16

Reactive Scattering Cross Sections III: Quasiclassical and Semiclassical Methods

Donald G. Truhlar and James T. Muckerman

1. Introduction

Classical trajectory methods for calculating inelastic scattering cross sections are covered in earlier chapters of this book, especially Chapters 10 and 12. This chapter covers the extension of this technique to treat reactive scattering. The first question which must be answered in a classical trajectory study of a reactive system is whether one should be using this method at all. Classical trajectory studies are useful not just because they yield reaction cross sections, angular distributions, reactivity as a function of initial and final energy distribution, and other observable reaction attributes, but also for the insight they may offer into the actual reaction event. One may look at the atomic motions in representative trajectories, and one may calculate such nonobservables as opacity functions (probability of reaction as a function of impact parameter) and dependence on features of the potential energy surface. But one must be careful not to overinterpret the reaction by a trajectory study. Because many reaction attributes depend sensitively on quantitative and qualitative features of the potential energy surfaces which are not quantitatively understood, one must be cautious about believing that the dynamical details of a particular trajectory calculation are in general accord with reality. Trajectory calculations are discussed from this point of view in Chapter 18 of this book.

Donald G. Truhlar • Chemical Dynamics Laboratory, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. James T. Muckerman • Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973.

Chapter 18 also discusses some simple theories which sometimes give as much reliable information as a full trajectory calculation and should be considered as alternative or complementary theoretical approaches.

Another consideration in deciding to use trajectory methods is the accuracy of classical mechanics. It is well known that quantum effects (e.g., tunneling and interference) play a role, and in some instances an extremely important one, in molecular collisions, so it is worthwhile to provide a few guidelines about when to expect a good first approximation to the nuclear motion problem from the quasiclassical trajectory method. These are as follows:

(i) The quasiclassical trajectory method becomes more reliable the larger the masses of the nuclei and the higher the energy in each degree of freedom of the system (within the validity of the Born–Oppenheimer approximation). This follows from the fact that the de Broglie wavelength becomes smaller as the momentum is increased. When the de Broglie wavelengths for motion along all generalized coordinates become smaller than the distances over which the potential energy changes rapidly as a function of those coordinates, the wave (quantum) nature of the internuclear motion need not be considered and it may be treated classically.

(ii) The quasiclassical method yields more reliable results when the desired information is highly averaged. This property is related to the Ehrenfest relations.[1] These relations show that the quantum-mechanical expectation values of position $\langle x \rangle$ and momentum $\langle p \rangle$ satisfy the classical equations of motion for the average potential $\langle V(x) \rangle$. But classical mechanics assumes they are governed by the potential $V(\langle x \rangle)$ at the average position. Thus the validity of classical mechanics requires that the spread Δx of coordinates covered by a representative wave packet be small. Unfortunately, wave packets representing atoms and molecules at chemical energies may have considerable spread. But classical mechanics may still be accurate for sufficiently averaged reaction attributes.

(iii) When the total energy of reactants is comparable to or below the minimum potential energy barrier separating reactants from products (i.e., low-energy collisions of internally "cold" molecules), trajectory methods may seriously underestimate reaction probabilities. The use of the method (without semiclassical corrections for classically forbidden paths as discussed in Section 3.4) in such threshold regions where tunneling or its multidimensional analogs are important should be avoided.

(iv) The quasiclassical trajectory method, when used to calculate state-to-state reaction probabilities, will misestimate probabilities which are "classically forbidden" in the classical S matrix sense[2] (see Section 3.4). The method is not reliable for predicting small transition probabilities.

(v) The quasiclassical trajectory method is not appropriate for predicting resonance features or other interference phenomena.

