

Statistical Adiabatic Channel Models

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Reprint

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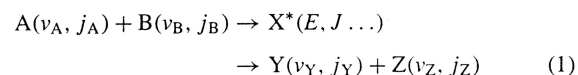
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Abbreviations

PST = phase space theory; SACM = statistical adiabatic channel model; TST = transition state theory.

1 INTRODUCTION

The statistical adiabatic channel model (SACM)¹⁻³ is one realization of the larger class of statistical theories of chemical reactions. Its goal is to describe, with feasible computational implementation, average reaction rate constants, cross sections, and transition probabilities and lifetimes at a detailed level, to a substantial extent with 'state selection', for bimolecular reactive or inelastic collisions with intermediate complex formation (symbolic sets of quantum numbers $v, j, E, J \dots$)



or unimolecular decay

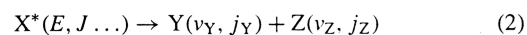


Figure 1 places the statistical adiabatic channel model in the general landscape of dynamical and statistical theories of chemical reactions. While this diagram stems originally from a review⁴ written in 1977 shortly after the development of the statistical adiabatic channel model (see also Refs. 5-28, cited in Figure 1), it is largely still valid today, when it is noted

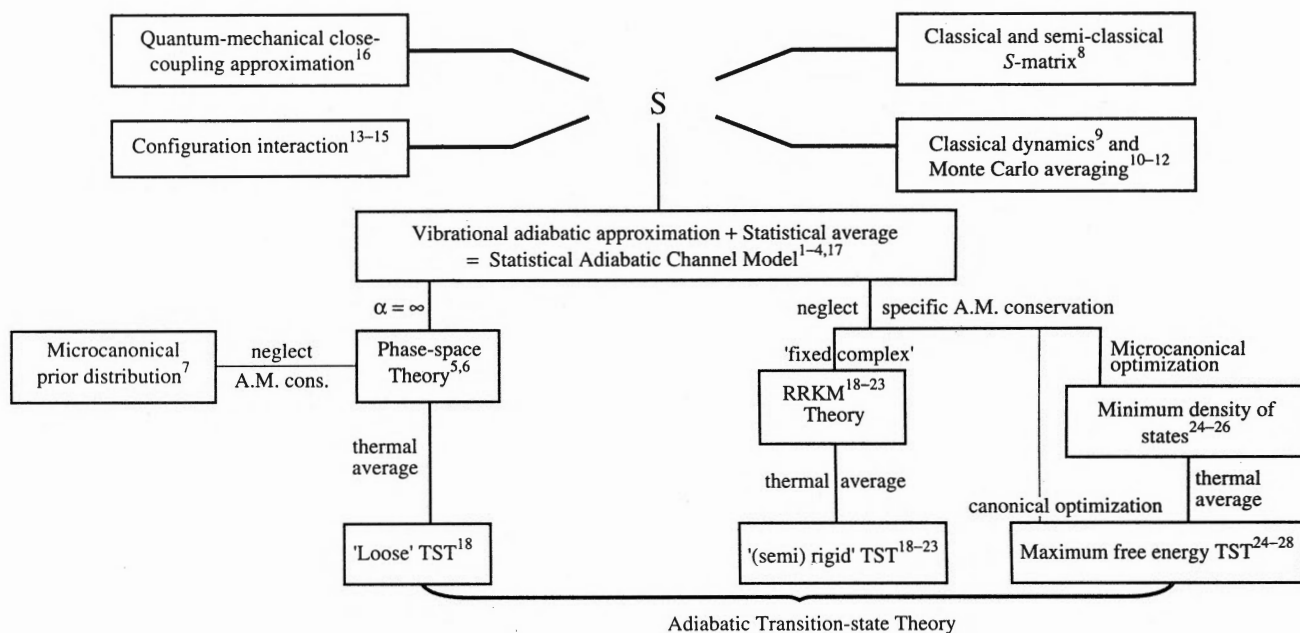


Figure 1 The theoretical description of unimolecular and bimolecular processes involving intermediate complexes in the framework of a general scattering theory (S-matrix) (after Ref. 4) (A.M. = angular momentum)

that many of the more recent developments, such as variational transition state theory, fall under the subclasses of canonical and microcanonical optimization (sometimes with dynamical assumptions differing slightly from the original adiabatic channel model). These developments, as well as the statistical adiabatic channel model, are now included in the more recent textbook literature on the subject.^{20–23} Nevertheless, because of the usual limitations of textbook material, it seems very pertinent to summarize the basic concepts, methods, and results of the SACM in this encyclopedia article, as the SACM has found wide applications in a variety of fields in modern reaction kinetics, including specialized subfields such as atmospheric chemistry, astrochemistry, combustion kinetics, mass spectrometry, and ion molecule reactions,²⁹ as well as laser chemistry³⁰ (see *Multiphoton Excitation*). In the present article we focus attention on the fundamental concepts and methods of the SACM, including also some recent developments. While we also make reference to some selected applications, a summary of the great multitude of applications in the various fields mentioned is beyond the scope of this short article.

2 BASIC STATISTICAL ADIABATIC CHANNEL MODEL AND FUNDAMENTAL EQUATIONS FOR UNIMOLECULAR AND BIMOLECULAR REACTIONS INVOLVING INTERMEDIATE COMPLEXES

2.1 The Statistical Scattering Matrix

We shall derive in this section the fundamental equations for the kinetic quantities in the adiabatic channel model from the point of view of the statistical S-matrix in scattering theory, which may seem to be the most logical approach following Refs. 2 and 17. In theoretical quantum dynamics we start from the time-dependent Schrödinger equation (3):

$$i \frac{\hbar}{2\pi} \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (3)$$

where Ψ depends upon all spin and space coordinates of the particles in the molecular system under consideration and upon time. Equation (3) is solved formally by the time evolution operator $\hat{U}(t, t_0)$ in equation (4), retaining only the dependence upon time explicitly in the notation:

$$\Psi(t) = \hat{U}(t, t_0) \Psi(t_0) \quad (4)$$

Considering the time evolution in a collision, it is useful in scattering theory to write the time evolution operator \hat{U} in a matrix representation \mathbf{U} in the basis of scattering states of the well separated, non-interacting collision partners, and to consider the formal limit of time $t_0 \rightarrow -\infty$ long before the interaction in the collision takes place and $t \rightarrow +\infty$, a time long after the collision. The resulting time evolution matrix in this formal limit³¹ is called the scattering matrix (S-matrix) in equation (5):

$$\mathbf{S} = \mathbf{U}(t \rightarrow +\infty, t_0 \rightarrow -\infty) \quad (5)$$

The scattering wavefunctions are given in equation (6) for large separation q of the collision partners (q is a reaction coordinate, asymptotically the center of mass distance, see section 4.2):

$$\begin{aligned} \Psi = q^{-1} k_a^{-1/2} \Phi_a Y_{\ell, m_\ell} \{ Q_1 \exp[-i(k_a q - \frac{1}{2} \ell \pi)] \\ - Q_2 \exp[+i(k_a q - \frac{1}{2} \ell \pi)] \} \end{aligned} \quad (6)$$

Φ_a is the product wavefunction for the combined (generally nu-rovibronic) internal states of the collision partners (i.e., $|a\rangle = |\{v_A, j_A, m_A\}\{v_B, j_B, m_B\}\rangle$, using various collective quantum numbers such as the vibrational quantum number v_A in a formal notation), Y_{ℓ, m_ℓ} is the normalized spherical harmonic for angular momentum quantum numbers ℓ and m_ℓ of relative rotation of the collision partners

and $k_a = 2\pi(2\mu E_{t,a})^{1/2}/h$ is the collision wavenumber with the translational energy $E_{t,a} = E - E_a$ (E_a = combined internal energy of collision partners, E = total energy) and $\mu = (m_A^{-1} + m_B^{-1})^{-1}$ is the reduced mass for the collision. Q_1 and Q_2 are constants. It is useful to transform to a basis which explicitly contains the constants of motion such as total angular momentum (with quantum number J) and its projection (with quantum number M), as well as parity (quantum number Π), and to write an incoming scattering channel formally as $|i\rangle = |J, M, a, \ell_i, E_{t,a}\rangle$ and an outgoing channel $f = |J, M, b, \ell_f, E_{t,b}\rangle$. With an incoming wave on $|i\rangle$ only, the total scattering wavefunction takes the form of equation (7):

$$|\Psi\rangle \propto |J, M, a, \ell_i, E_{t,a}\rangle - \sum_f S_{fi} |J, M, b, \ell_f, E_{t,b}\rangle \quad (7)$$

These equations show explicitly how the **S**-matrix maps the incoming wavefunction in the channel $|i\rangle$ onto the outgoing wavefunctions in all possible channels $|f\rangle$. Observable cross sections σ for collision processes are derived from appropriate sums and averages over the elementary cross section σ_{fi} in equation (8):

$$\sigma_{fi} = \frac{\pi |\delta_{fi} - S_{fi}|^2}{k_i^2} \quad (8)$$

with the Kronecker δ_{fi} ($= 1$ for $i = f$ and 0 for $i \neq f$). The fundamental assumption of the statistical **S**-matrix theories consists in a coarse grained (averaged) equipartition as described in Figure 2^{17,32} and summarized by equation (9):

$$\langle |S_{fi}|^2 \rangle_{f,i,\Delta E} = \begin{cases} W(E, J)^{-1} & \text{for strongly coupled channels} \\ \delta_{fi} & \text{for weakly coupled channels} \end{cases} \quad (9)$$

$W(E, J)$ is the number of strongly coupled channels (see below) at energy E and total angular momentum J . The **S**-matrix is block diagonal in certain good quantum numbers, such as J, M, Π etc. (see also below). The total number of asymptotically open channels (i.e., with $E_{t,a} > 0$) is given by $N(E, J)$, where $N(E, J)$ is usually larger than $W(E, J)$.

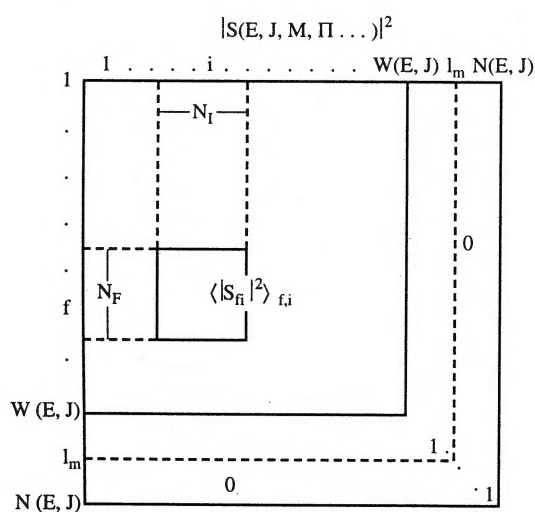


Figure 2 The structure of the statistical **S**-matrix in equation (9). $W(E, J)$ is the number of open channels in the adiabatic channel model. See detailed discussion in the text. (Reproduced by permission from *J. Phys. Chem.*, 1979, **83**, 150.)

One identifies the difference between $N(E, J)$ and $W(E, J)$ by considering dynamical constraints, distinguishing strongly coupled channels, which lead to intermediate complex formation, and weakly coupled channels, which do not lead to complex formation in a collision, or at least have a very low probability of giving complex formation. For the strongly coupled channels one assumes equal transition probability $|S_{fi}|^2$ from some initial to all final strongly coupled channels with total number $W(E, J)$. This leads automatically to the form of the $|S|^2$ -matrix given by equation (9), if one assumes that the $|S|^2$ -matrix is diagonal for the weakly coupled channels. The assumption of equal average transition probability may be further justified by two types of averaging process. The first averaging concerns large $N_I \gg 1$ of initial and $N_F \gg 1$ of final channels. The second kind of average concerns the energy interval ΔE over which the collision energy is statistically undetermined in a collision experiment. This energy interval can be supposed to cover many resonance scattering states of the intermediate complex. When the density of such resonance or metastable molecular intermediate levels is $\rho(E, J)$, then possible conditions for meaningful statistical averages are given by the inequalities (10) and (11):

$$\Delta E \rho(E, J) \gg 1 \quad (10)$$

$$\Delta E \rho(E, J) \gg W(E, J) \quad (11)$$

For a detailed discussion of these averaging procedures we refer to Refs. 2, 17, and 32. Without averaging, one might in addition describe fluctuations around the average values given by equation (9). So far we have not specified the dynamical properties or approximations which lead to the distinction between the strongly coupled channels and the weakly coupled channels indicated in equation (9) and Figure 2. The adiabatic channel model provides precisely such specifications.

