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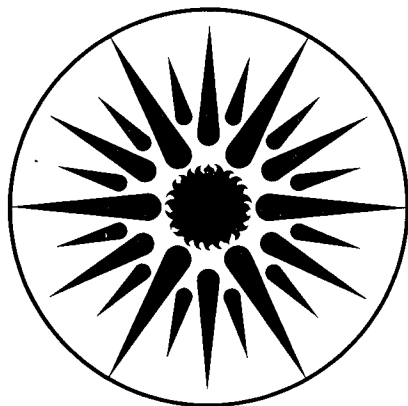
## APPLIED SCIENCE DIVISION

To be published as a chapter in  
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### Rate Coefficient Calculations for Combustion Modeling

N.J. Brown

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**RATE COEFFICIENT CALCULATIONS  
FOR COMBUSTION MODELING**

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## ABSTRACT

Transition state calculations and molecular dynamics approaches to rate coefficient calculations are discussed in this paper. Various inputs required for each type of calculation are also described. The reader is referred to a number of detailed reviews that explicitly describe how one performs various types of rate coefficient calculations. Hopefully, areas of difficulty and common misconception that frequently occur with respect to each approach or elements of the approach are clarified. The focus of the paper is to provide a list of essential ingredients, a description of approximations, limitations, and recent progress in the area.

## II. INTRODUCTION

The intent of this paper is to convey to the reader the elements of different approaches to rate coefficient calculations. Rate coefficient calculations range from rough back of the envelope estimates to highly sophisticated quantum mechanical calculations, and they include a variety of approaches that are classified as being either statistical or dynamical in nature. The intent of this paper is not to provide a review of this vast subject because extensive reviews covering speciality portions of the subject already exist. For more detailed reviews the reader is directed toward a number of references which contain descriptions of individual calculation methodologies. The focus here is to provide a list of the essential ingredients, a description of the approximations, limitations, and recent progress in the area.

## II. POTENTIAL ENERGY SURFACES

Potential energy surfaces (PES) have been discussed in the previous chapter by Page and Lengsfeld (1989). Here, we will briefly mention some details of potential energy systems that are important in rate coefficient calculations. Two books that describe the important features of potential energy surfaces are by Simons (1983) and by Murrell et al. (1984).

In general, a potential energy surface is a function of  $3N-5$  or  $3N-6$  internal co-ordinates. Most surfaces are calculated by invoking the Born-Oppenheimer (BO) approximation, and this implies that the wavefunction is a product of an electronic wavefunction and a nuclear wavefunction (the vibration/rotation wavefunction). Within the Born-Oppenheimer approximation, the electronic energy, which depends on the location of the nuclei, provides the potential energy surface on which the nuclei move. Within the clamped nuclei (BO) approximation where the electronic energy is computed parametrically as a function of fixed nuclear positions, wavefunctions that include spin/orbit interactions are frequently referred to as the adiabatic basis. However the term adiabatic is also used to refer to the wavefunctions which are eigenfunctions of the electronic Hamiltonian for the clamped nuclei which exclude the spin/orbit terms. This is the less correct but more commonly used definition of adiabatic and the one that is used in most PES calculations. Reactions on such surfaces are called adiabatic reactions because the electronic state of the system throughout the course of reaction is associ-

faces are usually called diabatic surfaces.

The information that one needs about a potential energy surface depends upon the type of rate coefficient calculation being pursued. In full dynamics calculations, be they quantum, semi-classical, or quasi-classical, the potential energy surface must be represented by a global function spanning the entire configuration space of nuclear motion. Frequently, a few ab initio points are calculated and an interpolation procedure is used to span the space. An excellent discussion of various criteria that a successful interpolating function must satisfy is given by Wright and Grey (1978). Connor (1979), in his review of reactive molecular collisions, discusses these criteria and previous research concerned with fitting. Another approach to obtaining a global PES is to approximate the overlap, coulomb and exchange integrals required for the surface calculation. This approach was pursued by Porter and Karplus (1964) for H<sub>3</sub> and by Silver and Brown (1980) for H<sub>4</sub>. In both approaches, integral parametrization was based upon ab initio results.

In reaction path treatments, the potential energy must be known in analytical form along the reaction path. There are accurate and efficient techniques for the ab initio quantum mechanical calculation of the gradient of the PES with respect to the nuclear coordinates. These are used most frequently to determine the saddle point, and the same techniques can be used to follow the path of steepest decent from the saddle point to reactants and products. If mass weighted Cartesian coordinates

are used, this defines, according to Fukui et al. (1975), the reaction path and the distance along it is the mass weighted reaction coordinate. Miller et al. (1980) describe the construction of a classical Hamiltonian for a general molecular system based upon the reaction path and a harmonic approximation to the PES about the reaction path.

Finally, in conventional transition state theory, where the saddle point is used as the transition state dividing surface, the barrier height geometry of the saddle point configuration and the vibrational frequencies of the transition state are required. In generalized transition state theory, there must be enough PES data to define and characterize the transition state.

Although not specifically concerned with potential energy surfaces, Benson's book (1976) entitled "Thermochemical Kinetics" is a veritable treasure house of information relating molecular structure characteristics to reactivity. The book provides an impressive discussion of semi-empirical methods for estimating Arrhenius parameters for a number of different types of reactions. It also gives additivity rules for estimating thermochemical properties. In this author's opinion, this book is an absolute requirement for every combustion modeler's shelf.