Once it has been determined that the quasiclassical trajectory method

is applicable and useful for a given system, one must determine the number of relevant potential surfaces as discussed in Chapter 18 and obtain analytic representations for them by, e.g., the methods of Chapters 2 and 3. If more than one surface is important, one must also characterize the non-adiabatic coupling terms. Trajectory techniques, like other theories of chemical reactions, have been applied most extensively to single-surface reactions, and these are emphasized in these chapters. The next questions which arise are: (i) How does one correspond the initial and final conditions of the trajectory to real (quantized) initial and final collision conditions? (ii) How does one minimize the errors in the classical treatment? Question (ii) may be restated: How does one incorporate semiclassical corrections? The answers to questions (i) and (ii) are closely related. The most straightforward way to incorporate quantized initial conditions is called the quasiclassical trajectory technique. This is explained in Section 2 of this chapter. This is the largest section of this chapter. It presents working equations for the quasiclassical trajectory method as applied to single-surface reactions of atoms with diatomic molecules.* The literature already contains several descriptions (mostly incomplete) of various techniques and equations for classical or quasiclassical forward trajectory calculations on three-dimensional atom–diatom reactions.[3-29] Rather than review all the computational schemes which have been used for various aspects of such calculations or compare the techniques used by various workers, we mainly present one set of approaches which we recommend as efficient and more-or-less optimal. However, we do present more than one approach to the calculation of product distributions since the optimum method may depend on the problem of interest.

The methods discussed in Section 2 are the ones we recommend in general for practical applications, but there are some problems where alternative correspondence methods for initial and final quantized degrees of freedom may be required or desirable. Section 3 presents a brief discussion of such alternative approaches to this correspondence.

Trajectory methods for studying multisurface reactions are discussed briefly in Chapters 13 and 18. We discuss some computational aspects of these methods in Section 4.

2. Quasiclassical Trajectory Method

The quasiclassical trajectory method assumes that each of the nuclei comprising a chemical system moves according to the laws of classical mechanics in the force field arising from the adiabatic electronic energy of

---

* Many of the techniques in this chapter are also applicable to reactions of atoms with polyatomic molecules and to molecule–molecule reactions. Nevertheless, we restrict our explicit considerations to atom–diatom reactions.

the system. The method may also be extended (see Section 4) to cases where the Born–Oppenheimer separation of electronic and nuclear motion breaks down provided that such breakdown is confined to localized regions of configuration space. The term "quasiclassical" is used to denote the manner in which molecules are prepared before collision (i.e., the *initial conditions*). In the quasiclassical trajectory method, molecules are prepared in discrete internal energy states corresponding to the quantum states of the molecule. Once the trajectory is begun, this quantum restriction is relaxed so that the time evolution of the system is governed solely by classical mechanics. A similar "quantization" is often employed in the analysis of *product molecule* internal energy states.

In accordance with the above, this section first considers the calculation of a single trajectory for an A + BC collision corresponding to specified initial quantized rotational and vibrational energies and a fixed initial relative translational energy. Then we consider the calculation of reaction cross sections and rate constants from a batch or batches of such trajectories. Finally, we consider the calculation of other reaction attributes, such as distributions of final conditions of the products and reactivity as a function of initial conditions.

2.1. Equations of Motion

It is assumed in the present discussion that the potential energy function (hypersurface) is an analytic function of the three internuclear distances, i.e., $V \equiv V(R_1, R_2, R_3)$, where R_1, R_2, and R_3 are the AB, BC, and AC distances, respectively, during the A + BC collision.

The first step in setting up a trajectory calculation is to define a coordinate system in which to express the Hamiltonian for the system. It is convenient to choose as a *reference* coordinate system a space-fixed Cartesian system consisting of the nine coordinates $\mathbf{x} \equiv \{x_i; i = 1, \ldots, 9\}$ of the three nuclei, denoted A, B, and C, respectively, and the nine momenta $\mathbf{p}_x \equiv \{p_{x_i}; i = 1, \ldots, 9\}$ conjugate to these coordinates. The Hamiltonian in this reference coordinate system is[5]

$$H(\mathbf{x}, \mathbf{p}_x) = T(\mathbf{p}_x) + V[R_1(\mathbf{x}), R_2(\mathbf{x}), R_3(\mathbf{x})] \qquad (1a)$$

where

$$T(\mathbf{p}_x) = \sum_{i=1}^{3} \left(\frac{1}{2m_A} p_{x_i}^2 + \frac{1}{2m_B} p_{x_{i+3}}^2 + \frac{1}{2m_C} p_{x_{i+6}}^2 \right) \qquad (1b)$$