2.2 Dynamical Assumptions of the Adiabatic Channel Model

The complete molecular Hamiltonian for the collision problem or for unimolecular dissociation is decomposed according to equation (12) into a dominant zero order part \hat{H}_0 and a part \hat{H}_1 , chosen in such a way that equations (13), (14) are satisfied:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad (12)$$

$$\hat{H}_0 \Psi_0 = E_0 \Psi_0 \quad (13)$$

$$\Psi_0 = \Phi_a(q, \{R\}) \xi_a(q) \quad (14)$$

The reaction coordinate q is identical to the scattering coordinate at large values of q , and is chosen according to an appropriate procedure (see below) for small values of q , when there is encounter of the collision partners in the complex. The set of coordinates $\{R\}$ contains all other degrees of freedom, including the electronic degrees of freedom in the most general description. In practice, however, one may start from an electronically adiabatic (Born–Oppenheimer) electronic potential for the atomic (nuclear) degrees of freedom only. The adiabatic channel wavefunctions satisfy a Schrödinger equation (15) for a ‘clamped q ’ Hamiltonian:

$$\hat{H}(q, \{R\}) \Phi_a(q, \{R\}) = V_a(q) \Phi_a(q, \{R\}) \quad (15)$$

One may explicitly decompose the ‘adiabatic channel potentials’ $V_a(q)$ into a contribution from the electronic degrees of freedom, i.e., the electronic potential $V(q)$ in equation (16), and a contribution $E_a(q)$ from the atomic (‘nuclear motion’) degrees of freedom:

$$V_a(q) = V(q) + E_a(q) \quad (16)$$

$V(q)$ is assumed here to be the electronic ground state, for definiteness. If excited electronic states are of interest, one can introduce excited state electronic potentials $V'(q)$, $V''(q)$, etc. The complete zero order solution is finally given by equation (17) with the kinetic energy operator \hat{T}_q along the reaction coordinate:

$$\{\hat{T}_q + V_a(q)\}\xi_{a,q}(q) = E_q\xi_{a,q}(q) \quad (17)$$

We have bound state solutions $\xi_{a,q}(q)$, when E_q is less than energy $V_0(q \rightarrow \infty)$ of the lowest dissociation channel of the intermediate complex (or the unimolecular reactant), quasibound solutions when E_q is less than $V_a(q \rightarrow \infty)$, tunneling quasibound states when $E_q < V_{a,\max}$, and finally continuum solutions otherwise. We note that the tunneling quasibound states will ultimately dissociate within the approximation specified by \hat{H}_0 , whereas the other quasibound states dissociate when the coupling due to \hat{H}_1 is included. So far, the dynamical assumptions are largely identical with the general assumption of ‘adiabatic transition state’ theory.^{15,17,33–37} In such a theory, adiabatic channel potentials would cross only if they differ in a good quantum number such as J , M , or Π . However, in the SACM additional, approximate adiabatically good quantum numbers are introduced by specifying \hat{H}_0 in such a way that it is adiabatically separable with respect to certain ‘high frequency’ or ‘conserved’ modes.¹ This results in the correlation diagram shown in Figure 3. The general channel wavefunction $\Phi_a(|a\rangle)$ is thus characterized by three different types of quantum numbers. The first type in the upper part of Figure 3 corresponds to exact constants of the motion such as J , M , Π , and other specific symmetries Γ (these may in part be only almost exact, see section 3 for a more detailed discussion of the symmetries). These are supposed to be constants of the motion for the collision or dissociation process as a whole, including reaction. The S-matrix is diagonal in these quantum numbers (or approximately so). The second type of quantum numbers, v_1 to v_r corresponds to the ‘adiabatically separable modes’ or ‘conserved’ modes, which are not at all good quantum numbers for the collision or reaction process. They are, however, good quantum numbers for the construction of the channel wavefunctions and channel potentials following equation (15). Therefore, channel potentials $V_a(q)$ differing in these quantum number may cross, since the v_r are in fact good quantum numbers for Φ_a . One quantum number v_r need not correspond to one degree of freedom, but might label energies from a subset of degrees of freedom strongly coupled among each other. The physical picture in introducing these adiabatically separable modes would typically correspond to high frequency modes, which in an inelastic long range collision, not proceeding through the collision complex, would not change their quantum number with appreciable probability. While other correlations are conceivable, a standard correlation for these modes would be $v_{in} = v_i = v_{ip}$ in the three regions for calculating channel potentials. In the collision of

Collision complex (reactant) region		Intermediate region		Separated collision partners (fragment) region
$ a_n\rangle$		$ a_q\rangle$		$ a_p\rangle$
J	...	J	...	J
M	...	M	...	M
Π	...	Π	...	Π
Γ	...	Γ	...	Γ
v_{1n}	...	v_1	...	v_{1p}
v_{2n}	...	v_2	...	v_{2p}
\vdots				
v_{rn}	...	v_r	...	v_{rp}
$\{v_{bn}, \tau_n\}$...	w	...	$\left\{ \begin{array}{l} j_A, m_A, \tau_A \\ j_B, m_B, \tau_B \\ \ell, m_\ell, (v_{bA}, v_{bB}) \end{array} \right\}$

Figure 3 Basic correlation diagram of the adiabatic channel model (after Ref. 1). The adiabatic channels $|a\rangle$ are characterized by a set of quantum numbers of three types: *good quantum numbers* (J, M, Π, Γ), which are conserved in the overall process, *adiabatically conserved quantum numbers* (v_1 to v_r), which are conserved in the channel correlation but not in the overall collision process, and finally *nonconserved quantum numbers* (w).

J is the total angular momentum quantum number excluding nuclear spin, M the corresponding magnetic quantum number, Π is the quantum number parity, and Γ is the quantum number corresponding to the irreducible representation of some appropriate further symmetry group (for instance nuclear spin symmetry⁴⁰ in the permutation group). The v_i stand for various types of vibrational quantum number, j, m for angular momentum and magnetic quantum numbers of fragments, τ for the asymmetric top rotational quantum number (K for symmetric tops) and ℓ, m_ℓ for the angular momentum and magnetic quantum numbers of the relative rotational motion of the fragments about their common center of mass

Cl with NO passing through the intermediate CINO, the high frequency NO stretching vibration could be such a mode.

Finally, the third set of modes corresponds to ‘low frequency’ vibrations and rotations of collision partners and collision complex which are so strongly coupled among each other at intermediate distances, that they cannot be labeled by separable quantum numbers, thus they are labeled by one channel quantum number w in the order of increasing energy. For a given set of quantum numbers ($J \dots v_r$) the noncrossing rule applies to these channels w . In the CINO example, the bending mode and asymmetric top quantum number τ for the collision complex (reactant) molecule would be combined in w , whereas for the separated fragments this would be the free rotation of the NO molecule (angular momentum quantum number j) and the relative ‘orbital’ rotation of the Cl and NO around their common center of mass (angular momentum quantum number ℓ), disregarding here the electronic and nuclear spin degrees of freedom for simplicity at this point, at least in the ‘half-collision’ corresponding to CINO formation and CINO dissociation, while nonadiabatic couplings may or may not be important during the lifetime of the intermediate complex (see also below). For more complicated systems, there are more such ‘soft’ (transitional) modes lumped together in the quantum number w . While there is always a minimum number of such degrees of freedom, characterized by the type of vibrational-rotational motion in the collision complex which has no correspondence in the separated fragments (for instance, disappearing vibrational modes), the precise specification, which modes are considered to be

adiabatically separable and which are not, has to be investigated for each dynamical system separately. Indeed, one may consider carrying out simple preliminary quantum or classical dynamical calculations to find out which assignment in the correlation of Figure 3 is best. In practice, one will often use the simplest empirical correlation and interpolation scheme¹ outlined further below. An extreme assumption would be to have no modes in the 'adiabatically separable class' ν_1 to ν_r .

Figure 4 provides a schematic representation of adiabatic channel potentials, which have been selected to represent some of the most important types of behavior. $V(q)$ is the electronic potential. The channel |a) might be close to the lowest adiabatic channel $V_0(q)$, containing perhaps in addition one quantum in an adiabatically separable mode. The channel |b) contains a large excitation in one or more adiabatically separable modes, which results in an asymptotically ($q \rightarrow \infty$) closed channel where the channel potential energy exceeds the total energy E . The channel |c) corresponds to a case with large excitation in a disappearing (transitional or 'soft') vibrational mode, which turns into rotational motion of the fragments. $V_c(q)$ has a maximum at intermediate fragment distances q . Channels of the type c and the type b may cross, as shown in the example, even if they share a set of good quantum numbers (J, M, Π, Γ), for the reasons discussed in relation to the correlation diagram. Finally the channel |d) would correspond to a high orbital and total angular momentum, leading to an essentially repulsive centrifugal type potential in the range shown. For the examples shown, only channel |b) is asymptotically closed, whereas |c) and |d) are adiabatically closed and channel |a) is open. Of these examples, in the SACM only channel |a) would contribute to the number $W(E, J)$ of strongly coupled channels to be used in equation (9).

A major achievement of the adiabatic channel model at the time of its invention¹ was, indeed, this complete correlation

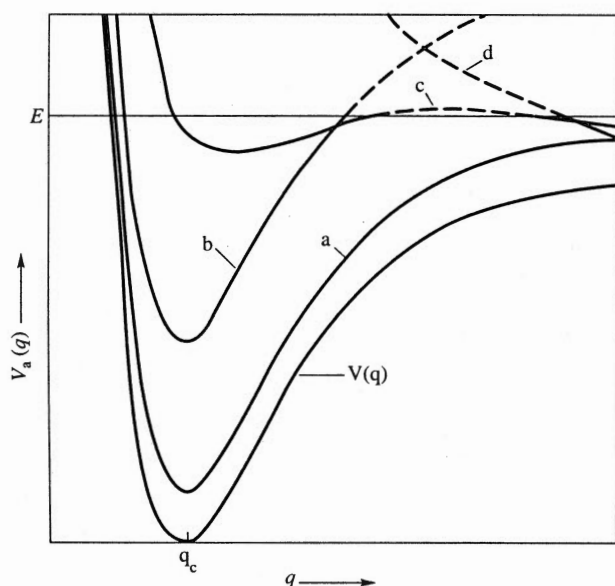


Figure 4 Schematic drawing of adiabatic channel potentials, illustrating the main types of behavior. The channels |b), |c), and |d) are adiabatically closed at the energy E , the channel |a) is adiabatically open. $V(q)$ is the electronic potential. (Reproduced by permission from *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 240)

and following of adiabatic channel potentials throughout the complete region of coordinate values from separated fragments to the bound collision complex (or the unimolecular reactant), including in particular complete labels involving the good quantum numbers ($J, M, \Pi, \Gamma \dots$). Previously, such complete specification had been available only for the outer region near the fragments in phase space theory,^{5,6} which can be considered to be a special limiting case of the adiabatic channel model as we shall show below. On the other hand, while traditional RRKM theory and related theories made wide use of abstract notation for total angular momentum quantum numbers J , etc., there was no realization of a proper assignment of such quantum numbers to channels, except for the trivial cases of bound molecule and tight transition states, but excluding the fragment region of freely moving collision partners. Indeed, for simple bond fission reactions the regions of freely moving collision partners and of close collision are both dynamically important, without there being a well defined location q^\ddagger of a 'transition state' and the adiabatic channel model was in part designed to resolve the questions and ambiguities arising from the absence of a well defined transition state structure. In the SACM all relevant kinetic quantities can be calculated without reference to such a structure.

