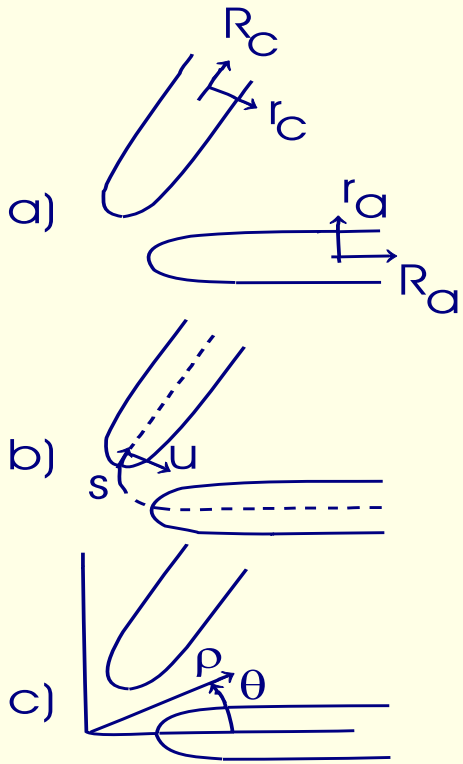
Coordinate systems

(a) Jacobi coordinates (good for one arrangement: A +BC; for analysis in the asymptotic region)

(b) reaction path ('natural coordinates') coordinates

(c) hyperspherical coordinates (good for the interaction region, not useful for analysis in the asymptotic region)



Which coordinate system for which quantum reactive procedure?

Jacobi coordinates: mass-scaled or non mass-scaled

collinear configuration:

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

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

$$T = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial R^2_{A-BC}} + \frac{\partial^2}{\partial r^2_{BC}}\right).$$

representation of the potential changes with the skewing angle φ_α depending on the masses of the atoms:

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

skewing angle: large (maximum 90^o) for $m_B >> m_A, m_C$; small (minimum 0^o) for $m_B << m_A, m_C$.

time-independent scattering:

- boundary value problem:

- R-matrix, - variational methods: Hulthen-Kohn, Schwinger, Newton

solution of linear equations, inversion of large matrices (grid (FEM, DVR) or conv. basis set)

for Hulthen-Kohn: ME collision energy independent

- starting value problem: close coupling

(a) propagation along a special coord. (grid), (b) in orthogonal coord.: eigenfunctions are needed (grid (FEM, DVR) or conv. basis set), ME collision energy independent

time-dependent scattering:

- starting value problem: propagation in time

coord.: grid (pseudo-spectral methods: FFT, DVR,..)

Potential energy matrix elements: simple to calculate within pseudo-spectral methods

How is the potential given? (a) local or global, (b) grid or functional Ansatz

Reactant and product coordinates

three independent sets of Jacobi-coodinates: A + BC (R_α, r_α), AB + C (R_β, r_β) and AC + B (R_γ, r_γ). R_α is the distance of atom A to the center of mass of diatom BC and r_α the distance in BC. With $\mathbf{x}_i$ and m_i (i=1,2,3 or A,B,C), the positions and masses of three particles, the centre of mass is

$$\mathbf{X} = \sum_{i=1}^{3} m_i \mathbf{x}_i / M \tag{1}$$

and the three types of mass normalised Jacobi coordinates are given as

$$\mathbf{r}_k = (\mathbf{x}_j - \mathbf{x}_i)/d_k, \quad \mathbf{R}_k = d_k[\mathbf{x}_k - \frac{m_i \mathbf{x}_i + m_j \mathbf{x}_j}{m_i + m_j}], \tag{2}$$

with the total mass M and the scaling parameters d_k

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

and the reduced mass

$$\mu = \sqrt{m_1 m_2 m_3 / M}, \tag{4}$$

where (i, j, k) is a cyclic permutation of $(1, 2, 3)$.

