Three-body dynamics using generalized angular momentum states

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ABSTRACT - The generalized angular momentum approach has successfully contributed to the understanding of many of the most interesting features of the three-body quantum mechanical problem and in particular of reactive scattering. A three-atom system possesses nine degrees of freedom, but the three which describe over-all translations can be eliminated because of centre-of-mass conservation. Accordingly, the complete description of the dynamics of three atoms requires the treatment of six coordinates.

In the hyperspherical coordinate system, this is accomplished by solving a quantization problem adiabatically in the hyperradius, treated as a quasi-separable variable, and next integrating a set of coupled-channel equations. The hyperradius acts as a natural reaction coordinate, at small values it describes the interaction among the three atoms while asymptotically it correlates with the reactant and product channels. The other variables are five angles which span a five-dimensional sphere.

Over the last two decades, a rigorous formalism for solving three-body scattering problems has been developed in our laboratory [1-2]. The mathematical tools are polynomials of a discrete variable properly weighted and normalized to be orthogonal on a lattice of points. In the application to atom-diatomic molecule chemical reactions, these quantities, which are generalized 3j symbols representing the discrete analogues of hyperspherical harmonics [1], i.e. the eigenfunctions of a generalized angular momentum operator, are used as basis set to expand the unknown wave functions of the triatomic system. Quantum scattering calculations using a computer code implementing this formalism (hyperquantization algorithm) have been carried out on benchmark reactions, see Ref.[3] and references therein for the F+H2 reaction and its isotopic variants.

In this presentation, the generalized angular momentum approach to quantum reactive scattering theory is reviewed, with emphasis placed on three-atom reactions. Some results will be also shown.

References

[1] V. Aquilanti and S. Cavalli, Few Body Systems Suppl. 6 (1992) 573.

[2] V. Aquilanti, S. Cavalli and D. De Fazio, J. Chem. Phys. 109 (1998) 3792; ibid J. Chem. Phys. 109 (1998) 3805.

[3] D. De Fazio, V. Aquilanti, S. Cavalli, A. Aguilar and J.M. Lucas, J. Chem. Phys. 129 (2008) 064303.

FIRST PRICIPLES THEORY OF CHEMICAL REACTIONS

In collision dynamics calculations use is made of the Born-Oppenheimer principle

1. the Schrödinger equation for electrons at fixed nuclei is solved for a large number of nuclear geometries and then the potential energy surface (PES) can be mapped as a function of internal coordinates describing the position of nuclei

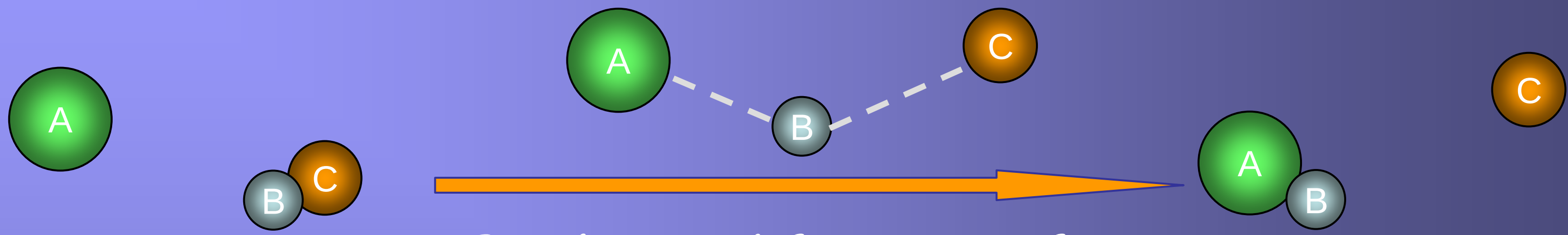
2. the Schrödinger equation (or classical equations) for the motion of nuclei controlled by the PES is solved (Scattering matrix)

3. cross sections and rate constants

Scattering calculations

- Quasi-classical trajectories calculations
- Semi-classical techniques
- Mixed quantum-classical methods
- Quantum scattering calculations :
  - Time dependent wave packet theories
  - Time independent Schrödinger equation
    - Variational methods
    - *Hyperspherical coordinate approach*

THREE-ATOM REACTIONS

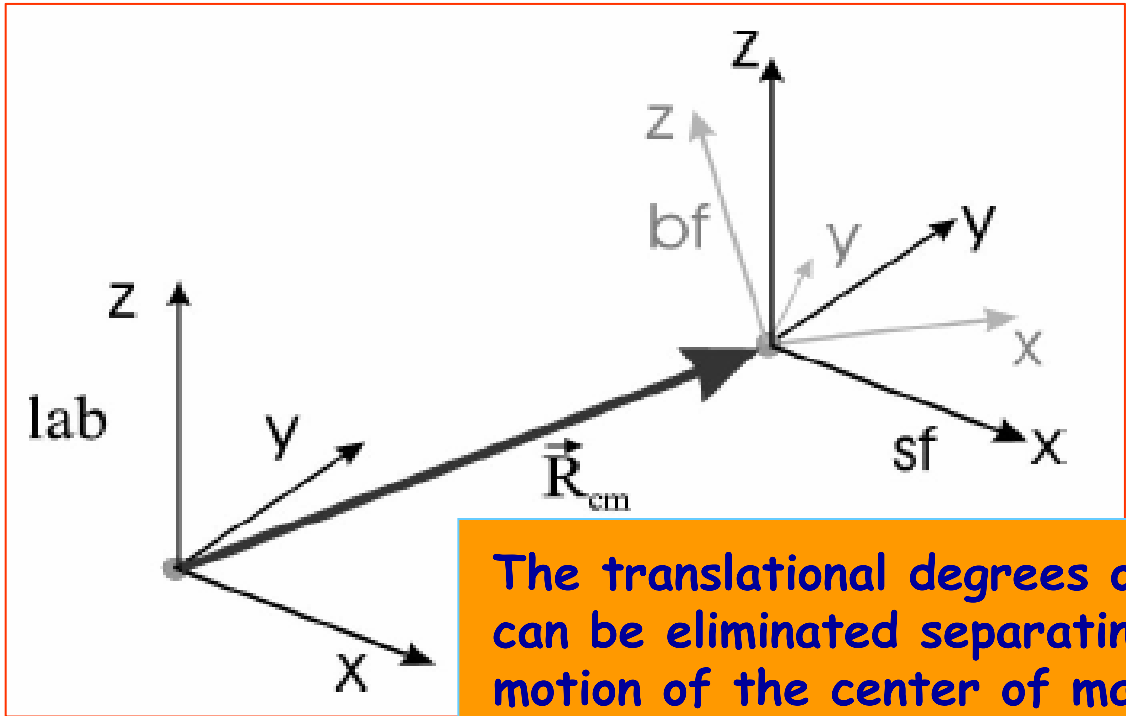


Breaking and formation of one chemical bond take place during the collision

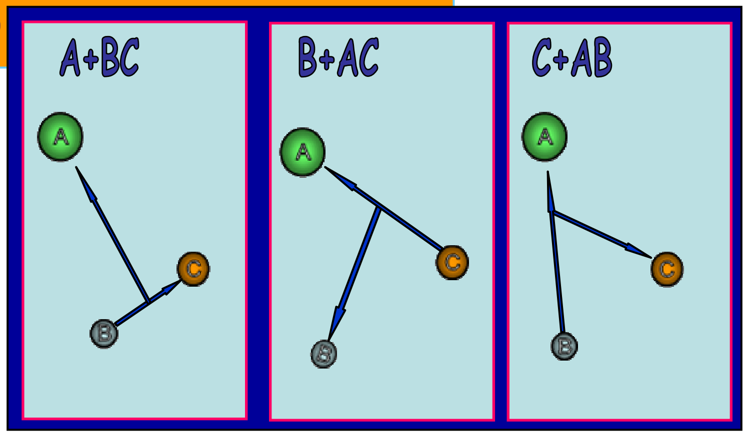
A three-atom system posses nine degrees of freedom