The most natural self-consistent assumption in specifying the number of strongly coupled channels would be through channel maxima $V_{a \max}$ in some region $q_{\min} \leq q \leq q_{\infty}$, leading to the count in equation (18):

$$W(E, J \dots) = \sum_{a(J \dots)} h(E - V_{a \max}) \quad (18)$$

with the Heaviside step function $h(x > 0) = 1$ $h(x < 0) = 0$ (only E and J are retained in the notation, the others being included implicitly). $a(J \dots)$ indicates the sum being extended over channels |a) with a given set of good quantum numbers $J \dots$. One may furthermore introduce transmission coefficients γ_a or consider a channel count different from the maximum. For instance, when many channel maxima fall into the region of small q , where the adiabatic assumptions are likely to fail, one may decide to count channels as open if their potential remains below E until entering a strong coupling region defined by some $q < q_s$. Also, the explicit inclusion of transitions between channels has been discussed as a possible variant of the SACM.¹⁷

A note may be useful concerning the use of the word 'adiabatic' in the SACM. This was introduced consistent with the original meaning in Greek from $\alpha\text{-}\delta\text{i}\alpha\beta\alpha\text{i}\nu\omega$ - 'I do not transgress', or 'walk through', implying that the dynamical system does not jump between different channel potentials in the outer regions of q . In thermodynamics and other application, 'adiabatic' has sometimes been used as 'following in an infinitely slow motion', which in the present case would lead to the noncrossing rule for all channels moving along q , except for those differing in a good quantum number. This led to some misunderstandings and misrepresentations in textbooks and elsewhere.^{21,23} There is, however, no fundamental reason why one should prefer the second usage of 'adiabatic' over the first,¹ etymologically more fundamental, one.³⁸ It has also been suggested to use the notion of 'quasiadiabatic' in order to explicitly include also possibilities for coupling between the channels.³⁹ In any case these are matters of terminology, not of the underlying physics.

2.3 Some Practical Equations for Cross Sections and Rate Constants

The definition of the S -matrix implies the cross sections for bimolecular collisions via intermediate complexes through the fundamental equation (8). In general, a reactant or product level a with degeneracy g_a comprises several channel states i and f . Averaging over all initial states and summing over final states one calculates, for instance, the integral inelastic or reactive cross section σ_{ba} connecting an initial (reactant) level a and a final (product or reactant) level b as given by equation (19):

$$\sigma_{ba}(E) = \frac{\pi}{g_a k_a^2} \sum_{J=0}^{\infty} (2J+1) \frac{W(E, J, a)W(E, J, b)}{W(E, J)} \quad (19)$$

The channel wavenumber k_a is given by the well defined asymptotic ($q \rightarrow \infty$) translational energy $E_{ta} = E - V_{a\infty}$ on the reactant channel $|a\rangle$, at total energy E through equation (20):

$$k_a = \frac{2\pi[2\mu(E - V_{a\infty})]^{1/2}}{h} \quad (20)$$

$\mu = (m_A^{-1} + m_B^{-1})^{-1}$ is the reduced mass for the collision. The degeneracy g_a is usually just the magnetic degeneracy arising from the angular momenta j_{Aa} and j_{Ba} of the collision partners on the entrance level a given by equation (21), resulting from magnetic sublevels which are not selected before the collision:

$$g_a = (2j_{Aa} + 1)(2j_{Ba} + 1) \quad (21)$$

However, it can also be useful to collect further channels at the same or very similar channel energy $V_{i\infty}$ into one entrance level a , resulting in degeneracies g_a defined in other ways. It can be useful to define cross sections for complex formation for the entrance level a by equation (22):

$$\sigma_a^c(E, J) = \frac{\pi}{g_a k_a^2} (2J+1)W(E, J, a) \quad (22)$$

Considering equations (19) and (22) together, one can interpret the cross section σ_{ba} as arising from a sum of contributions over angular momenta J consisting of a cross section for complex formation at E and J multiplied by a probability $P(E, J, b)$ for decay of that complex into a level b , given by equation (23):

$$P(E, J, b) = \frac{W(E, J, b)}{W(E, J)} \quad (23)$$

Finally, the total cross section for complex formation is given by equation (24):

$$\sigma_a^c(E) = \frac{\pi}{g_a k_a^2} \sum_{J=0}^{\infty} (2J+1)W(E, J, a) \quad (24)$$

The relative probability $P_a^c(E, J)$ of forming a complex with a given total angular momentum J by collisions from the entrance level a is given by equation (25):

$$P_a^c(E, J) = \frac{\sigma_a^c(E, J)}{\sigma_a^c(E)} \quad (25)$$

These expressions can be readily evaluated numerically, from $W(E, J)$, $W(E, J, a)$, and $W(E, J, b)$ and are useful in a

number of applications. Similar expressions can be derived for differential cross sections, which we shall not reproduce here.

Thermally averaged quantities, rate constants $k(T)$, can be calculated from these cross sections by means of the general equations (26) and (27):

$$\langle \sigma_{ba} \rangle = \int_0^{\infty} \left[\frac{E}{kT} \right] \sigma_{ba}(E) \exp\left(\frac{-E}{kT}\right) \left[\frac{dE}{kT} \right] \quad (26)$$

$$k_{ba}(T) = \left[\frac{8kT}{\pi\mu} \right]^{1/2} \langle \sigma_{ba} \rangle \quad (27)$$

The integration variable E in equation (26) is effectively E_{tb} . The condition for the validity of these equations for a thermally averaged rate constant $k_{ba}(T)$ is the existence of a well defined Maxwell-Boltzmann distribution of velocities of collision partners or relative collision energies ($E - E_a$) at temperature T , which remains unperturbed by the reaction process. If, furthermore the internal state distributions of the reactants also remain at an unperturbed Boltzmann distribution at temperature T , one finds a thermal rate constant for complex formation (or 'capture') given by equation (28):

$$k^c(T) = k_{\text{rec}\infty}(T) = \left[\frac{8kT}{\pi\mu} \right]^{1/2} \sigma^c(T) \quad (28)$$

$k_{\text{rec}\infty}(T)$ is the high pressure recombination (or 'capture') rate coefficient and $\sigma^c(T)$ is the thermally averaged cross section for complex formation in equation (29):

$$\sigma^c(T) = \frac{h^2}{8\pi\mu kT} \frac{Q^*}{Q_{A,\text{int}} Q_{B,\text{int}}} \quad (29)$$

Here, $Q_{A,\text{int}}$ and $Q_{B,\text{int}}$ are the canonical partition functions for all internal degrees of freedom of the collision partners A and B, and Q^* is given by equation (30):

$$Q^* = \sum_i \exp\left(\frac{-V_{i\text{max}}}{kT}\right) \quad (30a)$$

$$= \int_0^{\infty} W(E) \exp\left(\frac{-E}{kT}\right) \left[\frac{dE}{kT} \right] \quad (30b)$$

with the total number of adiabatically open channels in equation (31):

$$W(E) = \sum_a \sum_{J=0}^{\infty} (2J+1)W(E, J, a) \quad (31a)$$

$$= \sum_i h(E - V_{i\text{max}}) \quad (31b)$$

The zero of energy for the partition functions Q_A and Q_B and for Q^* must be the same, the most natural choice being the zero point levels of the collision partners A and B (i.e., $V_{0\infty}$, using the notation Q^0). If one chooses as a different reference energy for Q^* the maximum of the lowest adiabatic channel, i.e., one introduces equations (32) to (34):

$$V'_{i\text{max}} = V_{i\text{max}} - V_{0\text{max}} \quad (32)$$

$$Q^{*'} = \sum_i \exp\left(\frac{-V'_{i\text{max}}}{kT}\right) \quad (33)$$

$$E_0 = V_{0\text{max}} - V_{0\infty} \quad (34)$$

one obtains the frequently used transition state form in equation (35) for the rate coefficient, including the possibility of a barrier E_0 in the entrance channel for the reaction:

$$k^c(T) = \frac{kT}{h} \frac{\bar{Q}_\ddagger^*}{\bar{Q}_{\text{tA}}\bar{Q}_{\text{tB}}} \frac{Q^*}{Q_{\text{A,int}}^0 Q_{\text{B,int}}^0} \exp\left(\frac{-E_0}{kT}\right) \quad (35)$$

which makes use of the translational partition functions per unit volume defined by equation (36):

$$\bar{Q}_{\text{tx}} = \left[\frac{2\pi m_x kT}{h^2} \right]^{3/2} \quad (36)$$

The densities of states $\varrho(E, J)$ of the collision complex are not needed explicitly anywhere in these expressions, although they arise implicitly in the conditions of validity, equations (10) and (11). The densities are needed, however, for calculating lifetimes of collision complexes, and for specific rate constants of unimolecular decay.

2.4 Lifetimes of Collision Complexes, Specific Rate Constants $k(E, J)$ for Unimolecular Decay, and Transmission Coefficients

Lifetimes for collision complexes and specific rate coefficients for unimolecular decay of metastable states can be derived in several ways in the framework of the adiabatic channel model, resulting in similar fundamental expressions. The major differences between the various derivations of lifetimes are connected to the physical interpretation.

2.4.1 Statistical Lifetimes of Collision Complexes^{3,17}

The most general approach towards quantum lifetimes of collision complexes starts from the energy dependence of the statistical S-matrix.¹⁷ Following Smith,⁴¹ one can show that equation (37) holds:

$$N(E, J)^{-1} \text{Tr} [\mathbf{Q}(E, J)] = N(E, J)^{-1} \sum_{k=1}^{N(E, J)} \sum_{j=1}^{N(E, J)} |S_{kj}|^2 \Delta t_{kj} \quad (37)$$

where \mathbf{Q} is the lifetime matrix given by equation (38):

$$\mathbf{Q} = i \frac{h}{2\pi} S \frac{dS^\dagger}{dE} \quad (38)$$

$N(E, J)$ is the number of asymptotically open channels, which is the order of the block $S(E, J)$ of the S-matrix shown in Figure 2. Δt_{kj} is the delay time matrix defined by equation (39):

$$\Delta t_{kj} = \tau_{kj}^1 - \tau_{kj}^0 \quad (39)$$

where τ_{kj}^1 is the collision time between entrance channel j and exit channel k with the interaction potential, and τ_{kj}^0 is the hypothetical collision time without the interaction. Δt_{kj} is thus strictly speaking not an observable quantity, but this causes no difficulty for long lived collision complexes with $\tau_{kj}^1 \simeq \Delta t_{kj} \gg \tau_{kj}^0$. Similarly, one can define an excess density of states ϱ_e by equation (40):

$$\varrho_e(E, J) = \varrho^1(E, J) - \varrho^0(E, J) \quad (40)$$

where ϱ^1 is the density of states with the interaction potential between the collision partners and ϱ^0 the density of states

without the interaction. One can show^{42,43} that equation (41) holds:

$$\text{Tr}[\mathbf{Q}(E, J)] = h\varrho_e(E, J) \quad (41)$$

from which one can define an average delay time through equation (42):

$$\Delta t(E, J) = \frac{h\varrho_e(E, J)}{N(E, J)} \quad (42)$$

Introducing now the average density of metastable levels $\varrho(E, J)$ of the intermediate complex, which can be obtained by continuing the bound state spectrum in the framework of the adiabatic channel model or, in the case of isolated resonance scattering states, by counting the resonances and averaging over an interval $\Delta E \gg \varrho(E, J)^{-1}$, one has the approximate equivalence of average quantities in equation (43):

$$\langle \varrho_e(E, J) \rangle_{\Delta E} \simeq \varrho(E, J) \quad (43)$$

Noting that only scattering on adiabatically open channels with number $W(E, J)$ leads to long-lived complexes, and that furthermore the excess density $\varrho_e(E, J)$ at the location of a long-lived resonance is larger than the average given by equation (43), one finds finally the inequality for long-lived complex lifetimes given by equation (44):

$$\tau(E, J) \geq \langle \Delta t(E, J) \rangle_{\Delta E} = \frac{h\varrho(E, J)}{W(E, J)} \quad (44)$$

Similarly, one has equation (45) for the average specific rate constant $k(E, J)$ for unimolecular decay of metastable complexes:

$$k(E, J) \leq \frac{W(E, J)}{h\varrho(E, J)} \quad (45)$$

A more detailed discussion of this reasoning from formal scattering theory can be found in Ref. 17. One can express the inequality (45) as an equation (46):

$$k(E, J) = \langle \gamma \rangle \frac{W(E, J)}{h\varrho(E, J)} \quad (46)$$

where one interprets $\langle \gamma \rangle$ as an average transmission coefficient satisfying the inequality (47):

$$0 \leq \langle \gamma \rangle \leq 1 \quad (47)$$

From this discussion it becomes quite clear that the fundamental expression of statistical unimolecular rate theory in equation (46) is an average quantity. When considered as an energy average over many isolated long-lived resonance scattering states in the interval ΔE , one has the inequality (48):

$$\Delta E \gg \varrho(E, J)^{-1} \quad (48)$$

which is equivalent to the inequality (10).

The individual lifetimes and specific rate coefficients may scatter around this average value, as has been clearly pointed out in the early discussion of these quantities in the adiabatic channel model.² More recently, the concept of statistical fluctuations about this average has found renewed attention.⁴⁴⁻⁴⁶ Furthermore, the average transmission coefficient $\langle \gamma \rangle$ introduced somewhat formally through equations (45) to (47), can

be understood on the basis of two simple dynamical models, which we shall discuss here as well.