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

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{m_A m_C}{(m_A+m_B)(m_C+m_B)}} & -\sqrt{\frac{m_B(m_A+m_B+m_C)}{(m_A+m_B)(m_C+m_B)}} \\ \sqrt{\frac{m_B(m_A+m_B+m_C)}{(m_A+m_B)(m_C+m_B)}} & -\sqrt{\frac{m_A m_C}{(m_A+m_B)(m_C+m_B)}} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix} \tag{5}$$

or

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} \cos\,\phi_{\alpha\beta} & -\sin\,\phi_{\alpha\beta} \\ \sin\,\phi_{\alpha\beta} & \cos\,\phi_{\alpha\beta} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix}. \tag{6}$$

The skewing angle $\phi_{\alpha\beta}$ lies between π and $\pi/2$.

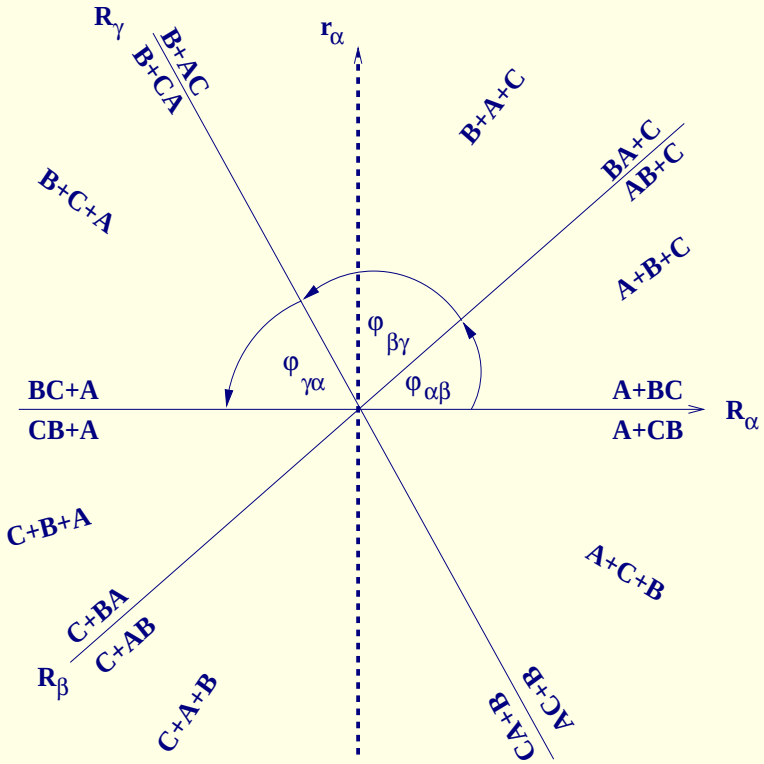


Figure 1: Configuration space of a triatomic system ABC with the arrangements α, β, γ.

Hyperspherical coordinates

• different ways of defining hyperspherical coordinates

- collinear Delves coordinates are defined in terms of the mass-scaled Jacobi vectors of the reactant arrangement a(A + BC) as

$$\rho = \sqrt{R_a^2 + r_a^2} \quad \text{and} \quad \theta_a = \tan^{-1}(r_a/R_a), \tag{7}$$

R_a: mass-scaled distance between A and the centre-of-mass of BC

r_a: mass-scaled distance between B and C

• hyperradius ρ in Eq. (7) is universal: it can equally well be defined in terms of mass-scaled Jacobi vectors of the product arrangement c(AB+C)

• Delves hyperangle θ_a is a function of the arrangement for which it is defined

relation between reactant hyperangle θ_a and product hyperangle θ_c: $\theta_a + \theta_c = \theta_{ac}$:

$$\theta_{ac} = \tan^{-1}(m_B/\mu) \quad \text{with} \quad \mu = \left(\frac{m_C m_B m_C}{m_A + m_B + m_C}\right)^{1/2} \tag{8}$$

- Johnson, Pack and Parker, Linderberg and Hinze and Wolniewicz: so-called "democratic" hyperspherical coordinates for reactive scattering

- Fock, Launay and LePetit: all channels cannot be treated equally

- Kuppermann: not so optimal for treating the Pauli-principle for identical nuclei