- three translations
- three vibrations
- three rotations

From Laboratory Frame to Space Frame

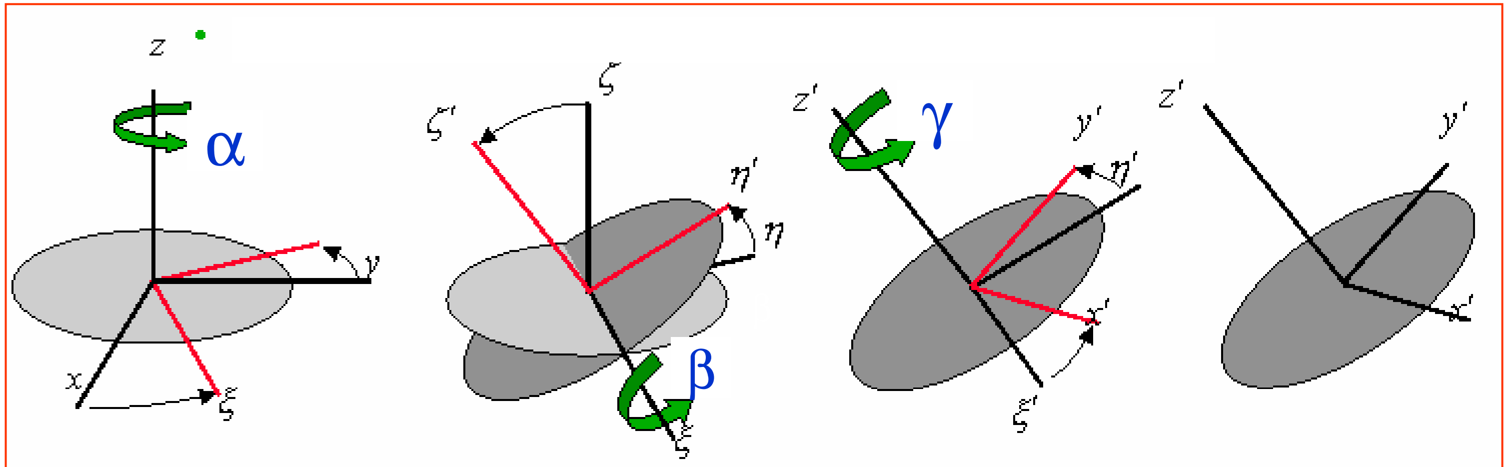


The translational degrees of freedom can be eliminated separating out the motion of the center of mass (e.g. JACOBI VECTORS)



Of the remaining six degrees of freedom

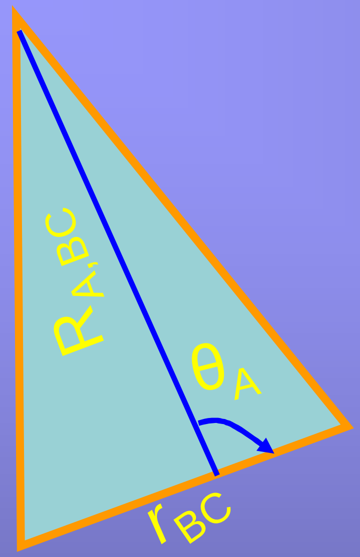
three describe the evolution of total angular momentum with respect to a body-fixed reference frame, *e.g.* the inertia principal axes frame



ORIENTATIONAL COORDINATES
α, β AND γ ARE THE EULER ANGLES

and the other three describe the shape of the triangle formed by the three atoms

" DEMOCRATIC " HYPERSPHERICAL COORDINATES

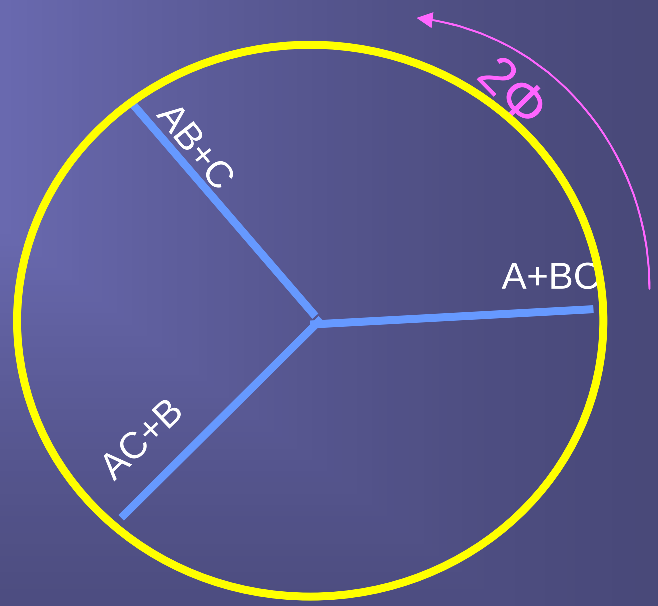


$$\rho = \sqrt{r_{BC}^2 + R_{A,BC}^2} = \sqrt{r_{AC}^2 + R_{B,AC}^2} = \sqrt{r_{AB}^2 + R_{C,AB}^2}$$

$$\sin 2\Theta = \frac{2}{\rho^2} R_{A,BC} r_{BC} \sin\theta_A = \frac{2}{\rho^2} R_{B,AC} r_{AC} \sin\theta_B = \frac{2}{\rho^2} R_{C,AB} r_{AB} \sin\theta_C$$

$$2\Phi_A = \arctan\left(\frac{2R_{A,BC} r_{BC} \sin\theta_A}{R_{A,BC}^2 - r_{BC}^2} \right)$$

- ❖the hyperradius ρ gives the size of the triangle
- ❖the angle Φ interpolates between the different sets of Jacobi coordinates
- ❖the angle Θ is related to the area of the triangle



HYPERSPHERICAL COORDINATE APPROCH TO REACTIVE SCATTERING

TIME-INDEPENDENT SCHRÖDINGER EQUATION

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V \right)\Psi = E\Psi$$

POTENTIAL ENERGY SURFACE (PES). IT DEPENDS ON THE INTERNAL COORDINATES ρ, Θ AND Φ

$$\nabla^2 = \rho^{-5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} + \frac{\Lambda^2(\omega_5)}{\rho^2}$$

LAPLACIAN OF A SIX-DIMENSIONAL SPACE

PARTITIONING OF THE GRAND-ORBIATAL ANGULAR MOMENTUM

$$\Lambda^2 = \Lambda_\Omega^2 + R$$

Ω IS THE PROJECTION OF J ON THE LEAST INERTIA AXIS

GRAND-ORBITAL ANGULAR MOMENTUM

$$\Lambda_\Omega^2 = \frac{1}{\sin 4\Theta}\frac{\partial}{\partial\Theta}\sin 4\Theta\frac{\partial}{\partial\Theta} + \frac{1}{\cos^2 2\Theta}\frac{\partial^2}{\partial\Phi^2} - \frac{4\Omega^2}{\sin^2 2\Theta}$$

