# Quantum reactive scattering: the time - independent approach (Part II)

Ralph Jaquet

Theoretische Chemie, Universität Siegen, D-57068 Siegen, Germany

ralph.jaquet@theo.chemie.uni-siegen.de

## 1. Introduction

In the first part of this overview we discussed coordinate systems used in quantum reactive scattering and how the first numerically exact calculations for the $H + H_2$ system have been performed in the seventies.
The second part of these lecture notes is based mostly on the work of Jaquet et al. [1], Launay [2], Kouri and Hoffmann [3], and Kuppermann [163]. We will discuss in detail the two main approaches, (a) linear algebraic variational approaches using jacobi coordinates and (b) propagation methods using hyperspherical coordinates. Recent devellopmentsi computer implementations and a few applications will be mentioned briefly in the last chapters.

## 2. Linear algebraic variational approach with Jacobi coordinates versus propagation methods with hyperspherical coordinates

### 2.1 Hulthén-Kohn variational principle

Variational principles play an important role in the solution of the Schrödinger equation, e.g. the Ritz-method [4] for the solution of partial differential equations and the Rayleigh-Ritz method [5] for the calculation of bound states for atoms and molecules. The oldest variational method for scattering problems was introduced by Hulthén [6](1944). Four years later Hulthén and Kohn [7, 8] developed independently the Hulthén-Kohn variational principle (**HKVP**), which is a Rayleigh-Ritz method combined with boundary conditions for the scattering. Two other famous variational principles are the one of Schwinger and Newton [9, 10], where matrix elements with Green'ss functions are needed. These are more difficult to calculate and are collision energy dependent. On the other hand in the Hulthén-Kohn variational principle just matrix elements of the Hamilton operator are needed. The problem of the HKVP is that it is not invariant with respect to the choice of boundary conditions, leading to problems with pseudo resonances. If one uses stationary wave boundary conditions for the calculation of the K-matrix and calculates the scattering matrix by $S=(1+iK)(1-iK)^{-1}$, we do not get the same S-matrix by using incoming and outgoing wave boundary conditions for the direct calculation of the S-matrix. The S-matrix version of the HKVP was developed by Miller and Jansen op de Haar [11]. First calculations for electron-molecule scattering were performed by McCurdy, Rescigno und Schneider [12, 13, 14].

### 2.2 Variational principle for scattering

The derivation of HKVP will be explained within a potential scattering problem [15]; $R$ is the translational coordinate and $V(R)$ the potential.
The radial Schrödinger equation for such a problem is ($\hbar$=1 and m=1):

$$\left(\frac{d^2}{2dR^2}-\frac{l(l+1)}{R^2}-V(R)+k^2\right)\Psi_l(R)=0 \tag{2.1}$$

with

$$k^2=E. \tag{2.2}$$

The wavefunction $\Psi_l(R)$ is regular at the origin

$$\Psi_l(0)=0 \tag{2.3}$$

and has following asymptotic form:

$$\Psi_l(R)\sim\sin(kR-\frac{l\pi}{2}+\eta_l), \tag{2.4}$$

with $\eta_l$ the exact phase-shift. The functional is defined as

$$I_l=\int_0^\infty\tilde{\Psi}_l(R)L\tilde{\Psi}_l(R)dR \tag{2.5}$$

with

$$L=\left(\frac{d^2}{dR^2}-\frac{l(l+1)}{R^2}-V(R)+k^2\right). \tag{2.6}$$

The trial wavefunction $\tilde{\Psi}_l(R)$ (approximation for the exact wavefunction $\Psi_l(R)$ ) fulfills (2.3) and (2.4) with the chosen phase shift $\tilde{\eta}_l$. The functional $I_l$ is 0, if the Ansatz for $\tilde{\Psi}_l(R)$ is equal to the exact wavefunction $\Psi_l(R)$. Varying the wavefunction by $\delta\tilde{\Psi}_l(R)$ a new function is obtained

$$\tilde{\Psi}_l(R)=\Psi_l(R)+\delta\tilde{\Psi}_l(R), \tag{2.7}$$

where $\delta\tilde{\Psi}_l(R)$ fulfils the boundary conditions

$$\delta\tilde{\Psi}_l(R\to 0)=0 \tag{2.8}$$

and

$$\lim_{R\to\infty}\delta\tilde{\Psi}_l(R)\sim\cos(kR-\frac{l\pi}{2}+\delta\tilde{\eta}_l). \tag{2.9}$$

With (2.7) in (2.5) one gets for the variation of the functional $\delta I_l$ in first order

$$\delta I_l = \int_0^\infty \delta\tilde{\Psi}_l(R) L \Psi_l(R) dR + \int_0^\infty \Psi_l(R) L \delta\tilde{\Psi}_l(R) dR. \tag{2.10}$$

Partial integration for the second integral in (2.10) gives

$$\int_0^\infty \Psi_l(R) L \delta\tilde{\Psi}_l(R) dR = \int_0^\infty \delta\tilde{\Psi}_l(R) L \Psi_l(R) dR$$
$$+ \left[ \Psi_l(R) \frac{d}{dR} \delta\tilde{\Psi}_l(R) - \delta\tilde{\Psi}_l(R) \frac{d}{dR} \Psi_l(R) \right]_0^\infty \tag{2.11}$$

and for the variation of the functional

$$\delta I_l = 2 \int_0^\infty \delta\tilde{\Psi}_l(R) L \Psi_l(R) dR +$$
$$\left[ \Psi_l(R) \frac{d}{dR} \delta\tilde{\Psi}_l(R) - \delta\tilde{\Psi}_l(R) \frac{d}{dR} \Psi_l(R) \right]_0^\infty . \tag{2.12}$$

The use of the boundary conditions (2.3), (2.4), (2.8) and (2.9) for $\Psi_l(R)$ and $\delta\tilde{\Psi}_l(R)$ in the second part of (2.12) leads to

$$\delta I_l = 2 \int_0^\infty \delta\tilde{\Psi}_l(R) L \Psi_l(R) dR + k\tilde{\eta}_l \tag{2.13}$$

Under the condition that $\Psi_l(R)$ fulfils (2.10 one gets for the variation of the functional

$$\delta I_l = k\tilde{\eta}_l. \tag{2.14}$$

Now, one defines a new functional

$$J = I_l + k\eta_l \tag{2.15}$$

With the exact wavefunction the functional is stationary ($I_l = 0$), and the exact phase shift is calculated from the stationary values of the functional in (2.15). In general the exact wavefunction is not known, and one uses $\Psi_t(R)$, which depends upon (n+1) parameters and fulfils the conditions in (2.8) and (2.9). Plugging the wavefunction into (2.15) and does the differentiation and integration one gets the functional $J$ depending upon (n+1) parameters $c_i, \eta_l$. The stationary values are calculated from

$$\frac{\partial J}{\partial c_i} = 0 \quad i = 1, 2, ..., n \quad \frac{\partial J}{\partial \eta_l} = k. \tag{2.16}$$

The approximate value for the phase shift is calculated by putting $\tilde{\Psi}_t(R)$, with parameters from (2.16), into (2.15). For the asymptotic boundary conditions for the trial wavefunction one can use also other relations:

$$\tilde{\Psi}_l(R) \sim \cos(kR - \frac{l\pi}{2}) + \cot\, \tilde{\eta}_l \sin(kR - \frac{l\pi}{2}) \tag{2.17}$$

or

$$\tilde{\Psi}_l(R) \sim \sin(kR - \frac{l\pi}{2}) + \tan\,\tilde{\eta}_l \sin(kR - \frac{l\pi}{2}). \tag{2.18}$$

Finally, one gets for the functional in (2.9)

$$J = I_l + k\,\cot\,\eta_l \tag{2.19}$$

or

$$J = I_l + k\,\tan\,\eta_l. \tag{2.20}$$

(2.20) is the original formulation of Kohn. The formulation in (2.19) (Hulthén) is called also the inverse Kohn-method [16].

### 2.3 S-matrix version of the Hulthén-Kohn- variational principle

In order to derive the S-matrix version of the Hulthén-Kohn variational principle (HKVP) (to make the derivation simpler everything will be formulated now in one dimension) one uses trial functions with incoming and outgoing wave boundary conditions [17, 11, 10]:

$$\tilde{\Psi}(R) = -u_0(R) + u_1(R)\tilde{S} + \sum_{i=2}^{N} u_i(R)c_i. \tag{2.21}$$

The first term is the incoming wave

$$u_0(R) = v^{-1/2}e^{-ikR} \tag{2.22}$$

with $v = \frac{\hbar k}{\mu}$ (asymptotic velocity) and wave vector $k = \hbar\sqrt{(2\mu E)}$. With the factor $v^{-1/2}$ one defines an unit flux for the incoming wave. The wavefunction has to be regular at the origin (R $\rightarrow$ 0) and is therefore multiplied with a cut-off function

$$u_0(R) = f(R)v^{-1/2}e^{-ikR}. \tag{2.23}$$

f(0) = 0 and f(R) = 1 for R$\rightarrow \infty$. The second term in (2.21) is a product of the outgoing wave

$$u_1(R) = f(R)v^{-1/2}e^{+ikR} \tag{2.24}$$

and the approximate S-matrix $\tilde{S}$. The third term in (2.21) defines a set of $N$ square-integrable $L^2$- basis functions, which have to describe the interaction region with variational parameters c$_i$. If we vary the trial wavefunction as in the last section, we get

$$\tilde{\Psi}(R) = \Psi(R) + \delta\tilde{\Psi}(R) \tag{2.25}$$

with

$$\delta\tilde{\Psi}(R) = u_1(R)\delta\tilde{S} + \sum_i \phi_i \delta c_i. \tag{2.26}$$

and plugging into the functional in (2.5)

$$\int_0^\infty \Psi(R)L\delta\tilde{\Psi}(R)dR = \int_0^\infty \delta\tilde{\Psi}(R)L\Psi(R)dR$$
$$\underbrace{-\frac{\hbar^2}{2\mu}\left[\Psi(R)\frac{d}{dR}\delta\tilde{\Psi}(R) - \delta\tilde{\Psi}(R)\frac{d}{dR}\Psi(R)\right]_0^\infty}_{Int}. \quad (2.27)$$

If we put $\delta\tilde{\Psi}(R)$ (Eq. (2.26)) and $\Psi(R)$ (Eq. (2.21)) into the second part of the integral, we get

$$\begin{aligned} Int = \left(-\frac{\hbar^2}{2\mu}\right)\Big[ & -\delta\tilde{S}u_0(R)\frac{d}{dR}u_1(R) + u_1(R)\frac{d}{dR}u_1(R)\delta\tilde{S}\tilde{S} \\ & +\frac{d}{dR}u_0(R)u_1(R)\delta\tilde{S} - u_1(R)\frac{d}{dR}u_1(R)\tilde{S}\delta\tilde{S}\Big]_0^\infty \\ = (-\frac{\hbar^2}{2\mu})\delta\tilde{S} & \left[-u_0(R)\frac{d}{dR}u_1(R) + \frac{d}{dR}u_0(R)u_1(R)\right]_0^\infty. \end{aligned} \quad (2.28)$$

The part within the parenthesis of the last equation in (2.280 is $(-2ik/v)$. We get now for the variation of the functional

$$\delta I_l = 2\int_0^\infty \delta\tilde{\Psi}(R)L\Psi(R)dR - \frac{\hbar}{i}\delta\tilde{S}. \quad (2.29)$$

If we define a new functional $J$

$$J = \tilde{S} + \frac{i}{\hbar}\int_0^\infty \tilde{\Psi}(R)L\tilde{\Psi}(R)dR \quad (2.30)$$

or in Dirac notation (the 'bra' is not taken complex conjugate)

$$J = \tilde{S} + \frac{i}{\hbar} < \tilde{\Psi}_l(R)|\hat{H} - E|\tilde{\Psi}_l(R) >, \quad (2.31)$$

then we get

$$\delta J = \frac{2i}{\hbar} < \delta\tilde{\Psi}(R)|\hat{H} - E|\tilde{\Psi}(R) > . \quad (2.32)$$

The variational conditions is now

$$\delta J = 0. \quad (2.33)$$

If the trial function $\tilde{\Psi}(R)$ is the exact wavefunction and therefore the solution of $(H - E)|\Psi(\mathrm{R}) >= 0$, the S-matrix is $S = \tilde{S} = J$. So we get the S-matrix version of the HKVP as

$$S = \mathrm{ext}\left[\tilde{S} + \frac{i}{\hbar} < \tilde{\Psi}(R)|\hat{H} - E|\tilde{\Psi}(R) >\right]. \quad (2.34)$$

With (2.21) into (2.34) we get the following relations

$$S = \frac{i}{\hbar}\mathrm{ext}[< u_0|\hat{H} - E|u_0 > +$$
$$\sum_{i,i'=1}^{N} c_i c_{i'} < u_i|\hat{H} - E|u_{i'} > -2\sum_{i=1}^{N} c_i < u_i|\hat{H} - E|u_0 >] \tag{2.35}$$

with

$$< u_0|\hat{H} - E|u_i > = < u_i|\hat{H} - E|u_0 >, \tag{2.36}$$
$$< u_i|\hat{H} - E|u_{i'} > = < u_{i'}|\hat{H} - E|u_i >, \tag{2.37}$$

for $i, i' = 2, N$ and

$$< u_0|\hat{H} - E|u_1 > = < u_1|\hat{H} - E|u_0 > -i\hbar \tag{2.38}$$

for $i, i' = 1$. For the calculation of the coefficients $c_i$ we perform the variation of (2.35) as

$$\frac{\partial S}{\partial c_i} = 0, \quad i = 1, ...N. \tag{2.39}$$

From this we get a set of $N$ linear equations, which can be solved by matrix inversion. The result is put back into (2.35) and for the S-matrix follows

$$S = \frac{i}{\hbar}[< u_0|\hat{H} - E|u_0 > - \sum_{i,i'=1}^{N} < u_i|\hat{H} - E|u_0 >$$
$$(< u_i|\hat{H} - E|u_{i'} >)^{-1} < u_{i'}|\hat{H} - E|u_0 >] \tag{2.40}$$

or in matrix notation:

$$S = \frac{i}{\hbar}(\mathbf{M}_{00} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0), \tag{2.41}$$

with

$$M_{00} = < u_0|\hat{H} - E|u_0 >, \tag{2.42}$$

$$(M_0)_i = < u_i|\hat{H} - E|u_0 >, \quad i = 1, ..., N \tag{2.43}$$

$$(M)_{i,i'} = < u_i|\hat{H} - E|u_{i'} > \quad i = 1, ..., N. \tag{2.44}$$

In order to simplify the time-consuming inversion of the complex matrix, it is better to separate out the real and imaginary part in (2.41). This has been done with Feshbach partitioning [18] and results into the following formulation:

$$S = \frac{i}{\hbar}(\mathbf{B} - \mathbf{C}^T (\mathbf{B}^*)^{-1} \mathbf{C}), \tag{2.45}$$

$$B = \mathbf{M}_{00} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0, \tag{2.46}$$

$$C = \mathbf{M}_{10} - (\mathbf{M}_0^*)^T \mathbf{M}^{-1} \mathbf{M}_0, \tag{2.47}$$

$$M_{1,0} =< u_0^*|\hat{H} - E|u_0 > . \tag{2.48}$$

In this specially formulated S-matrix there are no so-called Kohn-anomalies, which are found in the K-matrix version of the HKVP [10]. If the condition

$$\det|\mathbf{M}| = 0. \tag{2.49}$$

is fulfilled, then in (2.45) singularities may occur, which result from Siegert eigenvalues [19] (that are physically correct singularities of the S-matrix for complex energies). They characterise energies and lifetimes of resonances $(E - i\Gamma/2)$. In the scattering calculations the collision energies are real, and resonances will not occur in the S-matrix. The S-matrix can be calculated from the K-matrix

$$K = -2\left(\mathbf{M}_{00} - \mathbf{M}_0^T\mathbf{M}^{-1}\mathbf{M}_0\right), \tag{2.50}$$

by

$$S = (1 + iK)(1 - iK)^{-1}. \tag{2.51}$$

Whether one gets problems with singularities depends on the boundary conditions of $u_0$ and $u_1$ for the K-matrix:

$$u_0(R) \sim v^{-1/2} sin(kR) \quad u_1(R) \sim v^{-1/2} cos(kR). \tag{2.52}$$

Now $u_1$ is a real function and $\mathbf{M}$ is a real matrix, with real eigenvalues. For some special real values of the collision energy $E$ we get singularities in (2.50). In case of elastic scattering the S-matrix is just a number and the phase shift $\eta$ will be calculated from

$$S = \exp(2i\eta). \tag{2.53}$$

### 2.4 Multi-channel formulation: general aspects

We now summarize: In the S-matrix version of the HKVP [6, 7, 8, 16, 20] as derived by Miller and coworkers [21, 22, 23, 24, 25, 26, 27, 30, 32], the S-matrix at energy E is given by

$$S_{n_2,n_1} = ext[c_{1n_2n_1} + \frac{i}{\hbar}\langle\tilde{\Psi}_{n_2}|\hat{H} - E|\tilde{\Psi}_{n_1}\rangle], \tag{2.54}$$

where $\tilde{\Psi}_{n_i}(R)$ is a trial wave function (regular at $R = 0$) with the asymptotic form (for $R \to \infty$)

$$\tilde{\Psi}_{n_i}^E(R, \{q\}) = \sum_n (-u_{0n_i}(R)\delta_{nn_i} + \sum_{l=1}^N u_{ln}(R)c_{ln,n_i})\phi_n(\{q\}). \tag{2.55}$$

