Resonances

In Electron–Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics

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Bimolecular Reactive Collisions

Adiabatic and Nonadiabatic Methods for Energies, Lifetimes, and Branching Probabilities

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Several approximate methods for calculating resonance energies and widths for atom-diatom reactive collisions are discussed. In particular, we present resonance energy calculations by semiclassical and quantal vibrationally adiabatic models based on minimum-energy and small-curvature paths, by the semiclassical SCF method, by quantal SCF and configuration-mixing methods, and by close coupling calculations. We also present total width calculations based on analytic continuation by polynomials and Padé approximants of configuration-mixing stabilization graphs, and we present total width and partial-width calculations based on close coupling calculations and on the Feshbach formalism in reaction-path coordinates with a small-curvature tunneling approximation for adiabatic decay and a reaction-path-curvature coupling operator for nonadiabatic decay. The model calculations are judged by their agreement with the accurate close coupling calculations, and we also compare the resonance energies and total widths semiclassically from resonant periodic orbits. To illustrate the methods we consider the collinear reactions $H + FH \rightarrow HF + H$ and $D + FD \rightarrow DF + D$ on the low-barrier model potential of Muckerman, Schatz, and Kuppermann and the collinear and three-dimensional $H + H_2$ reactions on Porter-Karplus surface number 2. Finally we use an accurate potential energy surface for the three-dimensional $H + H_2$ reaction to predict the energies of several series of observable resonances for a real system.

Resonances in reactive collisions were first observed in quantum mechanical scattering calculations for the collinear $H + H_2$ reaction (1-9; for a review of early calculations on this system see reference 10 and for a recent review of the quantum mechanical treatment of reactive resonances see reference 11). Resonances

have subsequently been found in many converged quantum scattering calculations for this and other collinear reactions on realistic potential energy surfaces (8,11-61) and for two coplanar reactions (61,62) and in close coupling and coupled states calculations for two three-dimensional reactions (61,63-66): further results from the study of reference 64 are given in 67) as well as many approximate three-dimensional calculations (see, for example, references in 68,69, and other chapters in this volume). Resonances are observed in quantum scattering calculations as oscillations in the reaction cross sections (or probabilities) as functions of energy (10,11,69,70), and they can also be identified from eigenphase sums (71-74), Argand diagrams (75-78), lifetime analyses (79-86), wavefunction analyses (87,88), and direct calculation of poles of the reaction amplitude density on the real axis (89) or of poles of the resolvent (90,91) or the scattering matrix (86,92-97) in the complex energy plane.

Resonances are defined formally as poles of the scattering matrix in the complex energy or momentum plane (98-100). The pole location in the complex energy plane may be written as

$$\varepsilon_{res} = E_{res} - i\Gamma/2. \tag{1}$$

At such energies the Schroedinger equation has a solution with purely outgoing waves at large distances from the origin; this solution is a pure resonance state (101). Depending on the context either ε_{res} or E_{res} is called the resonance energy and Γ is called the width. The width notation is appropriate because if an incoming wavepacket has an energy spread large compared to Γ, a part of this wavepacket of width Γ will be delayed in the interaction region due to the resonance (98). The effect of a resonance on scattering attributes is easy to describe only for the case of an isolated, narrow resonance (INR); i.e., a resonance which is separated from other resonances by much more than the sum of their widths and which is narrow enough that the background ("direct") scattering does not vary appreciably over its width. (For discussions of overlapping resonances see references 102-104.) An INR decays by first-order kinetics with a rate constant equal to $\Gamma/\hbar$ (99,100,105); its contribution to a collisional delay time is $4\hbar/\Gamma$ at the energy E_{res} and is $2\hbar/\Gamma$ averaged over the resonance width (79,85). If Γ is small then the wave function for real energies close to E_{res}, corresponding to scattering energies or energies of predissociating complexes formed by absorption of electromagnetic radiation, may be very similar in the interaction region to the resonant state at the nearby complex energy ε_{res}. Since resonance states tend to be more localized than typical continuum states, they are easier to interpret and classify, and since the resonant state affects the scattering processes connecting all initial and final channels for a finite range of energies, identification and characterization of resonances provides a unifying feature for a variety of observable dynamical phenomena. In particular, resonances may be classified in terms of system quantum numbers just as usefully as bound states are so classified.

For scattering transition probabilities and photon-absorption oscillator-strength distributions, an INR contributes an energy-dependent feature with full width at half maximum (FWHM) of Γ. In the absence of background contributions, this feature is Lorentzian and is centered at E_{res}; otherwise it may interfere constructively and/or destructively with the background to yield a more complicated shape function for the energy dependence. Although an INR exhibits the same FWHM for all initial and final states, it does not have the same amplitude for all processes. The relative amplitude for a given transition $\alpha \rightarrow \alpha'$ is controlled by the residue of the α',α element of the scattering matrix at the resonant pole. In the vicinity of its pole this element may be written

$$S_{\alpha'\alpha} = S^d_{\alpha'\alpha} - \frac{i\gamma_{\alpha'}\gamma_\alpha}{E - \varepsilon_{res}}, \tag{2}$$

where E is the total energy, $S^d_{\alpha'\alpha}$ is the direct part, which is regular, and (99,100,105,106)

$$\sum_\alpha |\gamma_\alpha|^2 = \Gamma. \tag{3}$$

It is convenient to define the quantities

$$\Gamma_\alpha = |\gamma_\alpha|^2 \tag{4}$$

which are called partial widths and the quantities

$$\chi_\alpha = \gamma_\alpha \Gamma^{-\frac{1}{2}} \tag{5}$$

and

$$P_\alpha = |\chi_\alpha|^2 \tag{6}$$

which, respectively, are components of normalized scattering matrix eigenvectors and branching fractions or probabilities for the resonance to decay into state α. The latter interpretation is evident by noting that in the absence of direct scattering the resonance leads to a factorizable Lorentzian transition probability of the form

$$|S^r_{\alpha'\alpha}|^2 = \frac{\Gamma^2}{(E-E_{res})^2 + \Gamma^2/4} P_{\alpha'}P_\alpha, \quad \alpha'\neq\alpha, \tag{7}$$

and noting

$$\sum_\alpha P_\alpha = 1. \tag{8}$$

Clearly a complete description of an INR requires specification of E_{res}, Γ, and all γ_α or χ_α.

If a resonance is not narrow, then the partial widths may still be defined in terms of the residue at the pole, but Equation 4 is no longer valid (92,93,107). Branching probabilities are now defined by

$$\frac{P_\alpha}{P_\alpha{'}} = \frac{|\gamma_\alpha|^2}{|\gamma_\alpha{'}|^2} \tag{9}$$

plus the normalization condition of Equation 8.

Reactive resonances are interpreted as long-lived, quasi-bound complexes in the interaction region of the potential energy surface. The lowest-energy resonance of the collinear H + H$_2$ reaction was first interpreted in semiclassical terms as the result of the interference between direct and long-lived quasi-classical trajectories (5,108); in the resonance picture, the interference is between direct, short-lived, background scattering and long-lived trajectories representing the resonance. Wu and Levine (2) interpreted this resonance as an adiabatically trapped quasibound state. In the adiabatic model for a collinear atom-diatom reaction, vibrationally adiabatic potential curves $V_a(n,s)$ are constructed by adding local vibrational stretching energies $\varepsilon_{str}(n,s)$ to the Born-Oppenheimer potential $V_{MEP}(s)$ as a function of the distance s along the minimum energy path (MEP),

$$V_a(n,s) = V_{MEP}(s) + \varepsilon_{str}(n,s) \tag{10}$$

where n is the vibrational state for the motion perpendicular to the reaction coordinate. The lowest-energy resonance of H$_2$ was interpreted as a quasibound state in the local well of the first excited adiabatic potential curve. This view was confirmed by analysis of the scattering wavefunction which showed that it had over 90% vibrationally excited character when projected onto wavefunctions of the symmetric stretch vibration (109).