2.4.2 Recurrence Times and Transmission Coefficients for Quasibound Complex Dynamics

We consider the time-dependent wavefunction arising from a superposition of quasibound states of density $\varrho(E, J)$. For an equally spaced spectrum of density ϱ the recurrence time t_r generating a specific dynamical state is:⁴⁷

$$t_r = h\varrho(E, J) \quad (49)$$

For a nonequidistant spectrum with the same average density one has

$$t_r > h\varrho(E, J) \quad (50)$$

If the specific state considered is an outgoing translational state on the adiabatic channel $|a\rangle$ (Figure 4), one obtains an expression (51) for the specific rate constant on this adiabatic channel, if the quantum mechanical transmission probability for leaving the complex boundary is T_a , the rate constant being the frequency of generating the outgoing wave multiplied by the transmission probability:

$$k(E, J, a) = \frac{T_a(E)}{h\varrho(E, J)} \quad (51)$$

Summing over all channels, one obtains

$$k(E, J) = \frac{\sum_a T_a}{h\varrho(E, J)} \quad (52)$$

For simple analytical adiabatic channel model potentials one can derive simple analytical expressions for the transmission coefficients.¹ Often, one may replace T_a by the crudest quasi-classical model, giving a step function behavior with the Heaviside function $h(x > 0) = 1$ and $h(x < 0) = 0$ in equation (53):

$$T_a(E) = h(E - V_{a\max}) \quad (53)$$

Use of equation (18) results in equation (54):

$$k(E, J) = \frac{W(E, J)}{h\varrho(E, J)} \quad (54)$$

If one uses more generally $0 \leq T_a \leq 1$ one finds the inequality (45), where one must, however, accept some adiabatic channels as open below the classical thresholds due to the tunneling, if the tunneling probability is appreciable. A second reason for the inequality (45) arises from the inequality (50).

2.4.3 Transmission Coefficients from Analytically Solvable Resonance Scattering Models

Mies and Krauss¹³⁻¹⁵ derived analytical expressions for the decay rates from a set of resonance scattering states i with density ϱ coupled with equal coupling strength (parameter Γ_{ia}) to a continuum corresponding to channel $|a\rangle$. Their result can be written in the form¹⁷ of equation (55):

$$k_{ia} = \frac{\gamma_{ia}}{h\varrho} \quad (55)$$

with a transmission coefficient being given by equation (56):

$$\gamma_{ia} = \frac{2\pi\Gamma_{ia}\varrho}{(1 + \pi\Gamma_{ia}\varrho/2)^2} \quad (56)$$

γ_{ia} satisfies the condition (57):

$$0 \leq \gamma_{ia} \leq 1 \quad (57)$$

Both for very small coupling strengths Γ_{ia} in the model and for very large Γ_{ia} , the effective transmission coefficient decreases to zero as Γ_{ia} decreases to zero or increases to infinity. In the perturbation theory limit $\Gamma_{ia} \ll \varrho^{-1}$ ($\Gamma\varrho \ll 1$), one obtains isolated resonances with Lorentzian line shape and exponential decay rate coefficients given by equation (58):

$$k_{ia} = \frac{2\pi\Gamma_{ia}}{h} \quad (58)$$

Summing over all continua a one finds equation (59) for the total decay rate constant from the resonance i :

$$k_i = \frac{2\pi\Gamma_i}{h} = \frac{2\pi}{h} \sum_a \Gamma_{ia} \quad (59)$$

The maximum value $\gamma_{ia} = 1$ is obtained when $\pi\Gamma_{ia}\varrho/2 = 1$. Writing $\varrho \equiv \varrho(E, J)$, summing over all channels $|a\rangle$, and assuming that $\gamma_{ia} = 1$ for $W(E, J)$ adiabatically open channels and $\gamma_{ia} = 0$ otherwise, one obtains the usual right hand side inequality (60):

$$k(E, J) = \sum_a k_{ia} = \frac{\sum_a \gamma_{ia}}{h\varrho(E, J)} \leq \frac{W(E, J)}{h\varrho(E, J)} \quad (60)$$

The limiting case with $\pi\Gamma_{ia}\varrho \gg 1$ results in equation (61):

$$\gamma_{ia} = \frac{8}{\pi\Gamma_{ia}\varrho} \ll 1 \quad (61)$$

The decrease of the transmission coefficient with increasing coupling strength Γ_{ia} arises from interference between the overlapping resonances in this particular model.

Peskin, Reissler, and Miller⁴⁸ have proposed a different model for the effective transmission coefficient, which can be derived from simple one-dimensional scattering models or from a random matrix optical model. For the one-dimensional case of a coupling to a single continuum Γ , one obtains the one-channel rate constant of equations (62) and (63):

$$k(E) = \frac{\gamma}{h\varrho} \quad (62)$$

$$\gamma = 1 - \exp(-2\pi\varrho\Gamma) \quad (63)$$

γ interpolates smoothly between small values near zero for $\Gamma_1\varrho \ll 1$ in equation (64):

$$\gamma = 2\pi\varrho\Gamma_1 \quad (64)$$

giving the perturbation theory limit for an exponential decay in equation (65):

$$k = \frac{2\pi\Gamma_1}{h} \quad (65)$$

and $\gamma = 1$ for $\Gamma_1 \rho \gg 1$, giving the single channel rate constant in equation (66):

$$k = \frac{1}{h\rho} \quad (66)$$

For coupling a dense set of states with density $\rho(E, J)$ to $W(E, J)$ channels one finds similarly equations (67), (68):

$$k(E, J) = \frac{W(E, J)}{h\rho(E, J)} \langle \gamma \rangle \quad (67)$$

$$\langle \gamma \rangle = 1 - \exp \left[\frac{-2\pi \langle \Gamma^* \rangle \rho(E, J)}{W(E, J)} \right] \quad (68)$$

Again, the average transmission coefficient $\langle \gamma \rangle$ interpolates smoothly between 1 (for $\langle \Gamma^* \rangle \rho(E, J)/W(E, J) \gg 1$) and very small values for the perturbation theory limit for an exponential decay with a Lorentzian line shape ($\langle \Gamma^* \rangle =$ full width at half maximum) and a rate constant

$$k(E, J) = \frac{2\pi \langle \Gamma^* \rangle}{h} \quad (69)$$

We must note here that different forms for γ arise from the models because of the different nature of the models, and that there is a very different physical significance also for the quantities Γ_{ia} , Γ_1 and $\langle \Gamma^* \rangle$. It must also be clear that the rate coefficient of the adiabatic channel model does not depend on any of these model assumptions; rather, it can be derived in its general form from the very general considerations discussed in Section 2.4.1. However, the simple models for deriving transmission coefficients in Section 2.4.2 and 2.4.3 provide some physical insight and could also be made the basis for simple numerical calculations of transmission coefficients beyond the step function behavior, which leads to the most frequently used equation (54), i.e., equation (46) with $\langle \gamma \rangle = 1$. See also our calculation of transmission coefficients.⁹⁵

2.5 High Pressure Limiting Rate Constants for Unimolecular Reaction

The high pressure limiting rate coefficient for unimolecular reaction is the Boltzmann average over the specific rate constants, given by equation (70):

$$k_\infty(T) = Q_X^{-1} \int_{E=0}^{\infty} \sum_{J=0}^{\infty} (2J+1) k(E, J) \rho(E, J) \exp \left(\frac{-E}{kT} \right) dE \quad (70)$$

Q_X is the reactant (X) partition function. Inserting equation (46) with a double average over $\langle \langle \gamma \rangle \rangle$ (or assuming $\langle \gamma \rangle = 1$ and equation 54) one finds¹ equation (71):

$$\begin{aligned} k_\infty(T) &= \langle \langle \gamma \rangle \rangle \left(\frac{kT}{h} \right) Q_X^{-1} \int_{E=0}^{\infty} \sum_{J=0}^{\infty} (2J+1) W(E, J) \\ &\quad \times \exp \left(\frac{-E}{kT} \right) \left(\frac{dE}{kT} \right) \\ &= \langle \langle \gamma \rangle \rangle \frac{kT}{h} \frac{Q^*}{Q_X} \exp \left(\frac{-\Delta E_{X0}}{kT} \right) \end{aligned} \quad (71)$$

ΔE_{X0} is the energy difference between the maximum of the lowest adiabatic channel potential and the zero point level E_{0X} of the reactant X as given by equation (72):

$$\Delta E_{X0} = V_{a \max} - E_{0X} \quad (72)$$

Q^* has the same significance as in equation (35) and may conveniently be considered to be the 'partition function of the transition state' in the adiabatic channel model, referred to the zero point level of the transition state, equation (32).

One could also try to take the reverse route, starting from equation (35) (which implies $\langle \langle \gamma \rangle \rangle = 1$, not important for the present discussion). Then one derives $k_\infty(T)$ from detailed balance and the statistical thermodynamical expression for the equilibrium constant. Finally, one might obtain specific rate constants $k(E)$ by an inverse Laplace transformation (operator \hat{L}^{-1} in equation 73), with $\beta = (kT)^{-1}$:

$$\rho(E) k(E) = \hat{L}^{-1} \{ Q_X(\beta) k_\infty(\beta) \} \quad (73)$$

However, it is not possible to recover the nontrivial dependence of $k(E, J)$ on angular momentum J and other good quantum numbers by this procedure. The question has been discussed critically.²⁸ Formally, one might consider energy to be a sufficient index, if all decaying metastable states correspond to completely separated, isolated resonances. However, in practice this is rather the exception than the rule in unimolecular rate theory. Under normal circumstances one must allow for a dense set of heavily overlapping resonances with a variety of good quantum numbers.

3 SYMMETRY AND APPROXIMATE CONSTANTS OF MOTION IN THE ADIABATIC CHANNEL MODEL

A particular property of the adiabatic channel model is the ability to provide complete explicit specification of all good quantum numbers and symmetries for individual channels, throughout the correlation between all reactant and product levels (see Figure 3). At the time of introducing the adiabatic channel model this was a new feature in statistical theory, which can be systematically used both for obtaining simple computational results and for obtaining a deeper understanding of some of the basic properties of the reaction processes involved. We shall summarize here some of the ideas and results.

3.1 Fundamental Molecular Symmetries

The dynamical consequences of molecular symmetry arise from the invariance of the Hamiltonian \hat{H} and time evolution operator \hat{U} with respect to certain symmetry operations \hat{C} in equation (74) and (75):

$$\hat{H} \hat{C} = \hat{C} \hat{H} \quad (74)$$

$$\hat{U} \hat{C} = \hat{C} \hat{U} \quad (75)$$

The symmetry operations \hat{C} lead thus to certain 'constants of motion' or evolution, in particular also to 'reaction constants'.^{40,49-51} The general symmetry operations of relevance in the present context are with the related constants of motion:

- (i) translation in space (momentum conservation)
- (ii) translation in time (energy conservation)
- (iii) rotation in space (total angular momentum conservation)
- (iv) time reversal (symmetry of the S-matrix)
- (v) reflection of all particle coordinates in the center of mass (parity conservation)

- (vi) permutations of the indices of identical particles, i.e., electrons and certain nuclei (permutation symmetry and Pauli principle).

The first three invariances are generally believed to be exact. (i) leads in practice to the statement that in the center of mass frame for the reaction the center of mass stays at rest. (ii) is explicitly included in the adiabatic channel model through explicit specification of total energy E . (iii) corresponds to conservation of total angular momentum (F), including electronic and nuclear spin. (iv) leads to the symmetry of the S -matrix in an appropriate basis (i.e., $S = S^T$, see Ref. 17 for details. In general, S need not be symmetric, but it can be made symmetric by transformation to an appropriate basis, which is advisable for theoretical purposes). (v) leads to conservation of total parity and (vi) leads to the conservation of the irreducible representation of the corresponding permutation symmetry group. Because of the generalized Pauli principle, only one irreducible representation is allowed. Therefore (vi) leads to the (almost) trivial statement that this allowed representation is maintained. For a discussion of further, more general symmetries such as C , CP , CPT , etc., we refer to Ref. 51.

