

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

SYSTEM-BATH DECOMPOSITION OF THE REACTION PATH HAMILTONIAN FOR POLYATOMIC SCATTERING; QUANTUM PERTURBATIVE TREATMENT

### Permalink

<https://escholarship.org/uc/item/2602r4hw>

### Authors

Miller, W.H.  
Schwartz, S.

### Publication Date

1982-03-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

MAR 7 1982

LIBRARY AND  
DOCUMENTS SECTION

Submitted to the Journal of Chemical Physics

SYSTEM-BATH DECOMPOSITION OF THE REACTION PATH  
HAMILTONIAN FOR POLYATOMIC SCATTERING; QUANTUM  
PERTURBATIVE TREATMENT

William H. Miller and Steven Schwartz

March 1982

### TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782*



LBL-14205  
c-2

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

System-Bath Decomposition of the  
Reaction Path Hamiltonian for Polyatomic  
Scattering; Quantum Perturbative Treatment

By

William H. Miller\* and Steven Schwartz†

Department of Chemistry and Materials and Molecular Research Division,  
of the Lawrence Berkeley Laboratory, University of California,  
Berkeley, California 94720

This work was supported by the Director, Office of Energy Research,  
Office of Basic Energy Sciences, Chemical Sciences Division of the  
U.S. Department of Energy under Contract DE-AC03-76SF00098, and in  
part by the National Science Foundation grant CHE-79-20181.

Abstract

An approach to quantum mechanical reactive scattering in polyatomic molecular systems is described. The formulation is based on the reaction path Hamiltonian of Miller, Handy, and Adams [J. Chem. Phys. 72, 99 (1980)]. The essential physical idea is that the reaction coordinate in even polyatomic systems may be coupled strongly to only a few (one or two) of the vibrational modes orthogonal to it, and rather weakly coupled to the (perhaps many) remaining modes. This leads naturally to a "system-bath" decomposition of the reaction process, and this paper shows how this is carried through for the reaction path Hamiltonian. If only one transverse mode is included with the reaction coordinate to form the "system", for example, then the overall model is that of a collinear-like reaction, whose dynamics are treated accurately, taking place in a (harmonic) "bath" to which it is weakly coupled.

## I. Introduction.

Quantum mechanical reactive scattering for molecular systems is a topic of obvious importance, for it provides the rigorous theoretical description of chemical reactions, but the practical difficulties which hinder applications are substantial. The usual complication of inelastic molecular collisions, i.e., many strongly coupled channels, is compounded by the additional complexity of dealing with a rearrangement scattering process. The present status of the problem is that treatment of collinear atom-diatom reactions,  $A + BC \rightarrow AB + C$ , is relatively routine, but only a few calculations have been reported for more complex reactions.<sup>1</sup>

The purpose of this paper is to describe a practical framework for approaching the problem of quantum reactive scattering for three-dimensional polyatomic systems. The approach utilizes the reaction path Hamiltonian model for the polyatomic system, as formulated by Miller, Handy, and Adams,<sup>2</sup> and it also exploits the existing capability for carrying out collinear-like reactive scattering calculations.

The reaction path description<sup>3</sup> of a chemical reaction chooses the coordinates and momenta which characterize the system as a reaction coordinate, the distance along the reaction path (usually taken as the steepest descent path in mass-weighted cartesian coordinates through the transition state), and its conjugate momentum, plus local normal mode vibrations that are orthogonal to it. The potential energy surface in this model is thus a

(multidimensional) harmonic valley about the reaction path. The form of the Hamiltonian in these variables obtained by Miller, Handy, and Adams shows explicitly how couplings between the various degrees of freedom enter and also how the quantities characterizing them can be constructed from present quantum chemistry computational methodology.

The idea which we pursue in this paper is that for most reactions one expects the reaction coordinates to be strongly coupled to only a few of the transverse vibrational modes, and weakly coupled to the possibly large number of remaining modes. The validity of this notion is simply that most chemical reactions are local phenomena, so that the modes of the molecule physically close to the region of the bond-breaking and bond-making will be strongly affected (i.e., coupled) by the reaction, but those far from the region only weakly affected. Thus a "system-bath" decomposition of the process is natural: the reaction coordinate and the few (maybe only one) strongly coupled modes are the "system", whose dynamics should be treated accurately, and the remaining (many) weakly coupled modes constitute the (harmonic) bath that will be incorporated perturbatively.