The physical picture of a resonance as a long-lived, quasibound state has lead to the development of several approximate methods for calculating the locations and widths of resonances. The adiabatic model (see for example references 110-115) in reaction-path coordinates, also called natural collision coordinates, has been very successful for predicting both the locations and adiabatic partial widths for reactive resonances (46,56,116-119). Using Feshbach resonance theory (102,103), nonadiabatic partial widths can also be computed within the same framework (56,57,119, see also 120). In this method the nonadiabatic partial width is given by a golden-rule formula in which the operator is a reaction-path-curvature coupling term. The adiabatic approximation has also been used in other coordinate systems to locate reactive resonances, for example, the use of hyperspherical coordinates has been very successful for predicting resonance energies, especially for collinear heavy-light-heavy systems (11,47,121-126). In quantum mechanical stabilization calculations (127-130), bound-state linear variational methods are used instead of scattering calculations to calculate self-consistent-field (SCF) or configuration-interaction (CI) wave-

functions for the quasibound state; this method has recently been applied to bimolecular reactive resonances (131-135). Resonances are identified as the lowest-energy roots of the secular equation that are stable with respect to variation of a basis set parameter, e.g., the number of primitive basis functions or a scaling parameter. Total widths are obtained by analytically continuing approximate fits of the energy root, or two or more of them, as functions of the scaling parameter (133,135-138). [Although it is not considered here, the complex coordinate method provides a means of obtaining the complex resonance energy ε_{res} directly; i.e., without analytic continuation, using bound-state linear variational techniques (see for example, 91)]. The semiclassical SCF procedure (139) is essentially a generalization to multidimensional systems of the primitive WKB approximation (140) for bound state eigenvalues of one-dimensional potentials. This method has also been applied to locating reactive resonances (141-143) and evaluating the widths (142). Resonant periodic orbits (RPOs) are the basis of yet another pseudo-bound-state method for predicting resonances; RPOs are classical trajectories trapped in the interaction region of the potential energy surface with integer values of the classical action (144-147). These trajectories have been used to compute resonance energies, and widths are estimated from the instability of the RPOs (145).

To date, most of the work on reactive resonances has dealt with methods for calculating the resonance energy E_{res} and the total width Γ. However, a great deal can be learned from examination of the separate contributions of different decay channels to the total width. For example, as discussed above, branching ratios for decay into different channels are obtained from ratios of the partial widths or residue factors for those decay mechanisms. In the terminology of Taylor et al. (148) Feshbach internal-excitation resonances in adiabatic state n are denoted core-excited type I resonances if the resonance energy is below the threshold energy E_n^{thr} for this state and are called core-excited type II resonances if the resonance energy is above E_n^{thr} where the threshold energy is defined by

$$E_n^{thr} = \min[V_a(n,s=-\infty), V_a(n,s=+\infty)] \tag{11}$$

Core-excited type I resonances are sometimes called Feshbach resonances; they have only nonadiabatic contributions to the total width, but core-excited type II resonances have partial widths both for nonadiabatic decay in which n changes and for adiabatic decay by tunneling through the adiabatic barriers without changing n. Quasibound states of ground-state adiabatic potential curves are single-particle shape resonances, and they decay only adiabatically if they lie below the first excited-state threshold energy. Vibrational states of the ground-state adiabatic potential curve which lie below the ground-state threshold are truly bound states, and this phenomenon has been termed vibrational bonding (149-151). For larger polyatomic complexes more decay channels exist, e.g., decay can also occur nonadia-

batically by intramolecular vibration-to-vibration energy transfer. Limited, but significant, progress has been made in developing methods to obtain partial widths from complex wave-function calculations, e.g., by the Siegert method (107,152,153) or the complex-coordinate method (154,155). In the present article we summarize our recent work (56,57) using the Feshbach golden rule to calculate partial widths from real-valued wavefunctions.

In the present work we are interested in assessing the accuracy of several approximate methods for locating resonance energies and computing total widths and adiabatic and nonadiabatic partial widths. After a summary of the methods considered here we review and compare the results of these methods for the collinear H + FH → HF + H and D + FD → DF + D reactions on the low-barrier model potential surface of Muckerman, Schatz and Kuppermann (34). This system was chosen for review here because there are reliable quantum mechanical calculations of the resonance energies and widths (34,46,57) as well as several studies by approximate methods (46,57,117,118,131-133,135,141). Also, these systems display all three types of resonances, shape and type I and type II core-excited. We also review calculations on the lowest energy resonance of the collinear H + H₂ reaction on the Porter-Karplus surface number 2 (PK2,156). This resonance has also been thoroughly studied both by converged close coupling calculations (for example 4,61) and approximate methods (for example, for the methods discussed in this paper, see references (11,56,116-118,121,122,124,131-133,135,144-146). With a few exceptions, nearly all calculations of resonance energies and widths have been for collinear systems. We are also interested in the ease with which the approximate methods are extended to atom-diatomic reactions in three dimensions and to reactions involving more than three atoms. Therefore, we present new calculations of resonance energies for the three-dimensional H + H₂ reaction on the PK2 surface and on the accurate potential energy surface of Liu, Siegbahn, Truhlar, and Horowitz (LSTH, 157-159). Because of its current experimental interest (160-163), we also report calculations for the three-dimensional H + D₂ reaction on the LSTH surface.

Methods

Quantum mechanical scattering.

In conventional quantum mechanical scattering calculations, resonances show up as oscillations in the reactive cross sections (or reaction probabilities) or an increase of π in the eigenphase sum. [Narrow resonances are difficult to locate because of the need to take very small energy steps to find them. The difficulty in using the eigenphase sum is that usually it is only known modulo π and unless the eigenphase sum is tracked through a resonance with sufficiently small energy steps, the resonance is missed. The definition of an absolute eigenphase sum (74) removes this difficulty and simplifies the task of locating narrow resonances.] Once the resonance is

located, the width may be obtained by fitting the eigenphase sum in the vicinity of the resonance to a generalized Breit-Wigner form (72,73). The partial widths may be extracted from an analysis of the individual scattering matrix elements (46,56,164). The method used for the results presented here is given in the next paragraph.

Converged close coupling calculations were carried out using the R matrix propagation method of Light and Walker (165). These calculations yield the scattering matrix S as a function of energy E. There are several possible procedures one could use to extract resonance energies, total widths, and partial widths from close coupling calculations. For example, Macek and Burke (166) made 16-25-parameter nonlinear least-squares fits of reactance matrices to a resonant form analogous to Equation 6 to extract partial widths from 3- and 4-channel electron scattering calculations, and Fels and Hazi (167) used a nonlinear fitting procedure based on the variation of the eigenphases in the vicinity of a resonance and a transformation between partial widths corresponding to eigenchannels and those corresponding to physical channels to extract partial widths for a 2-channel model problem. A procedure for directly extracting the partial widths corresponding to physical channels for problems with an arbitrary number of channels was proposed by Ashton et al. (164), and a slightly modified version of this procedure was used in our previous work (56,57). In our work we first fit the eigenphase sum Δ(E) in the vicinity of E = E_res to the INR form (72,73)

$$\Delta(E) = \Delta_0(E) + \arctan \frac{\Gamma}{2(E_{res} - E)} \qquad (12)$$

where $\Delta_0(E)$ is a low-order real polynomial in E representing the background; this yields E_{res} and Γ. In step 2 each element of the upper triangular part of the scattering matrix is fit in the vicinity of $E = E_{res}$ to

$$S_{\alpha'\alpha} = S_{\alpha'\alpha}^d - \frac{i \, C_{\alpha'\alpha}}{E - \varepsilon_{res}} \qquad (13)$$

where $S_{\alpha'\alpha}^d$ is a low-order complex polynomial in E representing the background and $C_{\alpha'\alpha}$ is an additional complex fitting parameter. For step 3, Ashton et al. suggested minimizing the function

$$D_3 = \left\{ \sum_{\alpha} \sum_{\alpha' \leq \alpha} \left[\frac{|C_{\alpha'\alpha}| - (\Gamma_{\alpha'}\Gamma_\alpha)^{\frac{1}{2}}}{|C_{\alpha'\alpha}|} \right]^2 \right\}^{\frac{1}{2}} \qquad (14)$$

with respect to the set of Γ_α subject to the constraint

$$\sum_{\alpha} \Gamma_\alpha = \Gamma \qquad (15)$$

in order to obtain a "best" set of estimates of the partial
widths consistent with the INR constraint of Equation 3. [This
is the procedure we used in references (56,57) except we included
a spurious factor of one half in Equation 2 and hence also in
Equation 14; this affects the quantitative values of the partial
widths, but because of the constraint of Equation 15, the errors
are small and they do not affect the qualitative trends. The
partial widths given in this chapter are new values calculated
without the spurious factor of one half and are based on D_4
presented below rather than D_3.]