ROTATIONAL COUPLING

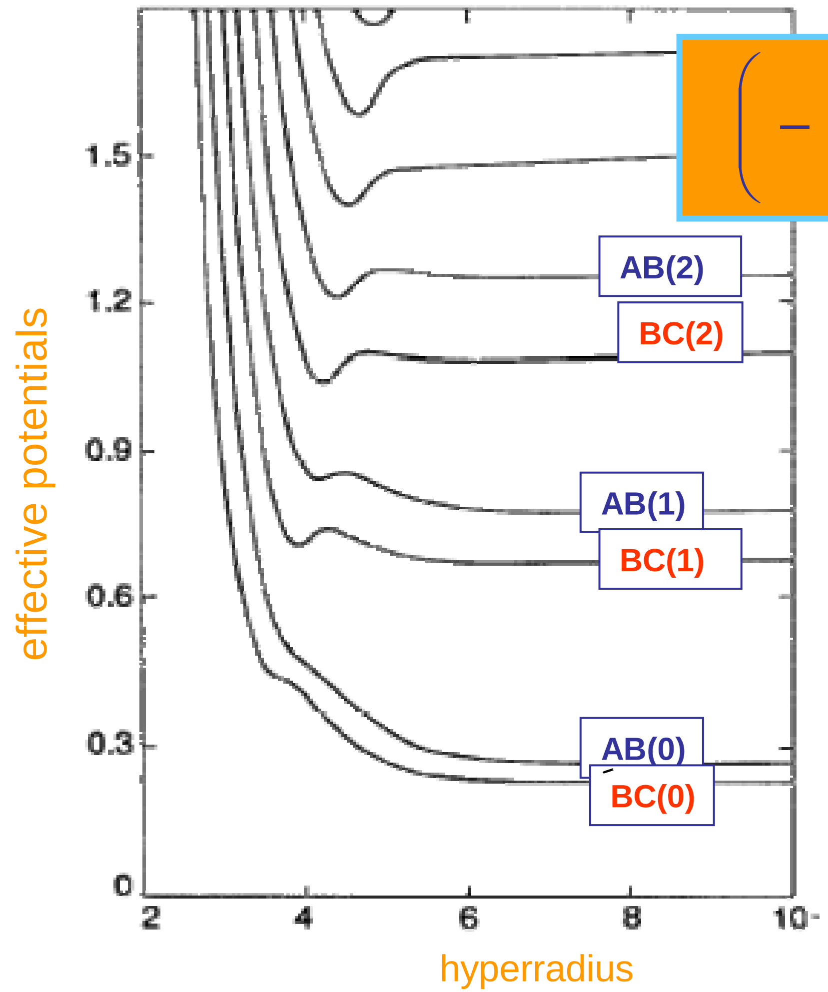
CORIOLIS COUPLING

$$R = \frac{\hat{J}_y^2}{\cos^2 2\Theta} + \frac{\hat{J}_x^2 + \Omega^2}{\cos^2 \Theta} + \frac{2i\sin 2\Theta}{\cos^2 2\Theta}\hat{J}_y\frac{\partial}{\partial\Phi}$$

Solving the time-independent Schrodinger equation in two stages

Quantization problem at fixed ρ (step 1)

$$\left(-\frac{\hbar^2}{2\mu\rho^2}\Lambda^2 + V \right)\varphi_n = \varepsilon_n \varphi_n$$



Effective potentials for multi-channel scattering as a function of ρ (step 2). When ρ→∞ they correlate with reactants' and products' rotation-vibration states.

The "Perugia" road to hyper-spherical effective potentials

$$\left\{-\frac{\hbar^2}{2\mu\rho^2}\left[\frac{1}{\sin 4\Theta}\frac{\partial}{\partial\Theta}\sin 4\Theta\frac{\partial}{\partial\Theta}+\frac{1}{\cos^2 2\Theta}\frac{\partial^2}{\partial\Phi^2}-\frac{4J_z^2}{\sin^2 2\Theta}\right]+V(\rho,\Theta,\Phi)\right\}\varphi_n=\varepsilon_n\varphi_n$$

HYPERSPHERICAL HARMONIC EXPANSION

$$\varphi_n=\sum_{\lambda,\sigma}t^{\Omega}_{n\lambda\sigma}(\rho)Y_{\lambda\sigma\Omega}(\varpi)$$

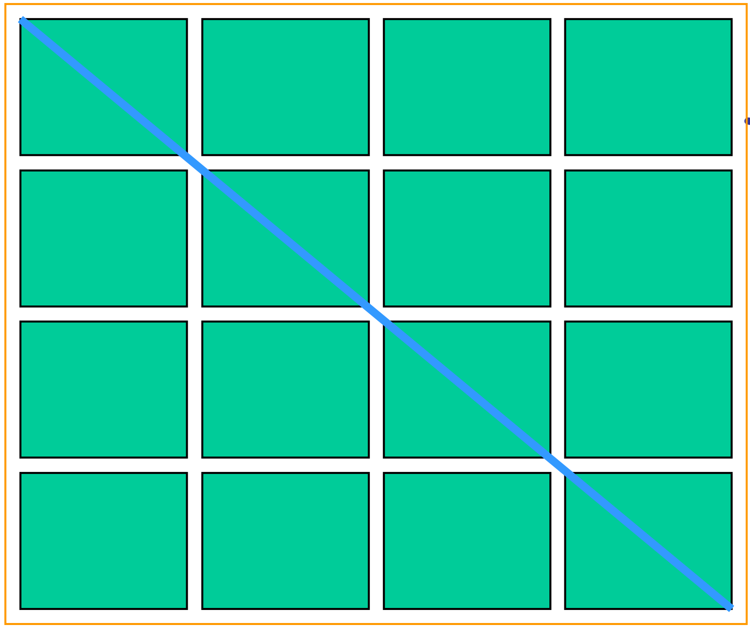
Wigner D-function

$$D^{\lambda/4}_{\frac{\sigma-2\Omega}{4},\frac{\sigma+2\Omega}{4}}(\Phi+\gamma,\Theta,\Phi-\gamma)$$

EIGENVALUE PROBLEM TO BE SOLVED AT EACH Ω

$$\left\{\sum_{\lambda',\sigma'}\frac{\hbar^2}{2\mu\rho^2}\frac{\lambda}{2}\left(\frac{\lambda}{2}+2\right)\delta_{\lambda\lambda'}\delta_{\sigma\sigma'}+V_{\lambda\sigma,\lambda'\sigma'}(\rho)\right\}t_{\lambda'\sigma'}=\varepsilon_n t_{\lambda\sigma}$$

THE HAMILTONIAN MATRIX:



$$K_{\lambda\sigma,\lambda\sigma} = \frac{\hbar^2}{2\mu\rho^2}\frac{\lambda}{2}\left(\frac{\lambda}{2}+2\right)$$

The kinetic energy matrix is diagonal

$$(K+V)T = T\varepsilon$$

The potential energy matrix is full

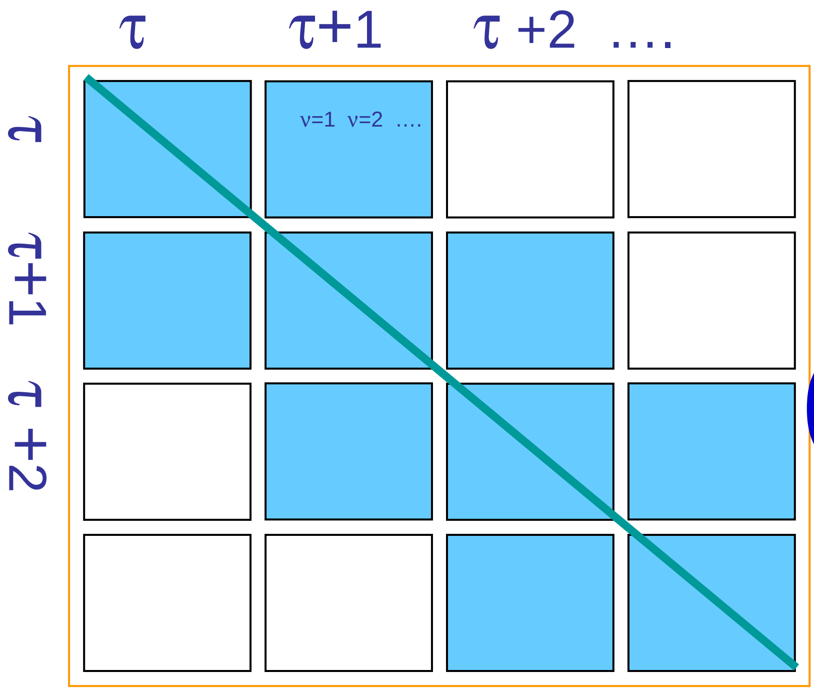
$$V_{\lambda\sigma,\lambda'\sigma'} = \iint\limits_{\Theta,\Phi} D^{\lambda/4}_{\frac{\sigma-2\Omega}{4},\frac{\sigma+2\Omega}{4}} V(\rho,\Theta,\Phi) D^{\lambda'/4}_{\frac{\sigma'-2\Omega}{4},\frac{\sigma'+2\Omega}{4}} d\cos 4\Theta \, d2\Phi$$

Orthogonal transformation

$$t^{\Omega}_{n,\lambda\sigma}(\rho) = \sum_{\tau\nu} G^{\lambda\sigma\Omega}_{\tau\nu} t_{n,\tau\nu\Omega}(\rho)$$