System-bath models have applications to many phenomena in physical chemistry, and there are a variety of theoretical methodologies for dealing with them. If the bath is harmonic and the coupling between system and bath linear in the bath coordinates, then the classical mechanical version of the treatment leads in an elementary fashion to a generalized Langevin equation (GLE)<sup>4</sup>

for the "system" dynamics; this has been discussed previously<sup>2b</sup> by one of us with respect to the reaction path Hamiltonian and the specific form of the GLE given. Presently, however, we wish to retain a fully quantum mechanical description. If a quantum representation in terms of tetradic operators were used one could proceed in a manner parallel to the classical GLE analysis,<sup>5</sup> but at the practical level the tetradic formulation does not accomplish any simplification unless additional approximations are introduced. In this paper, therefore, we treat the system-bath coupling by straight-forward quantum mechanical perturbation theory, which will be sufficient, of course, if the coupling is indeed weak.

Section II describes the system-bath decomposition of the reaction path Hamiltonian, and the perturbative treatment of the coupling between the two is described in Section III. This is essentially a distorted wave approximation where the zero<sup>th</sup> order Hamiltonian that defines the distorted wavefunction is the fully coupled "system" Hamiltonian plus the uncoupled "bath". If, for example, the "system" consists of the reaction coordinate and only one transverse vibrational mode, then it is equivalent to a collinear atom-diatom reaction. The solution of the zero<sup>th</sup> order problem thus involves the accurate solution of this collinear-like reactive scattering problem, and the coupling to the other ("bath") modes is then incorporated perturbatively. The overall picture is that of a collinear reaction taking place in a (harmonic) bath to which it is weakly coupled. It is useful to note that the zero<sup>th</sup> order version of the present approach is essentially



equivalent to an approximation utilized recently by  
Bowman, et al.<sup>6</sup> and found to give encouragingly good results.

II. System-Bath Decomposition of the Reaction Path Hamiltonian.

For total angular momentum  $J=0$  the reaction path Hamiltonian of Miller, Handy and Adams is

$$H(p_s, s, \{P_k, Q_k\}) = \frac{\frac{1}{2} [p_s - \sum_{k, k'=2}^F Q_k P_{k'} B_{k, k'}(s)]^2}{[1 + \sum_{k=2}^F Q_k B_{k, 1}(s)]^2} + V_0(s) + \sum_{k=2}^F (\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2) \quad (2.1)$$

where  $(s, p_s)$  is the reaction coordinate and its conjugate momenta, and  $(Q_k, P_k)$ ,  $k=2, \dots, F$ , the coordinates and momenta for normal mode vibrations in the hyper-plane normal to the reaction path.  $B_{k, 1}(s)$  are curvature coupling elements that couple vibrational mode  $k$  to the reaction coordinate (labeled here as mode 1), and  $\{B_{k, k'}(s)\}$  are coriolis-like coupled elements that couple vibrational modes  $k$  and  $k'$ .  $F=3N-6$ , where  $N$  is the number of atoms of the complete molecular system. More specifics of this Hamiltonian and its applications are described elsewhere,<sup>2,7</sup>

The "system" is chosen to be the reaction coordinate (mode  $k=1$ ) and vibrational modes  $k=2, \dots, f$ , and the "bath" consists of the remaining modes  $k=f+1, \dots, F$ . Retaining only the lowest order coupling terms between the system and the bath gives

$$H(p_s, s, \{P_k, Q_k\}) = H_0 + H_1 \quad (2.2a)$$

where

$$H_0 = H_{\text{sys}} + H_{\text{bath}} \quad (2.2b)$$

with

$$H_{\text{sys}}(p_s, s, \{P_k, Q_k\}, k=2, \dots, f) = \frac{\frac{1}{2} [p_s - \sum_{k,k'=2}^f Q_k P_{k'} B_{kk'}(s)]^2}{[1 + \sum_{k=2}^f Q_k B_{k,1}(s)]^2} + V_0(s) + \sum_{k=2}^f \left( \frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2 \right) \quad (2.2c)$$