In general, equation (76) applies for an observable constant of the motion C corresponding to an operator \hat{C} :⁴⁹

$$\begin{aligned} \langle \hat{C}(t) \rangle &= \langle \Psi(t) | \hat{C} | \Psi(t) \rangle = \langle \hat{U} \Psi(0) | \hat{C} | \hat{U} \Psi(0) \rangle \\ &= \langle \Psi(0) | \hat{U}^\dagger \hat{C} \hat{U} | \Psi(0) \rangle = \langle \Psi(0) | \hat{C} | \Psi(0) \rangle \\ &= \langle \hat{C}(0) \rangle \end{aligned} \quad (76)$$

In particular, if $\Psi(t)$ is an eigenfunction ζ_n of \hat{C} with eigenvalue c_n , then one has equation (77):⁴⁹

$$\langle \hat{C}(t) \rangle = \langle \zeta_n | \hat{C} | \zeta_n \rangle = c_n \quad (77)$$

Therefore we can label such a $\Psi(t)$, and also molecular energy levels, adiabatic channels and the like by the quantum numbers c_n the good quantum numbers under these conditions. (\hat{C} and c_n need not be dimensionless, thus the expression 'quantum number' should not be taken literally. However, one can always define numbers $c'_n = f(c_n)$, which are dimensionless.)

3.2 The Principle of Approximate Parity and Nuclear Spin Symmetry Conservation and Other Approximate Symmetries of Adiabatic Channels

In the framework of electroweak theory of molecules, parity is not a rigorous constant of the motion.⁵¹ Nevertheless, it remains a practical, approximately good quantum number in the framework of ordinary electromagnetic theory. Similarly, neglecting the weak coupling of nuclear spin with molecular motion, one may introduce the nuclear spin quantum numbers I , M_I and nuclear spin symmetry (i.e., the irreducible representation of the nuclear spin function and the corresponding complementary, Pauli-allowed irreducible representation of the 'motional' molecular wavefunction) as approximately good quantum numbers for scattering, chemical reactions, optical transitions, and for adiabatic channels.^{40,49} In practice, this amounts to classifying adiabatic channels with respect to the

symmetry group in equation (78):

$$S_{n_1, n_2, n_3}^* = S^* \otimes \prod_{i=1}^N S_{n_i} \quad (78)$$

or a subgroup M_{sm} of order m thereof. $S^* = \{E^*, E\}$ is the reflection group ('Spiegelungsgruppe') and S_{n_i} is the symmetric group of the permutations of n_i identical nuclei of type 'i' occurring in the molecular reaction system.⁴⁰ Similarly to molecular energy levels, every adiabatic channel in this approximation can be characterized by its 'motional' angular momentum J , its motional symmetry species Γ_k in the relevant molecular symmetry group and the corresponding Pauli-allowed nuclear spin statistical weights (corresponding to the Pauli-allowed nuclear spin angular momenta I , M_I occurring together with Γ_k). One thus arrives at the following practical procedure to obtain symmetry and angular momentum labels for adiabatic channels:

- (i) Obtain the 'motional' angular momentum coupling of reactants and products in the usual way,⁵² in a basis which explicitly specifies the total 'motional' angular momentum J (perhaps including electron spin if the coupling is important) for the adiabatic channels and molecular states.
- (ii) Obtain a classification of the adiabatic channels by irreducible representation Γ of an appropriate group S_{n_1, n_2, n_3}^* or subgroup M_{sm} , explicitly specifying also motional parity (by \pm in the notation).
- (iii) Count channels $W(E, J, M, \Gamma^\pm \dots)$ and densities $\rho(E, J, M, \Gamma^\pm \dots)$.
- (iv) Note degeneracy $(2J + 1) \times g_K(\Gamma^\pm)$ where g_K is the nuclear spin statistical weight for the irreducible representation Γ^\pm of the motional wavefunction.
- (v) Calculate cross sections with a statistical S -matrix, which is blockdiagonal in J, M, Γ^\pm , i.e.,

$$\langle |S_{fi}|^2 \rangle = W(E, J, M, \Gamma^\pm \dots)^{-1} \quad (79)$$

for strongly coupled channels, and specific rate constants

$$k(E, J, M, \Gamma^\pm \dots) = \langle \gamma \rangle \frac{W(E, J, M, \Gamma^\pm \dots)}{h \rho(E, J, M, \Gamma^\pm \dots)} \quad (80)$$

Further details of the procedures and examples can be found in Refs. 40 and 49. Here we shall quote a relatively simple example for illustration, which shows some of the main features of these procedures. The hydrogen bonded complex $(\text{HF})_2$ can dissociate into two HF momomers:



The complete group in equation (78) would be:^{39,53}

$$S_{2,2}^* = S_2^F \times S_2^H \times S^* \quad (82)$$

including exchange of nuclei between the two HF monomer units. However, if the latter remain intact, only the exchange (ab) of the monomers as a whole needs to be considered, leading to a group M_{s4} of order 4 defined by equation (83):

$$M_{s4} = \{E, E^*, (\text{ab}), (\text{ab})^*\} \quad (83)$$

where E is the identity, E^* the inversion operation, and (ab) represents the permutation of the two intact HF momomers,

(ab)* combined with inversion. The symmetry species (irreducible representations) of this group can be labeled A^+ , A^- , B^+ , B^- , where the exponent + and - indicates parity and A and B whether one has symmetry (A) or antisymmetry (B) with respect to the permutation (ab). Parity is easily obtained for the wavefunctions of a planar asymmetric top $(\text{HF})_2$ and the two diatomic rotors. The symmetric (A) nuclear spin functions have total nuclear spin $I = 2, 1, 0$ (twice for the latter, total weight $g_K = 10$) and combine with A motional symmetry. The antisymmetric nuclear spin function (B) has $I = 1$ (twice, total weight $g_K = 6$) combining with B motional symmetry.

Angular momentum coupling is particularly transparent for this example, as there is no electronic (spin) angular momentum for reactants and products in equation (81). One just combines two diatomic rotors with j_1 and j_2 to a channel angular momentum j in equation (84):

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \quad (84)$$

giving a total J by equation (85):

$$|j - \ell| \leq J \leq j + \ell \quad (85)$$

The motional parity of the product channels is given by equation (86):

$$\Pi = (-1)^{j_1+j_2+\ell} \quad (86)$$

and exchange symmetry by equations (87) and (88), if $(\nu_1, j_1) = (\nu_2, j_2)$:

$$A \text{ for } j + \ell = \text{even} \quad (87)$$

$$B \text{ for } j + \ell = \text{odd} \quad (88)$$

If $(\nu_1, j_1) \neq (\nu_2, j_2)$ one has a degenerate A, B pair. Figure 5 shows the corresponding symmetry correlations for the lowest adiabatic channels with $J = 0$ (and therefore $j = \ell$). For the bound complex $(\text{HF})_2$ with $J = 0$ the exchange symmetry (A, B) results from the tunneling splitting (tunneling vibrational mode ν_5), and parity from whether the only out of plane vibration ν_6 has an even (+) or odd (-) quantum number. There is thus a total of four different symmetry species on both sides of the correlation diagram for channels, with numerous crossings of channels of different symmetry. Additional crossings would arise at high energy, where the (HF) -stretching quanta are excited, because ν_{HF} is a conserved quantum number in the correlation. We shall return to this example below and note at present that statistical theory is not really applicable for vibrational predissociation of $(\text{HF})_2$ after (HF) -stretching excitation;⁵⁴ however, it may possibly be applicable to excitation of the low frequency modes.⁵⁵ In any case, the symmetry correlation is independent of whether statistical theory is applicable or not. It would also apply to other, symmetrically equivalent cases. Correlation diagrams of the type shown in Figure 5 are also very useful in discussing state selected predissociation into selected product channels.⁴⁹

More generally, further complications arise for angular momentum couplings when the fragments show electronic angular momentum, but the fundamental symmetry rules are not affected by this. Early examples for detailed correlations include triatomic systems,^{1,2} and another more recent example is the correlation for atom + linear molecule.⁵⁶ While for such simple cases, and planar molecules in general, parity is

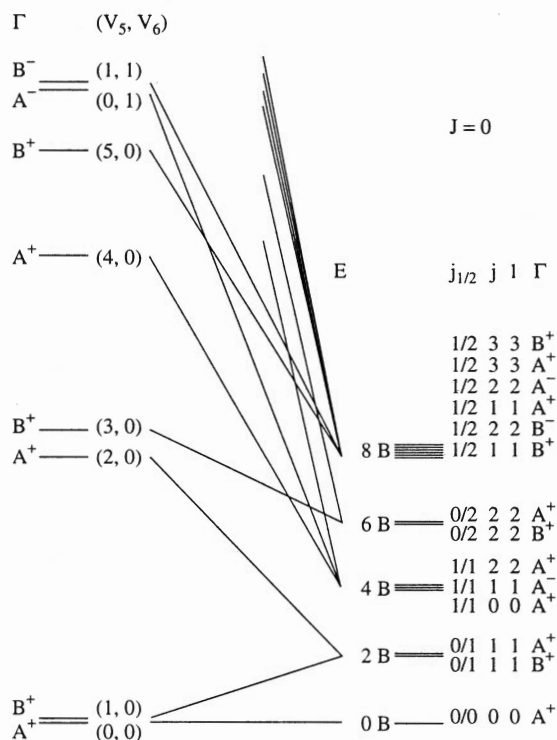


Figure 5 Symmetry correlation for adiabatic channels in the dissociation $(\text{HF})_2 \rightarrow 2\text{HF}$ (after Ref. 39)

easily identified as a quantum number, it must be stressed that, even for nonplanar molecules, parity can frequently be identified as a good quantum number of the spectroscopic states. This means, however, going beyond the usual point group classification of spectroscopic levels. Methane and CF_3I are relevant examples.^{40,49} However, the parity-violating weak nuclear interaction can introduce modifications at this point,^{57,58} which we shall not discuss in detail here. Further effects of interest arise when one includes explicit correlation with hyperfine levels, which in principle is possible in the adiabatic channel model,⁵⁹ (see also the discussion of hyperfine effects in H_3^+ in Ref. 63) and may become relevant with recent experimental detection of hyperfine distributions in reaction products.⁶⁰ These effects, as well as the role of coupling of scattering partial waves ℓ to symmetry and differential cross sections, are best treated separately.⁴⁰ Two recent results of importance in this context should be mentioned. Firstly, the detailed symmetry selection rules predicted⁴⁰ for $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ have been demonstrated in an elegant experiment.⁹² Secondly, ozone isotope anomalies⁹³ may well be related to the symmetry-dependent isotope effect predicted in 1977,⁴⁰ although the relationship may not be simple.⁴⁰

Finally, we should mention here the possibility of introducing further approximate constants of the motion beyond parity and nuclear spin symmetry. Recent spectroscopic evidence suggests that such approximately good additional quantum numbers should exist rather frequently on short time scales of a few picoseconds and less in intramolecular vibrational redistribution,^{51,61,62} and these may well persist in reactions, although experimental evidence for such effects remains to be established with certainty.

3.3 Approximate Calculation of Symmetrized Densities of States and Adiabatic Channel Numbers

While detailed symmetry correlations of adiabatic channels are possible, they are frequently unnecessary. One must distinguish here good quantum numbers arising from continuous groups, such as the total angular momentum quantum number, from those arising from discrete groups such as parity and nuclear spin-permutation symmetry. Whereas effects arising from angular momentum conservation have to be considered explicitly even in the classical limit at high energy, the discrete symmetries can be dealt with by simple correction factors at high energies, where the densities and numbers of channels are large.