### III. TRANSITION STATE THEORY

#### A. Theoretical Considerations

Transition state theory (TST) has been available for the calculation of rate coefficients for over fifty years and has been used extensively during this period. It is the theoretical approach most commonly used by combustion modelers to calculate



rate coefficients. Transition state theory has been the object of renewed theoretical interest since the early seventies. There are a number of texts that describe TST, and these are Gladstone (1941), Laidler (1969), and Eyring, Lin and Lin (1980); Eyring, Walter, and Kimball (1944); Johnston (1966); Bunker (1968); Weston and Schwartz (1972); Nikitin (1974); Smith (1980); and Levine and Bernstein (1987). Pechukas (1976 and 1981) has written two excellent reviews that describe characteristics of transition state theory and research in the area. More specialized reviews concerned with the theory have been written by Truhlar et al. (1985) and Truhlar and Garrett (1984). The first of these is especially useful in providing detailed information about methodology for actual rate coefficient determinations. Laidler and King (1983) have prepared a historical review of the theoretical developments of TST.

Transition state theory is paradoxical in that it is simple in construction and subtle in its consequences. To paraphrase some of the excellent material of Pechukas, TST is a statistical theory, and the statistics in this theory involve counting the number of ways a system can pass through a transition state. Although statistical concepts are employed to avoid the computational intensity of dynamical treatments, the essence of TST is founded in dynamical concepts. The idea of a transition state invokes dynamical considerations, specifically dynamical instability, in passing through the transition state, one has reactants on one side of the transition state and products on the

other.

There are two major assumptions which characterize transition state theory. First, a local equilibrium exists between reactants and species that originate as reactants and become transition state species. Second, any species passing through the transition state does so only once. The first of these is called the local equilibrium approximation and the second is the no-recrossing assumption. Within the framework of classical mechanics, the net rate of reaction in the forward direction is given by the flux of trajectories from the reactant phase space passing through the transition state dividing surface to the product phase space. The transition state is truly a point of no return, and implicit in the theory is the idea that once the system passes through the transition state from the reactant side of the PES it is by definition in product space forever more. The exactness of transition state theory at an energy  $E$  (microcanonical TST) can be verified by following all trajectories that leave the transition state, and if there is no recrossing, the theory is exact. Canonical TST is exact if and only if no trajectory of any energy crosses the transition state more than once, a significantly more stringent requirement. The rate coefficients from classical transition state theory are verified with a dynamical criterion, and they must be compared with rate coefficients calculated entirely classically, without quasiclassical quantization of initial states using standard trajectory calculations. When one speaks about TST being exact, it implies exact agreement between it and an exact classical trajectory calculation of the

rate coefficient.

For the reaction  $A + B \rightarrow C + D$ , the expression for the forward rate coefficient  $k_f$  is

$$k_f = \frac{k_B T}{h} \cdot \frac{Q^\ddagger}{Q_A Q_B} \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $h$  is Planck's constant and  $T$  is temperature in Kelvins. The partition function for molecule A per unit volume is given by

$$Q_A = h^{-3N_A} \int d\Gamma_A e^{(-H_A/k_B T)} \quad (2)$$

with  $N_A$  set equal to the number of atoms in A and  $H_A$  is the Hamiltonian of the isolated molecule A, and the volume element  $d\Gamma_A$  is such that A remains in a single electronic state. The volume elements are restricted such that the pertinent center-of-mass is confined to a unit volume. The partition function  $Q_B$  is defined in a similar manner. The partition function  $Q^\ddagger$  of the transition state per unit volume is a bit more complicated because it is not associated with a stable entity but rather that portion of phase space that the reactant system  $N = N_A + N_B$  must pass through to become products. For conventional transition state theory, the dividing surface is the saddle point region. With the reaction coordinate and its conjugate momentum separated out,  $Q^\ddagger$

$$Q^* = h^{-(3N-1)} \int d\Gamma e^{(-H^*/k_B T)} \quad (3)$$

is the integral over the remaining  $N-1$  coordinates and  $N-1$  conjugate momenta. The transition state has a fixed value of the reaction coordinate and thus one less degree of freedom than the reactants. Recall that the factors like  $h^{-3NA}$  are included in the classical partition function to give an approximate counting for quantum states. It is also assumed that all atoms are distinguishable.

If TST calculations are in error with respect to actual gas phase measurements, it is due to errors in the PES, errors in the theoretical formulation, or errors in the experiment. If transition state theory is in error relative to an exact classical dynamics calculation, it is because recrossing trajectories, which increase with energy in excess of the classical threshold, exist. This implies that classical TST provides an upper bound to the true classical rate coefficient, and this provides a variational criterion for TST, implying that one should choose the dividing transition state surface to minimize the reactant flux through it. Note that the variational criterion only exists with respect to the "true" classical rate coefficient calculated solely with classical mechanics with no quasi-classical considerations. In conventional TST, for a PES having a saddle point, the phase space dividing surface is chosen to be a function of only coordinates (momenta are excluded) and is located so that it passes through the saddle

point. The transition state is a plane determined by normal coordinate analysis of small vibrations around the saddle point with displacement along the reaction normal coordinate set equal to zero. Any other dividing surface is by definition a generalized transition state. Variational transition state theory is the name we apply to theory that uses the minimum flux (microcanonical) or maximum free energy of activation (canonical) criterion for locating the dividing surface. The minimum free energy criterion has been misinterpreted by Bunker and Pattengill (1968) to imply a minimum density of states criterion, and this does not yield the correct variational rate coefficient.