$$H_{\text{bath}}[\{P_k, Q_k\}, k=f+1, \dots, F] = \sum_{k=f+1}^F \left( \frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2 \right) \quad (2.2d)$$

$$H_1 = - \frac{[p_s - \sum_{k,k'=2}^f Q_k P_{k'} B_{kk'}(s)]}{[1 + \sum_{k=2}^f Q_k B_{k,1}(s)]^2} \sum_{k=2}^f \sum_{k'=f+1}^F (Q_k P_{k'} - Q_{k'} P_k) B_{k,k'}(s) - \frac{[p_s - \sum_{k,k'=2}^f Q_k P_{k'} B_{kk'}(s)]^2}{[1 + \sum_{k=2}^f Q_k B_{k,1}(s)]^3} \sum_{k=f+1}^F Q_k B_{k,1}(s) \quad (2.2e)$$

One sees that  $H_{\text{sys}}$  is the ordinary reaction path Hamiltonian for the  $f$  degrees of freedom that constitute the "system".

In many cases it may be reasonable to take the "bath" frequencies  $\{\omega_k(s)\}, k=f+1, \dots, F$  to be independent of the reaction coordinate  $s$ , but one may not always wish to do so. If the

S-dependence of mode  $k$  is retained, then it induces an additional coupling to the reaction coordinate. This is most easily seen in the classical version of the Hamiltonian if one transforms the bath variables from cartesian coordinates and momenta to action angle variables,  $(P_k, Q_k) \rightarrow (n_k, q_k)$   $k=f+1, \dots, F$ . Then the bath Hamiltonian becomes

$$H_{\text{bath}}(\{n_k, q_k\}, k=f+1, \dots, F) = \sum_{k=f+1}^F (n_k + \frac{1}{2}) \omega_k(s) \quad , \quad (2.3a)$$

and there is the following additional term in  $H_1$

$$-\frac{[p_s - \sum_{k,k'=2}^f Q_k P_{k'} B_{k,k'}(s)]}{[1 + \sum_{k=2}^f Q_k B_{k,1}(s)]^2} \sum_{k=f+1}^F Q_k P_k B_{kk}(s) \quad , \quad (2.3b)$$

where

$$B_{k,k}(s) \equiv \frac{-\omega'_k(s)}{2\omega_k(s)} \quad . \quad (2.3c)$$

The zero<sup>th</sup> order Hamiltonian thus conserves the action variables  $\{n_k\}, k=f+1, \dots, F$  of the bath, i.e., the bath is vibrationally adiabatic in zero<sup>th</sup> order

Rotation, i.e., non-zero values of the total angular momentum  $J$ , can be incorporated in the present description by including it in the "bath"; i.e., it seems reasonable that in most cases rotation will be weakly coupled to the reaction coordinate. (If

this is not the case, then rotation must be included in the "system" and treated non-perturbatively, perhaps, e.g., via an infinite-order sudden approximation.) To  $H_{\text{bath}}$ , and thus to  $H_0$ , is added the rotational energy of the rigid asymmetric rotor corresponding to the molecular geometry S=S and  $Q_k=0$ ,  $k=2, \dots, F$ ,  $E_{\text{rot}}^J(s)$ . The lowest order rotation-vibration coupling terms can then be included in  $H_1$ .

Finally, all of the above equations have been written in terms of the classical version of the reaction path Hamiltonian, but it is well known how one constructs the corresponding quantum mechanical Hamiltonian operators.

### III. Perturbative Treatment of System-Bath Coupling.

A method to include the effect of system-bath coupling within quantum mechanical perturbation theory is, for a scattering problem, standard distorted wave theory.<sup>9</sup> Thus the transmission amplitude  $t_{\tilde{n}, \tilde{n}'}(E)$  for reaction from initial quantum state  $\tilde{n} = \{n_k\}$ ,  $k=2, \dots, F$  of the reactants (i.e., the transverse vibrational modes at  $s = -\infty$ ) to final state  $\tilde{n}'$  of products (i.e., the transverse vibrational modes at  $s = +\infty$ ) with total energy  $E$ , is given by a perturbation series

$$t_{\tilde{n}, \tilde{n}'}(E) = t_{\tilde{n}, \tilde{n}'}^{(0)}(E) + t_{\tilde{n}, \tilde{n}'}^{(1)}(E) + \dots \quad (3.1)$$

The zero<sup>th</sup> term in Eq. (3.1) is the transmission amplitude resulting from the zero<sup>th</sup> order Hamiltonian  $H_0$  of Eqs. (2.2)-(2.3), and since the "bath" quantum numbers are conserved by  $H_0$ ,  $t_{\tilde{n}, \tilde{n}'}^{(0)}$  is diagonal in them.