The first important aspect to be considered is the role of rovibrational (Coriolis) coupling in calculating effective rovibrational densities of states, including all rotational levels of a given angular momentum J . This idea was, indeed, first implemented in the framework of the adiabatic channel model,¹ as the importance of a consistent inclusion of proper rovibrational coupling for effective densities $\varrho(E, J)$ was not recognized in earlier versions of statistical theories, such as RRKM theory. For a symmetric top with quantum numbers K , the density $\varrho(E, J)$ takes the approximate form given by equation (89):

$$\varrho(E, J) = \sum_{K=0}^J g_K \varrho_{\text{vib}}[E - J(J+1)B - (A-B)K^2 - E_z] \quad (89)$$

Here, E_z is the energy of the zero point level, A and B are rotational constants (in energy units, $g_K = 1$ for $K = 0$ and $g_K = 2$ for $K > 0$). The use of such densities in the statistical formulae implies that K is not a good quantum number for the reaction. The vibrational density of states ϱ_{vib} can be calculated in the separable harmonic or anharmonic oscillator approximations by simple formulae,⁶⁴ or fast convolution algorithms,^{65,66} which we have extended to include calculation of rovibrational states $\varrho(E, J)$ for the adiabatic channel model (see Ref. 17 and references cited therein). If K is considered to be a good quantum number on short time scales, one would effectively calculate equation (90):

$$k(E, J, K) = \frac{W(E, J, K)}{h\varrho(E, J, K)} = \frac{W_{\text{vib}}^{\ddagger}(E)}{h\varrho_{\text{vib}}(E)} \quad (90)$$

This is actually the most frequently used assumption in traditional RRKM theory. Near threshold, one has $W \simeq 1$ in the rate constant expressions (90) and (54). On the other hand, $\varrho(E, J)$ is substantially larger, for large J , than ϱ_{vib} - the increase being about a factor of $2J+1$ if the rotational energy is very small. Thus one finds that rovibrational coupling decreases the threshold rate constants for increasing J , compared to $k(E, J = 0)$. However, for very large J this effect is counteracted by an increase in the rotational energy, decreasing the factor ϱ_{vib} in equation (89), as was already observed in the first discussions of this effect.^{1,2} From a dynamical point of view, there is no particular reason to treat the symmetric top quantum number K as a 'better' quantum number than, say, vibrational angular momentum quantum numbers ℓ_{vib} or some other vibrational quantum numbers. Some or all of these may be conserved on very short time scales, but not on long time scales. None of them should be treated on an equal footing with J , which is certainly a very well conserved quantum

number, with the restriction of possible coupling to nuclear spin degrees of freedom on rather long time scales.

Symmetrized densities of states $\varrho(E, J, \Gamma_k^{\pm} \dots)$ and adiabatic channel numbers $W(E, J, \Gamma_k^{\pm} \dots)$ can be calculated by counting algorithms, for instance extending the Beyer-Swinehart algorithm in appropriate ways (see Refs. 40 and 50 also for further references), where Γ_k^{\pm} is an irreducible representation of the molecular symmetry group. In the classical limit of high energy and angular momentum, it can be shown that the total density can be decomposed according to a regular representation, leading to equation (91):⁵⁰

$$\frac{W(E, J, \Gamma_m^{\pm})}{W(E, J, \Gamma_n^{\pm})} = \frac{\varrho(E, J, \Gamma_m^{\pm})}{\varrho(E, J, \Gamma_n^{\pm})} \simeq \frac{[\Gamma_m^{\pm}]}{[\Gamma_n^{\pm}]} \quad (91)$$

$[\Gamma_m^{\pm}]$ stands for the dimension of the irreducible representation Γ_m^{\pm} . One notes that each channel and level entering the count in $W(E, J, \Gamma_m^{\pm})$ or in $\varrho(E, J, \Gamma_m^{\pm})$ has a further motional degeneracy $g_m = [\Gamma_m^{\pm}]$. If one introduces a count of nondegenerate motional states without considerations from the Pauli principle, one would obtain the densities in equation (92):

$$\varrho'(E, J, \Gamma_m^{\pm}) = [\Gamma_m^{\pm}] \varrho(E, J, \Gamma_m^{\pm}) \quad (92)$$

and channel numbers in equation (93):

$$W'(E, J, \Gamma_m^{\pm}) = [\Gamma_m^{\pm}] W(E, J, \Gamma_m^{\pm}) \quad (93)$$

In actual fact, each level of motional degeneracy $[\Gamma_m^{\pm}]$ combines with a nuclear spin wavefunction of spin symmetry degeneracy $[\Gamma_k^{\pm}]$ to give a nondegenerate Pauli allowed state following equation (94):

$$\Gamma_k \times \Gamma_m = \Gamma_{\text{Pauli}} + \dots \quad (94)$$

Γ_{Pauli} always corresponds to a nondegenerate species defined by its character χ_Q under the group operations Q :

$$\chi_Q = \prod_{i=1}^{N_F} (-1)^{P_{iQ}} \quad (95)$$

In equation (95), P_{iQ} is the parity of the permutation of the i th kind of fermions (total number N_F) in the operation Q . Of course, the degeneracy arising from angular momentum is retained. Thus, in counting levels that really exist, the densities in equation (91) are relevant. However, the densities in equation (92) are relevant when one counts molecular state densities $\varrho(E, J)$ using a model of oscillators and rotors disregarding the molecular symmetry group. One obtains the decomposition of this full 'motional' density according to equations (96) and (97):

$$\varrho(E, J) = \sum_m \varrho'(E, J, \Gamma_m) \quad (96)$$

$$W(E, J) = \sum_m W'(E, J, \Gamma_m) \quad (97)$$

In practice, one will usually calculate directly $\varrho(E, J)$ and $W(E, J)$ and then obtain $\varrho(E, J, \Gamma_m)$, $W(E, J, \Gamma_m)$, and $\varrho'(E, J, \Gamma_m)$, $W'(E, J, \Gamma_m)$ using equations (96) and (97) together with equations (91), (92), and (93). These general results⁴⁹ have been repeatedly checked by direct count for specific systems,^{63,67} and it is generally found that the convergence towards the classical limit of a regular density at high energy

is even faster than would be expected on the basis of the approach of the total density to the classical limit. At low energies, one should always use direct count. In the calculation of rate constants according to equation (80), q has usually already reached the regular limit, whereas W has not (in the extreme $W = 1$, only one channel being open). Therefore the threshold rate constants are larger when symmetry is taken into account, compared to a calculation with unsymmetrized total densities $q(E, J)$. However, when both W and q have reached the regular limit, the symmetry correction factor for $k(E, J)$ cancels completely, as it is the same in the numerator and in the denominator. In order to have such canceling one must take care, however, to use the same group and the same irreducible representations for the calculation of both $W(E, J, \Gamma)$ and $q(E, J, \Gamma)$. Indeed, this is necessary for a consistent definition of $k(E, J, \Gamma)$. This fact also makes it quite clear that one cannot simply use, say, different point groups for the molecule which dissociates (and $q(E, J, \Gamma)$) and the 'transition state' with $W(E, J, \Gamma')$.

3.4 Symmetry Numbers and Reaction Path Polytopy

For the thermal unimolecular reaction the expression (71) is extended by a further explicit summation over the symmetry index Γ with $W(E, J, \Gamma)$ with a nuclear spin statistical weight $g_K(\Gamma)$. The integral in equation (71) can be calculated, in the regular limit, using the approximation in equation (98):

$$\begin{aligned} W(E, \Gamma_{\text{Pauli}}) &= \sum_i \sum_{J=0}^{\infty} (2J+1) W(E, J, \Gamma_i) g_K(\Gamma_i) \\ &= \prod_j \frac{(2I_j+1) W_m(E)}{\sigma_{M_{sg^*}}} \end{aligned} \quad (98)$$

$W(E, \Gamma_{\text{Pauli}})$ is the total number of Pauli allowed channels including nuclear spin. I_j is the nuclear spin of the j th nucleus in the molecule, $W_m(E)$ the total number of open channels calculated 'mechanically' without regarding symmetry and nuclear spin, and $\sigma_{M_{sg^*}}$ is the symmetry number of the molecular symmetry group M_{sg^*} of order g^* as relevant for the calculation of $W(E)$. This could be the full permutation inversion group or a subgroup thereof. The symmetry number $\sigma_{M_{sg^*}}$ is just the order of the subgroup of permutations in either of these groups.⁵⁰ The partition function Q_X can be replaced similarly by

$$Q_X(\Gamma_{\text{Pauli}}) = Q_{mX} \cdot \prod_j \frac{(2I_j+1)}{\sigma_{M_{sgX}}} \quad (99)$$

The factor $\prod_j (2I_j+1)$ cancels and one arrives at the final expression (100) for the high pressure limiting rate constant

$$k_{\infty}(T) = \langle \langle \gamma \rangle \rangle \frac{kT}{h} \frac{Q_m^*}{Q_{mX}} \cdot \frac{\sigma_{M_{sgX}}}{\sigma_{M_{sg^*}}} \exp\left(\frac{-\Delta E_{X0}}{kT}\right) \quad (100)$$

Some observations may be useful in the interpretation of this expression. Firstly, both the Q_m must be computed consistently with a mechanical model, which is consistent with the assumed symmetry group. In principle this is completely arbitrary but one must satisfy quite generally equation (101):

$$\frac{Q_{m1}}{\sigma_{M_{sg1}}} = \frac{Q_{m2}}{\sigma_{M_{sg2}}} \quad (101)$$

When one uses a mechanical model 1 to compute Q_{m1} with a symmetry number $\sigma_{M_{sg1}}$ and compares this with calculation of Q_{m2} with another mechanical model 2 with symmetry number $\sigma_{M_{sg2}}$, the partition function for the true Pauli-allowed states given by equation (99) must remain unaffected by this change of models.

Secondly, the factor $\sigma_{M_{sgX}}/\sigma_{M_{sg^*}}$ is frequently interpreted as a 'reaction path degeneracy due to symmetry'. While this is a practical concept for rigid, classical transition states with a well defined point group (σ being computed for the point group of interest, then), this concept loses its meaning for nonrigid transition states and nonrigid molecules. For instance, one might choose in this case a model with the full permutation inversion group for calculating both Q_{mX} and Q_m^* . This group and the relevant $\sigma_{M_{sg}}$ are then the same for both and the ratio corresponding to the reaction path degeneracy would be 1. However, one might choose different symmetry models for Q_{mX} and Q_m^* and then the ratio is different from 1 (but $k_{\infty}(T)$ would not be affected by this change). For instance, a rather useful assumption for bond dissociation would be an ordinary rigid molecular reactant with some modest symmetry and a small symmetry number σ but a very nonrigid 'transition state' corresponding to a channel count with almost freely rotating fragments, say with some fragment symmetry numbers σ_1 and σ_2 . Then the 'reaction path degeneracy' would be $\sigma/(\sigma_1 \cdot \sigma_2)$, frequently less than 1. While this would appear counterintuitive, it is, of course, perfectly correct and consistent with the model assumptions used in the channel count.

Thirdly, one may consider a reaction path polytopy as a result of nonequivalent reaction paths. Here one would normally compute the total rate constant by the sum in equation (102):

$$k_{\infty}^{\text{total}}(T) = \sum_{i=1}^P k_{\infty i}(T) \quad (102)$$

If the $k_{\infty i}(T)$ are almost the same, one can replace the sum by a product ($p k_{\infty i}$) with a polytopy factor p . An example would be the existence of two enantiomeric reaction paths with $k_{\infty L} \simeq k_{\infty D}$ and $k_{\infty}^{\text{total}}(T) \simeq 2k_{\infty L}$. Because of the weak nuclear interaction the equation between $k_{\infty L}$ and $k_{\infty D}$ holds only approximately. For other isomeric reaction paths, the differences might be even larger and replacing the sum in equation (102) by a product for one $k_{\infty i}$ with some degeneracy factor may be less helpful.

4 THE STATISTICAL ADIABATIC CHANNEL MODEL AS AN *AB INITIO* THEORY AND AS AN EMPIRICAL FEW PARAMETER MODEL

The statistical adiabatic channel model was originally introduced as a simple empirical model to describe kinetic experiments with as few parameters as possible, providing nevertheless a connection to a more fundamental theory. While it was clear from the start that the model could also be used as an *ab initio* theory, the numerical computations necessary in this context seemed impractical at the time of the invention of the model.¹ Indeed, even the simple empirical approach was computationally demanding by the standard of the resources available then. During the past decades the computational

situation has changed drastically and today the *ab initio* use of the SACM is possible and coexists with the empirical use, which still provides most of the applications. We shall present here the two approaches in a logical (not the historical) order, starting with some recent results from the *ab initio* approach, proceeding to a description of the early empirical method, which is still useful, to end finally with the results from even more simplified models, which can be derived from the SACM.