The best dividing surface for variational microcanonical TST for collinear atom-diatom reactions was determined by Pechukas (1976), Pollack and Pechukas (1978), and Sverdlik and Koepfel (1978). The dividing surface is a curve joining the two equipotentials that bound the classically allowed region of the coordinate plane. Candidate best dividing surfaces are curves traced out by classical trajectories vibrating between the two equipotentials. If there is only one such vibrational energy, then that path is automatically the best dividing surface. If there is more than one, the one with less flux associated with it is best.

When the potential expands in either direction away from the saddle point, the best choice of the transition state dividing surface is in the vicinity of the saddle point. What is the optimum dividing surface for more complicated reactions in three dimensions? Considerable research on variational TST for

atom/molecule reactions in three dimensions and for some molecule/molecule reactions has been pioneered by Truhlar and Garrett. They provide considerable information regarding the choice of dividing surface in the review articles by Garrett and Truhlar (1984) and Truhlar, Isaacson, and Garrett (1985).

Our discussion has been confined to a discussion of classical transition state theory to illustrate to the reader the theoretical foundations of the theory, and the limits of applicability, and to clear up possible misconceptions. The next question to address is the "how to" issue--how does one calculate rate coefficients using transition state theory? The most popular approach is to perform a type of hybrid quantum calculation. In the quantization of conventional transition state theory we make three assumptions. First we assume that motion associated with the reaction coordinate is separable. Accordingly to Johnston (1966), this approximation is reasonable as long as the potential energy surface near the saddlepoint is well-approximated by a quadratic function over an area whose linear dimensions are much larger than the de Broglie wavelength. Second, we assume that the reaction coordinate motion can be treated classically and that the energy levels associated with the remaining bound degrees of freedom of the transition state and those of the reactant are quantized. Third, we frequently assume that the rate coefficient can be multiplied by a transmission coefficient to correct for non-classical motion along the reaction coordinate. Quantum mechanically there is the possibility of tunneling through the saddle point barrier at energies below the classical

threshold and the possibility of reflection at energies above threshold.

When the hybrid quantum approach is used, transition state theory no longer provides as upper bound to the true quantal equilibrium rate coefficient for a given potential energy surface. There is no variational principle associated with a rate coefficient calculated in this manner. This is also not a true quantum mechanical approach because the fundamental assumption of TST violates the uncertainty principle by requiring that one simultaneously must specify the position and momentum along the reaction coordinate.

There are a number of approximations that are similar for both hybrid conventional and generalized transition state theories. Rule number one is to always know what the zero of energy is for the reactant partition state functions and for the transition state partition functions. Be internally consistent. If there is more than one reactant, a relative translational partition function per unit volume,  $Q_{A,B}^T$ , must be included. This, for three-dimensional motion, is

$$Q_{A,B}^T(T) = (2\pi\mu k_B T/h^2)^{3/2} \quad (4)$$

where  $\mu$  is the reduced mass, and is not a function of the reaction coordinate and hence is the same for conventional and generalized transition states. The same is true for electronic partition functions, but one must remember that the electronic energy

is measured relative to the zero of energy, which for the transition state is the transition state energy. The expression for the electronic partition function for species A is

$$Q_A^e(T) = \sum_{\alpha} d_{A,\alpha} e^{(-\epsilon_{A,\alpha}/k_B T)} \quad (5)$$

where the degeneracy (multiplicity) is  $d_{A,\alpha}$  and the energy of the state  $E_{A,\alpha}$  is measured relative to the ground electronic state, which is the zero of energy. It is also important to include the electronic partition function for atoms.

The saddle point geometry and frequencies must be determined to evaluate rotational and vibrational partition functions in conventional transition state theory. The imaginary frequency associated with the reaction coordinate motion is required to correct reaction coordinate motion for non-classical effects, which frequently are not large for temperatures of interest in combustion studies. Truhlar et al. have given excellent descriptions of techniques for locating generalized transition states. Once transition states are defined, the moments of inertia and vibrational frequencies must be evaluated for the specific value of the reaction coordinate. Then the rotational partition function for non-linear molecules A (assuming temperature to be in the range appropriate for combustion) is

$$Q_A^R = \left(\frac{\pi}{\sigma}\right)^{1/2} (2k_B T / h^2)^{3/2} (I_A I_B I_C)^{1/2} \quad (6)$$



where  $I_A$ ,  $I_B$ , and  $I_C$  are the equilibrium moments of inertia associated with the principal axis of rotation. This formula holds for spherical top ( $I_A=I_B=I_C$ ) or symmetric top molecules (when  $I_A < I_B=I_C$  or  $I_A=I_B < I_C$ ). The rotational partition function for a linear molecule is

$$Q_A^R = \frac{1}{\sigma} (2k_B T / \hbar^2) I \quad (7)$$

The symmetry number,  $\alpha$ , must be included with the rotational partition functions and this corrects for repeated counting of indistinguishable configurations in the classical phase integral. The vibrational partition function for a molecule with  $m$  normal modes is

$$Q_A^V = \prod_m e^{(-hc\tilde{\nu}_m/2k_B T)} (1 - e^{-hc\tilde{\nu}_m/k_B T}) \quad (8)$$

The zero of energy is assumed to be located at the bottom of the potential well where the internuclear separation is the equilibrium value,  $\tilde{\nu}_m$  is the vibrational frequency in  $\text{cm}^{-1}$  for the  $m^{\text{th}}$  oscillator, and  $c$  is the velocity of light. Anharmonic effects become important and neglecting them results in rate coefficients that are too large. In particular, for stretching modes, anharmonic effects are especially important for tight transition states at low temperatures. For bends, anharmonicity becomes

important at higher temperatures. Anharmonic effects can be accounted for using the Pitzer-Gwinn (1942) techniques (PGT). The PGT is based upon the idea that the ratio of anharmonic vibrational partition function to the harmonic value is given correctly at the low and high temperature limits and assuming that the ratio is correct at all temperatures.