Discrete analogue of Wigner D-function

Representation of the Hamiltonian matrix in the new basis



The kinetic energy matrix is block-tridiagonal

$$(K+V)T = T\varepsilon$$

The potential matrix is diagonal

Explicit expression of the coefficients

$$G_{\tau\nu}^{\lambda\sigma} = (-)^{\frac{I}{2}+\nu-\frac{\lambda-\sigma}{2}} \sqrt{\frac{I+1}{N}} \begin{pmatrix} \frac{I}{2}+\frac{\Omega}{2} & \frac{I}{2}+\frac{\sigma}{4} & \frac{\lambda}{4} \\ -\tau-\frac{\Omega}{2} & \tau-\frac{\sigma}{4} & \frac{\Omega}{2}+\frac{\sigma}{4} \end{pmatrix} \exp(i\pi\sigma\nu/N)$$

Generalized 3-j symbol

or Hahn polynomials

$$\left(\frac{\lambda}{2}+1\right)^{1/2} \begin{pmatrix} \frac{I}{2}+\frac{\Omega}{2} & \frac{I}{2}+\frac{\sigma}{4} & \frac{\lambda}{4} \\ -\tau-\frac{\Omega}{2} & \tau-\frac{\sigma}{4} & \frac{\Omega}{2}+\frac{\sigma}{4} \end{pmatrix} = \exp\left[-\frac{i\pi(I+2\tau+2\Omega-\lambda)}{2}\right] Q^{\Omega,\frac{\sigma}{2},I}_{\frac{\lambda-\sigma-2\Omega}{4}}(\tau)$$

Hahn polynomials are classical orthogonal polynomials of a discrete variable

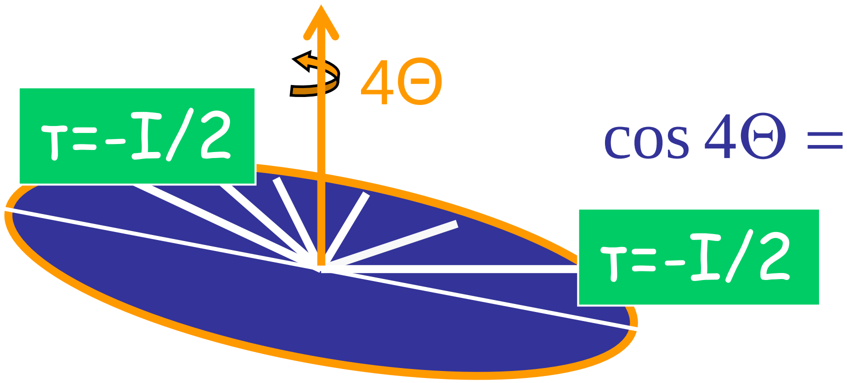
$$\lim_{I\to\infty}\left(\frac{I+1}{2}\right) Q_n^{\alpha\beta I}(\tau) = \mathrm{N}_{n\alpha\beta} \cos^{\beta}\frac{\vartheta}{2} \sin^{\alpha}\frac{\vartheta}{2} P_n^{\alpha\beta}(\cos\vartheta)$$

Hahn polynomials

Jacobi polynomials

$$\cos\vartheta = \frac{-2\tau}{I+1}$$

The indices τ and ν labeling the elements of the H-matrix are discrete variables



$$\cos 4\Theta = \frac{-2\tau}{I+1} \quad ; \quad -\frac{I}{2} \le \tau \le \frac{I}{2}$$

$$2\Phi = \frac{2\pi\nu}{N} \quad ; \quad \nu = 1, 2, \ldots, N$$

The grid points are evenly spaced in cos4Θ and 2Φ

Properties of Hahn polynomial

The Hahn polynomials are solutions of a difference equation

$$C(\xi)Q_n^{\alpha\beta X}(\xi-1) + D(\xi)Q_n^{\alpha\beta X}(\xi) +$$

$$+ C(\xi+1)Q_n^{\alpha\beta X}(\xi+1) = 0$$

and are orthogonal with respect to the discrete variable and to the degree of the polynomial

$$\sum_{\xi=0}^{X} Q_n^{\alpha\beta X}(\xi)Q_{n'}^{\alpha\beta X}(\xi) = \delta_{nn'}$$ Orthogonality relation

$$\sum_{n=0}^{X} Q_n^{\alpha\beta X}(\xi)Q_n^{\alpha\beta X}(\xi') = \delta_{\xi\xi'}$$ Dual orthogonality relation

The elements of the Hamiltonian H=K+V matrix: some details

$$V_{\tau\nu,\tau\nu} = V(\rho, \Theta_\tau, \Phi_\nu)$$

values of the potential energy surface at the grid points

$$\Theta_\tau = \frac{\arccos\left(-\tau/\left(\frac{I}{2}+\frac{1}{2}\right)\right)}{4} \; ; \quad -\frac{I}{2} \le \tau \le \frac{I}{2}$$

$$2\Phi_\nu = \frac{2\pi\nu}{N} \; ; \quad \nu = 1, 2, \ldots, N$$

$$K_{\tau\nu,\tau'\nu'} = \frac{1}{2\mu\rho^2} \sum_{\lambda,\sigma} G_{\tau\nu}^{\lambda\sigma\Omega} \frac{\lambda}{2}\left(\frac{\lambda}{2}+2\right) G_{\tau'\nu'}^{\lambda\sigma\Omega *}$$

the sum over λ can be performed analytically and the result is a tri-diagonal matrix with respect to the discrete variables τ

THE SCATTERING MATRIX

The S-matrix element $S_{nn'}(E,J)$ is the fundamental quantity linking the initial state n to a final state n' and it is related to the transition probability

$$P^J_{nn'}(E) = \left| S^J_{nn'}(E) \right|^2$$

Once the transition probabilities are known, the calculation of state specific reaction differential cross sections, integral cross sections and rate constants is straightforward.

Second part

Quantum resonance effects in Reaction dynamics

Definition of resonance

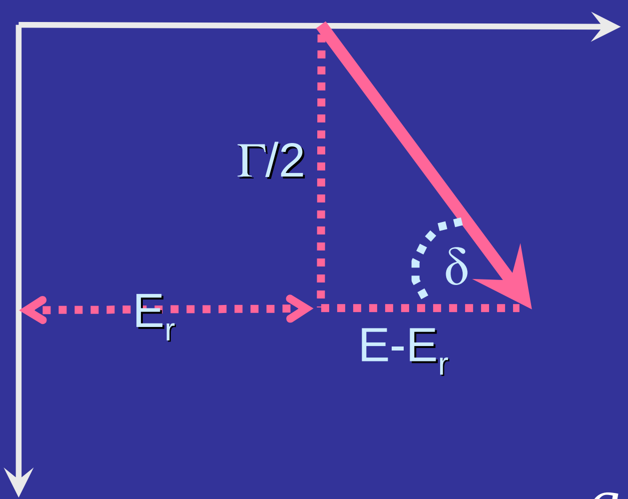
''RESONANCES ARE OBSERVABLE, ENERGY-LOCALIZED MANIFESTATIONS OF POLES OF THE SCATTERING MATRIX AT COMPLEX ENERGIES''

Width → Γ

$$z = E_r - i\frac{\Gamma}{2}$$

Position → E_r

$$lifetime \quad \tau = \hbar / \Gamma$$



The finite lifetime can manifest itself in a time-delay for scattering phenomenon relative to the free particle motion in the absence of a potential and in rapid variations in cross sections and reaction probabilities

$$q = 2\hbar \frac{\partial \delta}{\partial E} = \hbar \frac{\Gamma}{(E - E_r)^2 + (\Gamma / 2)^2}$$

Smith time-delay formalism

From the scattering matrix Smith defined the collision time-delay matrix

$$Q^J(E) = -i\hbar S^{J+} \frac{dS^J}{dE}$$

$Q_{vj,vj}$ is the average delay time of the collision in the initial state *vj*

$$q = T \; Q^J(E) T^+$$

q_α is the average delay time of the collision in the compound state α Eigenvalues provide the resonance position and lifetime