4.1 *Ab Initio* Calculation of Adiabatic Channels on Electronic Potential Hypersurfaces

From the point of view of pure theory, the most logical approach would be to calculate electronic potential hypersurfaces and adiabatic channel potentials *ab initio* and predict the relevant experimental quantities following Sections 2 and 3. Such a prediction would be approximate, because of the approximations involved in the model, but it would be fully *ab initio*, not involving any empirical adjustment. Indeed, the adiabatic channel model could furthermore be made the starting point of a numerically 'exact' reaction rate theory by explicitly including transitions between the adiabatic channels, as already proposed.¹⁷ A slightly more modest program would be to use empirically adjusted potential hypersurfaces and still compute adiabatic channel potentials *ab initio* by solution of the relevant Schrödinger equation (15) for this problem. Neither of these approaches can be used routinely today for complicated polyatomic reaction systems. However, some results along these lines are available, which can be used to

test the quality of some of the empirical model assumptions. Adiabatic channel potentials $V_a(q)$ in equation (15) can be calculated for relatively simple systems by (partly) analytical or various numerical methods.^{29,55,68-70} One numerically exact approach to solving the adiabatic channel Schrödinger equation for larger polyatomic systems is provided by the quasiadiabatic channel quantum Monte Carlo method.³⁹ This method is based on Anderson's diffusion Monte Carlo approach,⁷¹ applied here to the rovibrational part of the Schrödinger equation using the clamped reaction coordinate approximation, which is in essence the adiabatic channel model. While we refer to the original paper introducing this method,³⁹ we note that the 'adiabatic channel' part of the method scales very favorably, approximately linearly with the number of atoms. The question of calculating the electronic potential is to be considered separately. The method is straightforward only for the lowest adiabatic channel of a given symmetry, where it is numerically exact, providing statistical upper and lower bounds for the adiabatic channel potentials. Here it is ideally suited to provide benchmarks against which one can test other *ab initio* and also empirical approaches of the SACM. The result of one such test is shown in Figure 6 for the $(\text{HF})_2$ dissociation reaction already used for illustration in Section 3. Figure 6a shows the four lowest adiabatic channel potentials of the symmetries A^+ , B^+ , A^- , B^- . Figure 6b shows the corresponding rovibrational energy contribution in a logarithmic presentation following Ref. 1. As described below, for the empirical adiabatic channel interpolation method such a graph would be strictly linear for all channels, with the same slope $-\alpha$.

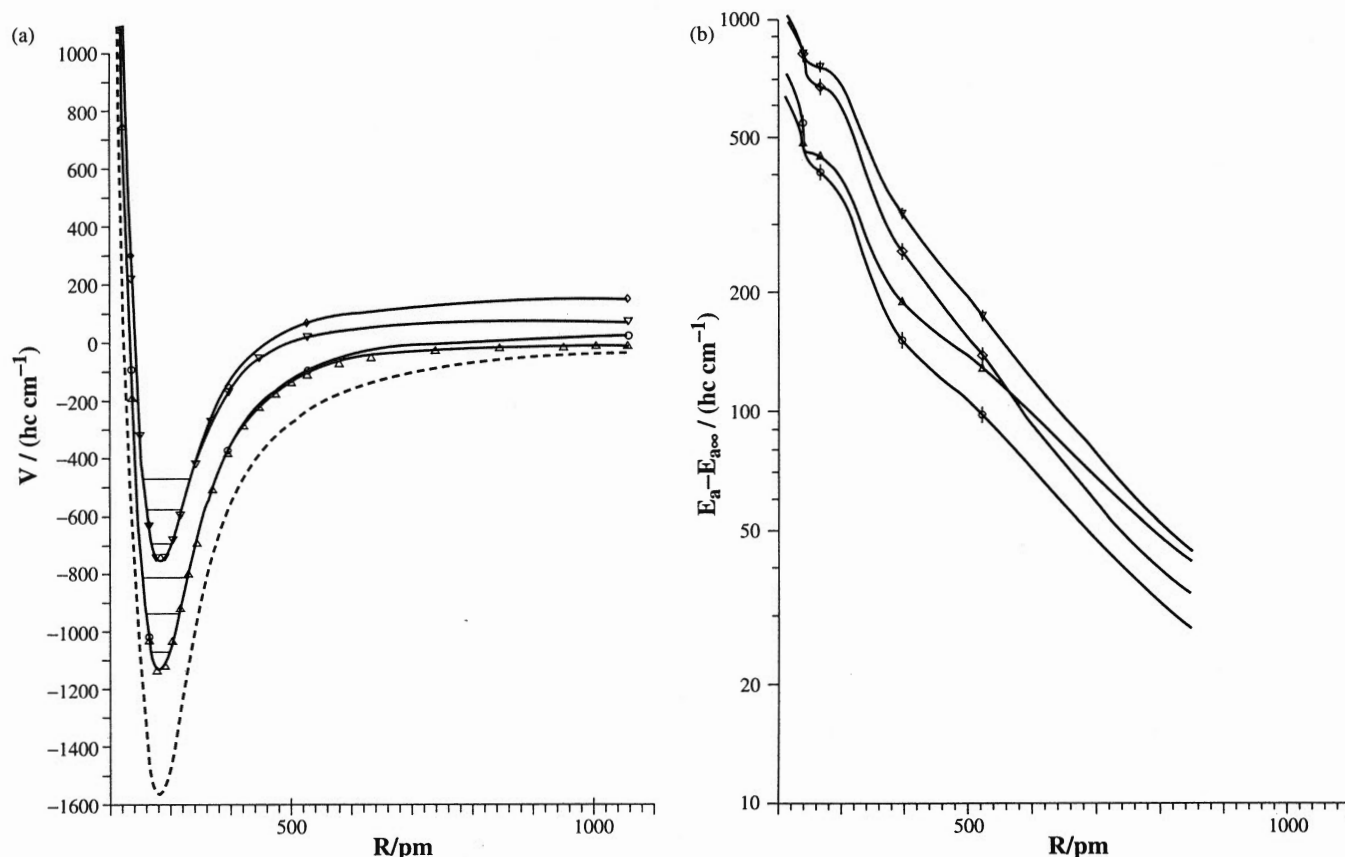


Figure 6 Adiabatic channels for $(\text{HF})_2 \rightarrow 2\text{HF}$ from quasiadiabatic channel quantum Monte Carlo calculations (after Ref. 39)

While this behavior is certainly not found exactly, one has a roughly linear behavior with $\alpha \simeq 0.3 \text{ \AA}^{-1}$ at long distance and a steeper slope ($\alpha \simeq 0.8 \text{ \AA}^{-1}$) at short distance. Such results can be used to test and calibrate the simple interpolation procedures of the adiabatic channels. We stress that the quasia-diabatic channel quantum Monte Carlo results correspond to exact $(6 - 1)$ dimensional solutions of the Schrödinger equation on a 6-dimensional potential hypersurface without making any separability assumptions. This test thus goes far beyond earlier tests following similar ideas using simple 1-dimensional hindered rotor potential functions.³² Such high-dimensional calculations correspond more or less to the current state of the art and further work along these lines is to be expected. We note that the method has also been used to calculate adiabatic channels for the isotope effects in the hydrogen bond isomerization reaction of $(\text{HF})_2$ ⁷² and the idea has also been taken up in calculations on bimolecular reactions.⁷³ Extension to higher $(\text{HF})_n$ clusters such as the reaction $(\text{HF})_3 \rightarrow (\text{HF})_2 + \text{HF}$ with even higher dimensionality on appropriate multidimensional potential hypersurfaces has been presented.⁷⁴

4.2 The Choice of a Reaction Coordinate q

Both in the *ab initio* calculation of adiabatic channels on a potential hypersurface and in the more empirical approaches described below, there may be a question as to the choice of the reaction coordinate q .¹ If there is a deep valley connecting reactants and products, possibly passing through a well defined saddle point, then this would define a natural choice of the reaction coordinate. In principle, one can also introduce additional dynamical constraints in the definition of the reaction coordinate and the question has been discussed in the early literature.^{33–37} Sometimes one may wish to introduce a certain practical definition of a reaction coordinate for reasons of simplicity and convenience. We take here the position that there is no a priori compelling choice of a reaction coordinate. Different choices simply result in slightly different versions of the theory. As long as the differences are not too large, this will not affect the calculated results by much. A frequently very good choice of the reaction coordinate is given by a normal coordinate near the potential minimum, changing then into a local bond distance coordinate for slightly larger values of q and finally into the center of mass distance of the fragments for very large q . One can in principle envisage an after the fact optimization of the reaction coordinate in the framework of the variational approximation to transition state theory to be discussed below. The choice of the reaction coordinate affects both the vibrational and the rotational contributions (via the centrifugal potentials). While individual contributions may be affected more importantly by differences in the choice of reaction coordinate, the total channel potentials will be less affected, because of some cancellation in consistent treatments.

A note on nomenclature may be useful. In the recent literature, the ‘reaction coordinate’ has frequently been called the ‘reaction path’, the two being synonymous when viewed as technical terms. However, ‘reaction path’ is frequently also supposed to imply that it is the physical path taken in the course of the reaction (classically a ‘typical’ trajectory). This is different from the definition of a mathematical reaction coordinate, which has no such intuitive connotations and is thus preferred here. Note also that the reaction coordinate need not be the minimum energy path (MEP) either.

4.3 The Few Parameter Empirical Interpolation for Electronic Potentials and Adiabatic Channel Potentials

In applications to a wide range of experimental results, one needs an efficient theoretical tool allowing for quick comparison of experiment and theory, perhaps followed by adjustment of theoretical parameters to experiment. With this goal in mind, the early formulation of the SACM included a simple empirical representation of the main features of the electronic potential by a very few adjustable parameters. Furthermore, the complicated calculation of adiabatic channels by a solution of the multidimensional clamped $-q$ -rovibrational Schrödinger equation, which is an exceedingly demanding task even today for larger than triatomic systems, was completely circumvented by a simple channel interpolation procedure. We shall present here a very brief description of this empirical approach for simple bond fission reactions.

The long range electronic potential in the reaction coordinate q can be represented by simple expressions of the form (103):

$$V(q) = \frac{C_n}{q^n} \quad (103)$$

with constants C_n and $n = 6$ for collisions of two neutral molecules, $n = 2$ for ion-dipolar⁷⁵ and $n = 4$ for other (e.g., quadrupolar) ion-molecule collisions. Further useful expressions for general long range potentials can be found in Ref. 76. In order to include short range repulsion one might use the Lennard-Jones (6-12) potential in equation (104):

$$V(q) = 4\varepsilon \left[\left(\frac{\sigma}{q} \right)^{12} - \left[\frac{\sigma}{q} \right]^6 \right] \quad (104)$$

with the usual parameters ε and σ .

Frequently, a better representation is given by the Morse potential:¹⁷

$$V(q) = D_e \{1 - \exp[\beta(q_e - q)]\}^2 \quad (105)$$

β is the ‘Morse steepness’ parameter, q_e is the value of the reaction coordinate at the potential minimum and D_e the energy difference between the potential minimum and the dissociated fragments. D_e can be derived empirically from the measurable thermodynamic or spectroscopic bond dissociation energy at 0 K, $\Delta H_0^0 \equiv D_0^0$ by means of equation (106):¹

$$D_e = D_0^0 + E_{zn} - E_{zp} \quad (106)$$

E_{zn} is the total zero point energy of the bound molecule and E_{zp} is the total zero point energy of the dissociated fragments. One must get as accurate an estimate as possible of these fully anharmonic zero point energies from the vibrational spectrum, if the complete potential is not known. The Morse parameters β and D_e can be further related to the force constant F_q for motion along q near the potential minimum by equation (107):

$$\beta = \sqrt{\frac{F_q}{2D_e}} \quad (107)$$

Other potentials, such as the Pöschl-Teller potential and related forms, have been suggested,^{39,76,77} and one should not

hesitate to choose the most appropriate form (including interpolated *ab initio* results), if enough is known about the specific potential.