Equating Equations 2 and 13 and using Equation 4 yields

$$\left| C_{\alpha'\alpha} \right| = \Gamma_{\alpha'}^{\frac{1}{2}} \ \Gamma_{\alpha}^{\frac{1}{2}} \tag{16}$$

For the three collinear reactive resonances for which a partial
width analysis is discussed in the present article, Equation 16
yields partial widths that sum to only about 50-90% of the total
width obtained from Equation 12. This indicates a breakdown of
the INR condition. Obtaining the best INR representation by
using Equations 14 and 15 systematically changes the branching
probabilities away from the values computed using Equations 4,9,
and 16. We found that the INR constraint could be enforced
without distorting the branching probabilities by replacing
Equation 14 by

$$D_4 = \left\{ \sum_{\alpha} \ \sum_{\alpha' \leq \alpha} \ \left[\left| C_{\alpha'\alpha} \right| - (\Gamma_{\alpha'}\Gamma_{\alpha})^{\frac{1}{2}} \right]^2 \right\}^{\frac{1}{2}}, \tag{17}$$

and Equation 17 (with the INR constraint of Equations 3 and 4)
was used for all the results presented here.

When the INR approximation breaks down it may be better to
use Equation 16 than to force satisfaction of the sum rule of
Equation 3, but space does not permit further discussion of this
point in this chapter. We do note though that the Feshbach
formalism discussed below and used to compute approximate partial
widths is consistent with the sum rule (102,103).

Vibrationally adiabatic models. In the adiabatic approximation
the dynamics of a multidimensional system is reduced to motion
in one mathematical degree of freedom governed by an effective
Hamiltonian. Calculations of the resonance energies and widths
for this one-dimensional model can be performed either
semiclassically or quantum mechanically.

The reaction probabilities that determine some of the E_{res}
and the adiabatic partial widths are nonzero only because of
tunneling. We have considered two semiclassical methods to
calculate the resonance energy and tunneling probabilities,
namely the primitive WKB method (140), which simply quantizes
the phase integral for motion in the well of the adiabatic
potential, and a uniform semiclassical method (168,169), which

also uses phase integrals in the classically allowed regions,
but combines them with phase integrals for classically forbidden
motion in the barrier region of the adiabatic potential curve.
In the present work we use the primitive WKB method for energies
of core-excited type I resonances, and we use the uniform
expression for energies of shape and core-excited type II
resonances. To obtain the adiabatic partial widths, it is
necessary to use a uniform semiclassical expression (168,169).
The calculation of the nonadiabatic partial widths is discussed
below.

Different adiabatic models are possible depending upon the
method used to incorporate reaction-path curvature effects in
the kinetic energy term of the effective Hamiltonian (120).
Several approximations have been used: in the minimum-energy-
path (MEP) approximation the system is assumed to follow the
minimum energy path [this has also been called the zero-curvature
approximation (5)]; in the Marcus-Coltrin-path approximation the
system is assumed to follow the path of outer turning points for
the vibrational motion normal to the MEP (116,120,170); in the
dynamical path (DP) approximation the system is assumed to follow
a path on which the internal centrifugal forces are balanced by
the potential energy surface (117); and in the small-curvature
(SC) approximation the system is assumed to follow the MEP in
classically allowed regions and to follow a path defined by the
small-curvature tunneling approximation (120,171) in tunneling
regions. In previous work (46,56,116,117) it was found that the
methods which include the effects of reaction-path curvature
generally give a better description of the adiabatic partial
width. The difference between resonance energies calculated
using these methods were small; typically the agreement was
better than a few tenths of a kcal/mol. The relative agreement
was not as good for the adiabatic partial widths obtained from
these methods; differences were as large as a factor of two. In
the following comparison, we limit our discussion to the SC
approximation.

Three different approximations to the local vibrational
energy $\varepsilon_{str}(n,s)$ have been considered: in Morse approximations
I and II (172) the potential along the cut perpendicular to the
reaction coordinate is fit to a Morse potential and the
eigenvalues are given by an analytic formula (173); and in the
WKB approximation the primitive semiclassical quantization
condition is used to find $\varepsilon_{str}(n,s)$ for the actual potential
along the cut perpendicular to the MEP. The WKB method was found
to give a better description of the adiabatic potential curve
near the adiabatic barrier maxima; however, the adiabatic
potential curves are not described well by this method in regions
of large reaction-path curvature because of a breakdown of the
natural collision coordinates (118). For the quantum mechanical
calculations only the Morse I approximation was used. When
calculating E_{res} and Γ using the semiclassical methods, the Morse
I approximation was found to give more reliable estimates of the
resonance energies for the H + FH and D + FD reactions, whereas

the Morse II approximation was better for H + H$_2$. For the collinear systems considered here, we will tabulate and discuss only those semiclassical resonance energies obtained using the adiabatic barriers computed using Morse approximation I, and for the three-dimensional cases considered here we only tabulate and discuss semiclassical results obtained by the Morse approximation II. The adiabatic partial widths have an exponential dependence upon the phase integrals in the tunneling regions of the adiabatic potential curves. Therefore, the calculated adiabatic partial widths have been found to be very sensitive to the energy at which they are computed and to the shape of the adiabatic barrier in the tunneling region (56,57,118). The most reliable estimates are obtained when the phase integrals are computed at the accurate resonance energy using the adiabatic potential curves obtained from the WKB approximation (118).

In the quantum mechanical calculations the resonance energy and widths are obtained by calculating adiabatic reaction probabilities and fitting these to a Lorentzian form. We have made calculations (46,116) in which reaction-path curvature is neglected (denoted the MEPVA method) and in which it is included using the Marcus-Coltrin path (denoted the MCPVA method). The differences between resonance energies calculated using these two methods were small (less than 0.1 kcal/mol for the cases studied) but the relative differences between adiabatic partial widths were larger (almost a factor of 2 in one case). Although the MCPVA results are presumably more accurate, we report here only the results of MEPVA calculations since they are available for more of the systems studied here.

Nonadiabatic Feshbach calculations. Using the reaction-path Hamiltonian and invoking an adiabatic separation of the reaction coordinate from all other coordinates, resonance energies and adiabatic partial widths are obtained by neglecting all off-diagonal terms of the Hamiltonian. The most important off-diagonal, nonadiabatic terms of the Hamiltonian are matrix elements of the kinetic energy term which includes reaction-path curvature. The diagonal elements of the reaction-path curvature operator are included, at least approximately, in the adiabatic calculations and the off-diagonal elements give rise to the nonadiabatic partial widths. The nonadiabatic partial width for decomposition of the resonance state into channel α is given by (56,57)

$$\Gamma^N_{nv;\alpha} = 2\pi \left[\left\langle \psi^{res}_{nv} | H_{QP} | \psi_\alpha(E_{res}) \right\rangle \right]^2 \tag{18}$$

where the resonance state is characterized by quantum numbers n and v for the vibrational and reaction coordinate motions, respectively. The wavefunction for the resonance state is approximated by

$$\psi^{res}_{nv} = f_{nv}(s)\,\phi_n(u,s) \tag{19}$$

where ϕ_n is the adiabatic basis function for motion perpendicular to the reaction coordinate and $f_{nv}(s)$ is the bound-state wavefunction for the trapped motion in the adiabatic well. The wavefunction of the continuum state for channel α at the resonance energy E_{res} is approximated by

$$\psi_\alpha(E_{res}) = f_\alpha(s)\,\phi_{n_\alpha}(u,s) \tag{20}$$

where $\phi_{n_\alpha}(u,s)$ is the adiabatic basis function for state n_α and $f_\alpha(s)$ is the continuum wavefunction for motion along the reaction coordinate in the adiabatic potential for state n_α, subject to the usual scattering boundary conditions. The coupling operator is approximated by

$$H_{QP} = \tfrac{1}{2}\left[H^{(I)} + h.c.\right] \tag{21}$$

where

$$H^{(I)} = -\frac{\hbar^2}{2\mu}\,[1+2\kappa(s)u]\,\frac{\partial^2}{\partial s^2} \tag{22}$$

h.c. is the hermitean conjugate of $H^{(I)}$, and $\kappa(s)$ is the curvature of the reaction coordinate. In previous work (57), the effect of anharmonicity and the neglect of parts of the coupling matrix elements on the nonadiabatic partial widths have been studied. In the present paper we report only those partial widths based on harmonic oscillator wavefunctions for the bound vibrational motion perpendicular to the reaction coordinate and including the effect of the reaction-path coupling operator on both vibrational and reaction coordinate wavefunctions.