$R$ is the translational coordinate and $\{q\}$ denotes the coordinates of all internal degrees of freedom with the channel eigenfunctions $\{\phi_n(\{q\})\}$. This is the multichannel formulation for $\tilde{\Psi}(R, \{q\})$ which can be used for elastic (without $\{q\}$ and $\phi_{n_i}$), inelastic and reactive processes (with introduction of the indices 1,2 for the arrangements A + BC and AB + C in the collinear case). The $\{u_{ln}(R)\}, l = 2, .., N$ is a square integrable basis set. $u_{0n}(R)$ and $u_{1n}(R)$ have the properties of incoming and outgoing waves, which can be "free" functions (the special form depends on the dimension of space to be included) or distorted functions. In order to regularize $u_{0n}$ and $u_{1n}$ ($u_{1n} = u_{0n}^*$), they are multiplied by a cutoff function f(R). In case of collinear reaction one chooses

$$u_{0n} = f(R)e^{-ik_nR}v_n^{-\frac{1}{2}}, \quad v_n = \frac{\hbar k_n}{\mu}, \quad k_n = (\frac{2\mu(E-E_n)}{\hbar^2})^{\frac{1}{2}} \tag{2.56}$$

$$f(R) = \frac{1}{2}\{1 + tanh[\alpha(R - R_\alpha)]\}. \tag{2.57}$$

Modifications for a 3D application are explained in the next section. Stationarity of (2.540 with respect to the expansion coefficients $c_{ln_i,n_j}$ (in (2.55)) leads to the matrix equation (details see [21])

$$\mathbf{S} = \frac{\mathbf{i}}{\hbar}(\mathbf{B} - \mathbf{C^T}\mathbf{B^{*-1}}\mathbf{C}), \tag{2.58}$$

where $\mathbf{S}, \mathbf{B}$ and $\mathbf{C}$ are matrices of the size of the number of open channels. $\mathbf{B}$ and $\mathbf{C}$ are given by

$$\mathbf{B} = \mathbf{M_{00}} - \mathbf{M_0^T}\mathbf{M^{-1}}\mathbf{M_0} \tag{2.59}$$

$$\mathbf{C} = \mathbf{M_{10}} - \mathbf{M_0^{*T}}\mathbf{M^{-1}}\mathbf{M_0} \tag{2.60}$$

$$(M_{00})_{nn'} = \langle u_{0n}\phi_n|\hat{H} - E|u_{0n'}\phi_{n'}\rangle \tag{2.61}$$

$$(M_{10})_{nn'} = \langle u_{1n}\phi_n|\hat{H} - E|u_{0n'}\phi_{n'}\rangle \tag{2.62}$$

$$(M)_{ln,l'n'} = \langle u_l\phi_n|\hat{H} - E|u_{l'}\phi_{n'}\rangle, \quad l, l' = 2, .., N \tag{2.63}$$

$$(M_0)_{ln,n'} = \langle u_l\phi_n|\hat{H} - E|u_{0n'}\phi_{n'}\rangle, \quad l = 2, .., N. \tag{2.64}$$

The translational functions in the bra symbols in (2.61), (2.62) are not the complex conjugate ones, and $n$ is the collective index of all internal quantum numbers.

The main numerical effort in this scattering method is the calculation of matrix elements. Those in (2.61), (2.62), (2.640 have to be recalculated for each energy. The matrix elements of the Hamiltonian and the overlap matrix over the basis $u_l\phi_n, \ l \geq 2$, in (2.63) have to be calculated only once, but the inversion of $\mathbf{M}$ has to be repeated for each energy.

In our work the wavefunction ($u_{ln}\phi_n, \ l \geq 2$) is built up from FE-functions in the interior region and analytical functions ($u_{ln}, \ l \leq 1$) in the asymptotic region.

We first solve the eigenvalue problem within FEM in 2D, resp. 3D

$$(\Psi^{FEM}|\hat{H}|\Psi^{FEM}) = E'(\Psi^{FEM}|\Psi^{FEM}) \tag{2.65}$$

up to a maximum eigenvalue $E_{max}$ or up to a finite number of eigenfunctions, which are then used as a new orthogonal basis for calculating the matrix elements in (2.63) and (2.64). The inversion of the large matrix $\mathbf{M}$ for different collision energies is then just the inversion of the diagonal elements.
In order to reduce the size of the matrices in (2.59) - (2.64), different polynomial orders for finite elements and different potential adapted basis sets have been tested.

### 2.5 S-matrix version of the HKVP: 3D formalism

In case of an atom-diatom system we have three arrangements $\alpha$: (A + BC, B+ AC, C + AB) $R_\alpha$ is the radial translational coordinate for arrangement $\alpha$ (the distance between the centers of mass of the two collision partners) and $q_\alpha$ denotes all the other coordinates, i.e. the internal coordinates for arrangement $\alpha$ (including the two angles of the three-dimensional vector $R_\alpha$). The functions $\phi_{\alpha\mathbf{n}}$ are the asymptotic internal eigenfunctions for arrangement $\alpha$, i.e. the eigenfunctions of the Hamiltonian $\hat{H}_\alpha$ without the radial kinetic energy for arrangement $\alpha$ including the asymptotic potential energy $v_\alpha$ for this arrangement,

$$\hat{H}_\alpha = \hat{H} - [-\frac{\hbar^2}{2\mu_\alpha}\frac{1}{R_\alpha}\frac{\partial^2}{\partial R_\alpha^2}R_\alpha] - V + v_\alpha, \qquad v_\alpha = \lim_{R_\alpha\to\infty} V. \tag{2.66}$$

$\alpha\mathbf{n}$ is the complete set of quantum numbers which characterize the channel. $u_{0\alpha\mathbf{n}}(R_\alpha)$ is an asymptotically incoming translational function for channel $\alpha\mathbf{n}$,

$$\lim_{R_\alpha\to\infty} R_\alpha u_{0\alpha\mathbf{n}}(R_\alpha) \sim v_{\alpha\mathbf{n}}^{-1/2} e^{-i(k_{\alpha\mathbf{n}}R_\alpha-(\pi/2)l_{\alpha\mathbf{n}})},$$
$$k_{\alpha\mathbf{n}} \equiv \mu_\alpha v_{\alpha\mathbf{n}} = \sqrt{2\mu_\alpha(E-\epsilon_{\alpha\mathbf{n}})}/\hbar. \tag{2.67}$$

$k_{\alpha\mathbf{n}}$ and $l_{\alpha\mathbf{n}}$ are the wave vector and orbital angular momentum for the channel $\alpha\mathbf{n}$. $u_{0\alpha\mathbf{n}}(R_\alpha)$ and $u_{1\alpha\mathbf{n}}(R_\alpha)$ have the same properties as given in the last section. The scattering wave function is expanded as

$$\Psi_{\alpha_1\mathbf{n_1}} = \sum_{\alpha\mathbf{n}} \phi_{\alpha\mathbf{n}}(q_\alpha)[-u_{0\alpha\mathbf{n}}(R_\alpha)\delta_{\alpha\alpha_1}\delta_{\mathbf{n}\mathbf{n_1}} + \sum_{t=1}^{N} u_{t\alpha\mathbf{n}}(R_\alpha)c_{t\alpha\mathbf{n},\alpha_1\mathbf{n_1}}] \tag{2.68}$$

where $\alpha_1\mathbf{n_1}$ is the initial channel, and the constants $c_{t\alpha\mathbf{n},\alpha_1,\mathbf{n_1}}$ are the variational parameters which are determined by the Hulthén-Kohn principle. The S-matrix is defined by the asymptotic form of the wavefunction, i.e.

$$\lim_{R_\alpha\to\infty} R_\alpha\Psi_{\alpha_1\mathbf{n_1}} \sim \sum_{\alpha\mathbf{n}} \phi_{\alpha\mathbf{n}}(q_\alpha)v_{\alpha\mathbf{n}}^{-1/2}$$
$$\times[-e^{-i(k_{\alpha\mathbf{n}}R_\alpha-(\pi/2)l_{\alpha\mathbf{n}})}\delta_{\alpha\alpha_1}\delta_{\mathbf{n}\mathbf{n_1}} + e^{i(k_{\alpha\mathbf{n}}R_\alpha-(\pi/2)l_{\alpha\mathbf{n}})}S_{\alpha\mathbf{n},\alpha_1\mathbf{n_1}}]. \tag{2.69}$$

In an atom-diatom system the internal coordinates $q_\alpha$ for a given arrangement are $q_\alpha = (r_\alpha, \hat{R}_\alpha)$ with $r_\alpha$ as the relative diatomic coordinate vector. The quantum numbers $\mathbf{n}$ are (vjlJM), (v,j) being the vibrational and rotational quantum numbers of the atom relative to the diatom, l the orbital angular momentum of the atom relative to the diatom, and (J,M) the total angular momentum and its projection onto a space fixed axis. The matrices are diagonal in J and M. The channel eigenfunctions $\phi_{\alpha\mathbf{n}}$ are

$$\phi_{\alpha\mathbf{n}}(q_\alpha) = \phi^{JM}_{\alpha vjl}(r_\alpha, \hat{R}_\alpha) =$$

$$\left(\frac{2J+1}{8\pi^2}\right)^{1/2} (-1)^{j+M} f_{vj}(r_\alpha) \sum_k C(jJl; k, -k) \Psi_{jk}(\gamma_\alpha) D^J_{Mk}(A, B, \Gamma) \tag{2.70}$$

where $f_{vj}(r_\alpha)$ is the diatomic vibrational eigenfunction, the $C$'s denote Clebsch-Gordan coefficients, $\Psi_{jk}(\gamma_\alpha)$ is the associated Legendre polynomial, $\gamma_\alpha$ defines the angle between $r_\alpha$ and $\hat{R}_\alpha$ and $D^J_{Mk}$ the Wigner rotation matrix. The matrix elements of $(\hat{H} - E)$ between typical basis functions $u_{t\alpha}(R_\alpha)\phi^{JM}_{\alpha vjl}(r_\alpha, \hat{R}_\alpha)$ are evaluated as usually. The three Euler angles $(A, B, \Gamma)$. are integrated out analytically, so that all matrix elements reduce to three-dimensional integrals that are evaluated numerically. The general expression for the matrix elements is

$$\begin{aligned}(M)^J_{t'\alpha'v'j'l',t\alpha vjl} &= < u_{t'\alpha'}\phi^{JM}_{\alpha'v'j'l'}|\hat{H} - E|u_{t\alpha}\phi^{JM}_{\alpha vjl} >= \\ &(-1)^{j'+j} \sum_{k,k'} C(j'Jl'; k', -k')C(jJl; k', -k) \\ \times \int & d\tau u_{t'\alpha'}(R_{\alpha'}) f_{\alpha'v'j'}(r_{\alpha'}) \Psi_{j'k'}(\gamma_{\alpha'}) d^J_{k'k}(\gamma_{\alpha'\alpha}) R^{-1}_\alpha \\ &\times[-\frac{\hbar^2}{2\mu_\alpha}\frac{d^2}{dR^2_\alpha} + \frac{\hbar^2 l(l+1)}{2\mu_\alpha R^2_\alpha} + \epsilon_{\alpha vj} + V - v_\alpha - E] \\ R^{-1}_\alpha u_{t\alpha}&(R_\alpha) f_{\alpha vj}(r_\alpha)\Psi_{jk}(\gamma_\alpha), d\tau = r^2_\alpha R^2_\alpha \sin\gamma_\alpha dr_\alpha dR_\alpha d\gamma_\alpha,\end{aligned} \tag{2.71}$$

where $d\tau$ is the three-dimensional volume element.
In (2.71) $\gamma_{\alpha',\alpha}$ is the angle between the two vectors $\hat{R}_{\alpha'}$ and $\hat{R}_\alpha$, $\epsilon_{\alpha vj}$ the vibration-rotational eigenvalues of potential $v_\alpha$, $\mu_\alpha$ is the translational reduced mass for channel $\alpha$. The integration variables can be chosen in a variety of ways. Because we do the scattering calculations (reactive and non reactive) only with one Jacobi coordinate, the angle $\gamma_{\alpha'\alpha}$ is identically zero, so that

$$d^J_{k'k}(\gamma_{\alpha'\alpha}) \rightarrow d^J_{k'k}(0) = \delta_{k,k'}, \tag{2.72}$$

and (2.71) reduces to a single sum and we do not have exchange matrix elements, i.e., those with $\alpha' \neq \alpha$. (2.71) applies for t and $t' = 0$ or 1, i.e., the "free" translational function for the matrices $\mathbf{M}_{00}$, $\mathbf{M}_{10}$, and $\mathbf{M}_0$, as well as for $L^2$ functions $t, t' > 2$ for the matrix $\mathbf{M}$. For the free functions $u_{0\alpha vjl}(R_\alpha)$ we use spherical Hankel functions where the regular and irregular parts can be multiplied with different cut-off functions $(f_1, f_2)$ (as in (2.56), (2.57))

$$R_\alpha u_{0\alpha vjl}(R_\alpha) = v_{\alpha vj}^{-1/2}(k_{\alpha vj}R_\alpha) \times [f_1(R_\alpha)n_l(k_{\alpha vj}R_\alpha) \\ -if_2(R_\alpha)j_l(k_{\alpha vj}R_\alpha)], \tag{2.73}$$

where $j_l$ and $n_l$ are regular and irregular spherical Bessel functions.