To make the formulae more transparent we specialize now to the case that the "system" consists of the reaction coordinate plus just one transverse vibrational mode, i.e.,  $f=2$  in Eq. (2.2). The "system" is thus equivalent to a collinear atom-diatom reaction, and the zero<sup>th</sup> order amplitude is of the form

$$t_{\tilde{n}, \tilde{n}'}^{(0)}(E) = t_{n_2', n_2}^{n_3 n_4 \dots n_F}(E) \delta_{n_3' n_3} \dots \delta_{n_F' n_F} \quad (3.2)$$

The reduced amplitude  $t_{n_2', n_2}^{n_3 \dots n_F}(E)$  is the result of a collinear-like scattering calculation with the vibrationally adiabatic bath

serving only to modify the effective potential along the reaction coordinate,

$$V_{\text{eff}}(s) = V_0(s) + \sum_{k=3}^F (n_k + \frac{1}{2}) \omega_k(s) \quad (3.3)$$

If the bath frequencies are essentially constant, then the bath adds a constant to the energy and the reduced amplitude has the even simpler form

$$t_{n_2', n_2}^{n_3 \dots n_F}(E) = t_{n_2', n_2}^{(2d)}(E - \sum_{k=3}^F (n_k + \frac{1}{2}) \omega_k) \quad (3.4)$$

when  $t_{n_2', n_2}^{(2d)}(E')$  is the two-dimensional collinear-like transmission amplitude as a function of the collinear energy  $E'$ .

(If, for example, the frequencies of the bath are approximated by their constant values of the transition state,  $\omega_k(0) \equiv \omega_k^\ddagger$ ,  $k=3, \dots, F$ , then Eq. (3.4) leads to a very useful expression for the thermal rate constant. The rate constant  $k(T)$  is given by

$$k(T) = (2\pi\hbar Q_T)^{-1} \bar{N}(\beta),$$

where  $Q_T$  is the partition function of the reactants and  $\bar{N}(\beta)$  is the Laplace transform of the cumulative reaction probability  $N(E)$ ,

$$\bar{N}(\beta) = \int_0^\infty dE e^{-\beta E} N(E) \quad (3.5a)$$

with

$$N(E) = \sum_{\underline{n}', \underline{n}} |t_{\underline{n}', \underline{n}}(E)|^2 \quad (3.5b)$$

Utilizing Eq. (3.4), it is relatively straight-forward to show that Eq. (3.5) gives  $\bar{N}(\beta)$  in terms of its two-dimensional counterpart,

$$\bar{N}(\beta) = Q_{\text{bath}}^\ddagger(\beta) \bar{N}_{2d}(\beta) \quad (3.6)$$

where

$$\bar{N}_{2d}(\beta) = \int_0^\infty dE' e^{-\beta E'} N_{2d}(E') \quad (3.7a)$$

with

$$\bar{N}_{2d}(E') = \sum_{n_2^f, n_2} |t_{n_2^f, n_2}(E')|^2 \quad (3.7b)$$

and where  $Q_{\text{bath}}^\ddagger$  is the partition function of the bath,

$$Q_{\text{bath}}^\ddagger(\beta) = \sum_{n_3, \dots, n_F} \exp[-\beta \sum_{k=3}^F \hbar \omega_k^\ddagger (n_k + \frac{1}{2})] \quad (3.7c)$$

If one adopts the language of transition state theory, then

Eq. (3.7) expresses the rate constant as



$$k(T) = \kappa(T) \frac{kT}{\hbar} \frac{Q^\ddagger}{Q_R} \quad (3.8)$$

where  $Q^\ddagger$  is the complete partition function of the transition state (bath plus system)

$$Q^\ddagger = Q_{2d}^\ddagger Q_{\text{bath}}^\ddagger \quad (3.9)$$

with the transmission coefficient  $\kappa(T)$  given by

$$\kappa(T) = \bar{N}_{2d}(\beta) / Q_{2d}^\ddagger \times \left( \frac{1}{2\pi\kappa T} \right) \equiv \kappa_{2d}(T) \quad (3.10)$$

The transmission coefficient of Eq. (3.10), however, is seen to be identical to the transmission coefficient for the two-dimensional collinear-like system. In zero<sup>th</sup> order, therefore, and with the assumption of constant frequencies, one sees that the transmission coefficient for the complete system of  $F$  degrees of freedom is the same as that for the smaller system of  $f$  degrees of freedom. This approximation has been utilized recently by Bowman, *et al.*<sup>10</sup> with quite good results.)