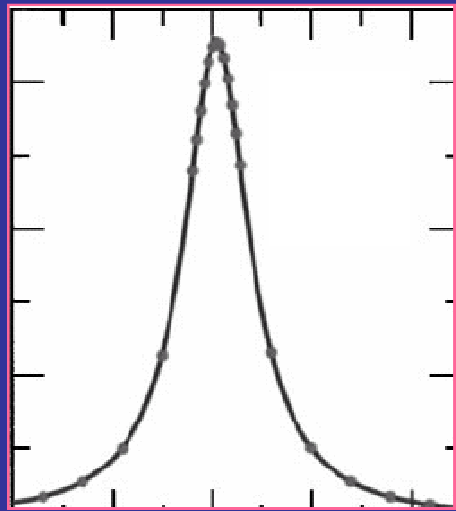
$$p_{Jvj} = \sum_l \left| t_{vjl} \right|^2$$

Eigenvectors provide the probability for the decay into a channel *v, j*

F.T. Smith, Phys. Rev. 118(1960)349

Eigen-lifetime analysis of time-delay matrix

AT AN ISOLATED RESONANCE ONE EIGENVALUE OF THE Q-MATRIX IS MUCH LARGER THAN THE OTHERS AND SHOWS A LORENTZIAN LIKE PROFILE

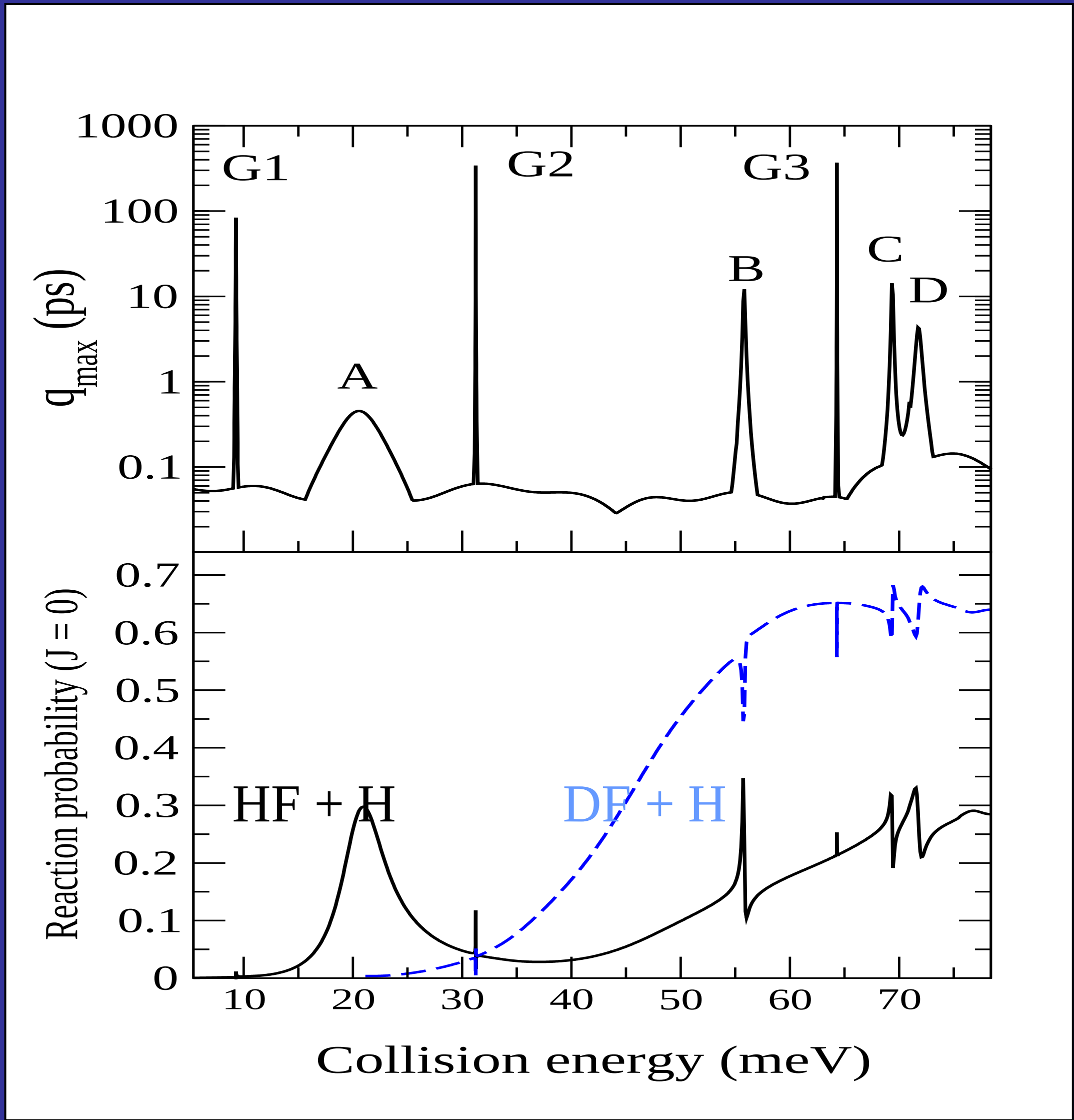


FITTING THE LARGEST EIGEN-LIFETIME

$$q_{\max} \approx \hbar \frac{\Gamma}{(E - E_r)^2 + \frac{\Gamma^2}{4}} + q_0$$

E_r is the resonance position and Γ is the width

Reaction probability and eigen-lifetime spectrum at J=0 for the F+HD reaction



J.Phys.Chem. A 111 (2007) 12538

✓A – Collinear Barrier

✓B,C,D – Exit Channel

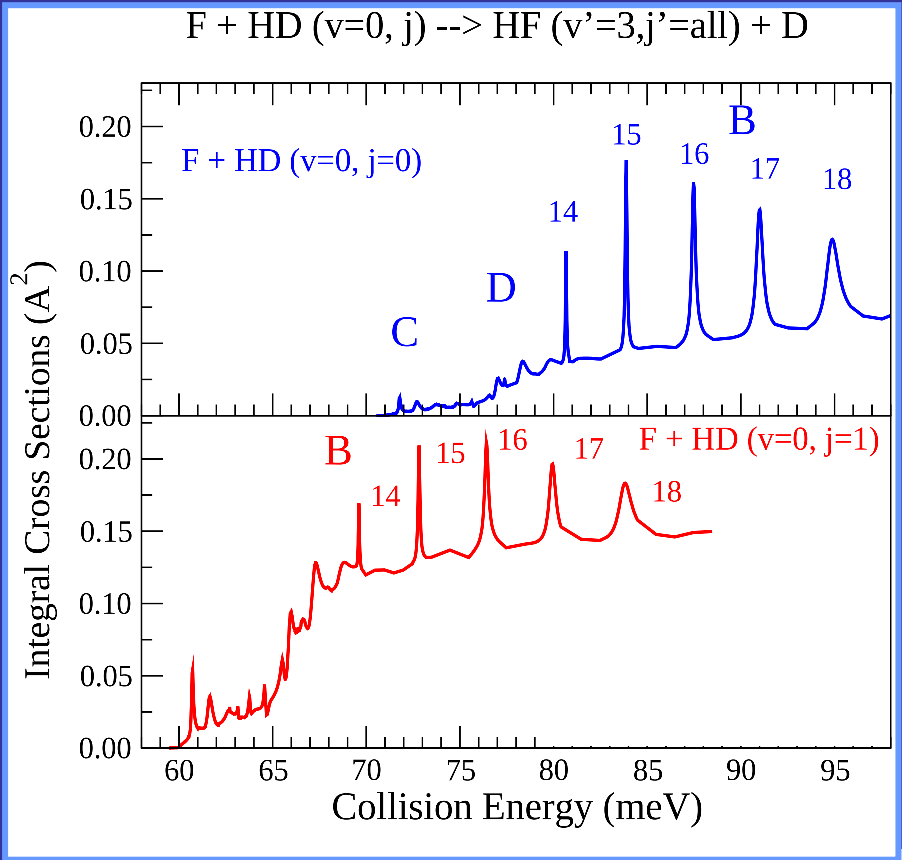
✓G1-G3 – Entrance Channel

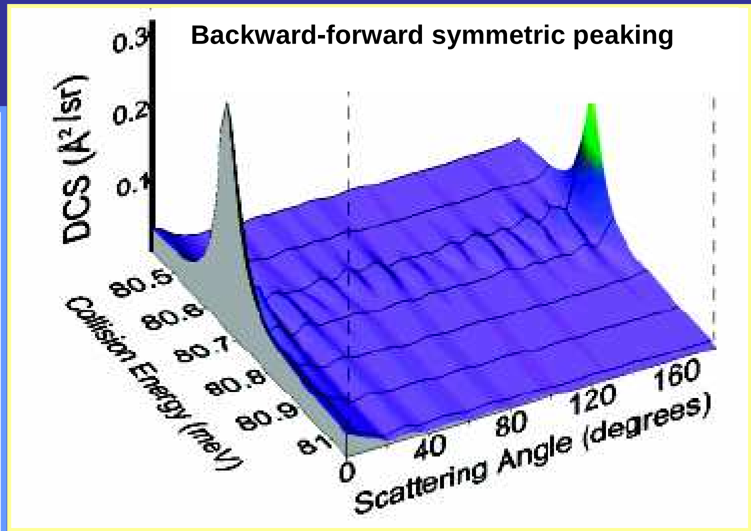
Resonance A has been studied in great detail, see: R.T. Skodje et al., J. Chem. Phys. 112(2000)4536; Phys. Rev. Lett. 85(2000)1206