## 2.6 3D potential adapted basis functions from 3D eigenvalue calculations

Similar to the scattering calculations [33] in the collinear case (2D) we are trying to solve the 3D eigenvalue problem for the interior region of the ABC - system. We are using the general formalism introduced by Sutcliffe, Tennyson and coworkers [34, 35, 36]. The body-fixed Hamiltonian can be written as

$$\hat{H} = K_V + K_{VR} + V(r, R, \gamma), \tag{2.74}$$

where $V$ is the electronic potential and the different kinetic energy operators $K_V$ and $K_{VR}$ include different vibrational ($V$) and rotational ($R$) terms. The symmetrized angular basis functions for $\hat{H}$ can be written as

$$|j,k> = 2^{-1/2}(1+\delta_{k0})^{-1/2}[\Psi_{jk}(\gamma)D^J_{Mk}(A,B,\Gamma) \\ +(-1)^p\Psi_{j-k}(\gamma)D^J_{M-k}(A,B,\Gamma)], \tag{2.75}$$

The total parity is given by $(-1)^{J+p}$ with $p = 0$ or 1 for e or f states, respectively. All symbols are already explained in the earlier section.
Letting the kinetic part of $\hat{H}$ act on $|j,k>$, multiplying from the left by $< j', k'|$ and integrating over all angular coordinates yields an effective kinetic energy operator ($J = 0$) which works only on functions of the radial variables:

$$K_V = \delta_{j'j}\delta_{k'k}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2}j(j+1)\left(\frac{1}{\mu_1 r^2} + \frac{1}{\mu_2 R^2}\right)\right] \tag{2.76}$$

The masses $\mu_1$ and $\mu_2$ are the usual reduced masses in Jacobi coordinates. Conventionally the approximation to the $l-$th energy level $E_l^J$ has the wavefunction

$$\Psi_l^J = \sum_k \sum_{jmn} d_{kjmn}^{Jl}|j,k>|m>|n> \tag{2.77}$$

in terms of radial basis functions for $r$ and $R$ ($|m>|n>$) and symmetrized angular basis functions ($|j,k>$). In case of our FE implementations we use instead of $|m>|n>$ a new set $|mn>$ (no separation in r and R).
For homonuclear diatomics the wavefunction should be either symmetric or antisymmetric with respect to interchange of the like atoms. This symmetry is naturally represented in scattering coordinates where functions with $j$ even and odd are symmetric and antisymmetric, respectively. Before we solve the full 3D problem we start with the 2D solution in $r$ and $R$

$$\hat{H}(r,R) = K_V + K_{VR} + \delta_{k'k} < j', k|V(r,R,\gamma)|j,k>_\gamma . \tag{2.78}$$

for a given angle $\gamma$, where the appropriate angular functions are given by

$$|j,k>=\Psi_{j,k}(\gamma)|J,M,k>, \tag{2.79}$$

with $|J,M,k>$ as the total angular momentum eigenfunctions.
This simplification to solve first a set of 2D problems is achieved by the transformation of the Hamiltonian of (2.78) to a discrete variable representation (DVR) in $\gamma$ by

$$\mathbf{H}^{DVR} = \mathbf{T}^T\mathbf{H}\mathbf{T}. \tag{2.80}$$

The transformation for the angular coordinate is given by

$$T^k_{j\alpha} = \omega^{1/2}_{k\alpha}\Psi_{jk}(\gamma_{k\alpha}), \tag{2.81}$$

where $\gamma_\mathbf{k}$ and $\omega_\mathbf{k}$ are the points and weights of an N-point Gauss-associated Legendre quadrature points of order k. An important feature of the DVR is the quadrature approximation. This is used to evaluate the contribution due to the potential which is diagonal in the DVR:

$$\sum_{j,j'=k}^{N+k-1} T^k_{j'\alpha'} < j'k|V(r,R,\gamma)|j,k>_\gamma T^k_{j\alpha} \simeq \delta_{\alpha\alpha'}V(r,R,\gamma_{k\alpha}). \tag{2.82}$$

The angular off-diagonal contributions arise from the kinetic energy operator via the $L$-matrix which is given by

$$L^k_{\alpha\alpha'} = \sum_{j=k}^{N+k-1} T^k_{j'\alpha'}j(j+1)T^k_{j'\alpha}. \tag{2.83}$$

The resulting $J=k=0$ effective radial Hamiltonian is

$$\begin{aligned}\hat{H}_{\alpha\alpha'} = \delta_{\alpha\alpha'}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial R^2} + V(r,R,\gamma_{k\alpha})\right]& \\ +\frac{\hbar^2}{2}\left(\frac{1}{\mu_1 r^2} + \frac{1}{\mu_2 R^2}\right)L^0_{\alpha\alpha'}&\end{aligned} \tag{2.84}$$

Our strategy is to solve the effective radial Hamiltonian for each $\alpha$ on the DVR grid by using finite elements. The lowest solutions, selected either by number or energy cut off, are then used to construct a full 3D Hamiltonian matrix which is diagonalised to yield the eigenenergies and values for the wavefunctions at the DVR grid points. In this approach there is a choice as to whether the diagonal parts of the angular kinetic energy term are included in the 2D or 3D problem.
In case of permutation symmetry of like atoms as in $AB_2$ systems one can modify the DVR in the $\gamma$-coordinate that leads to a modified, symmetrized $L$-matrix:

$$L^{kq}_{\alpha\alpha'} = 2\sum_{j=k}^{N/2+k-1} T^k_{2j+q,\alpha'}(2j+q)(2j+q+1)T^k_{2j+q,\alpha}, \quad q=0,1 \tag{2.85}$$

In a symmetrized DVR only the term which differs between even ($q=0$) and odd ($q=1$) calculations is provided by the $L$-matrix which means that the same solutions of the 2D problems can be used for both $q = 0$ and $q = 1$ calculations if the diagonal portion of $\mathbf{L}$ is only included in the 3D Hamiltonian.

### 2.7 Distorted waves

In order to reduce the computer time the number of basis functions in the interaction region and the number of functions in the asymptotic region must be kept as small as possible. The number of functions depends on the size of the area that must be described by the appropriate functions. If the $L^2$-basis functions are used for the strong interaction and 'inelastic' region the number of functions can become large. The idea is to solve first the inelastic problem with a close-coupling method [37, 38]. We use a procedure as developed by Groenenboom and coworkers [27, 29] and which we try in our finite element calculations (finite elements as $\mathrm{L}^2$- basis functions).
In the close-coupling method the wavefunction $\chi_j(R,r,\theta)$ is expanded in basis functions $\phi_i(r,\theta)$ for each scattering channel, which describe rotation ($\mathrm{j}_i$) and vibration ($\mathrm{v}_i$) along the reaction coordinate $R$. $i$ and $j$ are common indices for rotation ($j_i$) and vibration quantum numbers ($v_i$). Then we get a system of coupled equations for the translational matrix function $U_{ij}(R)$, which will be solved by a propagation method (renormalized Numerov method). In order to separate the different arrangement channels we add to the original potential in the area $\mathrm{R} < \mathrm{R}_{max}$ a distortion potential. We use two different distortion potentials to get two different solutions, from which by linear combination the distorted inelastic waves as incoming and outgoing waves for the HKVP results. The inelastic waves should fulfil the Schrödinger equation in the area $R = \infty \to R_{max}$. The close-coupling solutions overlap with the $\mathrm{L}^2$-basis functions, which are used only in the strong interaction region.
The use of distorted wave has several advantages:

- We do not need cut-off functions any more. The distorted wave automatically describe the boundary conditions at $R = 0$.
- Reduction of the area for the $\mathrm{L}^2$ basis functions.
- $(H - E)$ operating on the distorted waves is only a multiplicative operation and easy to calculate.

Further details are given in [28] and new studies to this subject are presented in the work of Groenenboom [29].

## 3. The hyperspherical method

In this section we will describe the hyperspherical method in more detail. The description of the formalism is based on extractions taken from the work of Launay [2]. The numerical calculation of the wavefunction $\Psi^{JM}$

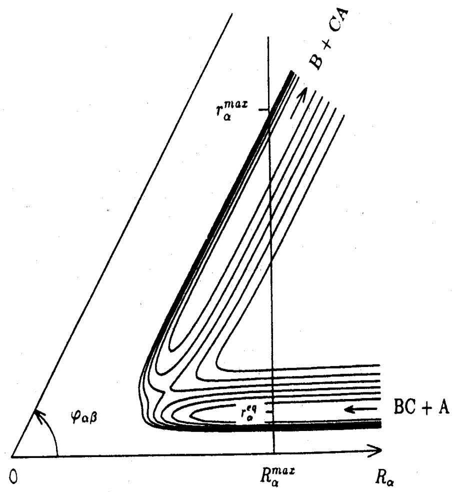


**Fig. 3.1.** Potential energy contours for an atom-diatom reaction. The Jacobi coordinates of arrangement $\alpha$ are sketched. (Reprinted, by permission, from Launay, J.M. in: *Dynamical Processes in Molecular Physics*, Delgado-Barrio, G. (Ed.) (Institute of Physics Publishing, Bristol and Philadelphia, 1991). Copyright 1991 Institute of Physics Publishing.)

$$\Psi^{JM}_{\lambda vjl} = \sum_{\lambda' v' j' l'} \frac{1}{R_{\lambda'}} f^J_{\lambda' v' j' l' \lambda vjl}(R_{\lambda'}) \Phi^{JM}_{\lambda' v' j' l'}(\mathbf{r}_{\lambda'} \hat{\mathbf{R}}_{\lambda'}) \tag{3.1}$$

and the analysis of its asymptotic behaviour at large atom-diatom distance

$$\begin{aligned} f^J_{\lambda' v' j' l' \lambda vjl}(R_{\lambda'}) \to & \frac{1}{k^{1/2}_{\lambda vj}} e^{-i(k_{\lambda vj} R_\lambda - l\pi/2)} \delta_{\lambda'\lambda} \delta_{v'v} \delta_{j'j} \delta_{l'l} \\ & - \frac{1}{k^{1/2}_{\lambda' v' j'}} e^{-i(k_{\lambda' v' j'} R_{\lambda'} - l'\pi/2)} S^J_{\lambda' v' j' l' \lambda vjl} \end{aligned} \tag{3.2}$$

in each arrangement $\lambda$ permits the evaluation of the $K$ and $S$ matrices. However, the appearance of different Jacobi coordinate systems in the asymptotic behaviour (3.2) renders reactive scattering calculations more complicated than inelastic scattering calculations, for which only one set of Jacobi coordinates is needed. Also, the calculation of the wavefunction in the reaction region needs to be performed with a different type of expansion. To see this feature, we consider a one-dimensional (collinear) model in which the wavefunction is expressed in the form of an expansion written in Jacobi coordinates of arrangement $\alpha$ as

$$\Psi = \sum_v \chi_{\alpha v}(r_\alpha) f_v(R_\alpha) \tag{3.3}$$

where the basis functions $\chi_{\alpha v}(r_\alpha)$ are the solutions of the *asymptotic* Hamiltonian of arrangement $\alpha$

$$[-\frac{1}{2\mu}\frac{\partial^2}{\partial r^2_\alpha} + v_\alpha(r_\alpha)]\chi_{\alpha v}(r_\alpha) = \varepsilon_\alpha \chi_{\alpha v}(r_\alpha) \tag{3.4}$$

In (3.4), $v_\alpha(r_\alpha)$ is the BC diatom potential, that is to say, the limit of the potential energy function $V(R_\alpha, r_\alpha)$ when $R_\alpha \to \infty$. The wavefunction components $f$ should be integrated from 0 to some limit $R_\alpha^{\max}$ situated in the region where the interaction potential has reached its asymptotic behaviour in both arrangements $\alpha$ and $\beta$. Very clearly, a large number of eigenstates $\chi_{\alpha v}(r_\alpha)$ are needed to represent accurately the wavefunction in arrangement $\beta$ because vibrational wavefunctions with a small $v$ quantum number are localized near the minimum $r_\alpha^{eq}$ of the potential $v_\alpha(r_\alpha)$. Moreover, since the number of bound vibrational states for a molecular potential is finite, a continuum of states $\chi_{\alpha\epsilon}(r_\alpha)$ with positive energy should also be included in the close-coupling expansion (3.3).

In an attempt to overcome this difficulty, one may use an expansion over eigenstates which are adapted to the *true* potential and not to the *asymptotic* potential. One thus defines *adiabatic states* by solving, for each $R_\alpha$, the equation

$$[-\frac{1}{2\mu}\frac{\partial^2}{\partial r_\alpha^2} + V(R_\alpha, r_\alpha)]\chi_{\alpha v}(R_\alpha; r_\alpha) = \varepsilon_\alpha(R_\alpha)\chi_{\alpha v}(R_\alpha; r_\alpha). \tag{3.5}$$

The first eigenstates of (3.5) concentrate into regions of low potential energy and thus will conveniently 'fill' the *two* arrangement valleys at large $R_\alpha$. The part of the wavefunction which goes into arrangement $\alpha$ is very well represented by an expansion over these eigenstates. This is however not the case for the part of the wavefunction which goes into arrangement $\beta$. Indeed, the wavefunction $\Psi$ is roughly localized between two equipotentials corresponding to the total energy $E$. Since lines of constant $R_\alpha$ cut these equipotentials obliquely, the length in the $r_\alpha$ coordinate is larger than in the $r_\beta$ coordinate. Solving a Schrödinger equation on a larger range of the variable means more effort and also more states to reach the limits of the domain of definition of the wavefunction. This difficulty is most pronounced for large skew angles $\varphi_{\alpha\beta}$ (i.e. for light-heavy-light collisions). For very small skew angles (heavy-light-heavy collisions), this difficulty does not appear and the expansion over the $\chi_{\alpha v}(R_\alpha; r_\alpha)$ states is a viable alternative.

Minimizing the number of basis states in each arrangement requires a coordinate system in which lines of constant values of the propagation variable cut the arrangement valleys at right or almost right angles, for large values of the propagation variable. Such coordinate systems are obviously *curvilinear*. The simplest of the coordinate systems which satisfies these requirements is *polar* coordinates

$$\rho = \sqrt{R_\alpha^2 + r_\alpha^2} \qquad \omega = \arctan\frac{r_\alpha}{R_\alpha} \tag{3.6}$$

In the case of three-dimensional reactive scattering, the generalization of polar coordinates yields the hyperspherical coordinates of six-dimensional space. Since the transformation

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{m_A m_B}{(m_A+m_C)(m_C+m_B)}} & -\sqrt{\frac{m_C(m_A+m_B+m_C)}{(m_A+m_C)(m_C+m_B)}} \\ \sqrt{\frac{m_C(m_A+m_B+m_C)}{(m_A+m_C)(m_C+m_B)}} & -\sqrt{\frac{m_A m_B}{(m_A+m_C)(m_C+m_B)}} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix} \tag{3.7}$$

or

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} \cos\,\phi_{\alpha\beta} & \sin\,\phi_{\alpha\beta} \\ -\sin\,\phi_{\alpha\beta} & \cos\,\phi_{\alpha\beta} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix}. \tag{3.8}$$

with

$$\tan\phi_{\alpha\beta} = m_C/\mu,\ \varphi_{\alpha\beta} = \phi_{\alpha\beta} - \pi,\ \phi_{\alpha\beta} = [\pi, 3\pi/2] \tag{3.9}$$

from one (mass-weighted) Jacobi coordinate to the other is a mere rotation, the *hyperradius* $\rho = \sqrt{R_\alpha^2 + r_\alpha^2}$ does not depend on the arrangement index $\lambda$. A set of five hyperangles denoted collectively as $\Omega$ completes the description of configuration space.

### 3.1 Hyperradial equations

Whatever the choice of $\Omega$ hyperangles, the six-dimensional Laplacian which enters the kinetic energy part of the Hamiltonian can be written as

$$\vec{\nabla}^2_{R_\lambda} + \vec{\nabla}^2_{R_\lambda} \equiv \frac{1}{\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} - \frac{\Lambda^2(\Omega)}{\rho^2}, \tag{3.10}$$

where $\Lambda^2(\Omega)$ is a second order differential operator called the *grand−angular momentum* whose explicit analytical form depends on the choice of hyperangles [41]. It commutes with $\vec{J}^2$ and $J_z$, the total angular momentum and its space-fixed projection. The Hamiltonian can thus be written as

$$H \equiv -\frac{1}{\mu\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} + \frac{\Lambda^2(\Omega)}{2\mu\rho^2} + V(\rho,\Omega). \tag{3.11}$$

Eigenfunctions of the grand-angular momentum $\Lambda^2$ are called hyperspherical harmonics. They form a complete set of eigenfunctions in $\Omega$-space and could be used to represent the variation of $\Psi(\rho,\Omega)$ at fixed $\rho$. However, too many of them are in general needed to represent the wavefunction accurately, especially at large $\rho$.

### 3.2 The adiabatic representation.

Let us consider the fixed-$\rho$ Hamiltonian

$$H(\rho) = \frac{\Lambda^2(\Omega)}{2\mu\rho^2} + V(\rho,\Omega), \tag{3.12}$$

and define a set of *potential adapted* adiabatic states $\Phi_k^{JM}(\rho;\Omega)$ which are eigenfunctions of $H(\rho)$

$$H(\rho)\Phi_k^{JM}(\rho;\Omega) = \epsilon_k^J(\rho)\Phi_k^{JM}(\rho;\Omega). \tag{3.13}$$

The partial wave $\Psi^{JM}$ can be expanded over the $\Phi_k^{JM}(\rho;\Omega)$ states as

$$\Psi^{JM} = \frac{1}{\rho^{5/2}}\sum_k \Phi_k^{JM}(\rho;\Omega) f_k^J(\rho), \tag{3.14}$$

and the hyperradial components $f_k^J(\rho)$ are the solutions of a set of coupled second order differential equations

$$\begin{aligned}&[-\frac{1}{2\mu}\frac{d^2}{d\rho^2} + \epsilon_k^J(\rho) + \frac{15}{8\mu\rho^2} - E]f_k^J(\rho) \ - \\ &\frac{1}{2\mu}\sum_{k'}[2P_{kk'}^J(\rho)\frac{df_{k'}^J}{d\rho} + Q_{kk'}^J(\rho)\ f_{k'}^J] = 0.\end{aligned} \tag{3.15}$$

The $non-adiabatic$ couplings in (3.15) are given by

$$P_{kk'}^J(\rho) =< \Phi_k^{JM}(\rho;\Omega)|\frac{\partial}{\partial\rho}\Phi_{k'}^{JM}(\rho;\Omega) >_\Omega \tag{3.16}$$

$$Q_{kk'}^J(\rho) =< \Phi_k^{JM}(\rho;\Omega)|\frac{\partial^2}{\partial\rho^2}\Phi_{k'}^{JM}(\rho;\Omega) >_\Omega . \tag{3.17}$$

Because of the large density of states $\Phi_k^{JM}$, numerous avoided crossings occur between adiabatic curves $\epsilon_k^J(\rho)$ and the functions $\Phi_k^{JM}$ have to be evaluated on a very fine grid of $\rho$ values to yield an accurate representation of the $P$ and $Q$ couplings. As a consequence, the equations (3.15) are in general difficult to integrate numerically.