To determine the first order term to the transmission amplitudes,  $t_{\underline{n}', \underline{n}}^{(1)}$  of Eq. (3.1), requires the zero<sup>th</sup> order wavefunctions, the scattering eigenfunctions of  $H_0$ ,  $f_{\underline{n}' \leftarrow \underline{n}}(s)$ . They are also diagonal in the bath quantum numbers,

$$f_{\underline{n}' \leftarrow \underline{n}}(s) = f_{\underline{n}' \leftarrow \underline{n}}^{n_3 \dots n_F}(s) \delta_{n_3 n_3} \dots \delta_{n_F n_F} \quad (3.11)$$

with the reduced function  $f_{\tilde{n}' \leftarrow \tilde{n}_2}^{n_3 \dots n_F}(s)$  being the result of the two-dimensional collinear-like scattering calculation. The asymptotic boundary conditions for  $f_{\tilde{n}' \leftarrow \tilde{n}}(s)$  are of the standard form,

$$f_{\tilde{n}' \leftarrow \tilde{n}}(s) \sim \frac{e^{\frac{ik_{\tilde{n}} s}{1/2}}}{k_{\tilde{n}}} \delta_{\tilde{n}', \tilde{n}} - \frac{e^{-\frac{ik_{\tilde{n}'} s}{1/2}}}{k_{\tilde{n}'}} r_{\tilde{n}', \tilde{n}}^{(0)}(E), \quad s \rightarrow -\infty \quad (3.12a)$$

$$\sim \frac{e^{\frac{ik_{\tilde{n}'} s}{1/2}}}{k_{\tilde{n}'}} t_{\tilde{n}', \tilde{n}}^{(0)}(E), \quad s \rightarrow +\infty \quad (3.12b)$$

where  $r_{\tilde{n}', \tilde{n}}^{(0)}$  and  $t_{\tilde{n}', \tilde{n}}^{(0)}$  are the zero<sup>th</sup> order reflection and transmission amplitudes, and these translate in an elementary way into corresponding boundary conditions on the two-dimensional-like scattering functions  $f_{\tilde{n}' \leftarrow \tilde{n}_2}^{n_3 \dots n_F}(s)$ .  $t_{\tilde{n}', \tilde{n}}^{(1)}(E)$  is then given by (with  $\hbar = 1$ )

$$t_{\tilde{n}', \tilde{n}}^{(1)}(E) = -i \sum_{\tilde{n}''', \tilde{n}''} \int ds f_{\tilde{n}''' \leftarrow \tilde{n}'}(s)^* H_{\tilde{n}''', \tilde{n}''}^{(1)} f_{\tilde{n}'' \leftarrow \tilde{n}}(s), \quad (3.13)$$

where  $H_{\tilde{n}''', \tilde{n}''}^{(1)}$  is the matrix of  $H_1$  in the vibrationally adiabatic basis of the transverse vibrational states; it is still an operator (multiplicative and differential) in the reaction coordinate degree of freedom. Since the translational scattering functions are diagonal in the bath quantum numbers, Eq. (3.13) simplifies to the following

$$t_{\tilde{n}', \tilde{n}}^{(1)}(E) = -i \sum_{n_2'', n_2'''} \int ds f_{n_2'' \leftarrow n_2'''}^{n_3^t, \dots, n_F^{t*}} H_{n_2'' n_3^t, \dots, n_F^t, n_2'' n_3^u, \dots, n_F^u}^{(1)} f_{n_2'' \leftarrow n_2'''}^{n_3^t, \dots, n_F^t} (s) \quad (3.14)$$