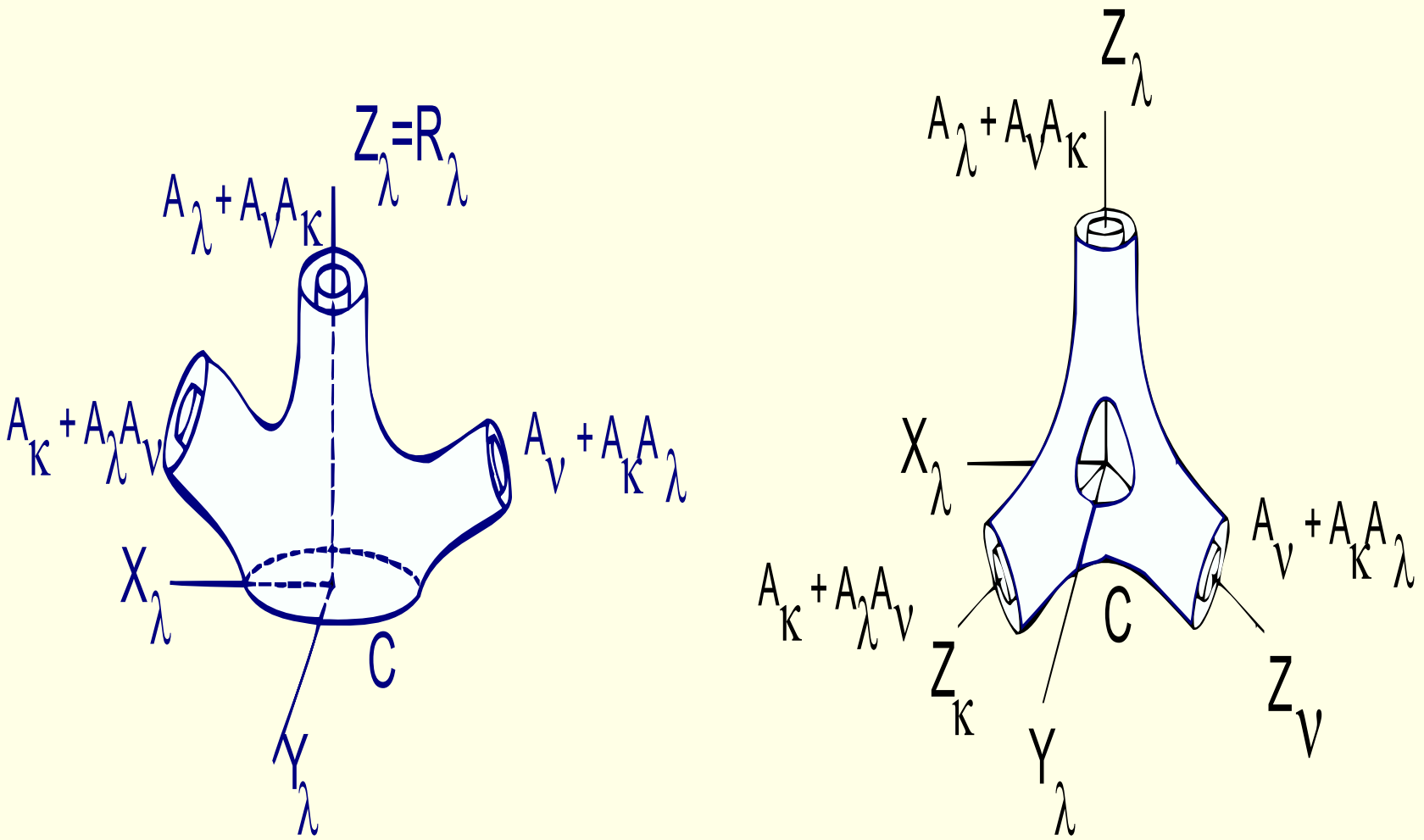


Figure 2: Equipotential surface for noncollinear $A_\lambda A_\nu A_\kappa$ triatomic system in spherical polar coordinates. a) $\rho = (R_\lambda^2 + r_\lambda^2)^{1/2}, \eta_\lambda = \tan^{-1}(r_\lambda / R_\lambda)$ and γ_λ, b) $\rho = (R_\lambda^2 + r_\lambda^2)^{1/2}, \omega_\lambda = 2\tan^{-1}(r_\lambda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