### 3.3 The diabatic representation

Instead of using an adiabatic representation, it is better to use a *diabatic* representation, i.e. an expansion over constant states, in small sectors $[\rho_p^{(l)}\rho_p^{(r)}]$ centred on $\rho_p$

$$\Psi^{JM}(\rho,\Omega) = \frac{1}{\rho^{5/2}}\sum_k \Phi_k^{JM}(\rho_p;\Omega) f_k^J(\rho_p;\rho) \tag{3.18}$$

The hyperradial components are solutions of the coupled equations

$$[-\frac{1}{2\mu}\frac{d^2}{d\rho^2} + \frac{15}{8\mu\rho^2} - E]f_k^J(\rho_p;\Omega) \ + \sum_{k'} H_{kk'}^J(\rho_p;\rho)\ f_k^J(\rho_p;\rho) = 0 \tag{3.19}$$

The diabatic coupling terms are given by

$$H_{kk'}^J(\rho_p;\rho) =< \Phi_k^{JM}(\rho_p;\Omega)|H(p)|\Phi_{k'}^{JM}(\rho_p;\Omega) >_\Omega \tag{3.20}$$

These diabatic couplings are smooth and well behaved, in contrast with the rapid variations of the non adiabatic $P$ and $Q$ couplings.

### 3.4 Propagation inside a sector

The sector width is an important parameter for the efficiency of the calculations. A small width facilitates the integration of the coupled equations because the couplings (3.20) are almost diagonal (they are exactly diagonal for $\rho = \rho_p$). However, the computational cost to determine the basis functions is large because a large number of diagonalizations is needed. On the contrary, a large sector width decreases the computational cost of the basis, but increases the one for the solution of the hyperradial equations, because matrix elements (3.20) become large when $p$ is far from the reference point $\rho_p$ and more channels are necessary to represent the wavefunction with a given accuracy. Several algorithms are currently in use for the solution of coupled equations in inelastic scattering theory. They can be used to solve the hyperradial equations. The experience is that the Johnson [42] algorithm modified by Manolopoulos [43] is very well suited to reactive problems, being both fast and accurate. It permits propagation of the logarithmic derivative matrix

$$\mathbf{Z}(\rho_p;\rho) = \mathbf{f}'(\rho_p;\rho)\mathbf{f}(\rho_p;\rho)^{-1} \tag{3.21}$$

from the left side $\rho_p^{(l)}$ to the right side $\rho_p^{(r)}$ of each sector. In (3.21), $\mathbf{f}$ and $\mathbf{f}'$ are square matrices of order $N$, where $N$ is the number of channels retained in the close-coupling expansion.

### 3.5 Propagation from one sector to the other

The condition of continuity of the quantity $\rho^{5/2}\Psi^{JM}$ and of its $\rho$-derivative permits to relate the hyperradial components and derivatives at the left boundary of the sector centred on $\rho_{p+1}$ to their values at the right boundary of the sector centred on $\rho_p$ as

$$f_k(\rho_{p+1};\rho_{p+1}^{(l)}) = \sum_{k'} U_{kk'}(\rho_{p+1};\rho_p) f_k(\rho_p;\rho_p^{(r)}) \tag{3.22}$$

$$f'_k(\rho_{p+1};\rho_{p+1}^{(l)}) = \sum_{k'} U_{kk'}(\rho_{p+1};\rho_p) f'_k(\rho_p;\rho_p^{(r)}), \tag{3.23}$$

where the elements of the transformation matrix $\mathbf{U}(\rho_{p+1};\rho)$ are given by

$$U_{kk'}(\rho_{p+1};\rho) =< \Phi_k^{JM}(\rho_p;\Omega)|\Phi_{k'}^{JM}(\rho_p;\Omega) > \tag{3.24}$$

(3.22) and (3.23) define starting conditions for integration of the coupled equations in sector $p+1$ and the transformation on the logarithmic derivative matrix $\mathbf{Z}$ can be written as

$$\mathbf{Z}(\rho_{p+1};\rho_{p+1}^{(l)}) = \mathbf{U}(\rho_{p+1};\rho_p)\mathbf{Z}(\rho_p;\rho_p^{(r)})U(\rho_{p+1};\rho_p)^{-1} \tag{3.25}$$

### 3.6 Asymptotic analysis

At a distance sufficiently large for the potential $V$ to have reached its asymptotic behaviour in each arrangement valley, the wavefunction $\Psi^{JM}$ can be matched to the asymptotic form in

$$f^J_{\lambda' v' j' l' \lambda v j l}(R_{\lambda'}) \to f^{(1)}_{\lambda v j l}(R_\lambda)\delta_{\lambda'\lambda}\delta_{v'v}\delta_{j'j}\delta_{l'l} - f^{(2)}_{\lambda v j l}(R_{\lambda'})K^J_{\lambda' v' j' l' \lambda v j l} \quad (3.26)$$

where

$$f^{(1)}_{\lambda v j l}(R_\lambda) = k^{1/2}_{\lambda v j} R_\lambda j_l(k_{\lambda v j} R_\lambda)$$
$$f^{(2)}_{\lambda v j l}(R_\lambda) = k^{1/2}_{\lambda v j} R_\lambda n_l(k_{\lambda v j} R_\lambda) \quad (3.27)$$

when the channel is open and

$$f^{(1)}_{\lambda v j l}(R_\lambda) = |k_{\lambda v j}|^{1/2} R_\lambda h^{(-)}_l(i|k_{\lambda v j}|R_\lambda)$$
$$f^{(2)}_{\lambda v j l}(R_\lambda) = |k_{\lambda v j}|^{1/2} R_\lambda h^{(+)}_l(i|k_{\lambda v j}|R_\lambda) \quad (3.28)$$

when the channel is closed ($h^{(\pm)}_l$ are spherical Hankel functions). On an hypersphere of radius $\rho_{\max}$, the quantity $\rho^{5/2}\Psi^{JM}$ and its $\rho$-derivative are continuous (the left and right values at $\rho = \rho_{\max}$ are the same for all $\Omega$). One can thus project the continuity equations onto the basis functions of the last sector $\rho_q$ whose right boundary $\rho^{(r)}_q = \rho_{\max}$. We define the matrix of regular asymptotic solutions $\mathbf{f}^{(1)}$ and its derivative $\mathbf{f}^{(1)'}$ with components

$$f^{(1)J}_{k,\lambda v j l} = < \Phi^{JM}_k(\rho_p;\Omega)|\rho^{5/2}\Psi^{(1)JM}_{k,\lambda v j l}(\mathbf{R}_\lambda \mathbf{r}_\lambda) >_\Omega \quad (3.29)$$

$$(f^{(1)J}_{k,\lambda v j l})' = < \Phi^{JM}_k(\rho_p;\Omega)|\frac{\partial}{\partial\rho}(\rho^{5/2}\Psi^{(1)JM}_{k,\lambda v j l}(\mathbf{R}_\lambda \mathbf{r}_\lambda)) >_\Omega, \quad (3.30)$$

where $\Psi^{(1)JM}_{k,\lambda v j l}$ is the full regular asymptotic function

$$\Psi^{(1)JM}_{k,\lambda v j l} \equiv \frac{1}{R_\lambda} f^{(1)}_{k,\lambda v j l}(R_\lambda)\Phi^{JM}_{k,\lambda v j l}(\widehat{\mathbf{R}}_\lambda \mathbf{r}_\lambda) \quad (3.31)$$

The quantities inside the ket in (3.29) and (3.30) are evaluated at $\rho = \rho_{\max}$ Similar expressions hold for the irregular asymptotic matrices $\mathbf{f}^{(2)}$ and $\mathbf{f}^{(2)\prime}$.The matching equations are obtained from the condition that the numerically integrated logarithmic derivative matrix $\mathbf{Z}$ is equal to its asymptotic form. Imposing $K$- matrix boundary conditions, we have

$$\mathbf{Z} = (\mathbf{f}^{(1)\prime} - \mathbf{f}^{(2)\prime}\mathbf{K})(\mathbf{f}^{(1)} - \mathbf{f}^{(2)}\mathbf{K})^{-1} \quad (3.32)$$

and the $K$-matrix is obtained as

$$\mathbf{K} = (\mathbf{Z}\mathbf{f}^{(2)} - \mathbf{f}^{(2)'})^{-1}(\mathbf{Z}\mathbf{f}^{(1)} - \mathbf{f}^{(1)\prime}) \quad (3.33)$$

$$\mathbf{S} = (\mathbf{1} + i\mathbf{K})/(\mathbf{1} - i\mathbf{K})^{-1}. \quad (3.34)$$

### 3.7 A remark on flux conservation

In the traditional inelastic scattering theory, one shows that the logarithmic derivative matrix $\mathbf{Z}$ is a symmetric matrix, because of the symmetry of coupling matrices. Moreover, the Wronskian of asymptotic functions is unity and it is easy to show that the $K$-matrix is symmetric and the $S$-matrix symmetric and unitary. In reactive collisions, the symmetry of the logarithmic derivative matrix is destroyed by the transformation (3.25) because $\mathbf{U}^{-1} \neq \mathbf{U}^t$. Also, the matrix Wronskian of the asymptotic solution matrices $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$ is not a unit matrix. As a consequence, the $K$-matrix is no longer symmetric and the $S$-matrix is no longer unitary. In practice, if enough closed channels are included in the wavefunction expansion, symmetry of the logarithmic derivative and $K$-matrices is preserved, at least for their open part.

### 3.8 Hyperspherical coordinate systems

Further remarks on coordinates, e.g. Fock [44] coordinates, Smith-Whitten [45] democratic coordinates and relations between Smith-Whitten and Fock coordinates are given in the work of Launay [2].

### 3.9 Computer implementation and applications

Several implementations of the hyperspherical method exist at present [46, 49, 50, 51, 52, 53]. It appears that Smith-Whitten coordinates are very convenient because they single out the projection of the total angular momentum onto the axis of least inertia. This axis is close to the atom-diatom axis in each arrangement and rotates slowly from the reactant atom-diatom axis to the product one for reactions in which symmetric top configuration is not accessible [54, 57]. When quantizing internal motion onto this axis, one finds that rotational coupling is minimal for reactions in which the saddle point is in a linear or near-linear configuration. The most expensive part of the computations lies in the solution of the close-coupling equations for all $J$ and $E$ values which are needed to get converged cross sections. Computer time scales as $N^3$, where $N$ is the number of channels because algorithms involve matrix inversions of order $N$. Using present day computers, systems involving about one thousand channels (or even more) can be treated and converged reaction cross sections have been recently obtained on systems like $H + H_2$ [51, 52, 53], $F + H_2$ [58, 59], $Cl + H_2$ [60], $He + H_2^+$ [61], $Ne + H_2^+$ [62], etc..

## 4. Reduced dimensionality and recent developments

### 4.1 Reduced dimensionality

For the past twenty years there have been developing, testing, and applying approximate theories of quantum reactive scattering to three-atom systems.

The terminology reduced dimensionality is used to characterize these theories. The reason for this terminology is that in these theories the number of dynamically coupled degrees of freedom is reduced relative to an exact approach. For nonrotating, three-atom systems there are three internal degrees of freedom that are coupled. Two of these can be chosen as radial distances, say the distance from one atom, A, to the center of mass of the other two, B and C, and the distance between B and C. The third degree of freedom is an angle which is needed to uniquely define the three-atom configuration. This angle plays a key role in the reactivity of many systems, since only restricted values of it will lead to appreciable reaction at thermal collision energies.

In several reduced dimensionality theories of reactive scattering the angle mentioned above is decoupled dynamically from the two radial degrees of freedom. In one approach the angular motion is treated in the sudden approximation [79, 80, 81], and in another it is treated adiabatically [82, 83, 84, 85, 81]. Perhaps the most significant difference between these two opposing pictures is the inclusion of quantised bending motion in the latter and its exclusion in the former.

Most of the work of Bowman in reduced dimensionality reactive scattering has concentrated on the adiabatic treatment of the bending motion. The accuracy of this approach has been demonstrated for every triatomic system for which an exact calculation has been done. It should be noted, however, that all these systems are collinearly dominated.

In comparison to the number and breadth of calculations of three-atom reactions, very few reactive scattering calculations have been done for four-atom reactions. The reasons for this are clear and compelling. Four-atom systems have twice as many internal degrees of freedom (six) compared to three-atom systems (which have three). This doubling of the number of internal degrees of freedom greatly complicates the problem. First, the number of conceivable arrangement channels changes from 3 for three-atom systems to 15 for four-atom systems. Second, the "size" of quantum methods based on a basis-set expansion or a grid representation of the wavefunction grows exponentially with the number of degrees of freedom. Third, and somewhat peripheral to the first two points, is the complexity of the potential function. While there has been significant progress in generating global potentials for four-atom systems recently citebow949, we are still far from the goal of having a general method that can exactly incorporate accurate ab initio or spectroscopic information into a global functional or numerical form.

In the reduced dimensionality quantum theory of reactive scattering for four-atom systems, AB + CD $\rightarrow$ A + ACD the theory assumes that the CD bond is inert, and in addition one treats the internal angular degrees of freedom in an adiabatic approximation. This results in a reduction in the number of dynamically coupled degrees of freedom from six, in an exact treatment, to three, the three radial distances, in the approximate theory. The scattering is treated in the reduced dimensionality space "exactly, " and for each bending

state of the four-atom system vibrational state-to-state scattering matrices and reaction probabilities are calculated. Of the three internal bending degrees of freedom (for the general nonlinear case), one bending degree of freedom correlates with the bend of the triatomic molecule. When summed over the quantum states of the two other bending degrees of freedom, the resulting reaction probabilities are vibrational state-to-state, but rotationally summed over the initial and final rotational states of the reactants and products. The theory is presented in detail for the nonrotating case, $J$ equal to zero, and simple energy shift approximations are made to relate reaction probabilities for $J \neq 0$ to the $J = 0$ ones. Energy shift approximations are also introduced to obtain reaction probabilities for excited bending states. These energy shifts are simply the rotational and bending energies of the four-atom transition state. Two reaction systems have been investigated in detail: $H_2$ + CN $\rightarrow$ HCN + H and OH + $H_2$ $\rightarrow$ $H_2O$ + H.
Authors: Bowman; Clary; Hayes, Walker (bending-corrected rotating linear model);
see: [63]

*Energy shift approximation.* Bowman: [63]

### 4.2 Recent developments

There has been a tremendous development of methods to handle theoretically quantum reactive scattering processes. In this section only a brief list with references and authors working with the different subjects will be given.

**Different variational principles:** Newton variational principle, Schwinger variational principle, amplitude density method: Truhlar, Kouri and coworkers; [65], [63]
Kohn variational principle: Miller, Zhang, Manolopolous, Wyatt and coworkers; [63], [64]
**Different body-fixed systems:** Pack, Parker and coworkers: [63]
**Different hyperspherical approaches:** Aquilanti et al. in [63]; Launay, Le Dourneuf (see refs. in [2]); Linderberg et al. [46]; Pack, Parker, Kress, Lagana, et al. (see refs. in [131]); Schatz et al. [66]; Manolopolous et al. (see refs. in [67]); Billing et al. [75]; Hinze, Wolniewiecz, Ahlijah [76];
**Different arrangement channel procedures:** Kouri, Truhlar et al. [3]; Micha [68, 69]; Tang [69]
**Integral equation approaches:** Kouri [69]; Truhlar et al. [63] ; Micha [68, 69]
**Time-independent wave packets:** Kouri [74]; Zhang [74]; Althorpe et al. [77]
**Approximate methods:** Angular momentum decoupling, reactive infinite order sudden (RIOS) and other methods: Kouri, Pack, Jellinek, Baer and coworkers; [69, 70]

Faddeev approach: Micha [68]
T-matrix approach: Tang [69]
Distorted wave Born approximation: Schatz, Miller, Tang and coworkers
**Negative imaginary potentials:** Last, Baer [63]; see Fig. 4.1, 4.2
**Four- and polyatomic reactions:** Bowman, Clary, Schatz and coworkers [63]
**Non-adiabatic reactions:** Schatz, Connor, Baer, Truhlar, Nakamura and coworkers [63]
**The geometric phase effect:** Some comments to this theme are given in the second next chapter. Further details, see e.g.: Kuppermann [63, 71]; Baer [69]

# 5. Computer implementations and methodologies

## 5.1 Basis sets, DVR, FEM, etc.

For detailed information the reader is referred to refs.[86], [72], [73].