One could in principle proceed to construct higher order distorted wave contributions, but a simpler (though approximate) way to take these effects into account is to unitarize the first order approximation via some ad hoc procedure, for example, the exponential DWBA model.<sup>11</sup> It is the composite matrix of reflection and transmission amplitudes in this case that is unitary,

$$U = \begin{pmatrix} \tilde{r} & \tilde{r} \\ \tilde{t} & \tilde{t} \end{pmatrix}, \quad (3.15)$$

where  $\tilde{r} = \{r_{\tilde{n}', \tilde{n}}\}$  and  $\tilde{t} = \{t_{\tilde{n}', \tilde{n}}\}$  are the reflection and transmission amplitudes as discussed above.  $\tilde{r}$  and  $\tilde{t}$  are the reflection and transmission amplitudes corresponding to the reverse reaction, i.e., beginning at  $s = +\infty$ . ( $\tilde{r}$  is the transpose of  $\tilde{t}$ , both of which are in general rectangular matrices;  $\tilde{r}$  and  $\tilde{t}$  are square matrices.) The exponential unitarization procedure expands  $U$  perturbatively,

$$U = U_0 + U_1, \quad (3.16)$$

and then determines the first two terms via Eq. (3.15);

$$U_{z_0} = \begin{pmatrix} r_H(0) & r_{H?}(0) \\ r_t(0) & r_{H?}(0) \end{pmatrix} \quad (3.17a)$$

$$U_{z_1} = \begin{pmatrix} r_H(1) & r_{H?}(1) \\ r_t(1) & r_{H?}(1) \end{pmatrix} \quad (3.17b)$$

Equation (3.16) is assumed to be the first two terms of the powers series of an exponential, which is then resummed symmetrically to give,

$$U_{z_1} = U_{z_0}^{1/2} \cdot \exp(U_{z_0}^{-1/2} \cdot U_{z_1} \cdot U_{z_0}^{-1/2}) \cdot U_{z_0}^{1/2} \quad (3.18)$$

With  $U_{z_0}$  and  $U_{z_1}$  known via Eq. (3.17) from the zero<sup>th</sup> and first order distorted wave results, Eq. (3.18) is used to determine  $U_{z_1}$ , and then Eq. (3.15) gives the unitarized transmission and reflection (i.e., reactive and non-reactive) amplitudes.

#### IV. Concluding Remarks.

One can, in principle, improve results given by the approach we have presented in one of two ways, namely, to treat the coupling between "system" and "bath" to higher order in perturbation theory, or to retain a first order perturbative treatment of the coupling and to include more of the transverse vibrational modes in the "system". There are practical limitations, however, in proceeding too far along either of these avenues. If one attempts to include more than one or two transverse vibrational modes with the reaction coordinate to form the "system", it will not generally be practical to solve the zero<sup>th</sup> order problem itself accurately. Conversely, if one must go beyond first order perturbative theory in a distorted wave calculation, then the perturbative approach is usually not the best way to attack the problem.

Our view, therefore, is that the approach we have described will be useful if indeed only one or two transverse modes are strongly coupled to the reaction coordinate, and together with it define the "system", while the coupling to the remaining transverse modes (the "bath") can be treated by first order perturbative theory. An encouraging note in this regard is that for the three-dimensional  $H + H_2$  reaction Bowman et al.,<sup>6</sup> obtain quite reasonable results already at the zero<sup>th</sup> order level of this approach with only one transverse mode included in the "system", i.e., the bending vibrations and rotation make up the "bath".

Finally, we note that sometimes it may not be most convenient to solve the collinear-like reactive scattering problem for the "system" in the reaction path coordinates  $(s, Q_2)$  (for example, if

the curvature coupling  $B_{2,1}(s)$  is very large). If such is the case, one can transform the collinear-like Hamiltonian  $H_{\text{sys}}$  of Eq. (2.2c) (with  $f=2$ ) to cartesian form,

$$H_{\text{sys}}(p_s, s, P_2, Q_2) \rightarrow H_{\text{sys}}(p_x, x, p_y, y) = \frac{1}{2} (p_x^2 + p_y^2) + V(x, y) \quad , \quad (4.1)$$

where  $V(x, y)$  is given by

$$V(x, y) = v_0(s) + \frac{1}{2} \omega(s)^2 [(x-x_0(s))^2 + (y-y_0(s))^2] \quad , \quad (4.2)$$