Hamilton's equations of motion[30] are

$$\dot{x}_i \equiv \frac{dx_i}{dt} = \frac{\partial H}{\partial p_{x_i}} = \frac{\partial T}{\partial p_{x_i}} \qquad (i = 1, \ldots, 9) \qquad (2a)$$

$$\dot{p}_{x_i} \equiv \frac{dp_{x_i}}{dt} = -\frac{\partial H}{\partial x_i} = -\frac{\partial V}{\partial x_i} = -\sum_{k=1}^{3} \frac{\partial V}{\partial R_k} \frac{\partial R_k}{\partial x_i} \qquad (i = 1, \ldots, 9) \quad (2b)$$

The three internuclear distances in terms of the reference coordinates are

$$R_1 \equiv R_{AB} = \left[\sum_{i=1}^{3} (x_i - x_{i+3})^2 \right]^{1/2} \tag{3a}$$

$$R_2 \equiv R_{BC} = \left[\sum_{i=1}^{3} (x_{i+3} - x_{i+6})^2 \right]^{1/2} \tag{3b}$$

$$R_3 \equiv R_{AC} = \left[\sum_{i=1}^{3} (x_i - x_{i+6})^2 \right]^{1/2} \tag{3c}$$

from which the required $\partial R_k / \partial x_i$ terms can readily be obtained. There are, of course, a total of 18 coupled first-order differential equations implied by equations (2a) and (2b).

It is indeed possible to carry out the entire trajectory calculation, including the specification of initial conditions, in this reference set of Cartesian coordinates. While it is usually convenient to transform the coordinate system as described below, it should be noted that it is not necessary to do so.

From equation (2b) it is seen that if the potential energy function is independent of some coordinate (i.e., the coordinate is *cyclic*), the momentum conjugate to that coordinate is a *constant of the motion* (independent of time). The elimination of any cyclic coordinate reduces the number of coupled equations which must be integrated to obtain each trajectory.

Anticipating that the coordinates of the center of mass of the entire system will prove to be cyclic, we wish to devise a new set of coordinates in which the three components of the position of the center of mass are three of the nine new coordinates. It would further prove convenient in the specification of initial conditions in A + BC to have internal coordinates corresponding to the displacement of A from the center of mass of the BC molecule. Hence we define[5]

$$q_i = x_{i+6} - x_{i+3} \qquad (i = 1, 2, 3) \tag{4a}$$

$$Q_i = x_i - \frac{1}{(m_B + m_C)} [m_B x_{i+3} + m_C x_{i+6}] \qquad (i = 1, 2, 3) \tag{4b}$$

$$S_i = \frac{1}{M} [m_A q_i + m_B q_{i+3} + m_C q_{i+6}] \qquad (i = 1, 2, 3) \tag{4c}$$

where $M \equiv m_A + m_B + m_C$, as our new system of *generalized coordinates*. These particular generalized coordinates for a three-body system are often called Jacobi coordinates. The coordinates in the three equations in equation (4) are called internal, relative, and center-of-mass coordinates, respectively.

The Hamiltonian can be obtained in terms of the generalized coordinates $\{q_i, p_i, Q_i, P_i, S_i, P_{S_i}; i = 1, 2, 3\}$, where p_i, P_i, and P_{S_i} are the momenta conjugate to q_i, Q_i, and S_i, respectively by employing the F_2-type

generator function[30]:

$$F_2(\mathbf{p}, \mathbf{P}, \mathbf{P}_S, \mathbf{q}, \mathbf{Q}, \mathbf{S}) = \sum_{j=1}^{3} \left[p_j q_j(\mathbf{x}) + P_j Q_j(\mathbf{x}) + P_{S_j} S_j(\mathbf{x}) \right] \tag{5}$$

Using equation (4) and the relation $p_{x_i} = (\partial F_2 / \partial x_i)$, one derives expressions for $p_{x_i}(\mathbf{p}, \mathbf{P}, \mathbf{P}_S)$ which are substituted into equation (1). The result is

$$H(\mathbf{q}, \mathbf{Q}, \mathbf{p}, \mathbf{P}, \mathbf{P}_S) = T(\mathbf{p}, \mathbf{P}, \mathbf{P}_S) + V[R_1(\mathbf{q}, \mathbf{Q}), R_2(\mathbf{q}, \mathbf{Q}), R_3(\mathbf{q}, \mathbf{Q})] \tag{6a}$$

$$T(\mathbf{p}, \mathbf{P}, \mathbf{P}_S) = \sum_{i=1}^{3} \left(\frac{1}{2\mu_{BC}} p_i^2 + \frac{1}{2\mu_{A,BC}} P_i^2 + \frac{1}{2M} P_{S_i}^2 \right) \tag{6b}$$