### **B. Symmetry in Rate Coefficient Calculations**

Symmetry in rate coefficient calculations must be properly accounted for. Although this section is concerned with TST calculations, the symmetry corrections described here are relevant to dynamics calculations as well. The literature is wrought with controversy over this subject, and many of the standard texts in chemical kinetics are in error. Two papers describe symmetry corrections correctly, and these are by Pollack and Pechukas (1978) and Coulson (1978), and they should be read because they clarify the misconceptions and capture the essence of the problem. Briefly, nuclear spin degeneracy can be ignored because nuclei are the same in the transition state as in the reactants and product and the degeneracies cancel. Symmetry numbers should be used rather than reaction path degeneracies or statistical factors. Rotational partition functions should be divided by molecular symmetry numbers to account for the effect of quantum statistics. Symmetry numbers should appear in classical and quantum partition functions. Symmetry numbers also should be used for the rotational partition functions of the

transition state. Pechukas (1976 and 1981) and Metiu et al. (1974) provide an excellent discussion of reaction path symmetry which should be used as input when transition state properties are deduced semi-empirically. For conventional transition state theory, the symmetry of the transition state is limited to the joint symmetries of the reactant and product unless they are physically indistinguishable or symmetry related, i.e., optical isomers. For the exceptional cases noted, the transition state may have additional symmetries.

### C. Tunneling Corrections

Frequently transition state calculations include a tunneling correction which is a quantum mechanical correction to reaction coordinate motion. The tunnel effect is the name given to the to describe the entire quantum mechanical barrier crossing problem which includes barrier penetration or transmission for energies less than the barrier height and barrier reflection corrections for energies which are greater. Tunneling is usually important for light atoms and molecules at low temperatures, and for combustion applications may be important for reactions involving H atoms.

Johnston (1966) very carefully gives some general criteria for assessing the nature of quantum effects on reaction coordinate motion. He suggests that one perform a normal coordinate analysis along the reaction coordinate to obtain the mass  $m^*$  and then compute the Boltzmann average de Broglie

wavelength as

$$\Lambda^* = (h^2/2\pi m^* k_B T)^{1/2} \quad (9)$$

If the potential is flat over distances large compared to  $\Lambda^*$  then the reaction coordinate motion is considered classical. If it is flat over a distance small compared with  $\Lambda^*$ , then the reaction coordinate motion is non-separable and very difficult to treat. If the potential energy surface near the saddlepoint is well approximated as a quadratic function over an area whose linear dimensions are comparable, then the motion is separable but not classical and requires a tunneling correction.

There are many approaches to treating tunneling. An especially fine description is given in the review paper by Truhlar et al. (1985). Here we will mention the more commonly used approaches. The imaginary frequency associated with reaction co-ordinate motion must be determined for all these corrections.

The simplest and most common method of approximating tunneling is the semiclassical Wigner (1932) approximation

$$\kappa^W = 1 + \frac{1}{24} \left| \frac{\hbar \nu^*}{kT} \right|^2 \quad (10)$$

This tunneling correction is the transmission coefficient obtained by Boltzmann averaging the semi-classical barrier pene-

tration probabilities. The symbol  $w^\ddagger$  is the imaginary frequency associated with reaction coordinate motion. For this approximation to be valid, tunneling contributions must come entirely from the saddle point region implying that transverse vibrations do not vary appreciably and the potential along the reaction path is well approximated by an inverted parabola. Wigner corrections are most likely to be valid when the correction is small and less than 2.

Other commonly used tunneling corrections are based upon assumptions of barrier shapes in the saddle point region. Two very common barriers which are worth noting are parabolic and Eckart barriers. The assumption of a fixed shape barrier sometimes leads to large errors in the tunneling correction. There is an excellent discussion of Eckart and Parabolic barriers in Chapter 2 of Johnston's book and in the paper by Truhlar and Kuppermann (1971). For those interested in using an Eckart-type correction, Eq. (2.22) in Johnston's book is in error. The  $2\pi^2$  should be replaced by  $4\pi^2$ .

#### D. Complex Reactions

Statistical theory for complex reactions is less secure, in its dynamical foundations, than the transition state theory of direct reactions. Many important combustion reactions have multiple transition states, and the dynamics in the region between the outermost transition states are very often complex rather than direct. In complex reactions, the variational

principle associated with classical transition state theory may fail. Assuming that potential wells are deep enough for at least one bound state, reactions along pathways with multiple transition states result in complex formation at some fixed energy. Formation of the complex is a bimolecular reaction and its dissociation is a unimolecular one. There is much confusion in the literature about complex reactions, and much of it concerns the boundedness of the calculated rate coefficient. Pollack et al. (1980), Pollack and Child (1980), and Pechukas and Pollack (1977) have investigated the bounds associated with rate coefficients of complex reactions in detail, and are careful in discussing the constraints on the reactive system that must occur for the rate coefficient to be bounded.