Quantum mechanical stabilization calculations. Quantum mechanical stabilization calculations provide a very convenient and efficient way to estimate the resonance characteristics by bound-state techniques. The first step of the method as we apply it involves calculating the eigenvalues of the Hamiltonion in a square-integrable basis as a function of a suitable basis-set scaling parameter. This basis may be restricted to a product of linear combinations of single-mode functions, which yields SCF stabilization, or it may be general, which is called configuration-mixing or configuration-interaction (CI) stabilization. The resonant eigenvalue $\varepsilon(\alpha)$ is then fit to a suitable polynomial (133) or appropriate Padé approximant (135) or $\varepsilon(\alpha)$ is represented as a polynomial root (174) and polynomial coefficients are fit (138). The stability condition is then employed to find the complex solution α_r of

$$d\varepsilon/d\alpha\big|_{\alpha=\alpha_r} = 0. \tag{23}$$

Finally the resonance position E_{res} and its width Γ may be approximated by

$$\varepsilon(\alpha_r) = E_{res} - i\Gamma/2 \tag{24}$$

with $\varepsilon(\alpha_r)$ computed from the fit. An important advantage of the stabilization method is that one can profitably use well developed bound-state methods to calculate $\varepsilon(\alpha)$ efficiently. In addition, one can treat systems involving many degrees of freedom more easily than by quantum mechanical scattering calculations, which may become prohibitively expensive. If scattering calculations are indeed too expensive to carry out for a given system, then stabilization results may be invaluable for qualitative interpretative purposes even if they are only semiquantitative in accuracy. It is useful to point out that the stabilization method does not rely on any fit to the shape of the cross section or scattering matrix as a function of energy.

Semiclassical SCF calculations. The use of the semiclassical SCF procedure to treat reactive resonances (141) is a straightforward extension of the work of Gerber and Ratner (139). Numerical complications do arise, however, and convergence of the SCF procedure can be much more difficult in the semiclassical method than in the quantum mechanical one or even impossible. A similarity to the quantum mechanical SCF procedure is that both give a clear picture of where the probability density for the resonance is localized (132,134,141).

Numerical comparison of methods for collinear reactions.

Resonance energies. In Table I, the resonance energies for three collinear atom-diatom reactions are compiled. These include three resonances each for the H + FH and D + FD reactions and the lowest-energy resonance for H + H_2 on the PK2 surface. All energies are relative to the minimum of the asymptotic reactant well.

In Table I, n and v are quantum numbers in natural collision coordinates: n is the quantum number of the vibrational motion perpendicular to the reaction coordinate and v is the quantum number for the bound reaction-path motion in the well of the adiabatic potential. These identifications were originally based on the vibrationally adiabatic approximation (46,117) and were confirmed by quantal stabilization calculations (131). For the systems included in Table I, reaction-path curvature is only small to moderate and we expect the adiabatic model in natural collision coordinates to give a good description of the resonance energies. Using a quantum mechanical treatment in the adiabatic model (MEPVA) gives slightly better results than using the semiclassical model (SCSA). The results of the adiabatic approximation in hyperspherical coordinates are only available for one of the three systems reported here. Although the earlier hyperspherical results (11) are not nearly as good as the SCSA or MEPVA ones for the H + H_2 system, including diagonal corrections in the effective Hamiltonian greatly improved the results (124). Also, we expect the hyperspherical coordinates to give a better description for systems with large reaction-path curvature. In the stabilization calculations no

Table I. Resonance Energies (kcal/mol) for Three Collinear Atom-Diatom Reactions

System	n	v	accurate quantal	MEPVA	SCSA[a]	Stabilization[b] SCF	Stabilization[b] CI	SCSCF[c]	hyper-spher.	RPOs[d]
H + FH	0	0	6.29[e]	6.34[f]	6.50	6.74	6.31	6.42	...[g]	...
	1	0	15.35[e]	...	15.22	14.57	15.41	14.25	...	...
	1	1	17.78[e]	...	17.56	16.82	18.43	17.11	...	...
D + FD	0	0	4.86[e]	4.88[f]	4.99	...	...	4.92	...	...
	1	0	11.25[e]	...	11.44	...	...	10.51	...	...
	1	1	13.20[e]	...	12.94	...	...	12.54	...	...
H + H_2 (PK2)	1	0	20.1[h]	20.4[i]	20.7	18.08	20.33	...	18.8[j] 20.17[k]	19.99

[a] reference 117, [b] reference 131, [c] reference 141, [d] reference 144, [e] reference 57, [f] reference 46, [g] ... indicates calculations not performed, [h] reference 56, [i] reference 116, [j] reference 11, [k] reference 124.

coordinate-dependent approximations are made, so this type of calculation should be valid for systems with small to large reaction-path curvature. The SCF description does not do as well for these systems as the adiabatic models; however, using configuration interaction the predictions of the resonance energies are greatly improved. The CI results are better than the MEPVA and SCSA results for the lowest-energy resonance of each system. The resonance energies predicted by the semiclassical SCF method are comparable in accuracy to the quantal SCF results. The resonant-periodic-orbit calculations appear very accurate for the H + H$_2$ resonance.

Partial widths. In Table II a compilation of adiabatic and nonadiabatic partial widths is given for the same resonances.

Table II. Partial Widths (kcal/mol) for Three Collinear Atom-Diatom Reaction

System	n	v	adiabatic[a]			nonadiabatic[b]	
			accurate quantal	MEPVA	SCSA[c]	accurate quantal	Feshbach
H + FH	0	0	0.0049[d]	0.0053[e]	0.0045	0.0[d]	0.0[d]
	1	0	0.0[d]	0.0[e]	0.0	0.479[d]	0.389[d]
	1	1	0.12	...[f]	0.107	0.15	0.184[d]
D + FD	0	0	0.0014[d]	0.0014[e]	0.0014	0.0[d]	0.0[d]
	1	0	0.0[d]	0.0[e]	0.0	0.309[d]	0.238[d]
	1	1	0.03	...	0.0435	0.10	0.127[d]
H + H$_2$ (PK2)	1	0	0.16	0.04[g]	0.16	0.37	0.48[h]

^{a} sum of all partial widths for decay channels with same n as resonant state, ^{b} sum of all partial widths for decay channels with n different from resonant state, ^{c} reference 118, ^{d} reference 57, ^{e} reference 46, ^{f} ... indicates calculations not performed, ^{g} reference 116, ^{h} reference 56.

For the lowest-energy resonances of H + FH and D + FD, the MEPVA and SCSA results give very similar-quality results for the adiabatic partial widths; however, for H + H$_2$ the MEPVA results underestimate the adiabatic partial width by a factor of 4 and the SCSA results are accurate to the number of significant figures quoted. This difference in the model calculations can be accounted for by the difference in the adiabatic potential used. In the MEPVA calculations the Morse I approximation is used in constructing the adiabatic potential curve, whereas for the SCSA calculations the WKB approximation is used to calculate $\varepsilon_{str}(n,s)$ in Equation 10. As discussed elsewhere (118), we expect the ground-state adiabatic barriers to be adequately described by the Morse I approximation, but for excited-state barriers a more accurate method for treating anharmonicities in the stretching vibration is needed. The Feshbach golden-rule .

formula is presently the only approximate method for calculating nonadiabatic partial widths. The typical errors are on the order of 0.03-0.09 kcal/mol, which is larger than the errors in the adiabatic partial widths as predicted by the SCSA method.

For the H + H$_2$ case, we can compare the partial width calculations to predictions made by Pollak (146) using an RPO analysis. His calculations indicated that the adiabatic partial width is "negligible" compared to the nonadiabatic one. Actually though, the accurate quantal results show an adiabatic/nonadiabatic ratio of 0.4, and the SCSA/Feshbach ratio is 0.3.

The useful accuracy obtained with the Feshbach golden rule formalism is encouraging because this approach is more general than the bimolecular reactive resonance calculations considered here. The same model used here for resonance energies and partial widths was applied to reactive tunneling in reference 120. More recently Carrington et al. (119) have treated the isomerization of vinylidene using a method that is similar in spirit to the one we applied to bimolecular resonances. One improvement made by these authors is to diagonalize the complex resonance energy operator. In their calculation the Hamiltonian matrix elements are quantized semiclassically using the Heisenberg correspondence principle and the derivative operator is not allowed to act on the vibrational wavefunction. (We found that the action of the derivative coupling operator on the vibrational wave function is very significant for collinear H + H$_2$ on the PK2 surface, for which it changes the predicted nonadiabatic partial width by a factor of 1.75.) In another application of the golden rule, Geiger et al. (175) have considered vibrationally nonadiabatic decay of the unimolecular decomposition resonances of C-O-H, as accessed in H + CO collisions. Since we have demonstrated that the intermode coupling responsible for vibrationally nonadiabatic decay in bimolecular reactive collision resonances of systems with single-saddlepoint potential energy surfaces and a system with a metastable well between two saddlepoints may be modelled quantitatively by the lowest-order reaction-path curvature operator, it would be interesting to see if this kind of treatment can also be applied successfully to similar intermode coupling effects that occur (176-178) in unimolecular decay resonances of systems with potential energy surfaces that exhibit stable wells. Although we (see also 179,180) have used the Feshbach approach to develop a formalism for the calculation of partial widths in the framework of natural collision coordinates, the Feshbach approach can also be applied in other coordinate systems. For example, Liedtke et al. applied the Feshbach method using Jacobi coordinates (26), although they did not calculate widths. Hyperspherical coordinates were mentioned in the introduction, and they often provide a useful separability in cases where reaction-path coordinates fail; furthermore, the coupling operator in hyperspherical coordinates is simpler than the reaction-path curvature operator of natural collision coordinates. Thus, golden-rule calculations in hyperspherical coordinates would be very interesting.