*The finite element method (FEM).* The general idea of FEM applied to solve the Schrödinger equation is to change over from the integration to a summation over many subdomains called elements [87, 1]. On each element the wavefunction is approximated by a parametrised function $u$. The simplest choice are polynomials of different degrees, e.g. in two dimensions

$$u(x,y) = \sum_{i,j} c_{ij} x^i y^j . \tag{5.1}$$

On each element $e$ a certain number of grid points is choosen and the function $u$ on the element is expanded as

$$u^{(e)}(x,y) = \sum_{i=1}^{p} u_i^{(e)} \tilde{N}_i^{(e)}(x,y) = \sum_{i=1}^{p} u_i^{(e)} N_i^{(e)}(\zeta_1,\zeta_2,\zeta_3)$$

$$u_i^{(e)} = u(x_i,y_i), \tag{5.2}$$

where the formfunctions $\tilde{N}_i^{(e)}$ $(N_i^{(e)})$ are defined to have interpolating properties inside each element $e$ and are zero or one at the grid points:

$$\tilde{N}_i^{(e)}(x_j,y_j) = \delta_{ij} \quad . \tag{5.3}$$

Integrals over the whole domain of the problem are then sums over all elements. We choose a triangular form of the elements. One obtains a simple integration formula, if one transforms from an arbitrary triangle to a unit rectangular triangle with the coordinates $\xi$ and $\eta$ and then to "natural triangular coordinates" $\zeta_i$ (see Fig. 1a, b in ref. [33]):

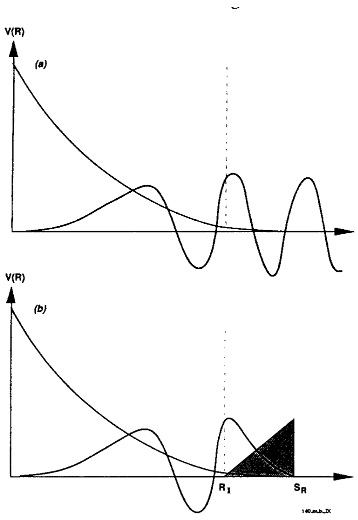


**Fig. 4.1.** Potential with a schematic wave function. (a) Without negative imaginary potential, (b) with negative imaginary potential. (Reprinted, by permission, from Last,I., Baer, M. in: Bowman, J.M. (Ed.): *Advances in Molecular Vibrations and Collision Dynamics*, Vol. 2 (JAI Press, Greenwich, CT, 1994)

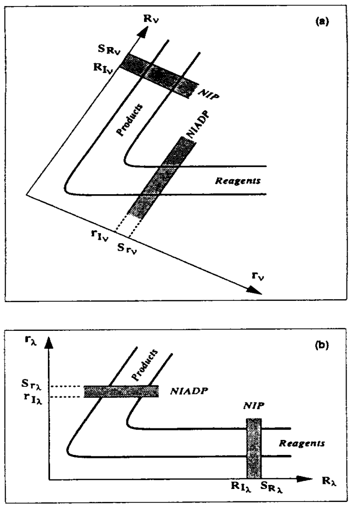


**Fig. 4.2.** Collinear potential energ with NIP and NIADP. (a) product arrangement channel, (b) reagent arrangement channel. NIP: negative imaginary potential, NIADP: negative imaginary potential decoupling potential. (Reprinted, by permission, from Last,I., Baer, M. in: Bowman, J.M. (Ed.): *Advances in Molecular Vibrations and Collision Dynamics*, Vol. 2 (JAI Press, Greenwich, CT, 1994)

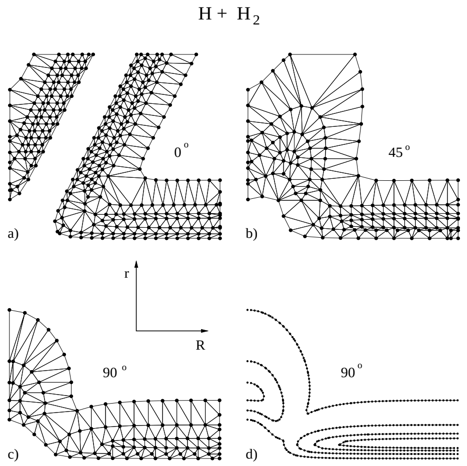


**Fig. 5.1.** H + $H_2$, **a-c):** Three different discretisations for the angles $0^o, 45^o$ and $90^o$ are shown $(r, R = [0, 8]\ a_0)$. The discretisation is based on a contour plot of the potential with energies $E = 0.12, 0.05, 0.02, 0.007\ E_h$. **d)** A contour plot for $90^o$ is shown. During the triangulation process some contours were discarded. (Reprinted, by permission, from Jaquet, R., A. Kumpf, M. Heinen: *J. Chem. Soc., Farad. Trans.* **93** (1997) 1027. Copyright 1997 by Royal Society of Chemistry.)

$$\begin{aligned} x &= x_1 + (x_2 - x_1)\xi + (x_3 - x_1)\eta \\ y &= y_1 + (y_2 - y_1)\xi + (y_3 - y_1)\eta \end{aligned} \tag{5.4}$$

$$\zeta_1 = 1 - \xi - \eta, \qquad \zeta_2 = \xi, \qquad \zeta_3 = \eta\ . \tag{5.5}$$

The formfunctions can then be expressed in terms of the $\zeta_i$. We have developed general formulas in one and two dimensions and these have been already given [88, 33]. In our calculations we are using regularly polynomials of 5th order, although other choices are possible.

*Grid schemes in FE for calculating a potential adapted basis..* In order to reduce the amount of computing time, that is related to solving linear equations (e.g. eq. (2.59)), we tested eigenfunctions that cover some or all different reaction channels and these eigenfunctions will build up an effective basis set for scattering. This will be even more interesting for polyatomic systems if for each channel, potential adapted eigenfunctions (in more than one dimension) can be made available. The problem that one has to deal with is the linear dependency. In an earlier work we tested it for collinear H + $H_2$. But the most appropriate version is to include the complete area for the whole reaction including the break up into the three atoms. This is the version we are applying in our work.
The advantage of FE is to have the choice to use an irregular grid that is adapted to the given problem. In our applications we normally use an equidistantly subdivided grid for that part of the potential area that is needed to describe the physics correctly. Within the multigrid methods the solution

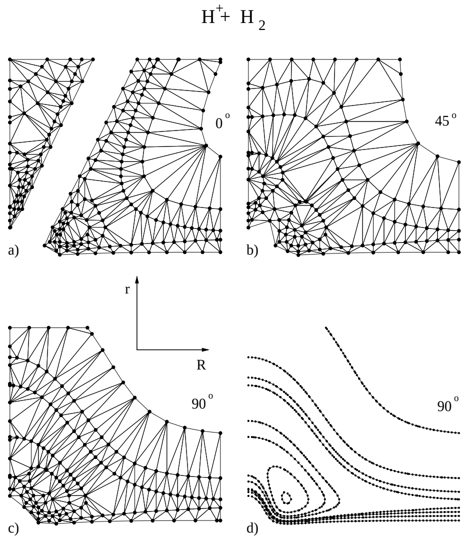


**Fig. 5.2.** $H^+ + H_2$, **a-c):** Three different discretisations for the angles $0^o, 45^o$ and $90^o$ are shown ($r, R = [0, 8]\ a_0$). The discretisation is based on a contour plot of the potential with energies $E = 0.3,\ 0.23,\ 0.2,\ 0.187,\ 0.12,\ 0.09,\ 0.046,\ 0.004\ \ E_h$. The first four energies match those of the $H + H_2$ potential. **d)** A contour plot for $90^o$ is shown. During the triangulation process some contours were discarded. (Reprinted, by permission, from Jaquet, R., A. Kumpf, M. Heinen: *J. Chem. Soc., Farad. Trans.* **93** (1997) 1027. Copyright 1997 by Royal Society of Chemistry.)

algorithm defines where to choose more grid points. This means a special grid for a special single solution. We would like to have an adapted grid that is nearly optimal for many solutions, e.g. many bound state wavefunctions or for scattering calculations with many collision energies. In an earlier work [88] we showed how to use the Bohr-Sommerfeld (BS) formula to create a 1D grid that leads to a small number of points for which many eigenvalues (up to $E_{max}$) can be calculated with the same high accuracy. We choose the grid points $x_i$ in such a way that $\int_{x_{i-1}}^{x_i} p(x)dx \approx \pi\hbar$ with $p(x) = \sqrt{2\mu_x(E_{max} - V(x)}$ as the classical momentum corresponding to the energy $E_{max}$. Now we try to optimise the grid in 2D in two different ways depending on the underlying potential energy surface (PES). In the first version the grid depends on the contour lines of the PES for well choosen energy values. Each contour line is described by a number of points which are used for triangulation. The energy values and the spacing of the points on the contour lines are defined by some rules, e.g. logarithmic or exponential spacing for the energy values depending on the problem and enlarged spacing on the contour lines for high energies, e.g. well above the collision energy. Results are given in Fig. 5.1. There is still a problem related to the shape of the triangles. The triangulation should not create triangles with too sharp angles and not to many triangles have to be connected in one point (around 6 would be optimal), otherwise the polynomial approximation in FEM becomes numerically problematic. Thus,

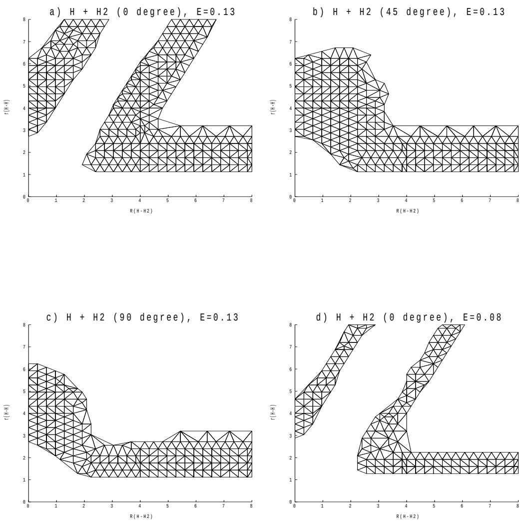


**Fig. 5.3.** H + $H_2$, **a-c):** Three different discretisations for the angles $0^o, 45^o$ and $90^o$ are shown ($r, R = [0, 8]\ a_0$). The discretisation is based on the combined use of the Bohr-Sommerfeld formula [??] in one dimension for $r$ and $R$ with $E_{max} = 0.13\ E_h$. **d)** A smaller range for triangulation is shown for $0^o$ and with $E_{max} = 0.08\ E_h$ (collinear arrangement). (Reprinted, by permission, from Jaquet, R., A. Kumpf, M. Heinen: *J. Chem. Soc., Farad. Trans.* **93** (1997) 1027. Copyright 1997 by Royal Society of Chemistry.)

all this depends on the number of grid points to start with and how dense they are lying. In Fig. 5.1 and 5.2 the grid is shown for H + $H_2$ [59] and $H^+$ + $H_2$ [90] for the angles $0^o, 45^o, 90^o$ (in Jacobi coordinates), whereas in Fig. 5.1d and 5.2d the starting points with the contour lines are shown. Beginning with these values triangles are created and after that a reduction of triangles will proceed. The automatic grid generation for the two examples is still not optimal, but shows the different features of dense grid points in the deep well for $H^+$ + $H_2$ and the less density for the barrier in H + $H_2$.
Because of the mentioned problems with the grid generation in the first version, we developed a second version that is related to our earlier work in 1D using the BS-formula. Starting with a relatively fine equidistant grid in 2D (e.g. in x, y ($r$ and $R$ in Jacobi coordinates)) we use the 1D formula for each stripe in x for a given y and vice versa for y for a given x values (symmetrisation can be included). We keep only those points of our grid that fulfil the requirements that the application of the 1D BS-formula leads to a solution in

x- and y-direction. In Fig. 5.3 we show a solution for the H + $H_2$ potential. The advantage is that we do not create too many points for the grid mesh, the angles of the triangles are not too small and practically no reduction of grid points has to be performed.

*Combination of FE and DVR..* In ABC-systems we have to deal with three coordinates (Euler angles are integrated out analytically), which are coupled more or less. If we choose Jacobi coordinates $R, r, \gamma$ at least in the reactant channel $R$ and $r$ are more strongly coupled, so we solve the $(R, r)$- problem with FE (no separation Ansatz) and describe the angular part by a discrete variable representation (DVR) [91]. The potential is expanded in Legendre polynomials, so for each fixed angle $\gamma$ a 2D solution using FE is performed.

### 5.2 Close coupling solvers

We now comment on methods that solve the equations as coupled ordinary differential equations (these considerations are taken as an extraction from the work of Kouri and Hoffman [92]). This approach can treat completely general scattering problems, including those involving rearrangements and breakup. However, to do so in a reasonably straight forward way, one must use coordinates that are able, with a single distance variable, to describe all possible arrangements. This is most easily achieved by use of hyperspherical coordinates (of which there are many possible choices). Our interest here is simply to indicate how solutions are generated that satisfy the boundary conditions, and what the principal complication is. It suffices to consider again the scattering of a projectile in $3D$ by a nonspherical scatterer. Thus, the potential, $V(\mathbf{r})$, depends on $r$, $\theta$, and $\varphi$, and the time-independent Schrödinger equation (TISE) is

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi = E\psi. \tag{5.6}$$

We expand $\psi$ in a truncated basis of spherical harmonics:

$$\psi(\mathbf{r}) = \sum_{l'}^{l_{\max}} \sum_{m'} Y_{l'm'}(\widehat{\mathbf{r}}) U_{l'm'}(r)/r. \tag{5.7}$$

We substitute (5.7) into (5.6) and project with a particular basis function, $Y_{lm}(\widehat{\mathbf{r}})$, to obtain the coupled equations

$$\begin{aligned}(E + \frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \frac{\hbar^2 l(l+1)}{2mr^2})U_{lm}(r) = \\ \sum_{l'}\sum_{m'} V(lml'm'|r)U_{l'm'}(r).\end{aligned} \tag{5.8}$$

In fact, if one includes a total of $N$-basis functions in the expansion, (5.8) will have $2N$ linearly independent solutions.

However, 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 the $U_{lm}$, to signify the linearly independent solution it represents:

$$(E + \tfrac{\hbar^2}{2m}\tfrac{d^2}{dr^2} - \tfrac{\hbar^2 l(l+1)}{2mr^2})U(lml_0m_0|r)$$
$$= \sum_{l'}\sum_{m'} V(lml'm'|r)U(l'm'l_0m_0|r), \tag{5.9}$$

(5.10) or in obvious matrix notation,

$$(E\mathbf{I} - \mathbf{K}) * \mathbf{U}(\mathbf{r}) = \mathbf{V} * \mathbf{U}(\mathbf{r}). \tag{5.10}$$

Note that $\mathbf{I}$ and $\mathbf{K}$ are diagonal matrices, and we interpret the $lm$ indices of $U(lml_0m_0|r)$ as "final state" indices and $l_0m_0$ as "initial state" indices. In addition to the regularity condition at $r = 0$ (which for typical potentials in atom-diatom scattering becomes the condition that $U(lml_0m_0|0) = 0$), we want to impose the asymptotic condition

$$\lim_{r\to\infty} U(lml_0m_0|r) =$$
$$\delta_{ll_0}\delta_{mm_0}j_l(kr) + h_l^+(kr)T(lml_0m_0). \tag{5.11}$$

This means that we must deal with a "two point" boundary condition problem, and we do not know the value of $T(lml_0m_0)$. This is equivalent to saying that although we know that $U(lml_0m_0|0) = 0$, we do *not* know what the correct value is for the derivatives, $dU(lml_0m_0|r)/dr$ at $r = 0$. The usual way to circumvent this difficulty is to convert the problem into a $pseudo - initial$ *value problem*. The initial conditions typically are taken to be

$$(a) \qquad U(lml_0m_0|0) = 0 \tag{5.12}$$

and

$$(b) \qquad \frac{d}{dr}U(lml_0m_0|r)|_{r=0} = \delta_{ll_0}\delta_{mm_0}. \tag{5.13}$$

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. This procedure generally requires solving a system of linear algebraic equations that yields the scattering amplitudes.