The importance of complex reactions to combustion is illustrated by a set of rate coefficient calculations by Miller and colleagues, Miller et al. (1986), Miller and Melius (1986 and 1988). The BAC-MP4 method of Melius and Binkley (1984 and 1985) is used to calculate transition state geometries, vibrational frequencies, and enthalpies for each of the molecular species. Rate coefficients were calculated using a hierarchy of statistical approximations: canonical theory, canonical theory with a Wigner tunneling correction, microcanonical theory, microcanonical theory with angular momentum conservation, and microcanonical theory with angular momentum conservation with one dimensional tunneling. The tunneling correction for the microcanonical rate coefficients was determined as recommended by Miller (1979), whereby a quantum mechanical flux through the

dividing surface was approximated. Three assumptions were invoked to calculate the rate coefficients: the RRKM or strong coupling assumption, the transition state theory assumption of no-crossing of the final transition state leading to products, and steady state approximations for all complexes. Rate coefficients and branching ratios were calculated for the product channels of the reactions  $O + HCN$ ,  $OH + HCN$ , and  $OH + C_2H_2$ .

#### IV. MOLECULAR DYNAMICS

Schrodinger's equation is the only rigorous and valid approach for treating dynamics and reactivity on the atomic scale. Three dimensional exact quantum mechanical calculations of reactivity have been performed to study reactivity and energy exchange in  $H + H_2$  and its isotopic analogs, and these calculations are described by Walker and Light (1980), and Conner (1979). Currently, there is substantial research activity ( see for example, Pack and Parker (1989), Pack et al. (1987), Zhang and Miller (1987), and Zhang et al. (1988)) devoted to improving quantum mechanical calculations on the  $H + H_2$  system, and one can expect exact calculations to be performed on the  $F + H_2$  system in the near future. The developments in the field of molecular quantum dynamics are occurring at an exciting pace and they will provide some intriguing results which should stimulate further progress in PES construction and in state-to-state experiments measuring reaction attributes.

Quantum mechanical calculations are not practical for

determining thermal rate coefficients for combustion applications due to the higher energies associated with combustion and the concomitantly large number of coupled opened and closed channels that must be included in the wavefunction expansion. Moreover, quantum effects: tunneling, interference phenomena, and resonances are not likely to be important for most reactions at temperatures in excess of 1000 K. For predicting ignition characteristics at temperatures lower than 1000 K, quantum effects, although small, may be important. The effects of combustion (i.e., higher energies and higher masses) tend to decrease the de Broglie wavelength

$$\lambda = \frac{h}{p} \quad (11)$$

of the reactive system, where  $p$  is the momentum. As  $\lambda$  decreases to a size smaller than the distance over which the potential changes significantly, the system can be treated classically. Furthermore, the amount of averaging necessary to compute a thermal rate coefficient from state-to-state ones is a smoothing process which washes out much of the quantum behavior while retaining the features produced by a classical calculation. Quantum mechanics are necessary for the calculation of transition probabilities for reactions where the energy is close to but less than the barrier height (for so-called classically forbidden processes) and for describing interference phenomena.



A very popular and often quite accurate approach to treating reactions between an atom and a molecule and between two molecules is classical mechanics. Hamilton's equations

$$\frac{\partial H}{\partial p} = \dot{q}_i \quad \frac{\partial H}{\partial q} = -\dot{p}_i \quad (12)$$

must be solved where  $H(p, q)$  is the system Hamiltonian and  $q_i$  and  $p_i$  are the  $i$ -th coordinate and momentum and the dot indicates the time derivative. For a given PES and selected values of  $p_i$  and  $q_i$  at some initial time, the classical laws of motion completely define the subsequent dynamical behavior of a system and the classical path or trajectory of the collision can be calculated by numerically integrating the  $6N-6$  differential equations (Hamilton's equations) where  $N$  is the number of atoms in the system. The calculation is called quasi-classical if the molecule is initially given energy which corresponds to a quantum mechanical eigenenergy. Classical trajectory calculations are useful because they yield reaction cross sections, angular distributions, product energy and angular momentum distributions, final energy and angular momentum distributions in unreactive reactants, and they also provide insight into the character of the reactions.

There are also semi-classical approaches to studying reactive collisions. Semiclassical treatments use real and complex valued solutions of Hamilton's equations to construct an asymptotic solution of Schrodinger's equation. Semiclassical

approaches will not be discussed further.

The classic paper in the field of quasiclassical dynamics is due to Karplus et al. (1965) and it describes their calculations on the  $H + H_2$  reaction. There are two excellent reviews that describe how to perform a quasiclassical calculation of a rate coefficient. The first of these is written by Truhlar and Muckerman (1979) and is concerned with all aspects of quasiclassical calculations for the system  $A + BC$ . The second is by Porter and Raff (1976) and it covers the calculation of reaction attributes by the quasiclassical method for  $A + B$ ,  $A + BC$ ,  $AB + CD$ , and  $A + BCD$  collisions, and is particularly good in describing the selection of initial conditions. Reviews have also been written by Conner (1979) and by Walker and Light (1980) and these are especially useful because they survey work which uses dynamical approaches to studies of reactivity and energy transfer. The books by Bernstein (1979) and Levine and Bernstein (1987), and the two volumes edited by Miller (1976) are highly recommended as sources describing the molecular dynamics approach to rate coefficient calculations.

There are three parts to a molecular dynamics calculation and these are 1) specification of the initial conditions, 2) integration of Hamilton's equations, and 3) determination of the molecular properties at the end of the collision when the collision partners are no longer interacting. To average over an ensemble of trajectories,  $N$  trajectories, each belonging to the same "state," must be computed. The initial values of the non-consequential (i.e., those not crucial to defining the "state.")

coordinates and momenta are selected according to their distribution in phase space at random. The phase space or ensemble average is usually accomplished by Monte Carlo Techniques. The number of trajectories required for convergence of the ensemble average depends on the precision required in the calculation of the variable of interest. Important work on improving sampling to render more rapid convergence has been performed by Faist et al. (1978) and Muckerman and Faist (1979).