Total resonance widths. The total resonance widths are compiled
in Table III. The reaction-path-Hamiltonian (RPH) method denotes
using the SCSA method for adiabatic partial widths and the
Feshbach golden-rule method for nonadiabatic partial widths and
summing these to obtain the total width.

Table III. Resonance Widths (kcal/mol) for Three Collinear
            Atom-Diatom Reactions

System	n	v	accurate quantal	RPH[a]	Stabilization cubic[b]	Stabilization Padé[c]	RPO
H + FH	0	0	0.0049[d]	0.0045[d]	0.0059	0.0040	...[e]
	1	0	0.479[d]	0.389[d]	0.37	0.36	...
	1	1	0.27[d]	0.291[d]	0.67	0.25	...
D + FD	0	0	0.0014[d]	0.0014[d]	...	...	...
	1	0	0.309[d]	0.309[d]	...	...	...
	1	1	0.13[d]	0.171[d]	...	...	...
H + H$_2$ (PK2)	1	0	0.53[f]	0.62[f]	0.48	0.48	1.06[g]

^{a} Reaction-path Hamiltonian model, see text for description.
^{b} reference 133, ^{c} reference 135, ^{d} reference 57, ^{e} ... indicates
calculations not performed, ^{f} reference 56, ^{g} references 145,146

The good agreement seen in the separate contributions to
the RPH methods is reflected in the good agreement for the total
widths.   Total widths can also be extracted from the
stabilization calculations. The simple polynomial fit of the
resonance energy as a function of scaling parameter is not as
accurate as the Padé approximant method. The Padé approximant
method gives total widths which are of about the same accuracy
as the RPH model for the H + FH resonances, but the Padé method
is more accurate for the H + H$_2$ resonance. Resonant periodic
orbits have also been used to calculate a width for the
lowest-energy resonance for H + H$_2$ (145,146); the result is too
large by a factor of 2.

Resonances in three-dimensional atom-diatom reactions

H + H$_2$. For H + H$_2$, a reactive resonance has been observed in
quantum mechanical scattering calculations for total angular
momentum J=0 (61,64). For F + H$_2$, more details of reactive
resonances in three dimensions have been uncovered. In plots
of the quantum mechanical opacity function versus energy and
total angular momentum J, peak values of the reaction probability
are observed to shift to higher energies as J is increased (63).
This "resonance ridge" indicates the dependence of the resonance
energy upon J. Resonances in three-dimensional reactions have
a much richer spectroscopy than those in collinear reactions;
in addition to having a dependence upon the state of the bound

stretching degrees of freedom in the interaction region, the
resonance energies also have a dependence upon the quantum
numbers for bending degree of freedom and the total angular
momentum. In the present section, we present calculations for
the H + H$_2$ reaction of resonance energies for various quantum
numbers for both the PK2 and LSTH surfaces using the adiabatic
model in natural collision coordinates.

For three-dimensional atom-diatom reactions with collinear
minimum-energy-paths, the adiabatic potential curve is given by

$$V_a(\underline{n},J,s) = V_{MEP}(s) + \varepsilon_{str}(n_{str},s) + \varepsilon_b(n_b,s) + \varepsilon_b(n_b',s)$$

$$+ \hbar^2 J(J+1)/[2I(s)] \qquad (25)$$

where $\varepsilon_b(n_b,s)$ is the energy level for the bending degree of
freedom, I(s) is the moment of inertia as a function of the
distance s along the MEP, and $\underline{n}$ is the collection of vibrational
quantum numbers (n_{str},n_b,n_b'). In the adiabatic model, the
resonances are interpreted as quasibound states in wells of these
one-dimensional potential curves. The resonance energies will
be labeled by the quantum number $\underline{n}$, by J, and by the quantum
number v for motion along the reaction path in the adiabatic
well. As described previously for collinear reactions, the
resonance energies are computed semiclassically, using a
primitive WKB method for core-excited type I resonances and a
uniform expression otherwise. Also, the small-curvature (SC)
method is used to incorporate the effects of reaction-path
curvature. Unlike the collinear case, we used the Morse
approximation II for fitting the local stretching vibrational
potential instead of Morse I approximation since the Morse II
approximation gave more accurate estimates of the resonance
energies for the collinear H + H$_2$ resonances. The bending
vibrational energies are evaluated by fitting the bending
potential to a harmonic-quartic potential and computing the
energy eigenvalues by a perturbation-variation method (181,182).

The results for the H + H$_2$ reaction on the PK2 and LSTH
surfaces are shown in Tables IV and V, respectively. In both
cases, we report all the sets of n_{str}, n_b, and n_b' with $n_{str}=$
1 and 2 for which we found resonance energies less than the
maximum in the adiabatic barrier. Rather than give the resonance
energies as a function of J, the resonance energies for the three
lowest J values were fit to the form

$$E_{res}(\underline{n},J) = E_{res}(\underline{n},J=0) + B_{\underline{n}}J(J+1) + D_{\underline{n}}[J(J+1)]^2 \qquad (26)$$

We note that, although the spacing between the resonances
differing only in J is very small, the INR approximation need
not be invalid for this reason because its validity only requires
narrow resonances well separated from others with the same total
angular momentum.

We compare the results in Table IV with the approximate
resonant periodic orbit (RPO) calculations of Pollak and Wyatt
(147) and with accurate quantal calculations (61). In the RPO
calculations, the bending degrees of freedom are included using

Table IV. Spectroscopic Properties of Three-Dimensional H + H$_2$ Reactive
Resonances on the PK2 Surface[a].

n_{str}	n_b	n_b'	v	$E_{res}(\underline{n}, J=0)$ SCSA[b]	$B_{\underline{n}}$	$D_{\underline{n}}$	$E_{res}(\underline{n}, J=0)$ RPO[c]	$B_{\underline{n}}$	$E_{res}(\underline{n}, J=0)$ Accurate[d]
1	0	0	0	22.68 .98	0.0281	4.9(-6)	22.01	0.0236	22.5 0.98
	1	0	0	25.53 1.11	0.0288	-4.3(-6)	...[e]	...	
2	0	0	0	29.16 1.26	0.0285	-2.4(-7)	30.90	0.0201	
			1	33.01 1.43	0.0251	7.0(-6)	...	...	
	1	0	0	31.97 1.39	0.0282	-7.6(-7)	32.43	0.0208	
	1	1	0	34.77	0.0280	-8.9(-7)	33.96	0.0215	
	2	0	0	34.97	0.0279	-8.3(-7)	34.25	0.0215	
	2	1	0	37.74	0.0278	1.7(-7)	35.78	0.0221	
	2	2	0	40.70	0.0279	1.0(-6)	37.60	0.0228	
	3	0	0	38.10	0.0278	-2.1(-8)	...	...	
	3	1	0	40.87	0.0279	1.1(-6)	...	...	
	3	2	0	43.86	0.0282	1.4(-6)	...	...	

[a] Rotational constants $B_{\underline{n}}$ and $D_{\underline{n}}$ are explained in Equation 26. Energies in kcal/mol relative to the bottom of the asymptotic reactant vibrational well. [b] The SCSA method uses Morse approximation II to evaluate $\varepsilon_{str}(n_{str}, s)$, [c] reference 147, [d] reference 61, [e] ... indicates that this method predicts no resonance would occur for these quantum numbers.