The second most important feature of the potential for simple bond fission reactions is the angular potential for those coordinates which correspond to free relative rotations for the separated fragments, changing into hindered rotations at shorter distances and finally vibrations in the bound molecule. Such potentials can be parametrized by general expressions of the form given in equations (108) and (109),^{17,32} where φ_e is the reference value of the angle φ :

$$V(\varphi, q) = 0.5 \sum_i V_{nj}(q) \{1 - \cos[nj(\varphi - \varphi_e)]\} \quad (108)$$

$$V_{nj}(q) = \frac{1}{3} V_{nj}(q_e) \{2 \exp[\alpha_j(q_e - q)] \pm \exp[2\alpha_j(q_e - q)]\} \quad (109)$$

These are to be added to $V(q)$. The α_j take the place here of the Morse steepness parameter. Because in the empirical approach one does not compute the corresponding hindered rotor eigenvalues exactly but rather by interpolation, one lumps all the α_j together into one α and uses the interpolation formula (110) for channel eigenvalues (see Figure 3 for the notation).

$$\begin{aligned} E_a(q) &= E_a(q_e, v_{in}, v_{bn}, \tau) \exp[-\alpha(q - q_e)] \\ &+ E_a(q = \infty, v_{ip}, j_1, j_2, \tau_1, \tau_2,) \\ &\times \{1 - \exp[-\alpha(q - q_e)]\} + E_{cent} \end{aligned} \quad (110)$$

The $E_a(q_e)$ and $E_a(q = \infty)$ are introduced in a correlation procedure by ordering the energy levels at q_e and $q = \infty$ by increasing energy for the relevant modes. The channel eigenvalues are added to the electronic potential in order to obtain the adiabatic channel potentials, according to equation (16). The centrifugal potential is interpolated in such a way that one obtains the pure J -dependent contribution to the ordinary rotational energy of the bound molecule (the τ dependence is included in the first term in equation (110) for small $q \simeq q_e$, and a pure centrifugal rotational energy for the two centers of mass of the two fragments rotating about their common center of mass. A useful interpolation is given by equations (111) and (112):

$$E_{cent} = B_s(q) \cdot P(P + 1) \quad (111)$$

$$P = J \exp[-\alpha(q - q_e)] + \ell \cdot \{1 - \exp[-\alpha(q - q_e)]\} \quad (112)$$

Here

$$B_s(q) = \frac{B(q) + C(q)}{2} \quad (113)$$

is the mean of the two small rotational constants calculated from the inertial tensor at the optimized structure for clamped q . Slightly more sophisticated treatments of the centrifugal energy have also been used and an essentially exact treatment of this highly nontrivial problem has become available by means of the quasiadiabatic channel quantum Monte Carlo method.³⁹ The parameter β can be obtained from spectroscopic data in the usual way. α could be obtained from mixed anharmonicities x_{ij} in practice has been adjusted to kinetic results,^{1,4,17,28} (frequently $\alpha \simeq 1 \text{ \AA}^{-1}$). It has also been suggested that α and β could be related by empirical relations, e.g., $\alpha = \beta/2$.^{78,79}

4.4 Treatments with Further Simplifications and Dynamical Limiting Cases

Even the empirical, detailed channel correlation and interpolation procedure described in Section 4.3 can be too cumbersome or expensive for some experimental applications. This provides motivation for further simplifications, which we shall mention here, providing also some insight into dynamical limiting cases of the SACM.

4.4.1 Variational Approximations for Specific (Microcanonical) and Thermal (Canonical) Rate Constants

Instead of following individual channel potentials and counting adiabatically open channels according to their individual maxima, one may define a number of locally open adiabatic channels^{1,4} by equation (114):

$$W(E, J, q) = \sum_{a(J)} h[E - V_a(q)] \quad (114)$$

One has obviously the inequality (115):

$$W(E, J, q) \geq W(E, J) \quad (115)$$

Therefore the best approximation to the true $W(E, J)$ is given by equation (116):

$$W(E, J, q^\ddagger) \equiv W^\ddagger(E, J) = W(E, J, q)_{\min} \quad (116)$$

$W^\ddagger(E, J)$ has an obvious interpretation as the number of open channels at the location q^\ddagger of the transition state. As one varies the position q^\ddagger of the transition state one finds the optimum choice at the position of a minimum value, $W(E, J, q)_{\min}$. Therefore, such approximations are also called microcanonical variational transition state theory. Sometimes the variational procedure has been used with the minimum density of states criterion in equation (117):^{24,26}

$$\varrho(E, J, q^\ddagger) = \varrho(E, J, q)_{\min} \quad (117)$$

or, using $W(E, q)$ in equations (118), (119),²⁵

$$W(E, q) = \sum_{J=0}^{\infty} (2J + 1) W(E, J) \quad (118)$$

$$W(E, q^\ddagger) = W(E, q)_{\min} \quad \text{at } q^\ddagger(E) \quad (119)$$

It has sometimes been claimed that the equalities in (115) must hold, but this would be clearly incorrect.

The microcanonical variational approaches had been introduced in various forms²⁴⁻²⁶ already prior to the statistical adiabatic channel model and have been reviewed before.^{1,4,17} One has the interesting sequence (120) of inequalities (subject to certain conditions):

$$\begin{aligned} k_{\text{variational}} &= \frac{W^\ddagger(E, J)}{h\varrho(E, J)} \geq \frac{W(E, J)}{h\varrho(E, J)} \geq \gamma \frac{W(E, J)}{h\varrho(E, J)} \\ &= \langle k(E, J)_{\text{true}} \rangle \end{aligned} \quad (120)$$

Quack and Troe¹⁷ suggested that the microcanonical variational theory is conceptually interesting but hardly worthwhile computationally (when viewed as an approximation to the SACM, although such computations may find use in other methods).

Similar to a microcanonical variational optimization, one can also carry out a canonical variational transition state theory defining a q -dependent partition function by equation (121):

$$Q(q) = \sum_a \exp \left[\frac{-V_a(q)}{kT} \right] \quad (121)$$

One obviously has again the inequality (122):

$$Q(q) \geq Q^* \quad (122)$$

and hence the best choice of an activated complex at q^\ddagger by means of equation (123):

$$Q^\ddagger(T) = Q(q, T)_{\min} \quad \text{at } q^\ddagger(T) \quad (123)$$

The notation takes explicitly into account that these quantities are temperature dependent, and in particular $q^\ddagger(T)$, which is in general different from $q^\ddagger(E)$.

One may use the statistical thermodynamical free energy function A defined in equation (124) by means of the partition function:

$$A(q) = -kT \ln [Q(q)] \quad (124)$$

Equation (123) results then in a maximum free energy criterion in equation (125):

$$A^\ddagger(T) = A(q, T)_{\max} \quad \text{at } q^\ddagger(T) \quad (125)$$

The idea that the best canonical choice of the transition state is given by the location of a maximum in the free energy is about as old as transition state theory, where one must note, however, that $A(q)$ is not the same as a normal molecular $A(T)$. It seems that the first quantitative calculation and graphical representation of a free energy function with a nontrivial dependence of its maximum on T , i.e., $q^\ddagger(T)$, was given²⁸ for unimolecular reactions with the example of the ethane dissociation methyl radical recombination reaction (see also the early work⁹⁶ for the reaction $\text{H} + \text{H}_2$). There have been numerous applications of the canonical variational transition state theory both in relation to the adiabatic channel model and other related procedures,⁸⁰ and we refer to the article by Truhlar in this encyclopedia (see *Transition State Theory*) as well as our earlier reviews^{4,17} and the diagram presented in Figure 1. There is no doubt that canonical variational transition state theory can be made the starting point of very simple and efficient computational procedures. However, the resulting approximation may sometimes not be good.^{4,17} One of the simplest approaches involves interpolation for $\ln Q$.²⁸

4.4.2 Product State and Product Translational Energy Distributions

Product state and product translational energy distribution from the statistical adiabatic channel model for collision experiments have been discussed in detail.¹⁷ They are in essence contained in the number of open adiabatic channels $W(E, J, b)$ leading to product levels of a specified characteristic, labeled by a quantum number b . For instance, in the case of product translational energy distributions arising from the unimolecular decomposition of molecules at total energy E , and angular momentum J , one would count all channels leading to translational energy in the range between $E_t = E - E_1$ and

$E_t + \Delta E$, as expressed by the sum \sum' in equation (126)^{32,81} (E_1 = internal quantum state energy of reaction products):

$$P(E_t, \Delta E, E, J) = W(E, J)^{-1} \sum'_{b(E_t, \Delta E)} W(E, J, b) \quad (126)$$

Measurable product translational energy distributions are then given by the weighted sum and integral with the distributions $P(E, J)$ of the reactant in equation (127):

$$P(E_t, \Delta E) = \int_0^\infty dE \sum_{J=0}^\infty P(E, J) P(E_t, \Delta E, E, J) \quad (127)$$

If necessary, one can furthermore take into account symmetry labels Γ and the adiabatic channel model can in principle be extended to account for 'inelastic' transitions between the adiabatic channels of the separating fragments, which are neglected in the above expressions.^{2,17} Of course, the complementary distribution over internal quantum state energies E_1 of the reaction products is given by perfectly similar, complementary expressions already used for the photodissociation of NO_2 ^{3,4} which has found recent interest again.⁸² As another interesting application we may mention the infrared multiphoton excitation and dissociation $\text{CF}_3\text{CN} \rightarrow \text{CF}_3 + \text{CN}$.⁸³

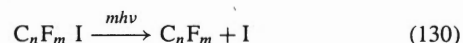
Particularly for the reverse problem of the analysis (for instance by least squares) of experimental product energy distributions in the framework of the SACM, the explicit use of the above equations may become quite demanding, computationally. It has been suggested^{17,84,85} that the following expression (128) is used with an adjustable parameter n .

$$P(E_t) = C E_1^n \varrho(E - E_t) \quad (128)$$

C is a normalization constant. $\varrho(E - E_1)$ is the total (combined) density of product internal states at total internal energy $E_1 = E - E_t$ given by the convolution in equation (129):

$$\varrho(E_1) = \int_0^{E_1} \varrho_Y(E_1 - x) \varrho_Z(x) dx \quad (129)$$

ϱ_Y and ϱ_Z are the complete internal (rovibrational) densities of states of the reaction products Y and Z . One can very roughly correlate the exponent n to the main potential parameters α and β in the adiabatic channel model.¹⁷ $n = 0$ corresponds to the 'loose' adynamic limit $\alpha = \infty$, $\beta = 0$, and $n = 3$ corresponds to the 'tight' limit, to $\alpha = 0$ and ordinary values of β in typical model calculations. Reasonable values of n , consistent with the statistical adiabatic channel model, should thus fall in the range $0 \leq n \leq 3$. Using efficient algorithms for $\varrho(E_1)$, the expression (128) with a single free parameter n can be used in least squares adjustments. As a recent application of this kind we may mention product translational energy distributions obtained from Doppler line profiles (300 MHz widths) measured at about 1 MHz resolution in the unimolecular reactions (130) after infrared multiphoton excitation.⁶⁰



This kind of analysis has also been used for Doppler line shapes of H-atom products in allyl photochemistry.⁸⁶

The limit with $\alpha = \infty$ in the adiabatic channel model corresponds to phase space theory⁴⁻⁶ (PST, see Figure 1). PST can thus be considered to be a simplified limiting model of the SACM. From this simple fact one can conclude that if

an experimental result agrees with PST, it agrees also with a dynamical limiting case of the SACM. This has been known for quite some time,²⁻⁴ but should be remembered in view of occasional discussions of apparent discrepancies between the SACM and experimental results, which are claimed to be consistent with PST.⁸⁷ This would be a logically inconsistent conclusion, as clearly pointed out in several places.^{4,88}

Another, more extreme simplification arises in the so called 'prior' distribution.⁷ The most frequently used prior distribution corresponds to equation (128) with $n = 0.5$. However, the most consistent logical choice corresponding to the adynamic postulate of the statistical prior distributions would correspond to $n = 0$.⁸⁹ This question has been discussed critically in Ref. 17, where further references can be found. In terms of the statistical S-matrix the adynamic prior distribution corresponds simply to replacing $W(E, J)$ in equation (9) by $N(E, J)$.

5 CONCLUSIONS AND OUTLOOK

The statistical adiabatic channel model (SACM) provides an easy computational access to the large class of chemical primary processes involving metastable intermediates, in particular unimolecular and bimolecular reactions. While in the present article we have concentrated on developing the principles and methods, the SACM has been in particular an enormously fruitful model for numerous applications. These include reactions important for atmospheric chemistry, combustion, pyrolysis and cracking processes, evaporation and condensation phenomena in hydrogen bonded complexes, ion-molecule reactions, reactions in interstellar space, ion fragmentations in mass spectroscopy, molecular beam scattering, vibrational relaxation, and infrared laser chemistry (see *Multiphoton Excitation*). There are far too many of these applications to include them in this review, but some exemplary applications of current interest have been mentioned and others can be found in the reviews cited. In the past, certainly, the emphasis was on applications of the simple empirical implementation of the SACM, often even with further simplifications. With the increasing power of *ab initio* methods (see Refs. 90, 91 and numerous articles in this encyclopedia), the future emphasis of the use of the SACM will be increasingly on its *ab initio* implementation. The fruitful interplay of *ab initio* potential hypersurface calculations and the SACM may indeed start a new era in the theory of inelastic and reactive processes involving metastable intermediate complexes.

6 RELATED ARTICLES

Monte Carlo Quantum Methods for Electronic Structure; Multiphoton Excitation; Photodissociation Dynamics; Rates of Chemical Reactions; Reaction Path Following; Symmetry in Chemistry; Transition State Theory.

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