Specification of initial conditions is relatively straightforward for  $A + B$ ,  $A + BC$ , and  $AB + CD$ , and is more complicated for  $A + BCD$ . The Porter and Raff paper gives an excellent discussion of this. There are, however, a number of things to be careful of and these will be described. In the quasiclassical approximation, the molecule is initially given energy corresponding to a quantum mechanical eigenenergy. It is important to separate out the rotational and vibrational contributions to the energy. For diatomic collisions, one frequently uses a rigid rotator Morse oscillator model for the diatom and equates the energy of this to a spectroscopically derived value of the energy for a given value of  $v$ , the vibrational quantum number and  $J$ , the rotational quantum number. The turning points,  $R^+$  and  $R^-$ , are solved for, and these and the angular momentum  $J$  are used to describe the initial state of the molecule. However, in order to separate rotational and vibrational motion and to determine the amount of energy in each degree of freedom, one must average over the vibrational period using the following equation

$$\epsilon_{\text{rot}} = \min \left\{ V_D(r) + \frac{J_r \cdot J_r}{2\mu r^2} \right\} - V_D(r_e) \quad (13)$$

where  $\epsilon_{\text{rot}}$  is the average rotational energy,  $V_D(r)$  is the diatomic potential energy (usually a Morse potential),  $r$  is the internuclear separation. The subscript  $e$  denotes the equilibrium separation. The vibrational energy is obtained from the total molecular energy, which is the quantum mechanical eigenenergy, minus the calculated average rotational energy. When the molecule is a triatomic or greater, the situation is more complex because the Coriolis interaction couples the vibrational and rotational degrees of freedom. Sometimes it is not necessary to know the individual contributions. In their studies of the unimolecular dissociation of  $\text{HO}_2$ , Miller and Brown (1982) and Brown and Miller (1984) analyzed various techniques of orthant sampling used to determine initial values for molecular coordinates and momenta when total molecular energy and angular momenta are specified. For studies with triatomics, the most efficient co-ordinate system for investigating collisions is the space-fixed frame. However, when a more rigorous separation between rotational and vibrational motion is sought, the individual contributions to the energy cannot be separated using the space-fixed frame because of the Coriolis interaction. Suzukawa et al. (1979) given a good description of how one separates vibrational and rotational motion in triatomics. Energy and angular momentum are deposited in the molecule, and a transformation to a body-fixed frame satisfying the Eckart condition is performed. The Eckart condi-

tions define a convenient molecule-fixed axis system in which the rotation-vibration interaction of the molecule become equal to zero when the molecule is in its equilibrium condition.

#### V. SENSITIVITY ANALYSIS

An important question to answer in rate coefficient calculations is: How sensitive is the calculated rate coefficient to the potential energy surface? The answer, of course, depends on the method used to calculate the rate coefficient, the particular identity of the reactants, and the initial states of the reactants. Frequently, answers to this question have been sought by attempting to systematically vary features of the potential energy surface and determining the concomitant effect on the rate coefficient. There are endless variations (many of which are non-unique) that can be attempted and it is quite difficult to organize the results of such an analysis in a very systematic manner. Isotopic substitution has also been used to gain insight into how different general parts of the PES affect observables. This is useful because the PES is the same for all the isotopes, but for each of them the dynamics probes different regions of the potential.

A more systematic approach to the problem of determining how structure in the PES maps itself into the observables associated with a reacting system is provided by functional sensitivity analysis. The combustion community is familiar with sensitivity analysis through its use in the detailed modeling of species and

temperature profiles in flames and from modeling of temporal species profiles in well stirred reactors. this approach has been pioneered by Rabitz (1985) and his colleagues. In these applications, parametric sensitivity analysis frequently has been employed since the rate and transport coefficients are usually thought of as discreet parameters. In rate coefficient calculations, the PES is actually a function of  $3N-5$  or  $3N-6$  coordinates despite the fact that it may be parametrized in numerical calculations. The PES is treated as a function and functional sensitivity analysis can be used to determine how the observables associated with the reacting system depend on features of the PES. In using functional sensitivity analysis, one calculates the gradient of an observable with respect to a perturbation to the potential at a particular point in configuration space. The sensitivity function directly indicates how a perturbation in the potential will be translated into a change in the observable. The application of functional sensitivity analysis to classical dynamics of molecular systems was initiated by Judson and Rabitz (1987). Functional sensitivity analysis has been used to treat inelastic collisions in the  $H_2 + H_2$  system and its isotopic analogs by Judson et al. (1989). Judson and Rabitz (1989) also used functional sensitivity analysis to investigate reactivity in the collinear  $F + H_2$  system. In both these calculations, classical mechanics has been used to treat the dynamics. Both these calculations have shown that the physics governing collisions in these problems are complex and that there is a highly structured relationship

between details in the potential energy system and the observables. The highly structured nature of the sensitivities implies that there are localized regions of the potential which are especially important to the dynamics. These localized regions are those very regions where a high density of ab initio points should be calculated and where minimal error should be introduced by fitting procedures. Although studies of this type are still in the nascent stage, sensitivity analysis provides a set of powerful tools to analyze models for their physical content and mathematical behavior. It provides a means in all its applications to probe the interrelationship between input (PES) and output (observables associated with the reacting system) functions. The development and application of functional sensitivity analysis to studies of reactive scattering will provide exciting new kinds of information regarding the mechanisms of reactivity on the microscopic level.