where  $x_0(s)$  and  $y_0(s)$  are given by

$$x_0(s) = \int_0^s ds' \sin \theta(s') \quad (4.3a)$$

$$y_0(s) = \int_0^s ds' \cos \theta(s') \quad (4.3b)$$

with

$$\theta(s) = \int_0^s ds' B_{2,1}(s') \quad , \quad (4.4)$$

and where  $s$  is determined as a function of  $x$  and  $y$  by the equation

$$\sin\theta(s) (x-x_0(s)) + \cos\theta(s) (y-y_0(s)) = 0 \quad . \quad (4.5)$$

Acknowledgments

This work has been supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098 and also in part by the National Science Foundation under grant CHE-79-20181. The author also thanks Professor G. L. Hofacker and his colleagues of the Lehrstuhl für Theoretische Chemie, Technische Universität München, for their warm hospitality while he visited as a U.S. Senior Scientist Humboldt awardee.

References

- \* Alexander von Humboldt U.S. Senior Scientist, Lehrstuhl für Theoretische Chemie, Technische Universität München, 1981-82.
- † University of California Regents Fellow.
1. For a recent review, see R. B. Walker and J. C. Light, Ann. Rev. Phys. Chem. 31, 401 (1980).
  2. (a) W. H. Miller, N. C. Handy, and J. E. Adams, J. Chem. Phys. 72, 99 (1980); (b) W. H. Miller, in Potential Energy Surfaces and Dynamics Calculations, ed. D. G. Truhlar, Plenum, N.Y., 1981, p. 265.
  3. A number of workers have contributed to the development of the reaction path description of chemical reactions, for example:
    - (a) G. L. Hofacker, Z. f. Naturforsch. 18a, 607 (1963);
    - (b) S. F. Fischer, G. L. Hofacker, and R. Seiler, J. Chem. Phys. 51, 3951 (1969);
    - (c) R. A. Marcus, J. Chem. Phys. 45, 4493, 4500 (1966); 49, 2610 (1968); 53, 4026 (1976);
    - (d) S. F. Fischer and M. A. Ratner, J. Chem. Phys. 57, 2769 (1972);
    - (e) P. Russegger and J. Brickmann, J. Chem. Phys. 62, 1086 (1976);
    - (f) M. V. Basilevsky, Chem. Phys. 24, 81 (1977);
    - (g) K. Fukui, S. Kato, and H. Fujimoto, J. Amer. Chem. Soc. 97, 1 (1975).



4. For application of this approach to atom-surface scattering, see S. A. Adelman and J. D. Doll, J. Chem. Phys. 61, 4242 (1974); 64, 2375 (1976), and M. Shugard, J. C. Tully, and A. Nitzan, J. Chem. Phys. 66, 2534 (1977).
5. See, for example, S. Mukamel, J. Chem. Phys. 70, 5834 (1979).
6. J. M. Bowman, G.-Z. Ju, and K. T. Lee, J. Chem. Phys. 75, 5199 (1981); 76, 0000 (1982).
7. (a) S. K. Gray, W. H. Miller, Y. Yamaguchi and H. F. Schaefer, J. Chem. Phys. 73, 2733 (1980).  
(b) S. K. Gray, W. H. Miller, Y. Yamaguchi and H. F. Schaefer, J. Am. Chem. Soc. 103, 1900 (1981).  
(c) C. J. Cerjan, S.-h. Shi, and W. H. Miller, J. Phys. Chem. 86, 0000 (1982).
8. See, for example,  
(a) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, N.Y., 1955;  
(b) J. T. Hougen, P. R. Bunker, and P. C. Cross, J. Mol. Spectrosc. 34, 136 (1970).
9. See, for example, A. Messiah, Quantum Mechanics, Wiley, N.Y., 1962, pp. 822.
10. J. M. Bowman, G.-Z. Ju, K. T. Lee, A. F. Wagner, and G. C. Schatz, J. Chem. Phys. 75, 141 (1981).
11. See, for example, S. Bosanac and G. C. Balint-Kurti, Mol. Phys. 29, 1797 (1975); and R. D. Levine and G. C. Balint-Kurti, Chem. Phys. Lett. 6, 101 (1970).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720