Johnson and others:
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

$$\mathbf{A} = \frac{1}{2}(\mathbf{r} \times \mathbf{R}). \tag{9}$$

internal coordinates ρ, θ and ϕ:

$$\rho^2 = |\mathbf{r}|^2 + |\mathbf{R}|^2, \qquad \cos\theta = 4|\mathbf{A}|/\rho^2 \tag{10}$$

$$\cos\phi_k = 2(\mathbf{r}_k \cdot \mathbf{R}_k)/(\rho^2 \sin\theta), \tag{11}$$

ϕ: depends on k, the index of the particular set of Jacobi coordinates

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

distance between the particles:

$$|\mathbf{x}_j - \mathbf{x}_i| = d_k \rho [1 + \sin\theta \sin\phi_k]^{\frac{1}{2}}, \quad d_k = \sqrt{(1 - m_k/M) m_k/\mu} \tag{12}$$

$$\mu = m_1 m_2 m_3 / M, \quad M = m_1 + m_2 + m_3. \tag{13}$$

volume element:

$$d^6 v = \frac{1}{8} \rho^5 d\rho \sin\theta \cos\theta d\theta d\phi d\omega \tag{14}$$

$$d\omega = d\alpha \sin\beta d\beta d\gamma \tag{15}$$

$$\begin{aligned} &0 \leq \rho \leq \infty, 0 \leq \theta \leq \frac{\pi}{2}, 0 \leq \phi \leq 4\pi, \\ &0 \leq \alpha \leq 2\pi, 0 \leq \beta \leq \pi, 0 \leq \gamma \leq 2\pi. \end{aligned} \tag{16}$$

