282 (1979).
- [335] Y-S M. Wu, A. Kuppermann and B. Lepetit, Theoretical calculation of experimentally observable consequences of the geometric phase on chemical reaction cross sections, Chem. Phys. Lett. 186: 319 (1991).
- [336] Y Aharonov and D. Bohm, Significance of electromagnetic potentials in the quantum theory, Phys. Rev. 115: 485 (1959).
- [337] Y-S.M. Wu and A. Kuppermann, Prediction of the effect of the geometric phase on product rotational state distributions and integral cross sections, Chem. Phys. Lett. 201: 178 (1993).
- [338] M. V. Berry, Quantal phase factors accompanying adiabatic changes, Proc. R. Soc. Lond. A 392: 45 (1984).
- [339] J. W. Zwanziger, M. Koenig, and A. Pines, Berry's phase, Ann. Rev. Phys. Chem. 41: 601 (1990).
- [340] G. Schatz et al, Faraday Discuss. 110, 139 (1998)

- [341] G. Wolken and M. Karplus, J. Chem. Phys. 60, 351 (1974).
- [342] Kuppermann, A. (1975). Chem. Phys. Lett. 32, 374-375.
- [343] A. M. Arthurs and A. Dalgarno, Proc. R. Soc. London Ser. A 256, 540 (1960).
- [344] J. O. Hirschfelder and E. P. Wigner, Prod. Natl. Acad. Sci. 21, 113 (1935).
- [345] C. F. Curtiss, J. O. Hirschfelder, and F. T. Adler, J. Chem. Phys. 18, 1638 (1950).
- [346] R. T. Pack, J. Chem. Phys. 60, 633 (1974).
- [347] L. S. Davydov, Quantum Mechanics. translated by D. ter Haar.(Addison-Wesley, Reading, MA. 1965), Chap. VI.
- [348] P. McGuire and D. J. Kouri, J. Chem. Phys. 60, 7488 (1974).
- [349] Handbook of Mathematical Functions, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington. D.C., 1964).
- [350] G. C. Schatz and A. Kuppermann, J. Chem. Phys. 65, 4624 (1976).
- [351] M. E. Rose, Elementary Theory of Angular Momentum, (Wiley, New York, 1957), Chap. 3.
- [352] A. Messiah, Quantum Mechanics, (North-Holland, Amsterdam, 1966), Vol. 11, Eq. X111. 54, p. 530.
- [353] D. J. Vezzetti and S. I. Rubinow, Ann. Phys. 35, 373 (1965).
- [354] P. M. Morse and H. Feshbach, Methods of Theoretical Physics (McGraw-Hill, New York, 1953), Vol. 11, p. 1721.
- [355] A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais, Jour. Chem. Phys. 86, 6258 (1987).
- [356] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, Jour. Chem. Phys. 95, 4343 (1991).
- [357] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, Jour. Chem. Phys. 104, 7139 (1996).
- [358] L. Banares, F. J. Aoiz, V. J. Herrero, M. J. D'Mello, B. Niederjohann, K. Seekamp-Rahn, E. Wrede, and L. Schnieder. "Experimental and quantum mechanical study of the H+D2 reaction near 0.5 eV: The assessment of the H3 potential energy surfaces. " Jour. Chem. Phys. 108, 6160 (1998)

- [359] M. P. Miranda, D. C. Clary, J. F. Castillo, and D. E. Manolopoulos. "Using quantum rotational polarization moments to describe the stereodynamics of the $\text{H}+\text{D}_2(\nu=0, j=0) \rightarrow \text{HD}(\nu', j')+\text{D}$ reaction." *Jour. Chem. Phys.* 108, 3142 (1998)
- [360] E. Wrede, L. Schnieder, K. H. Welge, F. J. Aoiz, L. Banares, J. F. Castillo, B. Martinez-Haya, and V. J. Herrero. "The Dynamics of the Hydrogen Exchange Reaction at 2. 20 eV Collision Energy: Comparison of Experimental and Theoretical Differential Cross Sections." submitted to *Jour. Chem. Phys.* (1999)
- [361] R. Jaquet, A. Kumpf, M. Heinen, *J. Chem. Soc., Farad. Trans.*, **93**, 1027 (1997)
- [362] Baer, M., Kouri, D. J., in [2], p. 167.
- [363] Jellinek, J., Kouri, D. J., in [1], Vol. 2, Chap. 1.
- [364] Ohsaki, A.; Nakamura, H. *Phys. Rep.* 1990,187, 1.
- [365] Bowman, J. M. *Adv. Chem. Phys.* 1985, 61, 115.
- [366] Bowman, J. M.; Wagner, A. F., in [2], p. 47.
- [367] Walker, R. B.; Hayes, E. F., in [2], p. 105.
- [368] Bowman, J. M. *J. Phys. Chem.* 1991,95,4960.
- [369] Schatz, G. C. In *Advances in Molecular Electronic Structure Theory*, Dunning, T. H., Jr., Ed.; JAI: Greenwich and London, 1990; Vol. 1, pp. 88-127; Varandas, A. J. C. *Adv. Chem. Phys.* 1988, 74, 255; Truhlar, D. G.; Steckler, R.; Gordon, M. A. *Chem. Rev.* 1987,87,217.
- [370] A. C. Allison, *Adv. At. Mol. Phys.*, 25, 323 (1988)

Textbooks on Scattering Theory:

N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1965), 3rd ed., Chaps. 2-5.

R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966).

L. S. Rodberg and R. M. Thaler, *Introduction to the Quantum Theory of Scattering* (Academic Press, New York, 1967).

Electronic and Ionic Impact Phenomena, edited by H. S. W. Massey, E. H. S. Burhop, and H. B. Gilbody (Clarendon Press, Oxford, 1969-1974), Vols. 1-5.

M. R. C. McDowell and J. P. Coleman, *Introduction to the Theory of Ion-Atom Collisions* (North-Holland, Amsterdam, 1970).

M. S. Child, *Molecular Collision Theory* (Academic Press, New York, 1974).

C. J. Joachain, *Quantum Collision Theory* (North Holland, Amsterdam, 1975).

L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics* (Pergamon Press, Oxford, 1976), 3rd ed., Vol. 1, Chap. 4, p. 41.

H. Eyring, S. H. Lin, and S. M. Lin, *Basic Chemical Kinetics* (Wiley, New York, 1980), Chap. 3, p. 81.

B. H. Bransden, *Atomic Collision Theory* (Benjamin Cummings, Menlo Park, 1983), 2nd ed.

B. H. Bransden and C. J. Joachain, *Physics of Atoms and Molecules* (Wiley, New York, 1983).

E. E. Nikitin and S. Ya. Umanskil, *Theory of Slow Atomic Collisions* (Springer-Verlag, Berlin, 1984).

E. W. McDaniel, *Atomic Collisions: Electron and Photon Projectiles* (Wiley, New York, 1989), Chaps. 3 and 4, p. 71.

M. S. Child, *Semiclassical Mechanics with Molecular Applications* (Clarendon Press, Oxford, 1991). A. G. Sitenko, *Scattering Theory* (Springer-Verlag, Berlin, 1991).

E. W. McDaniel, J. B. A. Mitchell, and M. E. Rudd, *Atomic Collisions: Heavy Particle Projectiles* (Wiley, New York, 1993), Chap. 1, p. 1.