For resonances G_1, G_2, G_3 see: T. Takayanagi et al., J. Chem.Phys. 109 (1998) 8929

For resonances B, C, D see: T. Takayanagi , Chem. Phys. Lett. 433 (2006) 15

NARROW RESONANCE SIGNATURES:
Breit-Wigner peaks in ICS and forward backward symmetry in DCS



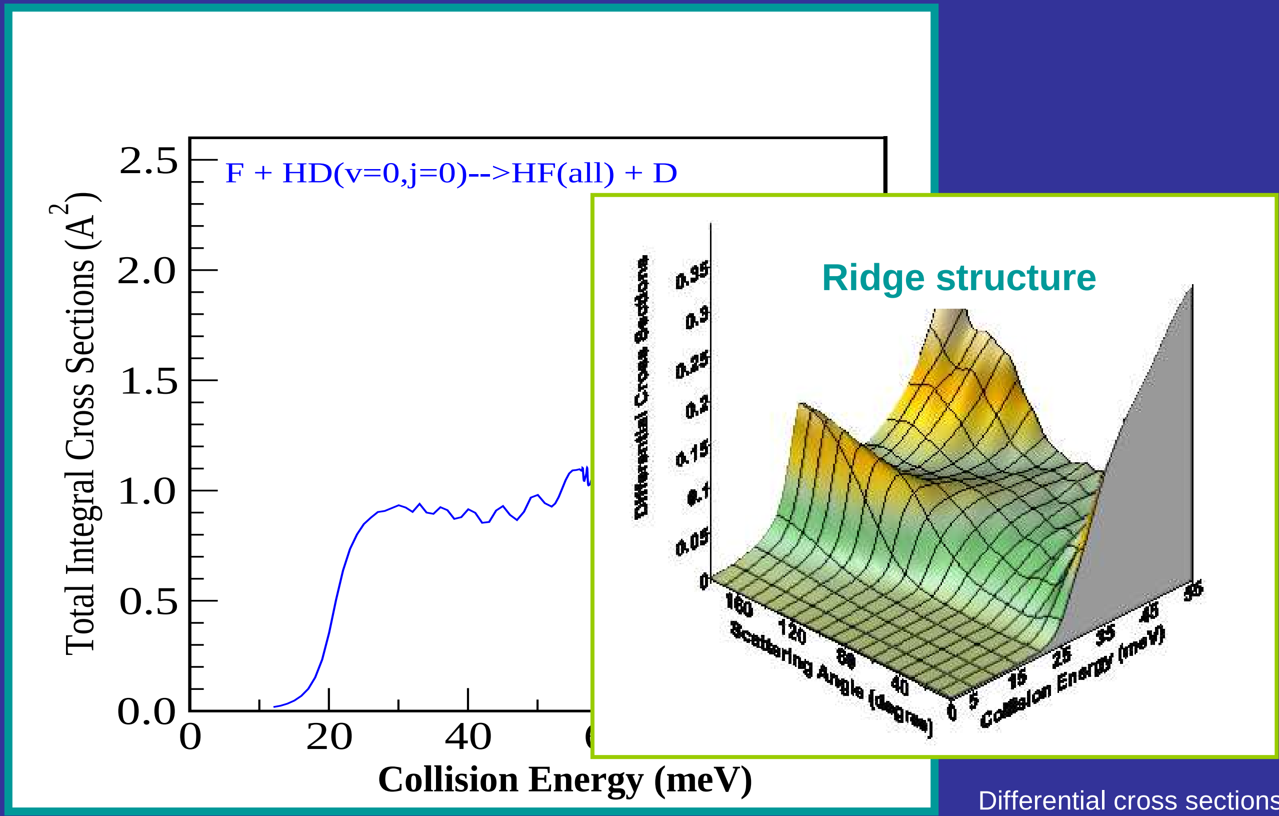


Differential cross section for the F+HD(v = 0, *j* = 0) reaction summed over all open channels of HF(v = 3). The collision energy corresponds to the resonance B at *J* = 14 in the neighborhood of the HF(v = 3, *j* = 0) threshold.

J-selected peaks are observed at the energies of resonance states B,C and D

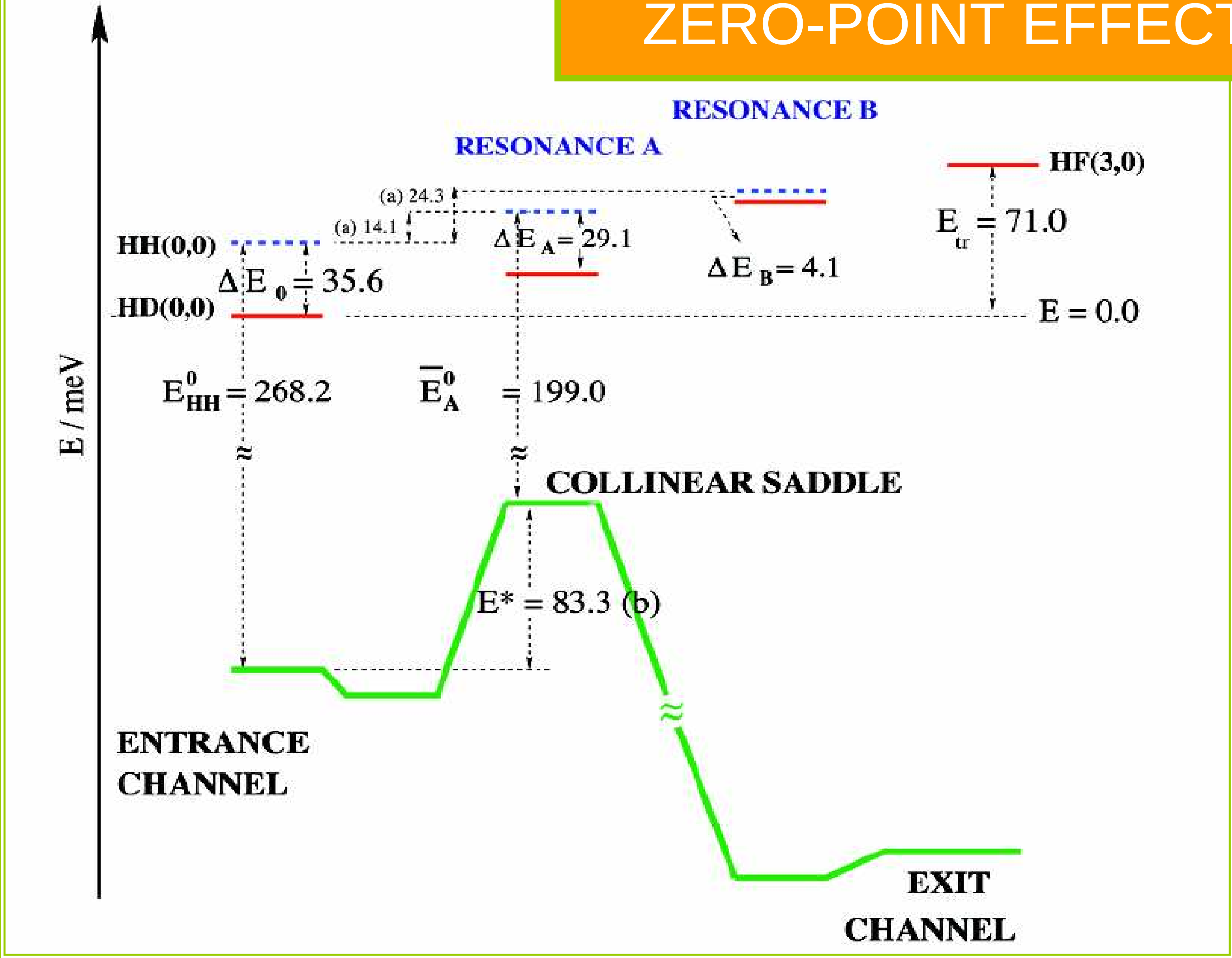
BROAD RESONANCE SIGNATURES

step-like feature in ICS and ridge like structure in DCS



Differential cross sections for the F + HD(v = 0, *j* = 0) reaction summed over all open channels of HF(v = 2)