Here

$$\mu_{BC} \equiv m_B m_C / (m_B + m_C) \tag{7a}$$

and

$$\mu_{A,BC} \equiv m_A (m_B + m_C) / M \tag{7b}$$

are the *reduced masses* corresponding to internal and relative motion, respectively, and $\{R_i(\mathbf{q}, \mathbf{Q}); i = 1, 2, 3\}$ are given by[5]

$$R_1 = \left[\sum_{i=1}^{3} \left(\frac{m_C}{m_B + m_C} q_i + Q_i \right)^2 \right]^{1/2} \tag{8a}$$

$$R_2 = \left[\sum_{i=1}^{3} Q_i^2 \right]^{1/2} \tag{8b}$$

$$R_3 = \left[\sum_{i=1}^{3} \left(\frac{m_B}{m_B + m_C} q_i - Q_i \right)^2 \right]^{1/2} \tag{8c}$$

While the generator function method has the advantage of generality, the transformation of the kinetic energy to conjugate momenta of Jacobi coordinates can be achieved more simply by the mobile method.[31]

As was anticipated, the R_i are independent of S_1, S_2, and S_3, the coordinates of the center of mass. These coordinates are therefore cyclic and the conjugate momenta P_{S_1}, P_{S_2}, and P_{S_3} are constants of the motion. We may without loss of generality define the center of mass to be stationary (or, equivalently, define our coordinate system to move with the uniform motion of the center of mass) and delete the terms involving P_{S_1}, P_{S_2}, and P_{S_3} from the Hamiltonian. The resulting set of twelve Hamilton's equations is

$$\dot{q}_i = \frac{\partial H}{\partial p_i} = \frac{\partial T}{\partial p_i} \qquad (i = 1, 2, 3) \tag{9a}$$

$$\dot{Q}_i = \frac{\partial H}{\partial P_i} = \frac{\partial T}{\partial P_i} \qquad (i = 1, 2, 3) \tag{9b}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} = -\frac{\partial V}{\partial q_i} = -\sum_{k=1}^{3} \frac{\partial V}{\partial R_k} \frac{\partial R_k}{\partial q_i} \qquad (i = 1, 2, 3) \qquad (9c)$$

$$\dot{P}_i = -\frac{\partial H}{\partial Q_i} = -\frac{\partial V}{\partial Q_i} = -\sum_{k=1}^{3} \frac{\partial V}{\partial R_k} \frac{\partial R_k}{\partial Q_i} \qquad (i = 1, 2, 3) \qquad (9d)$$

where $\{R_i(\mathbf{q}, \mathbf{Q}); i = 1, 2, 3\}$ is given by equations (8). This is the usual form in which the equations of motion are integrated, although some workers[32,33] have found it convenient to use the equivalent second-order form obtained from Newton's or Lagrange's instead of Hamilton's equations of motion.

It is, of course, possible to reduce the number of equations even further by recognizing the total energy and total angular momentum (three components) as constants of the motion. This would reduce the number of equations from 12 to 8, but the form of the resulting equations would be much more complicated and will not be discussed here. Moreover, the conservation of these quantities can serve as an accuracy criterion when integrating equations (9) numerically.