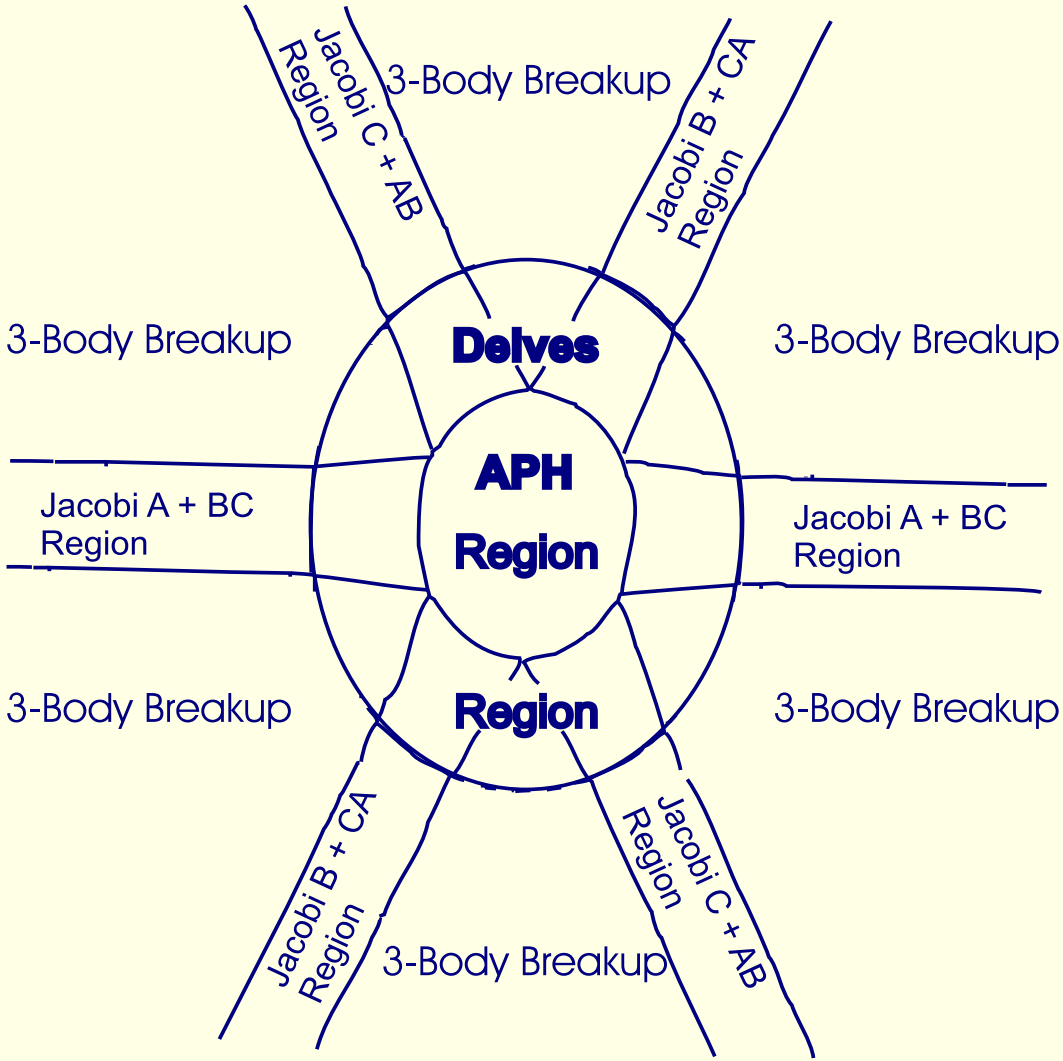


Figure 3: Schematic showing the two hyperspherical regions (APH and Delves) and the Jacobi region. There are six arrangement channels as a result of covering the configuration space twice.

Pack, Parker and coworkers:

- use of 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

- 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 coordinate components (S_τ,$\widehat{S}_\tau$,s_τ,$\widehat{s}_\tau$) are the space-fixed (SF) Jacobi coordinates, whereas the coordinates (S_τ, s_τ, Θ_τ, α_τ, β_τ, γ_τ) are the body-fixed (BF) Jacobi coordinates

– the angles $\widehat{S}_\tau$ and $\widehat{s}_\tau$ are the two sets of polar and azimuthal angles associated with the vectors $\mathbf{S}_\tau$ and $\mathbf{s}_\tau$ respectively, and the angle between these vectors is

$$\theta_\tau = \cos^{-1}[\frac{\mathbf{S}_\tau \cdot \mathbf{s}_\tau}{S_\tau \; s_\tau}]. \tag{17}$$

– 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 $\mathbf{S}_\tau$ or $\mathbf{s}_\tau$ depending on the relative masses of the particles involved. Delves hyperspherical coordinates for arrangement τ are:

$$\rho = (S_\tau^2 + s_\tau^2)^{\frac{1}{2}} \quad \text{and} \quad \theta_{D\tau} = \tan^{-1}(\frac{s_\tau}{S_\tau}). \tag{18}$$

In addition to ρ and $\theta_{D\tau}$, the four SF or four BF angles of the arrangement complete the Delves coordinate set.

APH coordinates:

$$\rho = (S_\tau^2 + s_\tau^2)^{\frac{1}{2}} \tag{19}$$

$$\tan\theta = \frac{[(S_\tau^2 - s_\tau^2)^2 + (2\mathbf{S}_\tau \cdot \mathbf{s}_\tau)^{\mathbf{2}}]^{\frac{\mathbf{1}}{\mathbf{2}}}}{2S_\tau s_\tau \sin\Theta_\tau} \tag{20}$$

$$\sin(2\chi_\tau) = \frac{2\mathbf{S}_\tau \cdot \mathbf{s}_\tau}{[(S_\tau^2 - s_\tau^2)^2 + (2\mathbf{S}_\tau \cdot \mathbf{s}_\tau)^{\mathbf{2}}]^{\frac{\mathbf{1}}{\mathbf{2}}}} \tag{21}$$

– to complete the APH coordinate specification one chooses the 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