Table V. Spectroscopic Properties of the Three-Dimensional H + H$_2$ Reactive
Resonances on the LSTH surface [a]

n_{str}	n_b	n_b'	v		$E_{res}(\underline{n}, J=0)$ SCSA[b]	$B_{\underline{n}}$	$D_{\underline{n}}$	$E_{res}(\underline{n}, J=0)$ Accurate[c]
1	0	0	0	.98	22.58	0.0262	2.5(-6)	22.7 0.98
	1	0	0	1.09	25.18	0.0241	6.1(-5)	
2	0	0	0	1.24	28.65	0.0264	-4.0(-6)	
			1	1.38	31.88	0.0229	4.7(-6)	
	1	0	0	1.35	31.20	0.0261	-7.1(-7)	
	1	1	0		33.76	0.0259	-6.8(-7)	
	2	0	0		33.94	0.0259	-7.0(-7)	
	2	1	0		36.47	0.0258	2.9(-7)	
	2	2	0		39.18	0.0260	1.2(-6)	
	3	0	0		36.79	0.0258	5.1(-7)	
	3	1	0		39.33	0.0260	1.2(-6)	
	3	2	0		42.07	0.0262	-3.1(-7)	

[a] Rotational constants $B_{\underline{n}}$ and $D_{\underline{n}}$ are explained in Equation 26. Energies in kcal/mol relative to the bottom of the asymptotic reactant vibrational well. [b] The SCSA method uses Morse approximation II to evaluate $\varepsilon_{str}(n_{str}, s)$, [c] reference 64

a sudden-like approximation and the rotational constant B_n is evaluated using an adiabatic reduction scheme. Therefore, it is interesting to compare these results with the vibrationally adiabatic ones which are based upon different approximations. The only accurate quantal results available for three-dimensional $H + H_2$ are for $n_{str}=1$, $n_b=n_b'=0$, and $J=0$. The adiabatic model (SCSA) is in better agreement with the accurate results than the RPO calculations, but both are very close and the two approximate calculations differ by only 0.7 kcal/mol. The two approximate calculations show similar trends in the dependence of the resonance energies on the bending state but also show some marked differences. For $n_{str}=1$, the SCSA calculations show that the $n_b=1$, $n_b'=0$, $J=0$ adiabatic curve should hold one resonance level, which is calculated to be about 0.05 kcal/mol below the maximum of the adiabatic curve. The RPO results do not predict a resonance for this state. For $n_{str}=2$, the SCSA and RPO predictions of the lowest resonance energy (for $n_b=n_b'=0$) differ by about 1.7 kcal/mol. This disagreement reflects the increased difficulty of predicting accurate resonance energies as the quantum numbers increase. Also of interest is the dependence of the resonance energy on the bending quantum numbers for this state. The SCSA method predicts that the adiabatic curves up to $n_b=3$ and $n_b'=2$ will hold resonance energy levels, whereas the RPO method predicts resonance levels only through $n_b=n_b'=2$. Also, the resonance energies go up faster with increasing numbers of bending quanta for the SCSA method. The trends in the dependence of the resonance energies upon J is fairly clear. The rotational constants B_n for the SCSA model are consistently higher than those for the RPO method. The values obtained from the SCSA model are all just slightly lower than the value of the rotational constant evaluated at the saddle point, $n^2/[2I(s=0)]$ = 0.0295 kcal/mol.

The agreement between the SCSA and accurate quantal results is as good for the LSTH surface (Table V) as for the PK2 surface. It is also interesting to compare the results on the two surfaces. Although the surfaces have substantially different bending potentials, the resonance energies are surprisingly similar for the two systems. However, the rotational constants B_n are consistently lower on the LSTH surface.

$H + D_2$. The adiabatic model (SCSA) was also applied to the H $+ D_2$ reaction using the accurate potential energy surface (LSTH). For this reaction we found the adiabatic potential energy curves for $n_{str}=1$ and 2 would not support any resonance energy levels. Therefore, we predict that no low-energy reactive resonances will be observed for this system.

Concluding remarks.

Several approximate models for computing resonance energies and widths have been compared, with numerical illustrations for bimolecular reactive resonances for which an adiabatic separation in reaction-path coordinates is reasonable. For systems in which the reaction-path curvature is not too great, the adiabatic model

in natural collision coordinates provides a good zero-order description of resonance states and reasonably accurate resonance energies and adiabatic partial widths, and it is most easily extended to reaction in three dimensions. When the reaction-path curvature is too large for natural collision coordinates to be useful, one can retain some of these advantages by making the adiabatic approximation in hyperspherical coordinates. We also consider three ways to go beyond the adiabatic approximation: (i) SCF stabilization calculations, in which the motion along two or more coordinates is assumed separable in an average sense, but neither coordinate is assumed to be adiabatic with respect to the other; (ii) configuration-mixing stabilization calculations, in which no separability is assumed at all; and (iii) Feshbach-theory calculations in which nonadiabatic coupling is added perturbatively to an adiabatic zero-order description. The stabilization calculations are reasonably accurate and are not limited to systems with small-to-moderate reaction-path curvature, but they provide only total widths and are slightly more complicated than adiabatic-based methods to extend to three-dimensional reactions. The Feshbach golden-rule calculations in an adiabatic basis have the advantage of providing partial widths, and the initial successes of this approach are very encouraging.

Literature Cited

1. Truhlar, D. G.; Kuppermann, A. J. Chem. Phys. 1970, 52, 3841.
2. Wu, S.-F.; Levine, R. D. Chem. Phys. Lett. 1971, 11, 557.
3. Wu, S.-F.; Levine, R. D. Mol. Phys. 1971, 22, 881.
4. Diestler, D. J. J. Chem. Phys. 1971, 54, 4547.
5. Truhlar, D. G.; Kuppermann, A. J. Chem. Phys. 1972, 56, 2232.
6. Johnson, B. R. Chem. Phys. Lett. 1972, 13, 172.
7. Wu, S.-F; Johnson, B. R.; Levine, R. D. Mol. Phys. 1973, 25, 609.
8. Wu, S.-F.; Johnson, B. R.; R. D. Levine Mol. Phys. 1973, 25, 839.
9. Schatz, G. C.; Kuppermann, A. J. Chem. Phys. 1973, 59, 964.
10. Truhlar, D. G.; Wyatt, R. E. Annu. Rev. Phys. Chem. 1976, 27, 1.
11. Kuppermann, A. In "Potential Energy Surfaces and Dynamics Calculations"; Truhlar, D. G., Ed., Plenum: New York, 1981; p. 375.
12. Schatz, G. C.; Bowman, J. M.; Kuppermann, A. J. Chem. Phys. 1973, 58, 4023.
13. Baer, M. Mol. Phys. 1974, 27, 1429.
14. Baer, M.; Halavee, U.; Persky, A. J. Chem. Phys. 1974, 61, 5122.
15. Kouri, D. J.; Baer M. Chem. Phys. Lett. 1974, 24, 37.

16. Chapman, F. M., Jr.; Hayes, E. F. J. Chem. Phys. 1975, 62, 4400.
17. Schatz, G. C.; Bowman, J. M.; Kuppmann, A. J. Chem. Phys. 1975, 63, 674.
18. Schatz, G. C.; Bowman, J. M.; Kuppmann, A. J. Chem. Phys. 1975, 63, 685.
19. Adams, J. T. Chem. Phys. Lett. 1975, 33, 275.
20. Connor, J. M. L.; Jakubetz, W.; Manz, J. Mol. Phys. 1975, 29 347.
21. Rosenthal, A.; Gordon, R. G. J. Chem. Phys., 1976, 64, 1641.
22. Chapman, F. M., Jr.; Hayes, E. F. J. Chem. Phys. 1976, 65, 1032.
23. Bowman, J. M.; Leasure, S. C.; Kuppmann, A. Chem. Phys. Lett. 1976, 43, 374.
24. Light, J. C.; Walker, R. B. J. Chem. Phys. 1976, 65, 4272.
25. Chapman, F. M., Jr.; Hayes, E. F. J. Chem. Phys. 1977, 66, 2554.
26. Liedtke, R. C.; Knirk, D. L.; Hayes, E. F. Int. J. Quantum Chem. Symp. 1977, 11, 337.
27. Wyatt, R. E.; McNutt, J. F.; Latham, S. L.; Redmon, M. J. Faraday Disc. Chem. Soc. 1977, 62, 322.
28. Wyatt, R. E. In "State-to-State Chemistry"; Brooks, P.R.; Hayes, E. F., Eds., American Chemical Society: Washington, 1977; p. 185.
29. Connor, J. N. L.; Jakubetz, W.; Manz, J. Mol. Phys. 1978, 35, 1301.
30. Gray, J. C.; Truhlar, D. G.; Clemens, L.; Duff, J. W.; Chapman, F. M.; Morrell, G. O.; Hayes, E. F. J. Chem. Phys. 1978, 69, 240.
31. Latham, S. L.; McNutt, J. F.; Wyatt, R. E.; Redmon, M. J. J. Chem. Phys. 1978, 69, 3746.
32. Askar, A.; Cakmak, A. S.; Rabitz, H. A. Chem. Phys. 1978, 33, 267.
33. Connor, J. N. L.; Jakubetz, W.; Manz, J. Mol. Phys. 1980, 39, 799.
34. Schatz, G. C.; Kuppmann, A. J. Chem Phys. 1980, 72, 2737.
35. Garrett, B. C.; Truhlar, D. G.; Grev, R. S.: Walker, R. B. J. Chem. Phys. 1980, 73, 237.
36. Garrett, B. C.; Truhlar, D. G.; Grev, R. S.; Magnuson, A. W.; Connor, J. N. L. J. Chem. Phys. 1980,73, 1721.
37. Hauke, G.; Manz, J.; Römelt, J. J. Chem. Phys. 1980, 73, 5040.
38. Kuppmann, A.; Kaye, J. A.; Dwyer, J. P. Chem. Phys. Lett. 1980, 74, 257.
39. Römelt, J. Chem. Phys. Lett. 1980, 74, 263.
40. Manz, J.; Römelt, J. Chem. Phys. Lett. 1980, 76, 337.
41. Manz, J.; Römelt, J. Chem. Phys. Lett. 1981, 77, 172.
42. Kaye, J. A.; Kuppmann, A. Chem. Phys. Lett. 1981, 77, 573.
43. Kuppmann, A., Kaye, J. A. J. Phys. Chem., 1981, 85, 1969.
44. Manz, J.; Römelt, J. Chem. Phys. Lett. 1981, 81, 179.
45. Walker, R. B.; Zeiri, Y.; Shapiro, M. J. Chem. Phys. 1981, 74, 1763.
46. Garrett, B. C.; Truhlar, D. G.; Grev, R. S.; Schatz, G. C.; Walker, R. B. J. Chem. Phys. 1981, 85, 3806.
47. Launay, J. M.; Le Dourneuf, M. J. Phys. B 1982, 15, L455.