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## REFERENCES

1. Benson, Sidney W.; (1976); **Thermochemical Kinetics, Second Edition**; New York: John Wiley & Sons.
2. Bernstein, R. B.; (1979); **Atom-Molecule Collision Theory, A Guide for the Experimentalist.**; New York and London: Plenum.
3. Bernstein, R. B.; (1982); **Chemical Dynamics via Molecular Beam and Laser Techniques**; New York: Oxford University Press.
4. Bowman, Joel M. and Aron Kuppermann; (1975); **Chem. Phys. Let.**; 34; 523.
5. Brown, Nancy J. and James A. Miller; (1984); **J. Chem. Phys.**; 80; 5568.
6. Brown, N. J. and O. Rashed; (1986); **J. Chem. Phys.**; 85; 4348.
7. Bunker, Don L.; (1966); **Theory of Elementary Gas Reaction Rates**; Oxford: Pergamon Press.
8. Bunker, Don L. and M. Pattengill; (1968); **J. Chem. Phys.**; 48; 772.
9. Connor, J. N. L.; (1979); **Computer Phys. Comm.**; 17; 117.
10. Coulson, D. R.; (1978); **J. Am. Chem. Soc.**; 100; 2992.
11. Dunning, Thom H. Jr., Lawrence B. Harding, Raymond A. Bair, Robert A. Eades and Ron L. Shepard; (1986); **J. Phys. Chem.**; 90; 344.
12. Dunning, Thom H. Jr., Lawrence B. Harding; Albert F. Wagner, George C. Schatz and Joel M. Bowman; (1988); **Science**; 240; 453.
13. Eyring, H., S. H. Lin and S. M. Lin; (1980); **Basic Chemical Kinetics**; New York: John Wiley & Sons.
14. Eyring, H., J. Walter and G. E. Kimball; (1944); **Quantum Chemistry**; New York: Wiley.
15. Faist, M. B., J. T. Muckerman and F. E. Schubert; (1978); **J. Chem. Phys.**; 69; 4087.
16. Forst, Wendell; (1973); **Theory of Unimolecular Reactions**; New York: Academic Press.

17. Fukui, K., S. Kato and H. Fujimoto; (1975); **J. Amer. Chem. Soc.**; 97; 1.
18. Geiger, Lynn C. and Schatz, George C.; (1985); **Chem. Phys. Lett.**; 114; 520.
19. Glasstone, Samuel, Keith J. Laidler and Henry Eyring; (1941); **The Theory of Rate Processes**; New York: McGraw-Hill Book Company, Inc.
20. Golden, D. M. and C. W. Larson; (1984); **Twentieth Symposium (International) on Combustion**; 595.
21. Ho, P., M. E. Coltrin, J. S. Binkley and C. F. Melius; (1985); **J. Am. Chem. Soc.**; 89; 4647.
22. Johnston, Harold S.; (1966); **Gas Phase Reaction Rate Theory**; New York: Ronald Press Company.
23. Judson, R. S. and H. Rabitz; (1989); **A Classical Functional Sensitivity Analysis of Coplanar Inelastic Scattering for  $H_2 + H_2$  and its Isotopic Analogs** ; **J. Phys. Chem.** 93; 2400.
24. Judson, Richard S. and Herschel Rabitz; (1987); **J. Chem. Phys.**; 86; 3886.
25. Judson, R. S. and H. Rabitz; (1989); **J. Chem. Phys.**; 90; 2283.
26. Karplus, M., R. N. Porter and R. D. Sharma; (1965); **J. Chem. Phys.**; 43; 3259.
27. Laidler, K. J.; (1969); **Theories of Chemical Reaction Rates**; New York: McGraw-Hill.
28. Laidler, K. J. and M. C. King; (1983); **J. Phys. Chem.**; 87; 2657.
29. Levine, Raphael D.; (1969); **Quantum Mechanics of Molecular Rate Processes**; Oxford: Clarendon Press.
30. Levine, Raphael D.; (1969); **Quantum Mechanics of Molecular Rate Processes**; London: Oxford University Press.
31. Levine, Raphael and Richard B. Bernstein; (1987); **Molecular Reaction Dynamics and Chemical Reactivity**; New York: Oxford University Press.
32. Melius, C. F. and J. S. Binkley; (1984); **ACS Combustion Symposium**; 103.