2.2. Initial Conditions

Before Hamilton's equations of motion, equations (9), can be integrated to obtain a trajectory, initial values of the coordinates and momenta, $\{q_i^0, Q_i^0, p_i^0, P_i^0; i = 1, 2, 3\}$, must be specified. These initial values depend on the chosen set of *collision parameters*, which are those geometric parameters which characterize a collision and make one collision differ from another. For collisions of an atom A with some selected vibrational–rotational state (n, j) of the molecule BC at some fixed center-of-mass collisions energy E_{rel}, there are *five* collision parameters. Defining (without loss of generality) the atom A and the center of mass of the BC molecule to lie initially in the yz plane on the $-z$ side of the origin of the reference set of Cartesian coordinates with the initial relative velocity vector $\mathbf{v}_{rel}$ directed along the $+z$ axis, the five collision parameters are as follows:

b the impact parameter (the y component of the initial relative coordinate, i.e., Q_2^0)

θ the initial azimuthal orientation angle of the BC internuclear axis (the angle between $\mathbf{q}$ and the $+z$ axis)

ϕ the initial polar orientation angle of the BC internuclear axis (the angle between the projection of $\mathbf{q}$ onto the xy plane and the $+x$ axis)

η the initial orientation of the BC angular momentum (the angle between $\mathbf{q} \times \mathbf{p}$ and some reference vector normal to the BC internuclear axis)

ζ the initial phase angle of the BC vibration (defined to be zero at the inner turning point, π at the outer turning point, and to vary linearly with time)

It now remains to express the initial values of the generalized coordinates and momenta $\{q_i^0, Q_i^0, p_i^0, P_i^0; i = 1, 2, 3\}$ in terms of these colli-

sion parameters. If ρ is the initial separation between A and the center of mass of BC and b is the impact parameter of the collision, then

$$Q_1^0 = 0 \tag{10a}$$

$$Q_2^0 = b \tag{10b}$$

$$Q_3^0 = -(\rho^2 - b^2)^{1/2} \tag{10c}$$

$$P_1^0 = 0 \tag{10d}$$

$$P_2^0 = 0 \tag{10e}$$

$$P_3^0 = (2\mu_{A,BC}E_{rel})^{1/2} = P^0 \tag{10f}$$

Let $r \equiv |\mathbf{q}|$ and let θ and ϕ be defined as above so that

$$q_1^0 = r^0 \sin\theta \cos\phi \tag{11a}$$

$$q_2^0 = r^0 \sin\theta \sin\phi \tag{11b}$$

$$q_3^0 = r^0 \cos\theta \tag{11c}$$

One convenient method for specifying the remaining variables $\mathbf{p}^0$ and r^0 (the as yet undetermined initial internuclear separation) in terms of η, ξ, θ, and ϕ is to place r^0 at the inner turning point and to define ρ, the initial separation of A and BC, as

$$\rho = \rho_0 + \frac{\xi}{2\pi} v_{rel} \tau_{BC}^{n,j} \tag{12a}$$

$$= \rho_0 + \frac{\xi}{2\pi} \frac{P^0 \tau_{BC}^{n,j}}{\mu_{A,BC}} \tag{12b}$$

so that when along the trajectory the separation of A and BC decreases to ρ_0, the BC vibrational phase angle has the value ξ. Here $\tau_{BC}^{n,j}$ is the vibrational period of BC in the state (n, j) and ρ_0 is the "collision shell" radius, which must be sufficiently large so that the interaction between A and BC is negligible. For very long-range interaction potentials corrections for nonvanishing interaction can be made but these will not be discussed here. To minimize the distance beyond ρ_0 that the trajectory is started, it is more efficient to use a random number to choose r between r_- and r_+, the inner and outer turning points of BC, respectively, in each trajectory (or, alternatively, select either r_- and r_+ randomly) and replace the vibra-

tional period in equation (12) by the half-period*

$$\frac{1}{2} \tau_{BC}^{n,j} = \left(\frac{\mu_{BC}}{2} \right)^{1/2} \int_{r_-}^{r_+} \left[\varepsilon_{n,j} - V_{BC}(r) - \frac{j(j+1)\hbar^2}{2\mu_{BC}r^2} \right]^{-1/2} dr \qquad (13)$$

where $\varepsilon_{n,j}$ is the internal energy of the state (n, j) of the BC molecule and $V_{BC}(r)$ is defined as

$$V_{BC}(r) \equiv V_{BC}(R_2) = \lim_{R_1, R_3 \to \infty} V(R_1, R_2, R_3) \qquad (14)$$

The calculation of $\varepsilon_{n,j}$ and of $(1/2)\,\tau_{BC}^{n,j}$ will be discussed below.