48. Lee, K. T.; Bowman, J. M.; Wagner, A. F.; Schatz, G. C. J. Chem. Phys. 1982, 76, 3563.
49. Bondi, D. K.; Clary, D. C.; Connor, J. N. L.; Garrett, B. C.; Truhlar, D. G. J Chem. Phys. 1982, 76, 4986.
50. Manz, J.; Pollak, E.; Römelt, J. Chem. Phys. Lett. 1982, 86, 2
51. Alvariño, J. M.; Gervasi, O.; Laganà, A. Chem. Phys. Lett. 1982, 87, 254.
52. Römelt, J. Chem. Phys. Lett. 1982, 87, 259.
53. Bondi, D. K.; Connor, J. N. L. Chem. Phys. Lett. 1982, 92, 570
54. Kaye, J. H.; Kuppmann, A. Chem. Phys. Lett. 1982, 92, 574.
55. Shyldkrot, H.; Shapiro, M. J. Chem. Phys. 1983, 79, 5927.
56. Skodje, R. T.; Schwenke, D. W.; Truhlar, D. G.; Garrett, B. C. J. Phys. Chem. 1984, 88, 628.
57. Skodje, R. T.; Schwenke, D. W.; Truhlar, D. G.; Garrett, B. C. J. Chem. Phys. 1984, 80, 3569.
58. Laganà, A.; Hernandez, M. L.; Alvariño, J. M. Chem. Phys. Lett 1984, 106, 41.
59. Bondi, D. K.; Connor, J. N. L.; Manz, J.; Römelt, J. Mol. Phys 1983, 50, 467.
60. Abusalbi, N.; Kouri, D. J.; Lopez, V.; Babamov, V. K.; Marcus, R. A. Chem. Phys. Lett. 1984, 103, 458.
61. Schatz, G. C.; Kuppmann, A. Phys. Rev. Lett. 1975, 35, 1266.
62. Baer, M. J. Chem. Phys. 1976, 65, 493.
63. Redmon, M. J.; Wyatt, R. E. Int. J. Quantum Chem. Symp. 1977, 11, 343.
64. Walker, R. B.; Stechel, E. B.; Light, J. C. J. Chem. Phys. 1978, 69, 2922.
65. Redmon, M. J.; Int. J. Quantum Chem. Symp. 1979, 13, 559.
66. Redmon, M. J.; Wyatt, R. E. Chem. Phys. Lett. 1979, 63, 209.
67. Bowman, J. M.; Lee, K-T. Chem. Phys. Lett. 1979,64,291.
68. Lee, Y. T. Ber. Bunsenges. physik. Chem. 1982, 86, 378.
69. Wyatt, R. E.; McNutt, J. F.; Redmon, M. J. Ber. Bunsenges. physik. Chem. 1982, 86, 437.
70. Gerjuoy, E. In Autoionization (Proc. Symp. At. Interactions and Space Phys.); A. Temkin, Ed.; Mono Book Corp.: Baltimore, 1966, p. 33.
71. Danos, M.; Greiner, W. Phys. Rev. 1966, 145, 708.
72. Nesbet, R. K. Adv. At. Mol. Phys. 1977, 13, 315.
73. Hazi, A. Phys. Rev. A 1979, 19, 920.
74. Truhlar, D. G.; Schwenke, D. W., Chem. Phys. Lett. 1983, 95, 8
75. Bohm, A. "Quantum Mechanics"; Springer-Verlag: New York, 1979; pp. 478-83.
76. Levine, R. D.; Shapiro, M.; Johnson, B. R. J. Chem. Phys. 1970 52, 1755.
77. Levine, R. D.; Johnson, B. R. Chem. Phys. Lett. 1969, 4, 365.
78. Levine, R. D.; Bernstein, R. B. J. Chem. Phys. 1970, 53, 686.
79. Smith, F. T. Phys. Rev. 1960, 118, 349.
80. Smith, F. T. In "Kinetic Processes in Gases and Plasmas", Hochstim, A. R., Ed., Academic Press, New York, 1969, p. 321.
81. Celenza, L.; Tobocman, W. Phys. Rev. 1968, 174, 1115.
82. Gien, T. T. Can. J. Phys. 1969, 47, 279.
83. Kinsey, J. L. Chem. Phys. Lett. 1971, 8, 349.
84. LeRoy, R. J.; Bernstein, R. B. J. Chem. Phys. 1971, 54, 5114.
85. Yoshida, S. Annu. Rev. Nucl. Sci. 1974, 24, 1.

86. Korsch, H. J.; Möhlenkamp, R. J. Phys. B 1982, 15, L559.
87. Allison, A. C. Chem. Phys. Lett. 1969, 3, 371.
88. Jackson, J. L.; Wyatt, R. E. Chem. Phys. Lett. 1970, 4, 643.
89. Johnson, B. R.; Balint-Kurti, G. G.; Levine, R. D. Chem. Phys. Lett. 1970, 7, 268.
90. Numrich, R. W.; Kay, K. G.; J. Chem. Phys. 1979, 71, 5352.
91. Reinhardt, W. P. Annu. Rev. Phys. Chem. 1982, 33, 223.
92. Basilevsky, M. V.; Ryaboy, V. M. Int. J. Quan, Chem. 1981, 19, 611.
93. Basilevsky, M. V.; Ryaboy, V. M. Chem. Phys. 1984, 86, 67.
94. Atabek, O.; Lefebvre, R.; Jacom, M. J. Phys. B 1982, 15, 2689.
95. Meyer, H.-D.; Walter, O. J. Phys. B 1982, 15, 3647.
96. Meyer, H.-D. J. Phys. B 1983, 16, 2265.
97. Meyer, H.-D. J. Phys. B 1983, 16, 2785.
98. Brenig, W.; Haag, R. In "Quantum Scattering Theory"; Ross, M., Ed.; Indiana University Press: Bloomington, 1963; p. 13.
99. Newton, R. G. "Scattering Theory"; McGraw-Hill: New York, 1966.
100. Taylor, J. R. "Scattering Theory"; John Wiley & Sons: New York, 1972.
101. Siegert, A. F. Phys. Rev. 1939, 56, 750.
102. Feshbach, H. Ann. Phys. (N.Y.) 1958, 5, 357.
103. Feshbach, H. Ann. Phys. (N.Y.) 1962, 19, 287.
104. Feshbach, H. Ann. Phys. (N.Y.) 1967, 43, 410.
105. Goldberger, M. L.; Watson, K. M. "Collision Theory"; John Wiley & Sons: New York, 1964.
106. Rodberg, L. S.; Thaler, R. M. "Introduction to the Quantum Theory of Scattering"; Academic Press: New York, 1967.
107. McCurdy, C. W.; Rescigno, T. N. Phys. Rev. A 1979, 20, 2346.
108. Stine, J. R.; Marcus, R. A. Chem. Phys. Lett. 1974, 29, 575.
109. Bowman, J. M.; Kuppermann, A.; Adams, J. T.; Truhlar, D. G. Chem. Phys. Lett. 1973, 20, 229.
110. Hirschfelder, J. O.; E. Wigner J. Chem. Phys. 1939, 7, 616.
111. Marcus, R. A. J. Chem. Phys. 1966, 45, 4493.
112. Marcus, R. A. J. Chem. Phys. 1966, 45, 4500.
113. Marcus, R. A. J. Chem. Phys. 1968, 49, 2610.
114. Truhlar, D. G. J. Chem. Phys. 1970, 53, 2041.
115. Miller, W. H.; Handy, N. C.; Adams, J. E. J. Chem. Phys. 1980, 72, 99.
116. Garrett, B. C.; Truhlar, D. G. J. Phys. Chem. 1979, 83, 1079; 1980, 84, 628(E); 1983, 87, 4553(E).
117. Garrett, B. C.; Truhlar, D. G. J. Phys. Chem. 1982, 86, 1136; 1983, 87, 4554(E).
118. Garrett, B. C.; Truhlar, D. G., J. Chem. Phys., 1984, 81, in press.
119. Carrington, T., Jr.; Hubbard, L. M.; Schaefer, H. F., III; Miller, W. H. J. Chem. Phys., 1984, 80, 4347.
120. Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. J. Chem. Phys. 1982, 77, 5955.
121. Dywer, J. P.; A. Kuppermann, unpublished.
122. Dywer, J. P.; Ph.D. Thesis, California Institute of Technology, Pasadena, 1978.
123. Babamov, V. K.; Kuppermann, A., J. Chem. Phys. 1982, 77, 1891.
124. Römelt, J. Chem. Phys. 1983, 79, 197.