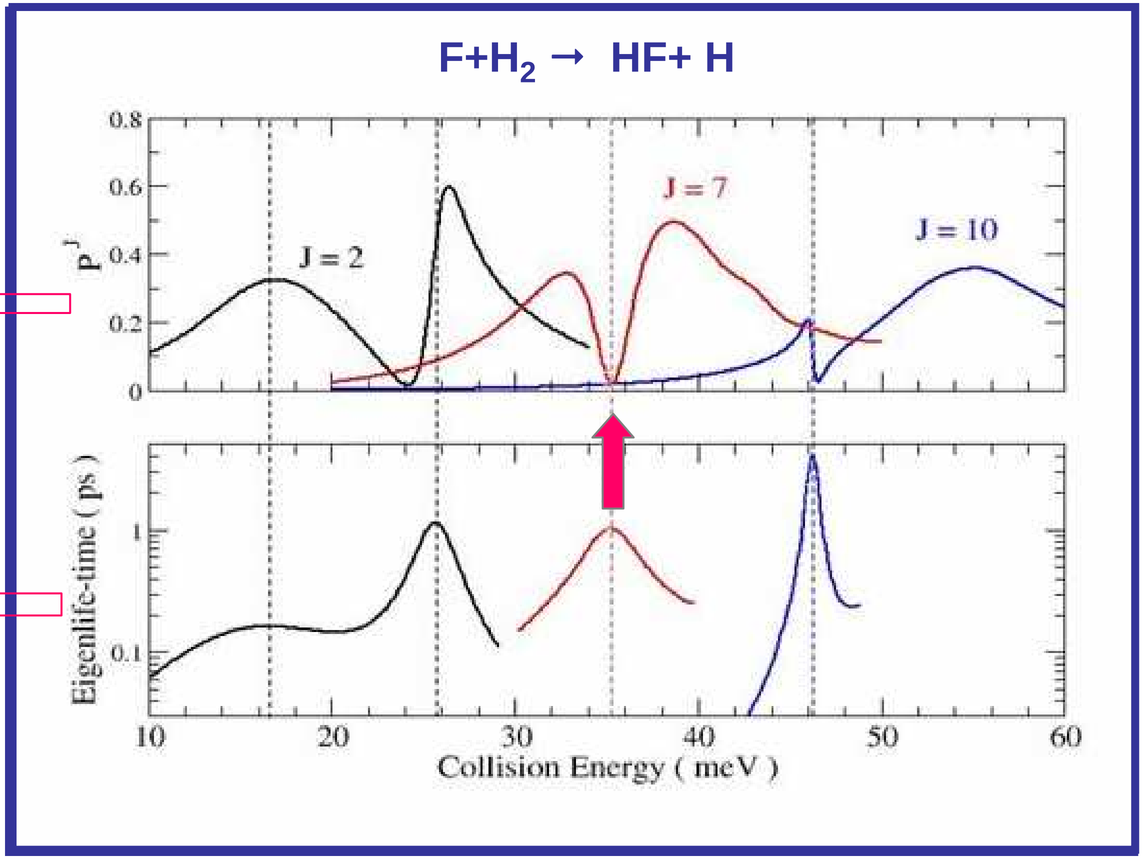
ZERO-POINT EFFECTS



ENERGY PROFILE OF THE REACTION PROBABILITY AND OF THE LARGEST EIGENVALUE OF THE COLLISION DELAY-TIME MATRIX

$$P^{J}_{nn'}(E) = \left| S^{J}_{nn'}(E) \right|^2$$

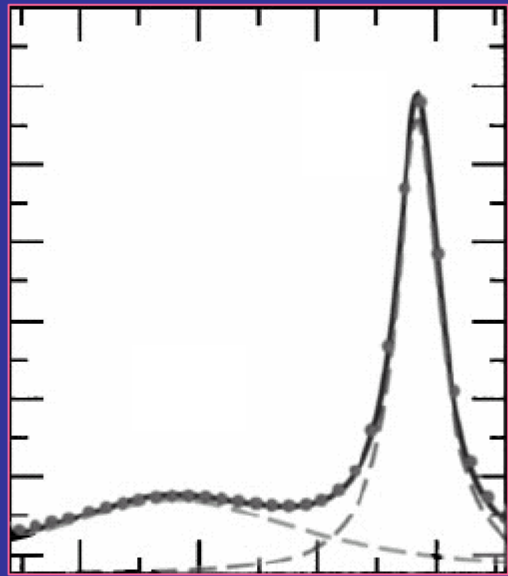
Largest eigenvalue, q_{max}, of the collision time-delay matrix



The reaction probability, in the collision energy range of 10-50 meV, exhibit two maxima separated by a minimum which, at the smallest values of the total angular momentum, are peaked near the maxima of the spectrum of q_{max}. As J increases, the two peaks get closer and the discrepancy between the maxima of $P_{nn'}$ and the maxima of q_{max} becomes more evident. At J = 7 the two features have a near specular shape but only one maximum, which is peaked where $P_{nn'}$ has a minimum, shows up in the spectrum of q_{max}.

fitting the largest eigen-lifetime

In the vicinity of two overlapping and interacting resonance states, q_{max} is fitted to the sum of two Lorentzian like profiles



E_A and E_B are the positions
Γ_A and Γ_B are the widths

$$q_{\max} \approx \hbar \left(\frac{\Gamma_A^2}{(E - E_A)^2 + \frac{\Gamma_A^2}{4}} + \frac{\Gamma_A^2}{(E - E_B)^2 + \frac{\Gamma_B^2}{4}} \right)$$

Interacting resonances

Positions and widths of A and B resonance states as a function of total angular momentum