An even more efficient method[27] is always to choose $\rho = \rho_0$, but before integrating the three-body equations of motion to integrate the diatomic equation of motion from $r = r_-$ for a time $(\xi/2\pi)\,\tau_{BC}^{n,j}$. If $\xi \geq \pi$, one can do this more efficiently by integrating from $r = r_+$ for a time $[(\xi - \pi)/2\pi]\,\tau_{BC}^{n,j}$.

With the selection of $r = r_\pm$, all the initial momentum of the BC molecule is angular momentum, i.e., at a turning point there is no radial component of $\mathbf{J}_r$, where $\mathbf{J}_r$ is the BC angular momentum vector which has the magnitude $J_r = [j(j+1)]^{1/2}\,\hbar$ or $(j + 1/2)\,\hbar$, depending on the correspondence scheme chosen. We will use the former in the rest of this chapter, although in many cases there is not much difference between the two choices. We may therefore write

$$\mathbf{q}^0 \cdot \mathbf{J}_r = 0 \qquad (15)$$

and

$$J_r^2 = j(j+1)\,\hbar^2 = (r_\pm p^0)^2 \qquad (16)$$

Let $\boldsymbol{\kappa}$ be a reference vector normal to the BC internuclear axis defined by

$$\boldsymbol{\kappa} = \mathbf{q}^0 \times \hat{\mathbf{e}}_z = q_2^0 \hat{\mathbf{e}}_x + q_1^0 \hat{\mathbf{e}}_y \qquad (17)$$

where $\hat{\mathbf{e}}_x$, $\hat{\mathbf{e}}_y$, $\hat{\mathbf{e}}_z$ are the unit vectors along Cartesian axes so that

$$\mathbf{p}^0 \cdot \boldsymbol{\kappa} = q_2^0 p_1^0 - q_1^0 p_2^0 = J[(q_1^0)^2 + (q_2^0)^2]^{1/2} \cos\eta \qquad (18)$$

where the second equality in equation (18) follows from the definition of η as the angle between the angular momentum of BC and the reference vector $\boldsymbol{\kappa}$. Combining equations (11), (15), (16), and (18) leads to the follow-

---

* Alternatively one could alternate r^0 between r_- and r_+ in successive trajectories. If one does not pick new values for all the other random variables in the alternate trajectories this is a form of cluster sampling and is less efficient than the procedure recommended in the text. If one does pick new values for all the other random variables this is a form of stratified sampling which slightly complicates the error analysis without any expected significant increase in accuracy.

ing initial values of internal (BC) momenta

$$p_1^0 = J_r(\sin\phi\cos\eta - \cos\theta\cos\phi\sin\eta)/r_\pm \qquad (19a)$$

$$p_2^0 = -J_r(\cos\phi\cos\eta + \cos\theta\sin\phi\sin\eta)/r_\pm \qquad (19b)$$

$$p_3^0 = J_r(\sin\theta\sin\eta)/r_\pm \qquad (19c)$$

Given some set of values for the collision parameters, these values are used in equations (10), (11), (12), and (19) with $r^0 = r_\pm$ and $J_r = [j(j + 1)]^{1/2}\hbar$. The constant ρ_0 must be determined for the particular system studied. The calculation of $r_\pm$, $\varepsilon_{n,j}$, and $(1/2)\tau_{BC}^{n,j}$ will now be considered.

In the semiclassical theory of bound states, the internal energy of the BC molecule, $\varepsilon_{n,j}$, is defined by the implicit equation[34]

$$\tfrac{1}{2}J_v - \pi\hbar(n + \tfrac{1}{2}) = 0 \qquad (20a)$$

where

$$J_v = 2\int_{r_-}^{r_+} \left\{ 2\mu_{BC}\left[\varepsilon_{n,j} - V_{BC}(r) - \frac{J_r^2}{2\mu_{BC}r^2} \right] \right\}^{1/2} dr \qquad (20b)$$