33. Melius, C. F. and J. S. Binkley; (1985); **Twentieth Symposium (International) on Combustion**; 575.
34. Metiu, H., J. Ross, R. Silbey and T. F. George; (1974); **J. Chem. Phys.**; 61; 3200.
35. Miller, James A.; (1981); **J. Chem. Phys.**; 75; 5349.
36. Miller, James A. and Nancy J. Brown; (1982); **J. Phys. Chem.**; 86; 772.
37. Miller, James A. and Carl F. Melius; (1988); Accepted for publication in **Twenty-second Symposium (International) on Combustion**.
38. Miller, James A. and Carl F. Melius; (1988); **Twenty-first Symposium (International) on Combustion**; 919.
39. Miller, J. A., C. Parrish and N. J. Brown; (1986); **J. Phys. Chem.**; 90; 3339.
40. Miller, W. H.; (1976); **Dynamics of Molecular Collisions**; Parts A & B; New York and London: Plenum.
41. Miller, William H.; (1979); **J. Am. Chem. Soc.**; 101; 6810.
42. Miller, William H.; (1976); **Accounts Chem. Res.**; 9; 306.
43. Miller, William H.; (1976); **Dynamics of Molecular Collisions, Modern Theoretical Chemistry, Volumes 1 and 2**; New York: Plenum Press.
44. Miller, William H.; (1974); **J. Chem. Phys.**; 61; 1823.
45. Miller, W. H., N. C. Handy and J. E. Adams; (1980); **J. Chem. Phys.**; 72; 99.
46. Muckerman, J. T. and M. B. Faist; (1979); **J. Phys. Chem.**; 83; 79.
47. Murrell, J. N., S. Carter, S. C. Farantos, P. Huxley and A. J. C. Varandas; (1984); **Molecular Potential Energy Functions**; New York: John Wiley & Sons.
48. Nikitin, E. E.; (1974); **Theory of Elementary Atomic and Molecular Processes in Gases**; London: Oxford University Press.
49. Pack, R. T. and G. A. Parker; (1987); **J. Chem. Phys.**; 87; 3888.
50. Pack, Russell T. and Gregory A. Parker; (1989); **J. Chem. Phys.**; 90; 3511.

51. Page, M. and B. Lengsfeld; (1989); **Ab Initio Quantum Calculation**; in this volume.
52. Parker, G. A., R. T. Pack, B.J. Archer and R. B. Walker; (1987); **Chem. Phys. Lett.**; 137; 564.
53. Pechukas, Philip; (1981); **Ann. Rev. Phys. Chem.**; 32; 159.
54. Pechukas, Philip; (1976); **"Statistical Approximation in Collision Theory"** in **Dynamics of Molecular Collisions, Part B**; edited by William H. Miller, New York: Plenum Press, 269.
55. Pechukas, Philip and E. Pollak; (1979); **J. Chem. Phys.**; 71; 2062.
56. Pechukas, Philip and E. Pollak; (1977); **J. Chem. Phys.**; 67; 5976.
57. Pitzer, K. S. and W. D. Gwinn; (1942); **J. Chem. Phys.**; 10; 428.
58. Pollak, E. and M. S. Child; (1980); **J. Chem. Phys.**; 73; 4373.
59. Pollak, E., M. S. Child and P. Pechukas; (1980); **J. Chem. Phys.**; 72; 1669.
60. Pollak, E. and P. Pechukas; (1978); **J. Am. Chem. Soc.**; 100; 2984.
61. Porter, R. N. and M. Karplus; (1964); **J. Chem. Phys.**; 40; 1105.
62. Porter, R. N. and L. M. Raff; (1976); **"Classical Trajectory Methods in Molecular Collisions"** in **Dynamics of Molecular Collisions, Part B** edited by William H. Miller, New York: Plenum Press, 1.
63. Rabitz, Herschel; (1985); **"Frontiers in Applied Mathematics"**; Ed. J. Buckmaster; SIAM; Philadelphia.
64. Rabitz, Herschel; (1987); **Chem. Rev.**; 87; 101.
65. Silver, D. M. and N. J. Brown; (1980); **J. Chem. Phys.**; 72; 3859.
66. Simons, Jack; (1983); **Energetic Principles of Chemical Reactions**; Boston: Jones and Bartlett Publishers, Inc.
67. Smith, Ian W. M.; (1980); **Kinetics and Dynamics of Elementary Gas Reactions**; London: Butterworths.

68. Suzukawa, H. H. Jr., M. Wolfsberg and D. L. Thompson;  
(1978); **J. Chem. Phys.**; 68; 455.
69. Sverdlik, D. I. and G. W. Koepl; (1978); **Chem. Phys. Lett.**;  
59; 449.
70. Truhlar, Donald G. and Bruce C. Garrett; (1984); **Ann. Rev.**  
**Phys. Chem.**; 35; 159.
71. Truhlar, Donald G., Alan D. Isaacson and Bruce C.  
Garrett; (1985); **Generalized Transition State Theory in**  
**The Theory of Chemical Reaction Dynamics**; 4; 65.
72. Truhlar, Donald G. and Aron Kuppermann; (1971); **J. Amer.**  
**Chem. Soc.**; 93; 1840.
73. Truhlar, D. G. and J. T. Muckerman; (1979); "Reactive  
**Scattering Cross Sections III: Quasiclassical and**  
**Semiclassical Methods**" in **Atom-Molecule Collision Theory, A**  
**Guide for the Experimentalist.**; Edited by R. B. Bernstein;  
New York and London: Plenum; 505-566.
74. Walker, Robert B. and John C. Light; (1980); **Ann Rev. Phys.**  
**Chem.**; 31; 401.
75. Webster, Frank and J. C. Light; (1989); **J. Chem. Phys.**; 90;  
265.
76. Webster, Frank and J. C. Light; (1989); **J. Chem. Phys.**; 90;  
300.
77. Weston, R. E., Jr. and Schwartz, H. A.; (1972); **Chemical**  
**Kinetics**; New Jersey: Prentice Hall.
78. Whetten, Robert L., Gregory S. Ezra and Edward R. Grant;  
(1985); **Ann Rev. Phys. Chem.**; 36; 277.
79. Wigner, E. P.; (1932); **Z. Phys. Chem. Abt. B**; 19; 203.
80. Wright, J. S. and S. K. Gray; (1978); **J. Chem. Phys.**; 69;  
67.
81. Zhang, J. Z. H. and W. H. Miller; (1987); **Chem. Phys. Lett.**;  
140; 329.

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