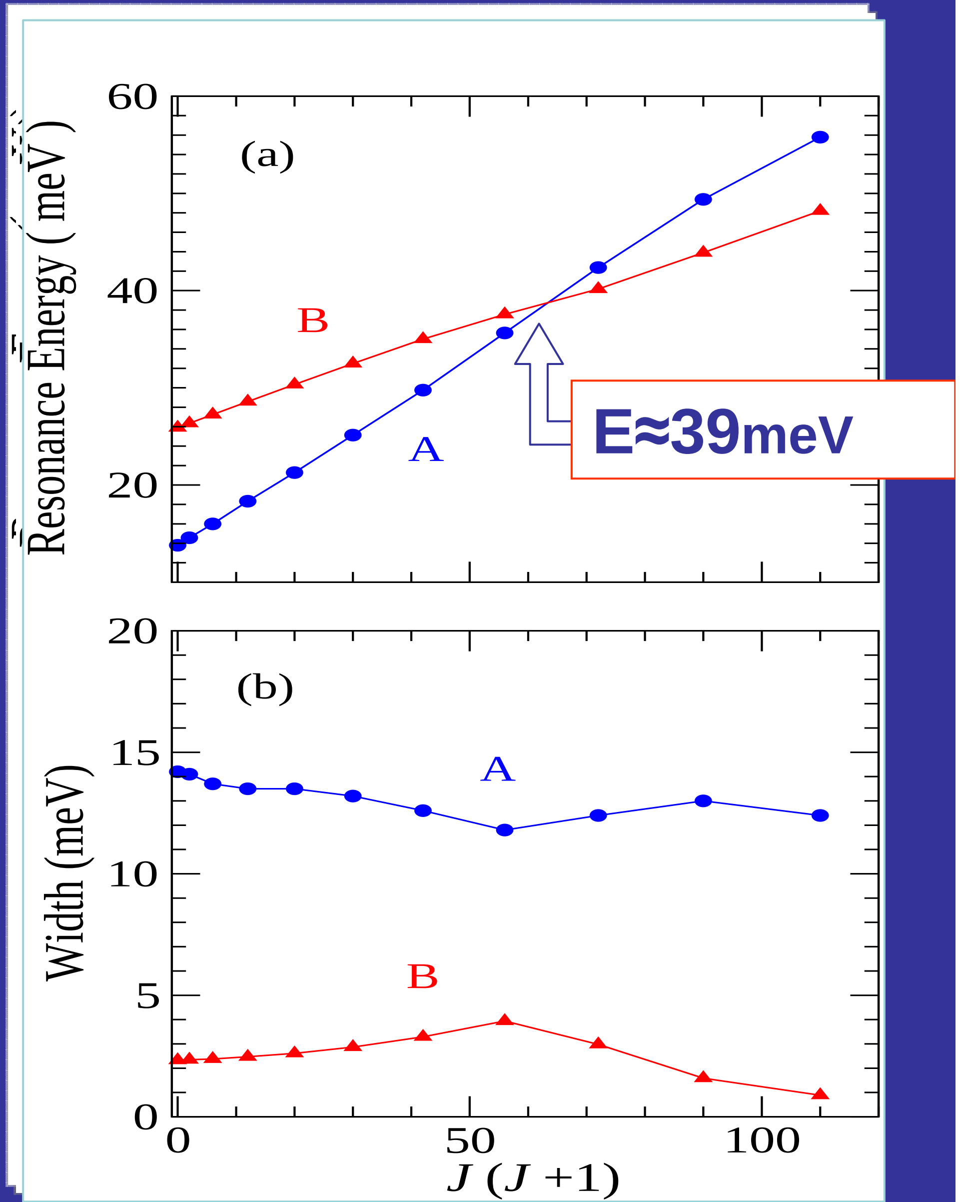
The resonance energy depend on J as a linear rigid rotator

$$E_A = E_A^{J=0} + B_A J(J+1)$$
$$E_B = E_B^{J=0} + B_B J(J+1)$$

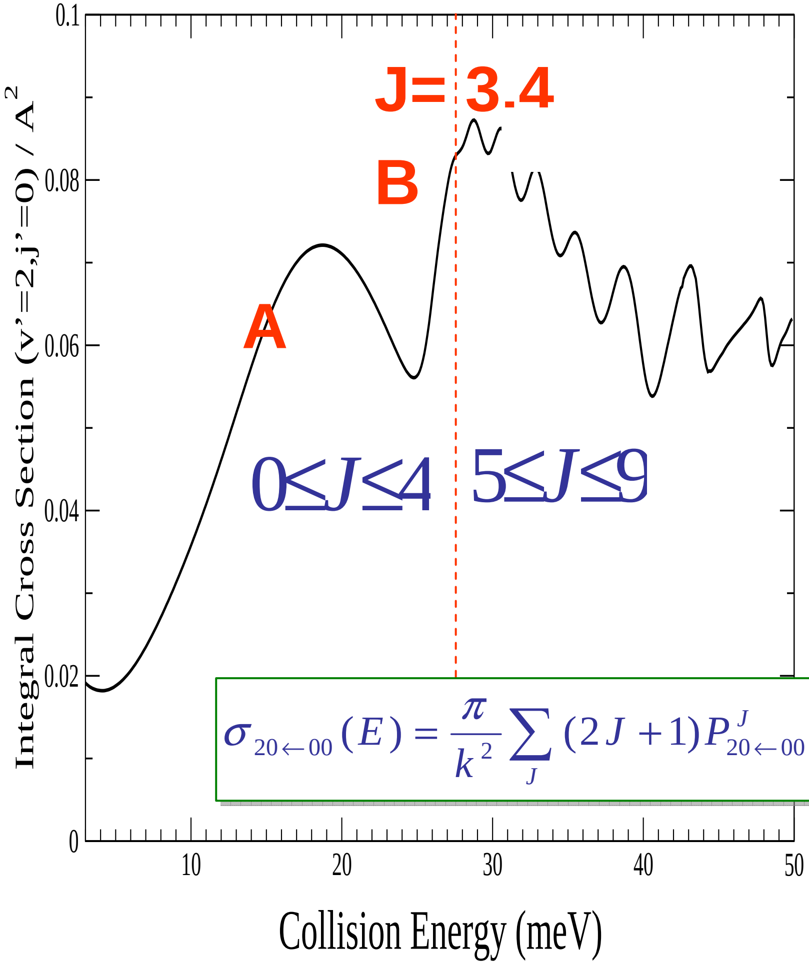
Slopes of the approximately straight lines

$B_A = 0.367$ meV

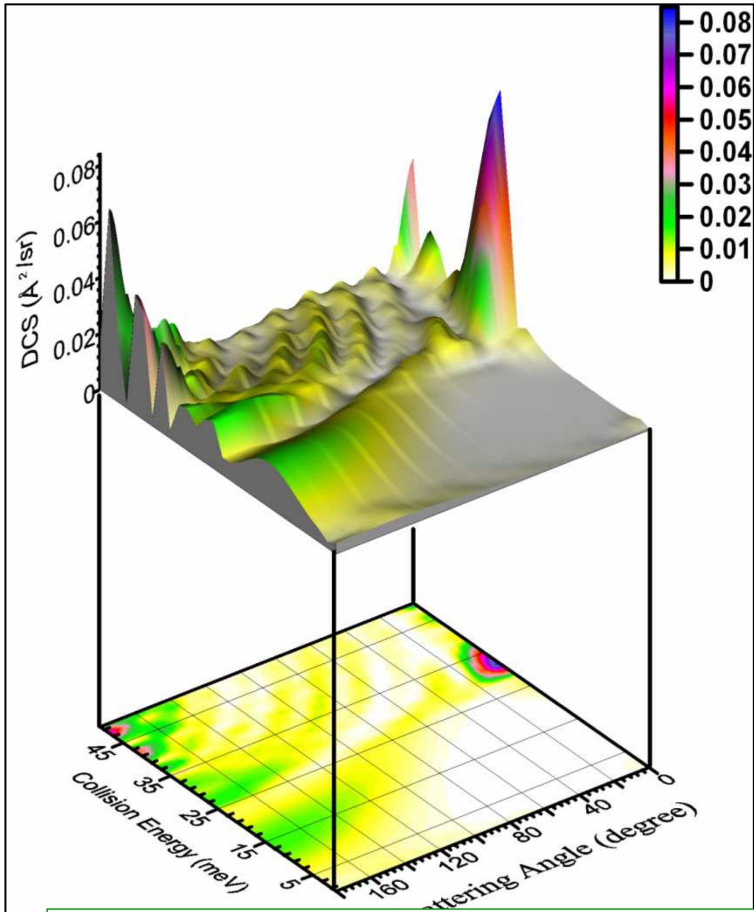
$B_B = 0.216$ meV



F+H2 (v=0, j=0) ⟶ HF(v=2, j=0) + H: quantum oscillations in the ICS and forward scattering peak in the DCS



$$\sigma_{20\leftarrow 00}(E) = \frac{\pi}{k^2}\sum_J (2J+1)P^J_{20\leftarrow 00}$$



$$\sigma_{20\leftarrow 00}(E,\vartheta) = \frac{1}{4k^2}\left|\sum_J (2J+1)P^J(\cos\vartheta)\tilde{S}^J(E)\right|^2$$

SUMMARY

- HYPERQUANTIZATION ALGORITHM

- QUANTUM SCATTERING CALCULATIONS
  - ICS, DCS, Q-matrix

- F+HD → HF+D
  - Breit-Wigner peaks in ICS (narrow van der Waals states); forward backward symmetry in DCS
  - step-like feature in ICS; ridge like structure in DCS (broad compound state)

- $F+H_2 \rightarrow HF(v=2, j=0)+H$
  - Quantum oscillations in the ICS
  - Forward scattering peak in the DCS

The End