125. Aquilanti, V.; Cavalli, S.; Laganà, A. Chem. Phys. Lett. 1982, 93, 179.
126. Pollak, E.; Römelt, J. J. Chem. Phys. 1984, 80, 3613.
127. Holøien, E.; Midtal, J. J. Chem. Phys. 1966, 45, 2209.
128. Taylor, H. S. Adv. Chem. Phys. 1970, 17, 91.
129. Taylor, H. S.; Thomas, L. D. Phys. Rev. Lett. 1972, 17, 1091.
130. Bačić, Z.; Simons, J. J. Phys. Chem. 1982, 86, 1192.
131. Thompson, T. C.; Truhlar, D. G. J. Chem. Phys. 1982, 76, 1790; 1982, 77, 3777(E).
132. Thompson, T. C.; Truhlar, D. G. Chem. Phys. Lett. 1983, 101, 235.
133. Thompson, T. C.; Truhlar, D. G. Chem. Phys. 1982, 92, 71.
134. Thompson, T. C.; Truhlar, D. G. J. Phys. Chem. 1984, 88, 210.
135. Thirumalai, D.; Thompson, T. C.; Truhlar, D. G. J. Chem. Phys., 1984, 80, in press.
136. Simons, J. J. Chem. Phys. 1981, 75, 2465.
137. McCurdy, C. W.; McNutt, J. F. Chem. Phys. Lett. 1983, 94, 306.
138. Isaacson, A. D.; Truhlar, D. G., to be published.
139. Gerber, R. B.; Ratner, M. A. Chem. Phys. Lett. 1979, 68, 195.
140. Landau, L. D.; Lifshitz, E. M. "Quantum Mechanics", 2nd ed., Pergamon Press, Oxford, 1965, p. 163.
141. Garrett, B. C.; Truhlar, D. G. Chem. Phys. Lett. 1982, 92, 64.
142. Farrelly, D.; Hedges, R. M., Jr.; Reinhardt, W. P. Chem. Phys. Lett. 1983, 96, 599.
143. Smith, A. D.; Liu, W.-K. Chem. Phys. Lett. 1983, 100, 461.
144. Pollak, E.; Child, M. S. Chem. Phys. 1981, 60, 23.
145. Pollak, E.; Wyatt, R. E. J. Chem. Phys. 1982, 77, 2689.
146. Pollak, E. J. Chem. Phys. 1982, 76, 5843.
147. Pollak, E.; Wyatt, R. E. J. Chem. Phys. in press.
148. Taylor, H. S.; Nazaroff, C. V.; A. Golebiewski J. Chem. Phys. 1966, 45, 2822.
149. Clary, D. C.; Connor, J. N. L. Chem. Phys. Lett. 1983, 94, 81.
150. Pollak, E. Chem. Phys. Lett. 1983, 94, 84.
151. Manz, J.; Meyer, R.; Römelt, J. Chem. Phys. Lett. 1983, 96, 607.
152. Yaris, R.; Taylor, H. S. Chem. Phys. Lett. 1979, 66, 505.
153. Atabek, O.; Lefebvre, R. Chem. Phys. 1981, 55, 395.
154. Noro, T.; Taylor, H. S. J. Phys. B 1980, 13, L377.
155. Bačić, Z.; Simons, J. Int. J. Quantum Chem. 1982, 21, 727.
156. Porter, R. N.; Karplus, M. J. Chem. Phys. 1964, 40, 1105.
157. Liu, B. J. Chem. Phys. 1973, 58, 1925.
158. Siegbahn, P.; Liu, B. J. Chem. Phys. 1978, 68, 2457.
159. Truhlar, D. G.; Horowitz, C. J. J. Chem. Phys. 1978, 68, 2466; 1979, 71, 1514E.
160. Gerrity, D. P.; Valentini, J. J. J. Chem. Phys. 1983, 79, 5203.
161. Rettner, C. T.; Marinero, E. E.; Zare, R. N. In "Physics of Electronic and Atomic Collisions: Invited Papers from the XIIIth ICPEAC"; Eichler, J.; Hertel, I. V.; Stolterfoht, N., Eds; North Holland: Amsterdam, in press.
162. Marinero, E. E.; Rettner, C. T.; Zare, R. N. J. Chem. Phys., in press.
163. Gerrity, D. P.; Valentini, J. J. J. Chem. Phys., in press

164. Ashton, C. J.; Child, M. S.; Hutson, J. M. J. Chem. Phys. 1983,
     78, 4025.
165. Light, J. C.; Walker, R. B. J. Chem. Phys. 1976, 65, 4272.
166. Macek, J.; Burke, P. G. Proc. Phys. Soc. London 1967, 92, 351.
167. Fels, M. F.; Hazi, A. U. Phys. Rev. A 1972, 5, 1236.
168. Connor, J. N. L. in "Semiclassical Method in Molecular
     Scattering and Spectroscopy", Child, M. S., Ed.; Reidel,
     Dordrecht, Holland, 1980.
169. Connor, J. N. L.; Smith, A. D. Mol. Phys. 1981, 43, 347.
170. Marcus, R. A.; Coltrin, M. E. J. Chem. Phys. 1977, 67, 2609.
171. Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. J. Phys. Chem.
     1981, 85, 3019.
172. Garrett, B. C.; Truhlar, D. G. J. Phys. Chem. 1979, 83,
     1052; 1979, 83, 3058(E).
173. Herzberg, G. "Molecular Spectra and Molecular Structure".
     Vol. I, "Spectra of Diatomic Molecules", 2nd ed., Van Nostrand,
     Princeton, NJ, 1950, p. 101.
174. Downing, J. W.; Michl, J. In "Potential Energy Surfaces and
     Dynamics Calculations"; Truhlar, D. G., Ed.; Plenum: New York,
     1981; p. 199.
175. Geiger, L. C.; Schatz, G. C.; Garrett, B. C., contribution
     included in this volume.
176. Wolf, R. J.; Hase, W. L. J. Chem. Phys. 1980, 73, 3779,
     1980, 72, 316.
177. Hedges, R. M.; Reinhardt, W. P. Chem. Phys. Lett. 1982, 91, 241.
178. Kulander, K. C. J. Chem. Phys. 1983, 73, 1279.
179. Shoemaker, C. L.; Wyatt, R. E. J. Chem. Phys. 1982, 77, 4982.
180. Shoemaker, C. L.; Wyatt, R. E. J. Chem. Phys. 1982, 77, 4994.
181. Truhlar, D. G. J. Mol. Spectrosc. 1971, 38, 415.
182. Garrett, B. C.; Truhlar, D. G. J. Phys. Chem. 1979, 83, 1915.