In principle, the above procedure works, However, there is a practical difficulty that makes additional computational effort necessary, because different $l$-values lead to different classical turning points at a given total energy $E$. As a result, 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, (5.9), including varieties of the Numerov method, the so-called log- derivative method (which essentially calculates $\mathbf{U^{-1}} * \mathbf{dU/dr}$), etc.
Finally, we should comment on how the computational effort scales with problem size, since some methods may be very efficient for small problems but rapidly become impractical as the complexity increases. Similarly, some methods may not be so efficient for smaller problems, but have slow scaling with problem size. Generally, all of the methods discussed involve either matrix-matrix multiplications or solutions of linear algebraic equations. Both procedures scale as the cube of the matrix dimensions. However, 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). Thus, these types of approaches involve of the order of $N^3$ multiplications at each step in prop, agating 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 $f_n$

$$U = \sum_{n=1}^{N} f_n, \tag{5.14}$$

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.
We can introduce an "average" number of basis functions, $\langle f_n \rangle$, such that

$$U = N \langle f_n \rangle , \tag{5.15}$$

and 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.

Further information is given, by Lester [93], Johnson, Manolopolous, Alison [95], Mrugala [94], Secrest [93] and for R-matrix-method [96].

## 6. Examples: "Exact" calculations for $H + H_2$, $F + H_2$, etc.

**6.0.1 Some remarks to Jacobi coordinates and scattering applications.** It should be clear from Fig. 2b (Part I) that either set of mass-scaled Jacobi coordinates alone provides a complete description of the available collinear coordinate space. However, it should be equally clear that while $R_a$ and $r_a$ are better suited to describing translational and vibrational motions in the reactant channel, $R_c$ and $r_c$ are more appropriate for a corresponding description of the products. It therefore seems natural to retain both sets of coordinates at once, using each set for convenience as required. Moreover, formulations of quantum reactive scattering based on this idea are quite easy to construct. Indeed a comprehensive account of such a formulation, for the general case of a 3D atom-diatom reaction, was given by Miller [97]. Several other formulations have also been proposed by Baer, Kouri, and coworkers over the last years [98] and have been reviewed and extended by Baer [99].
Because the translational and vibrational motions in the reactant channel are coupled non-locally to those in the product channel, it is usually most convenient to use basis functions to describe the motions in each arrangement. The non-local couplings between the reactant and product channels then appear as exchange integrals between basis functions in different chemical arrangements's [97]. These exchange integrals are simply a mathematical manifestation of the interactions which cause the reaction to proceed. They are augmented by direct interaction potential integrals between basis functions in the same chemical arrangement, which in turn are responsible for all the elastic and inelastic scattering effects.
Having chosen to adopt this description of reactions one must still find some way of extracting the desired scattering information. The best way to do this is to use a variational principle for the scattering matrix of interest, which is then obtained one order more accurately in the error than the scattering wave function itself [100]. The advantage of the approach stems in part from the fact that the scattering wave function is only very rarely explicitly required. In fact it is never required in purely reactive scattering problems.
The computational effort in variational reactive scattering has two main sources. First one must evaluate costly multi-dimensional exchange integrals between basis functions in different chemical arrangements, and then one must solve a large system of linear algebraic equations for the scattering matrix of

interest. While it is probably fair to say that these computational problems have both been solved by 'brute force' in most applications to date, several ingenious approaches to their solution have also recently been proposed.

The three variational principles in common use in scattering theory are due to Kohn [8], Schwinger [104] and Newton [105]. Two of these variational principles, those due to Kohn and Newton, have been successfully developed and applied to reactive scattering problems in recent years: there is the 'S-matrix Kohn' method of Zhang, Chu, and Miller, the related 'log derivative Kohn' method of Manolopoulos, D'Mello, and Wyatt and the '$L^2$- Amplitude Density Generalized Newton Variational Principle' ($L^2$-AD GNVP) method of Schwenke, Kouri, and Truhlar.

The Kohn variational principle is perhaps the simplest of the three scattering variational principles mentioned above [8]. In particular, it requires that one calculate matrix elements only over the total Hamiltonian $H$ of the system, and not over the Green's function $G_0(E)$ of some reference Hamiltonian $H_0$. While matrix elements of $H$ between energy-independent basis functions are also energy-independent, all matrix elements of $G_0(E)$ have to be re-evaluated at each new scattering energy E. The Kohn variational principle is therefore somewhat easier to apply than the Schwinger and Newton variational principles, which involve the use of $G_0(E)$, when calculations are required on a tight energy grid. This is invariably the case, for example, in any detailed analysis of quantum mechanical resonance effects [102].

Unfortunately, traditional applications of the Kohn variational principle in electron-atom and electron-molecule scattering have been plagued by spurious singularities, or 'Kohn anomalies', of the kind observed originally by Schwartz [106]. A convenient solution to this problem did not really arrive until 1987, when Miller and Jansen op de Haar published a paper describing a new basis set method for quantum scattering problems [107]. Their method is based on a variational basis set expansion for matrix elements of the full scattering Green's function

$$G^+(E) = \lim_{\epsilon \to 0} (E + i\epsilon - H)^{-1} \tag{6.1}$$

and involves, in addition to the usual square integrable basis functions of bound state calculations, certain damped scattering functions which enforce the outgoing wave boundary conditions implied by the $+i\epsilon$ [108]. This direct application of outgoing wave boundary conditions leads to a complex symmetric matrix representation of $(E - H)$, rather than the real symmetric matrix representation obtained when conventional standing wave boundary conditions are applied [100, 8]. The Kohn anomalies found by Schwartz are now known to be an artifact of these standing wave boundary conditions, and so are not expected to appear in Miller and Jansen op de Haar's approach [109, 110].

In their original paper Miller and Jansen op de Haar only applied their method to simple elastic and inelastic scattering tests [107].The first practical demonstration of its efficiency came, when Zhang and Miller used the method

to calculate $J = 0$ reaction probabilities, over quite a wide energy range, for the already heavily studied H+$H_2$ reaction [103]. Their results agreed well with the earlier calculations, and appeared to be quite easy to converge.
The next development came at the beginning of 1988, when Zhang, Chu, and Miller recast their approach in terms of a direct variational expression for the scattering matrix S [111]. This paper uses the Löwdin-Feshbach partitioning identity to separate out the real and complex parts of the problem, and exploits the complex conjugation symmetry between incoming and outgoing wave scattering functions to reduce the number of integrals and linear equations involved. Interestingly, the resulting methodology bears more relation to the original (K-matrix) version of the Kohn variational principle than does the earlier work of Miller and Jansen op de Haar. However, Miller has since shown quite explicitly that both versions of his methodology are at least formally, if not practically, the same [112, 113].
The final streamlined version of the S-matrix Kohn method proposed by Zhang, Chu, and Miller has been applied quite successfully in recent years. In particular, and after a preliminary calculation of $J = 0$ reaction probabilities for F+$H_2$ [114], Zhang and Miller have concentrated more or less exclusively on the calculation of high energy integral and differential cross sections for the H + $H_2$ and D + $H_2$ reactions. Their first major application came at the end of 1988, when they reported fully converged integral cross sections for H+$H_2(v = 0, j = 0) \rightarrow$ $H_2$ $(v' = 1, j = 1, 3)$+H in the energy range $E_{tot} =$ 0.9 to 1.4 eV [115]. This was the first calculation of integral cross sections for the hydrogen exchange reaction at sufficiently many energies above the $v' = 1$ threshold, and on a sufficiently accurate potential energy surface, to allow for a detailed comparison with the resonant structure observed in the bulk experiments of Nieh and Valentini [116]. However, while Zhang and Miller's calculations did show resonant structure in the low partial waves, this structure was 'washed out' of their integral cross-sections by the angular momentum averaging in the partial wave sum [117].
Since they had observed some resonant structure in their low total angular momentum calculations, semi-classical arguments led Zhang and Miller to suggest that Nieh and Valentini's experimental apparatus might preferentially be measuring differential cross sections in the backward direction, rather than the integral cross sections that were claimed. In order to test this suggestion Manolopoulos and Wyatt [118] and Zhang and Miller [124] have since calculated these differential cross sections in the relevant energy range. While some resonant structure as a function of the scattering energy is indeed seen in these calculations, this structure is not nearly so pronounced as, nor even really compatible with, that which is experimentally observed [125]. This and other attempts to 'explain' the Nieh and Valentini experiment have recently been reviewed in some detail by Miller [126].
Further details on other variational approaches, see the review of Manolopolous and Clary [64].

**6.0.2 Some remarks to hyperspherical coordinates and scattering applications.** In short, the various 3D hyperspherical coordinate methods can be classified into two distinct groups. The methods in the first group, which we shall simply lump together under the heading of 'Delves coordinate' (DC)) methods, are characterized by the use of 3D Delves hyperspherical coordinates in the close interaction region, irrespective of whether or not they are used doubled in one arrangement [119] or, as originally defined [120], in all three [121]. The methods in the second group, which we shall refer to as 'principle axis' (PA) methods, are characterized by the use of a single hyperspherical coordinate system that treats all three arrangements in an equivalent way [125, 127, 128, 129].
The adiabatically adjusting principle axis hyperspherical (APH) coordinate method of Pack and Parker is well known [54, 130, 122, 131, 132, 123]. The APH coordinates were first introduced by Pack, in 1984, as a route to an optimum centrifugal sudden (CS) approximation for reactions [125]. These coordinates are similar to the earlier PA hyperspherical coordinates of Smith and Whitten [127] and of Johnson [129], but differ in that they do not require the use of half-integer angular momenta [127, 129] and are better suited to the prolate symmetric top (e.g. collinear and asymptotic atom plus diatom) configurations that are most often energetically preferred [54].
The earliest applications of the APH coordinate method were to the calculation of $J = 0$ and $J = 1$ reaction probabilities for the H + $H_2$ and D + $H_2$ reactions [54, 124, **?**]. While these calculations demonstrated the feasibility of the method they used a general finite element program to solve the surface eigenvalue problem [54] and were found to be comparatively expensive to perform. A careful comparison of other approaches to the eigenvalue problem, including variational basis set expansion and the discrete variable representation (DVR) developed by Light and coworkers [133] soon suggested that this bottleneck might more easily be overcome.
In [134] a symmetry adapted DVR is used, combined with the sequential diagonalisation and truncation procedure of Light and coworkers, to solve the surface eigenvalue problem for the PES representation of F + $H_2$. These calculations of Bacic and coworkers on the F + $H_2$ reaction provide an impressive demonstration of the APH coordinate and DVR surface eigenproblem approach.
Launay and Le Dourneuf use essentially, although not exactly, the same PA hyperspherical coordinates as Pack and Parker. In particular, they choose the quantisation axis for the internal motion as the axis of least inertia, so that the rotational couplings about this axis are minimised in a variational way [**?**, **?**]. This leads to rapid convergence of reaction probabilities with respect to the total angular momentum projection quantum number $\Omega$, and so allows one to use far smaller basis sets for large $J$ values than are required when all possible projections are retained.

The method proposed by Launay and Le Dourneuf differs from that of Pack and Parker in the choice of the hyperangular surface Hamiltonian. Pack and Parker retain as many of the kinetic energy terms in this Hamiltonian as is possible, leaving fewer terms to be incorporated later in the solution of the coupled hyperradial equations [54]. Launay and LeDourneuf retain fewer terms in the surface Hamiltonian, all of which are essentially independent of the total angular momentum $J$ [51]. This approach is only possible for atom-diatom reactions in which equilateral triangle configurations are energetically forbidden, but it does mean that for these reactions, of which there are several, the surface eigenproblern can be solved once and for all independent of $J$. Launay and Le Dourneuf also describe a simple variational basis set expansion for the surface eigenvalue problem, and show how many of the required matrix elements can once again be evaluated independent of $J$ [51].

The work of Linderberg and coworkers is based on finite elements, which are used both for solving the surface eigenvalue problem [46, 135, 136, 137] and the variational $R$-matrix propagation within the coupled hyperradial equations problem [137]. However, they also adopt the early PA hyperspherical coordinates of Mead [128], which are probably less appropriate for reactions than $H_3$ or $FH_2$.

Kuppermann and co-workers [119], and Schatz [121] have used the Delves coordinate (DC) method and applied it to novel reactive scattering problems in recent years. Kuppermann introduced his symmetrised hyperspherical coordinates in 1975, at a time when the original quantum reactive scattering calculations on the hydrogen exchange reaction were just beginning to appear. These coordinates are essentially the same as the 3D hyperspherical coordinates introduced by Delves [120], except that the angle $\theta_a$ is doubled to allow a more useful symmetric mapping of three-atom potential energy surfaces. Pack and Parker refer to Kuppermann's coordinates as 'doubled Delves' coordinates [54].

In 1986, more than a decade after they were first introduced, Kuppermann and Hipes reported the successful application of a method based on doubled Delves coordinates to the hydrogen exchange reaction for total angular momentum $J = 0$ [55]. ($H+H_2(v = 0, j = 0) \rightarrow H_2(v', j')+H$) and was the first 3D application of an exact quantum mechanical method without natural collision coordinates. Hipes and Kuppermann extended this work to higher energies [49] and gave detailed Eisenbud-Wigner time delays [138] and Smith collision lifetimes [150] analyses of the observed $J = 0$ resonance effects.

In their early calculations Hipes and Kuppermann used the finite element method to solve the surface eigenvalue problem at each required value of the hyperradius $\rho$. However, like Parker and co-workers, they have since found that other techniques may make their calculations easier to do. Specifically, Cuccaro, Hipes, and Kuppermann have published two papers in which they describe a variational approach to the surface eigenvalue problem [139] and apply it to the calculation of $J = 0$ and $J = 1$ reaction probabilities and

collision lifetime matrices for the PK2 and LSTH potential energy surface representations of $H+H_2$;
this work provides the first practical demonstration of the doubled Delves coordinate method for $J > 0$.
The last of the competing hyperspherical coordinate methods was introduced in 1988 by Schatz [121]. In order to avoid the problems caused by the non-equivalent treatment of the different arrangements, Schatz chooses to retain all three sets of 3D Delves coordinates at once. This can in principle lead to linear dependence problems if the coupled-channel basis functions, which in this case are only very roughly analogous to the surface eigenfunctions described above, are not chosen with some care. Schatz defines his basis functions in terms of the solutions to certain one-dimensional reference Schrödinger equations in each arrangement, which seems in practice to work quite well [56, 151]. The resulting methodology has much in common with the Fock coupling scheme proposed earlier by Schwenke and coworkers [152], who used a mixed hyperspherical and Jacobi coordinate set. It also effectively bridges the gap between the earlier hyperspherical coordinate methods and the Jacobi coordinate variational methods.
At the same time as triatomic systems had been investigated by hyperspherical methods, several 3D hyperspherical coordinate schemes for reactions involving polyatomic molecules have also been proposed [153, 154]. In 1990 calculations on a (diatom + diatom) to (atom + triatom) reaction had already been carried out by Brooks and Clary [155]. This paper develops a collinear four-atom hyperspherical coordinate system and reports the first converged collinear reaction probabilities for $H_2$ + CN. Further details, up to 1990, are given in the review of Manolopolous and Clary [64]. Most recent developments and applications are given in the book of Bowman [63], in the new special issues in Physical Chemistry Chemical Physics (1999), Faraday Discussion 110 (1998) and Faraday Transactions Vol. 93 (1997) and are presented at the 5th workshop on "Quantum reactive scattering" in Perugia, Italy, 1999.

## 6.1 H + $H_2$

This reaction has attracted theoretions ever since and original work before 1980 is presented by Kuppermann et al. [140, 141, 142], Wyatt et al. [143, 144, 145], Light et al. [146] and reviews up to 1990 are presented by Truhlar, Miller, etc. (Ann. Rev. Phys. Chem.: 1990).
The potential energy surfaces for H + $H_2$ that have been used over the last years are given in: PK: [147], LSTH: [148], DMBE: [156], BKMP: [157], BKMP2: [158].
Newest work on H + $D_2$ is presented in [159, 160, 161].

**6.1.1 The geometric phase effect in H + $H_2$.** Over the years there had been a long discussion of what might be the reason for deviations between theoretical and experimental work on the reaction probabilities in $H + H_2$. One of these topics are related to the geometric phase effect and the next subsection is extracted from the work of Kuppermann [149, 163].

In diatomic systems the potential energy curves of two electronically adiabatic states will only intersect if the states have different symmetries or differ in some other crucial manner. For a polyatomic system, on the other hand, two electronically adiabatic potential energy surfaces (PESs) can intersect even if the corresponding states have the same symmetry and spin multiplicity [164]. This possibility stems from the fact that such systems have more than one independent nuclear coordinate. Let us assume that the spin terms in the system's Hamiltonian can be neglected and that two of its electronically adiabatic PESs display an intersection that is conical. Furthermore, let us require that the corresponding adiabatic electronic wave functions be real and as continuous a function of the nuclear coordinates as possible. Then, if the system is transported around a closed loop in nuclear configuration space (a so-called pseudorotation) that encircles an intersection geometry, those wave functions must change sign [164, 165]. Reciprocally, if such an adiabatic electronic wave function changes sign upon a motion of the polyatomic system around a closed loop in nuclear configuration space, somewhere on or inside that loop there must exist a conical intersection. These conical intersections are a generalization of those associated with the Jahn-Teller effect [166]. Conical intersections between electronically adiabatic potential energy surfaces are not only possible but actually quite frequent, if not prevalent, in polyatomic systems. Some examples are triatomic systems whose isolated atoms have $^2S$ ground states [164, 165] such as $H_3$ and its isotopomers ($DH_2$, HD, HDT, etc.), $LiH_2$ and its isotopomers, and tri-alkali systems such as $Na_3$ and LiNaK. Many other kinds of polyatomic molecules also display such intersections. The reason is that they have three or more internal nuclear motion degrees of freedom, and only two independent relations between electronic Hamiltonian matrix elements are sufficient for the existence of doubly degenerate electronic energy eigenvalues; as a result, these relations are easy to satisfy [165]. The systems $C_2H$ [167, 168], $NH_2$ [169], $NO_2$ [170, 171], and $HO_2$ [172, 173] represent just a few examples.

The change in sign of the real adiabatic electronic wave functions associated with a pair of intersecting PESs upon a pseudorotation around a conical intersection of the system has consequences for its structure and dynamics. It requires that the corresponding nuclear wave functions undergo a compensating change of sign, known as the geometric phase effect [174]. This change in sign, in turn, profoundly affects the nature of the solutions of the corresponding nuclear motion Schrödinger equation (SE) [53]. For systems whose conical intersection geometry is either an equilateral triangle or close to one, symmetrised hyperspherical coordinates [53] are very convenient for enforcing such sign change.

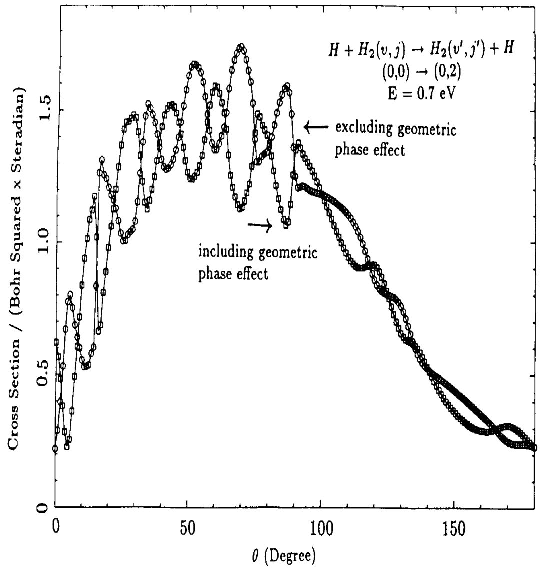


**Fig. 6.1.** Degeneracy-summed differential cross sections for the $H+H_2(v = 0, j = 0) \to H_2(v' = 0, j' = 2)+H$ reaction, at a total energy of 0.7 eV, as a function of scattering angle. (Reprinted, by permission, from Kuppermann, A. in: Tsipis, C.A., Popov, V.S., Herschbach, D.R., Avery, J.S. (Eds.): *New methods in quantum theory*, NATO ASI Series 3/8 (Kluwer, Dordrecht, 1997). Copyright 1997 by Kluwer.)

The geometric phase effect associated with chemical reactions [174] and with the motion of electrons in magnetic fields [175] was generalized in 1984 by Berry [176] to systems which are transported around a loop or circuit C in parameter space. If $\hat{H}$ is the system's Hamiltonian and $\mathbf{R}$ a set of parametric variables on which $\hat{H}$ depends, he showed that an eigenstate of $\hat{H}$, when the system is transported slowly (i.e., adiabatically) around $C$, will acquire a geometrical phase factor $e^{i\gamma(c)}$, independent of time, in addition to the familiar dynamical phase factor. He also derived an explicit general formula for $\gamma(c)$ in terms of the spectrum and eigenstates of $\hat{H}(\mathbf{R})$ over a surface spanning $C$. The geometric phase angle $\gamma(c)$ is now widely known in the literature as Berry's phase. This phase is an example of a holonmy, the extent to which some variables change when other variables or parameters characterizing a system return to their initial value. Berry's basic concept was the separation of a system into an internal part, involving rapidly varying internal degrees of freedom, and an external part, involving slowly varying external (i.e., para-

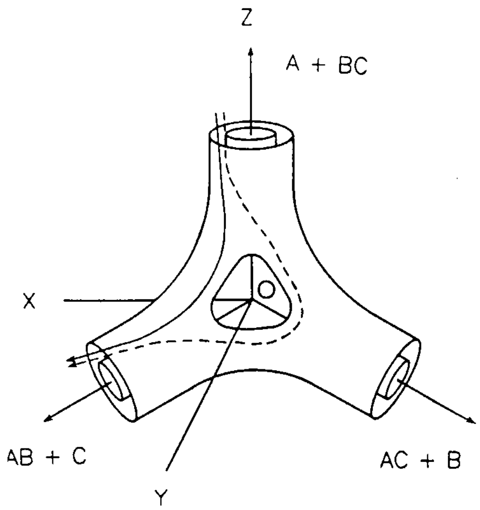


**Fig. 6.2.** This figure depicts two kinds of semiclassical paths which contribute to exchange scattering amplitude for a triatomic system ABC. The dashed path partially encircles the conical intersection line, whereas the solid one does not. (Reprinted, by permission, from Kuppermann, A. in:Tsipis, C.A., Popov, V.S., Herschbach, D.R., Avery, J.S. (Eds.): *New methods in quantum theory,* NATO ASI Series 3/8 (Kluwer, Dordrecht, 1997). Copyright 1997 by Kluwer.)

metric) degrees of freedom. The geometric phase arises from the coupling between the motions of the internal and external parts. For molecular systems, the internal "fast" degrees of freedom are the electronic ones, and the external "slow" ones are the nuclear ones. The geometric phase arises from the coupling between these two kinds of degrees of freedom. The applications of Berry's phase to spectroscopic phenomena has been extensively reviewed [177].
For including the geometric phase effect in the hyperspherical close-coupling equations for the calculations of the $H_3$-system the wavefunctions has to be modified by the phase factor $e^{i\gamma}$. This formulation is especially simple in hyperspherical coordinates. Examples: see Fig. 6.1 and 6.2.

## 6.2 F + $H_2$, Ne + $H_2^+$, N + $H_2$, etc. and miscellaneous

Beside the H + $H_2$ reaction the F + $H_2$ reaction is the most investigated system [162, 67]. For other reactions like Ne + $H_2^+$ or N + $H_2$ detailed investigations have been performed most recently. Results of different hyperspherical applications are presented by Nakamura in [63] and the influence of spin-orbit effects in reactions can be taken from the work of Schatz et al. [179].

## 7. Summary

It should be clear from the preceding sections that there are now a variety of 'exact' ways to solve the Schrödinger equation for three dimensional atom-diatom reactions.

At present the two leading approaches to quantum reactive scattering are hyperspherical coordinate methods, and variational methods based on the simultaneous use of mass-scaled Jacobi coordinates in each of the chemical arrangements involved. These two approaches are somewhat complementary: both have already seen numerous important applications, and it is as yet unclear which will ultimately prove the 'best' to use.

Hyperspherical coordinate methods provide a different physical picture of reactive scattering in terms of adiabatic hyperradial potential energy curves, which correlate asymptotically with the bound rovibrational energy levels of the reactant and product fragments and are useful for interpreting dynamical resonance effects. They also lead quite naturally to optimum angular momentum decoupling approximations of the 'coupled states' or 'centrifugal sudden' form. Jacobi coordinate variational methods do not at present provide such a useful physical picture of the dynamics, but are nevertheless somewhat more amenable to perturbation theory approximations of the 'distorted wave' type. Natural collision coordinate methods, which still give the most intuitive physical picture of all, appear to be computationally intractable for the more demanding reactions studied to date.

Converged $J = 0$ and $J \neq 0$ reaction probabilities can now be obtained 'quite routinely' for a wide variety of atom-diatom reactions. Moreover, differential and integral cross sections, can also be obtained, at quite high scattering energies, for all the deuterium substituted analogues of $H + H_2$. However, cross sections for highly exoergic reactions with heavier atoms are still quite difficult to obtain. Since a large number of experimentally interesting reactions fall into this latter category the need for further methodological developments is clear.

Several other important problems also await detailed theoretical formulations and efficient three dimensional numerical implementations. These include the study of electronically non-adiabatic reactions, the description of subtle geometric effects caused by the conical intersection of ground and excited electronic potential energy surfaces, collision induced dissociation, and reactions involving polyatomic molecules. However, since potential energy surfaces and dynamics calculations appear at last to be converging on a realistic ab initio quantum theory of reactive scattering, the future prospect for each of these problems is good.

We have mostly talked about triatomic reactions. For further information on four-atomic and polyatomic systems the reader is referred to the work presented in [63, 74, 71, 180] and the new special issues in Physical Chemistry Chemical Physics (1999), Faraday Discussion 110 (1998) and Faraday Transactions Vol. 93 (1997).

## A.1 List of abbreviations

BCRLM - bending corrected linear model
BF - body-fixed
BO - Born-Oppenheimer
CG - Clebsch-Gordan
CRP - cumulative reaction probability
DCS - differential cross section
DIM - diatomics-in-molecules
GP - geometric phase
LAB - laboratory
NGP - non geometric phase
PDE - partial differential equation
PES - potential energy surface
QM - quantum mechanical
RIOSA - reactive infinite order sudden approximation
SE - Schrödinger equation
SF - space-fixed
TDSE - time-dependent Schrödinger equation
TISE - time-independent Schrödinger equation

## A.2 Credits

The following work from the literature was in some parts extracted and built into this review:

(a) "Jaquet, R., A. Kumpf, M. Heinen: J. Chem. Soc., Farad. Trans. **93** (1997) 1027" contributed to chapter 2.
(b) "Launay, J.M. in: Dynamical Processes in Molecular Physics, Delgado-Barrio, G. (Ed.) (Institute of Physics Publishing, Bristol and Philadelphia, 1991)" contributed to chapter 3.
(c) "Kouri, D.J. and Hoffman, D.K. in: *Multiparticle quantum scattering with applications to nuclear, atomic and molecular physics*, Tuhlar, D.G., Simon,B. (Eds.) (Springer, 1997)" contributed to chapter ???.
(d) "Kuppermann, A. in: New methods in quantum theory, Tsipis et al. ( Eds.), NATO ASI Series 3/8 (Kluwer, Dordrecht, 1997)" contributed to chapter ???.

*Acknowledgement.* The author thanks Christian Morari for help and discussions.

## References

1. Jaquet, R., Kumpf, A., Heinen, M.: *J. Chem. Soc., Farad. Trans.* **93** (1997) 1027.

2. Launay, J.M. in: *Dynamical Processes in Molecular Physics*, ed. G. Delgado-Barrio (Institute of Physics Publishing Bristol and Philadelphia, 1991) p. 97.
3. Kouri, D.J., Hoffman, D.K. in: *Multiparticle quantum scattering with applications to nuclear, atomic and molecular physics*, Truhlar, D.G., Simon B. (Eds.) (Springer, NY, 1997).
4. Elsgolc, L.E. in: Calculus of Variations (Pergamon Press, 1961).
5. J. P. Boyd, J.P. in: Chebyshev and Fourier Spectral Methods (Springer, NY, 1989).
6. Hulthén, L., *Kgl. Fysiogr. Sallsk. Lund Forh.* **14** (1944) 21.
7. Hulthén, L., *Arkiv. Mat. Ast. Fys.* **35A** (1948) 25.
8. Kohn, W.: *Phys. Rev.* **74** (1948) 1763.
9. Wu, T.-Y. and Ohmura, T. in: Quantum Theory of Scattering (Prentice Hall, Englewood Cliffs, New Jersey, 1962), p. 64.
10. Miller, W.H., *Comments At. Mol. Phys.* **22** (1988) 115.
11. Miller, W.H. and Jansen op de Haar, B.M.D.D.: *J. Chem. Phys.* **86** (1987) 6213.
12. McCurdy, C.W., Rescigno, T.N., Schneider, B.I.: *Phys. Rev. A.* **36** (1987) 2061.
13. McCurdy, C.W., Rescigno, T.N.: *Phys. Rev. A.* **37** (1988) 1044.
14. McCurdy, C.W., Rescigno, T.N., Schneider, B.I.: *Phys. Rev. Lett.* **63** (1989) 248.
15. Farina, J.E.G. in: Quantum Theory of Scattering (Pergamon Press, 1973).
16. Nesbet, R.K. in: Variational Methods in Electron-Atom Scattering Theory(Plenum Press, NY 1980).
17. Zhang, J.Z.H., Chu, S.-I. and Miller, W.H.: *J. Chem. Phys.* **88** (1988) 6233.
18. Feshbach, H.: *Ann. Phys. (N.Y.)* **5** (1958) 357, **19** (1962) 287.
19. Siegert, A.J.F. : *Phys. Rev.* **56** (1939) 750.
(1944) 21.
20. Joachain, C.J. in: *Quantum collision theory*, Elsevier, Amsterdam, 1983.
21. Zhang, J.Z.H., Chu, S.I., and Miller, W.H.: *J. Chem. Phys.* **88** (1988) 6233.
22. Miller, W.H., *Comments At. Mol. Phys.* , **22** (1988) 115.
23. Zhang, J.Z.H., Miller, W.H.: *Chem. Phys. Lett.* **140** (1987) 329.
24. Zhang, J.Z.H.: *J. Chem. Phys.* **94** (1991) 6047.
25. Colbert, D.T., Miller, W.H.: *J. Chem. Phys.* **96** (1992) 1982.
26. Belyaev, A.K., Colbert, D.T., Groenenboom, G.C., Miller, W.H.: *Chem. Phys. Lett.* **209** (1993) 309.
27. Groenenboom, G.C., Colbert, D.T.: *J. Chem. Phys.* **99** (1993) 9681.
28. Kumpf, A.: Doctoral thesis, 1998, Siegen, Germany.
29. Groenenboom, G.C.: *J. Chem. Phys.* 1993 **108** (1998) 5670; 5677.
30. Zhang, D.H., Zhang, J.Z.H.: *J. Chem. Phys.* **100** (1994) 2697.
31. Miller, W.H. (Ed.) in: *Dynamics of Molecular Collisions*, Parts A and B (Vols. 1 and 2 of Modern theoretical Chemistry) (Plenum, NY, 1976).
32. Miller, W.H., in [31], p. 1
33. Jaquet, R., Gribkova,J.: *Theoret. Chim. Acta* **89** (1994) 363.
34. Tennyson, J., Miller, S.: *Comput. Phys. Commun.* **55** (1989) 149.
35. Tennyson, J., Henderson, J.R.: *J. Chem. Phys.* **91** (1989) 3815.
36. Sutcliffe, B.T., Tennyson, J.: *Mol. Phys.* **58** (1986) 1053.
37. Johnson, B.R. Secrest, D.: *J. Math. Phys.* **7** (1966) 2187.
38. Pechukas P., Light, J.C.: *J. Chem. Phys.* **44** (1966) 3897.
39. M . Abramowitz and I. A. Stegun, Handbook of Mathematical Functions (National Burreau of Standarts, Washington, D. C. 1968)
40. Johnson, B.R.: *J. Chem. Phys.* **67** (1977) 4086.
41. Johnson, B.R.: *J. Chem. Phys.* **79** (1983) 1916.
42. Johnson, B.R.: *J. Comp. Phys.* **14** (1973) 445.

43. Manolopoulos, D.E.: *J. Chem. Phys.* **85** (1986) 6425.
44. Fock, V.: *D. Kon. Nors. Vidensk. Selsk. Forh.* **31** (1958) 138.
45. Whitten, R. C., Smith F.T.: *J. Math. Phys.* **9** (1968) 1103.
46. Linderberg, J., Padkjaer, S. B., Öhrn, Y., Vessal, B., : *J. Chem. Phys.* **90** (1989) 6254.
47. Johnson, B.R.: *J. Chem. Phys.* **73** (1980) 5051.
48. Aquilanti, V., Grossi, G., Lagana, A.: *J. Chem. Phys.* **76** (1982) 1587.
49. Hipes, P.G., Kuppermann, A.: Chem. Phys. Letters **133** (1987) 1.
50. Launay, J.M., Lepetit B.: *Chem. Phys. Lett.* **144** (1988) 346.
(1989) 6254
51. Launay, J.M., Le Dourneuf, M.: *Chem. Phys. Lett.* **163** (1989) 178.
52. Wu, Y.S.M., Cuccaro, S.A., Hipes, P.G., Kuppermann, A.: 1991 *Theoret. Chim. Acta* **79** (1991) 225.
53. Wu, Y.S.M., Kuppermann, A., Lepetit, B.: *Chem. Phys. Lett.* **186** (1991) 319.
54. Pack, R.T., Parker G.A.: 1987 *J. Chem. Phys.* **87** 3888.
55. Kuppermann, A., Hipes, P. G., : *J. Chem. Phys.* **84** (1986) 5962.
56. Schatz, G.C.: *J. Chem. Phys.* **90** (1989) 3582.
57. Pack, R.T., Parker, G.A.: *J. Chem. Phys.* **90** (1989) 3511.
58. Launay, J.M., Le Dournef, M.: *Chem. Phys. Lett.* **169** (1990) 473.
59. Launay, J.M.: *Theoret. Chim. Acta* **79** (1991) 183.
60. Launay, J.M., Padkjaer, S.B.: *Chem. Phys. Lett.* **181** (1991) 95.
61. Lepetit, B., Launay, J.M.: *J. Chem. Phys.* **95** (1991) 5159.
62. Huarte-Larranaga, F., Gimenez, X. Lucas, J.M., Aguilar, A., Launay, J.M.: *Phys. Chem. Chem. Phys.* **1** (1999) 1125.
63. Bowman, J.M. (Ed.) in: *Advances in Molecular Vibrations and Collision Dynamics*, Vol. 2 (JAI Press, Greenwich, CT, 1994).
64. Manolopoulos, D.E. and Clary, D.C., *Ann. Rep. C Roy. Soc. of Chem.* **80** (1989) 95.
65. The amplitude density for non-reactive scattering was introduced by B. R. Johnson and Secrest, D., J. Math Phys. **7**, (1966) 2187 and generalized to reactive scattering by Kouri, D.J.: *J. Chem. Phys.* **51** (1969) 5204. The solution method for the amplitude density was introduced by Baer, M., Kouri, D.J.: *J. Chem. Phys.* **56** (1972) 1758 .
66. Bowman, J. (Ed.) in: *Advances in Molecular Vibrations and Collision Dynamics* (JAI Press, Greenwich, CT, 1991).
67. Castillo, J.F., Manolopolous, D.E.: *Faraday Discuss.* **110** (1998) 119.
68. Micha, D.: *Adv. Chem. Phys.* **30** (1975) 7.
69. Baer, M. (Ed.) in: *Theory of Chemical Reaction Dynamics*, Vols. I-IV, CRC Press, Boca Raton, FL, 1985.
70. Bernstein, R.B. (Ed.) in : *Atom-Molecule Collision Theory: a Guide for the Experimentalist* (Plenum, NY, 1979).
71. Tsipis, C.A., Popov, V.S., Herschbach, D.R., Avery, J.S. (Eds.) in: *New methods in quantum theory*, NATO ASI Series 3/8 (Kluwer, Dordrecht, 1997)
72. Cerjan, C. (Ed.) in: *Numerical Grid Methods and their Application to Schrödinger's Equation*, NATO ASI Series C 412 (Kluwer, Dordrecht, 1993)
73. Lagana, A. (Ed.) in: *Supercomputer algorithms for reactivity, dynamics and kinetics of small molecules* (Kluwer, Dordrecht, 1989).
74. Zhang, J.Z.H. and Wyatt, R.E. (Eds.) in: *Dynamics of molecules and chemical reactions* ( Dekker, 1996).
75. Billing ??
76. Hinze ??
77. Althorpe, S.C. et al.: *J. Chem. Soc. Faraday Trans.* **93** (1997) 703.

78. Clary, D.C. (Ed.) in: *The Theory of Chemical Dynamics* (Reidel,Dordrecht, 1986).
79. Baer, M., Kouri, D.J. in: [78], p. 167.
80. Jellinek, J., Kouri, D.J. in: [69] Vol. 2, Chap. 1.
81. ?????? Ohsaki, A.; Nakamura: *H. Phys. Rep.* **187** (1990) 1.
82. Bowman, J.M.: *Adv. Chem. Phys.* **61** (1985) 115.
83. Bowman, J.M., Wagner, A.F. in: [78], p. 47.
84. Walker, R. B., Hayes, E.F. in: [78], p. 105.
85. Bowman, J.M.: *J. Phys. Chem.* **95** (1991) 4960.
86. Wyatt, R.E. in: [70].
87. Jaquet, R.: *Theoret. Chim. Acta* , **71** (1987) 425.
88. Jaquet, R.: *Comput. Phys. Commun.* , **58** (1990) 257.
89. Porter, R.N., Karplus, M.: *J. Chem. Phys.* **40** (1964) 1105.
90. Röhse, R., Kutzelnigg, W., Jaquet, R., Klopper, W. : *J. Chem. Phys.* **101** (1994) 2231.
91. Light, J.C., Hamilton, I.P., Lill, J.V.: *J. Chem. Phys.* **82** (1985) 1400.
92. Secrest, D. in [70], chap. 8.
93. (a) Lester, W.A. in: [31], p. 1. (b) Light, J.C. in: [70] p. 239. (c) Secrest, D. in: [70] p. 265, 377.
94. Mrugala, F.: *Int. Rev. Phys. Chem.* **12** (1993) 1.
95. Allison, A.C.: *Adv. Atom. Mol. Phys.* **25** (1988) 323.
96. Reeves, M.S., Unekis, M.J., Schwenke, D.W., Harvey, N.M., Truhlar, D.G.: RMPROP-Version 2. 1, University of Minnesota, Minneapolis, 1994.
97. Miller, W.H.: *J. Chem. Phys.* **50** (1969) 407.
98. Baer, M., Kouri, D.J.: *Phys. Rev. A.* **4** (1971) 1924; *J. Chem. Phys.* **56** (1972) 4840; *J. Math. Phys.* **14** (1973) 1637.
99. Baer, M.: *Phys. Rev.* **178** (1989) 99.
100. Nesbet, R.K. in: *Variational Methods in Electron-Atom Scattering Theory* (Plenum, NY, 1980) chap. 2.
101. Kohn, W.: *Phys. Rev.* **74** (1948) 1763.
102. Kuppermann, A. in : 'Potential Energy Surfaces and Dynamics Calculations', ed. Truhlar, D.G., Plenum Press, NY, 1981, p. 375.
103. Zhang, J.Z.H., Miller, W.H.,: *Chem. Phys. Lett.* **140** (1987) 329.
104. Schwinger, J.: *Phys. Rev.* **72** (1947) 742.
105. Newton, R.G. in: *Scattering Theory of Particles and Waves* (Springer, NY, 1982) p. 320.
106. Schwartz, C.: *Phys. Rev.* **124** (1961) 1468; *Ann. Phys.* **10** (1961) 36.
107. Miller, W.H., Jansen op de Haar, B.M.D.: *J. Chem. Phys.* B **86** (1987) 6213.
108. Messiah, A.: *Quantum Mechanics* (Wiley, NY, 1962) chap. 19.
109. Gaucher, L.F.X, Miller, W.H.: *Israel J. Chem.* **29**, (1989) 349.
110. Lucchese, R.: *Phys. Rev. A.* (1991).
111. Zhang, J.Z.H., Chu, S-I., Miller, W.H.: *J. Chem. Phys.* **88**, (1988) 6233; **89**, (1988) 4454.
112. Miller, W.H.: *Collect, Czech. Chem. Commun.* **53**, (1988) 1873.
113. Miller, W.H.: *Comments At. Mol. Phys.* **22**, (1988) 115.
114. Zhang, J.Z.H., Miller, W.H.: *J. Chem. Phys.* **88** (1988) 4549; **90** (1989) 7610.
115. Zhang, J.Z.H., Miller, W.H.: *Chem. Phys. Lett.* **153** (1988) 465.
116. Nieh, I-C., Valentini, J.J.: *Phys. Rev. Lett.* **60** (1988) 519; *J. Chem. Phys.* **92** (1990) 1083.
117. Schatz, G.C.: *Ann. Rev. Phys. Chem.* **39** (1988) 317.
118. Manolopoulos, D.E., Wyatt, R.E.: *Chem. Phys. Lett.* **152** (1988) 23 ; **159** (1989) 123 ; *J. Chem. Phys.* **91** (1989) 6096 ; **93** (1990) 403.
119. Kuppermann, A. : *Chem. Phys. Lett.* **32** (1975) 374.

120. Delves, L.M.: *Nucl. Phys.*, **9** (1959) 391; **20** (1960) 275.
121. Schatz, G. C., in: The Theory of Chemical Dynamics, edited by Clary, D.C. (Dordrecht: Reidel, 1986), p. 1; *Chem. Phys. Lett.* **150** (1988) 92; *J. Chem. Phys.* **90** (1989) 3582.
122. Pack, R.T., Parker, G.A.: *J. Chem. Phys.* **90** (1989) 3511.
123. Bacic, Z., Kress, J.D., Parker, G.A., Pack, R.T., : *J. Chem. Phys.* **92** (1990) 2344.
124. Zhang, J.Z.H., Miller,W.H.: *Chem. Phys. Lett.* **159** (1989) 130.
125. Pack, R.T.: *Chem. Phys. Lett.* **108** (1984) 333.
126. Miller, W.H.: *Ann. Rev. Phys. Chem.* (1991)
127. Smith, F.T.: *J. Math. Phys.* **3** (1969) 735; Whitten, R.C., Smith, F.T.: *J. Math. Phys.* **9** (1968) 1103; Whitten, R.C.: *J. Math. Phys.* **10** (1969) 1631.
128. Mead, C.A. *Chem. Phys.* **49** (1980) 23; *J. Chem. Phys.* **72** (1980) 3839.
129. Johnson, B.R.: *J. Chem. Phys.* **73** (1980) 5051; **79** (1983) 1906, 1916.
130. Parker,G.A., Pack, R.T., Archer, B.J., Walker, R.B.: *Chem. Phys. Lett.* **137** (1987) 564.
131. Parker, G.A, Pack, R.T, Lagani, A, Archer, B.J, Kress, J.D., Bacic, Z. in: [73] p. 105.
132. Kress, J.D., Bacic, Z., Parker, G.A., Pack, R.T.: *Chem. Phys. Lett.* **157** (1989) 484.
133. Light, J.C., Hamilton, P., Lill, V.: *J. Chem. Phys.* **82** (1985) 1400.
134. Whitnell, R.M., Light, J.C.: *J. Chem. Phys.* **89** (1988) 3674.
135. Mishra, M., Linderberg, J., Öhrn, Y.: *Chem. Phys. Lett.* **111** (1984) 4A
136. Linderberg, J.: *Int. J. Quant. Chem.* , **19** (1986) 467.
137. Linderberg, J., Vessal, B.: *Int. J. Quant. Chem.* , **31** (1987) 65.
(1989) 6254.
138. Eisenbud, L., Ph. D. Thesis, Princeton, 1948; Wigner, E.P.: *Phys. Rev.* **98** (1955) 145.
139. Cuccaro, S.A., Hipes, P.G., Kuppermann, A. : *Chem. Phys. Lett.* **154** (1989) 155.
140. Kuppermann, A., Schatz, G.C.: *J. Chem. Phys.* **62** (1975) 2502.
141. Schatz, G.C. and Kuppermann, A.: *Phys. Rev. Lett.* **35** (1975) 1266.
142. Schatz, G.C., Kuppermann, A. : *J. Chem. Phys.* **65** (1976) 4668.
143. Elkowitz, A.B., Wyatt, R.E. : *J. Chem. Phys.* **62** (1975) 2504.
144. Elkowitz, A.B., Wyatt, R.E. : *J. Chem. Phys.* **63** (1975) 702.
145. Wyatt, R. E. in [70] p.477.
146. Light, J.C., Walker, R.B.: *J. Chem. Phys.* **65** (1976) 472. Stechel, E.B., Walker, R.B., Light, J.C.: *J. Chem. Phys.* **69** (1978) 3518.
147. Porter, R.N., Karplus, M.: *J. Chem. Phys.* **40** (1964) 1105.
148. Truhlar, D. G. and Horowitz, C. G. : *J. Chem. Phys.* **68** (1978) 2466
149. Kuppermann in [74]
150. Smith, F.T.: *Phys. Rev.* B **118** (1960) 349.
151. Schatz, G.C.: *Chem. Phys. Lett.* **151** (1988) 409.
152. Schwenke, D.W., Truhlar, D.G., Kouri, D.J.: *J. Chem. Phys.* **86** (1987) 2772.
153. Öhrn, Y., Linderberg, J.: *Mol. Phys.* **49** (1983) 53.
154. Chapuisat, X.: *Chem. Phys. Lett.* **136** (1987) 153.
155. Brooks, N., Clary, D.C.: *J. Chem. Phys.* **92** (1990) 4178.
156. Varandas, A.J.C., Brown, F.B., Mead, C.A., Truhlar, D.G., Blais, N.C.: *J. Chem. Phys.* **86** (1987) 6258 .
157. Boothroyd, A.I., Keogh, W.J., Martin, P.G., Peterson, M.R.: *J. Chem. Phys.* **95** (1991) 4343.
158. Boothroyd, A.I., Keogh, W.J., Martin, P.G., Peterson, M.R.: *J. Chem. Phys.* **104** (1996) 7139.

159. Banares, L., Aoiz, F.J., Herrero, V.J., D'Mello, M.J., Niederjohann, B., Seekamp-Rahn, K., Wrede, E., Schnieder, L.: *J. Chem. Phys.* **108** (1998) 6160.
160. Miranda, M.P., Clary, D.C., Castillo, J.F., Manolopoulos, D.E.: *J. Chem. Phys.* **108** (1998) 3142.
161. Wrede, E., Schnieder, L., Welge, K.H., Aoiz, F.J., Banares, L., Castillo, J.F., Martinez-Haya, B., Herrero, V.J.: submitted to *J. Chem. Phys.* (1999)
162. Manolopolous, D.E.: *J. Chem. Soc. Faraday Trans.* **93** (1997) 673.
163. Kuppermann, A. in: [71]
164. Herzberg, G., Longuet-Higgins, H.C.: *Discussion Faraday Soc.* **35** (1963) 77.
165. Longuet-Higgins, H.C.: *Proc. R. Soc. Lond A* **344** (1975) 147.
166. Jahn, H.A., Teller, E.: *Proc. R. Soc. A* **161** (1937) 220.
167. Carrick, P.G., Merer, A.J., Curl, R.F.: *J. Chem. Phys.* **78** (1983) 3652.
168. Yan, W.B., Hall, J.L., Stephens, J.W., Richnow, M.L., Curl, R.F.: *J. Chem. Phys.* **86** (1987) 1657.
169. Petrongolo, C., Hirsch, G., Buenker, R.J.: *Mol. Phys.* **70** (1990) 835.
170. Hirsch, G., Buenker, R.J., Petrongolo, C.: *Mol. Phys.* **70** (1990) 835.
171. Robie, D.C., Hunger, M., Bates, J.L., Reisler, H.: *Chem. Phys. Lett.* **193** (1992) 413
172. Walch, S.P., Duchovic, R.J.: *J. Chem. Phys.* **94** (1991) 7068.
173. Kendrick, B., Pack, R.T.: *J. Chem. Phys.* **102** (1995) 1994.
174. Mead, C.A., Truhlar, D.G.: *J. Chem. Phys.* **70** (1979) 2282.
175. Aharonov, Y., Bohm, D.: *Phys. Rev.* **115** (1959) 485.
176. Berry, M.V.: *Proc. R. Soc. Lond. A* **392** (1984) 45.
177. Zwanziger, J.W., Koenig, M., Pines, A.: *Ann. Rev. Phys. Chem.* **41** (1990) 601.
178. Wu, Y-S.M., Kuppermann, A.: *Chem. Phys. Lett.* **201** (1993) 178.
179. Schatz, G.C, McCabe, P., Connor, J.N.L.:, Faraday Discuss. **110** (1998) 139.
180. Thompson, D.L.(Ed.) in: *Modern methos in multidimensional dynamics computations in chemistry* (World Scientific, Singapore, 1998)