The integral in equation (20b) is readily evaluated by numerical integration. A particularly efficient scheme is obtained by defining a new variable

$$y \equiv \frac{2r - r_+ - r_-}{r_+ - r_-} \qquad (21a)$$

and using a Chebyshev quadrature of the second kind[35]:

$$\int_{-1}^{1} f(y)(1 - y^2)^{1/2} \, dy \cong \sum_{i=1}^{k} w_i f(y_i) \qquad (21b)$$

where

$$w_i = \frac{\pi}{k + 1}\sin^2\frac{i\pi}{k + 1} \qquad (21c)$$

and

$$y_i = \cos\frac{i\pi}{k + 1} \qquad (21d)$$

After an initial estimate of $\varepsilon_{n,j}$, the Newton–Raphson method[36] may be used to solve iteratively for the correct value of $\varepsilon_{n,j}$. Very few points ($k \leq 15$) are required to evaluate the integral in equation (20b). The integral

$$\frac{\partial J_v}{\partial \varepsilon_{n,j}} = \mu_{BC}\int_{r_-}^{r_+} \left\{ 2\mu_{BC}\left[\varepsilon_{n,j} - V_{BC}(r) - \frac{J_r^2}{2\mu_{BC}r^2} \right] \right\}^{-1/2} dr \qquad (22)$$

which also arises in the application of the Newton–Raphson method to find the zero of equation (20a), is simply the half-period as defined in equation (13) and is readily evaluated using numerical differentiation of J_v (see

Reference 27) or by another numerical integration. If the latter procedure is chosen it is convenient again to make the substitution of equation (21a) and to use a Chebyshev quadrature of the first kind[35]:

$$\int_{-1}^{1} \frac{f(y)}{(1 - y^2)^{1/2}} dy = \sum_{i=1}^{k} w_i f(y_i) \tag{23a}$$

where

$$w_i = \frac{\pi}{k} \tag{23b}$$

and

$$y_i = \cos \frac{(2i - 1)\pi}{2k} \tag{23c}$$

Chebyshev quadratures are also called Gauss–Mehler quadratures[37] and are widely used for this kind of semiclassical integral.[38,39] In evaluating the integrals in equations (20) and (13), one must first solve for the appropriate turning points $r_{\pm}$ at each trial energy using, for example, the Newton–Raphson method as described in Reference 5.

2.3. Calculation of a Trajectory

Having obtained the equations of motion and the initial conditions, the next problem is to calculate a trajectory. This is accomplished by numerical integration of the equations of motion for the given initial values of the $\{q_i, Q_i, p_i, P_i; i = 1, 2, 3\}$. There are a large number of well-tested algorithms for integrating coupled sets of differential equations, and these are described sufficiently well in the numerical-analysis literature.[40] The most popular integrators for trajectory studies of chemical reactions have been the fourth-order Runge–Kutta–Gill and the Adams–Moulton method. The latter is a predictor–corrector scheme and is most often used with fourth-order predictor and fifth-order corrector, although higher orders are used sometimes. Many problems have been solved with a fixed-size time step, but variable-step-size Runge–Kutta and variable-step-size predictor–corrector schemes have also been widely used. Predictor–corrector schemes are more efficient but more complicated than Runge–Kutta schemes for this kind of calculation if a fixed step size is used. Variable-step-size algorithms are more problematic. For many problems, they are actually less efficient than fixed-step-size schemes because of the extra "overhead" involved in the variable-step-size routines. But for some problems significant savings in computer time were achieved by using variable-step-size predictor–corrector schemes. A good program library will include a choice of more than one of these kinds of algorithms. If the computer costs

for the project being undertaken are small, then it is probably most efficient just to use any one of these which is handy. If the computer costs will be significant, one should test several algorithms for cost efficiency on the particular problem of interest. The algorithm which is most efficient for one problem (with a given potential energy function, set of atomic masses, range of energies and initial conditions, and number of significant figures of precision required on given trajectories) is not necessarily the most efficient for another problem.

There has not been much work reported in systematically comparing the efficiencies of various numerical integration schemes specifically as applied to chemical dynamics problems. In general it is difficult to tell how efficient an integration scheme will be for practical work on the basis of formal properties like order of the finite difference error, stability regions, or number of function evaluations per step. Matzen and Riley[41] made an interesting study of two $F + H_2$ trajectories (with H_2 initially in the ground state, E_{rel} equal to about 2 kcal/mol, and the potential given by an extended LEPS function). For each trajectory they systematically varied the numerical parameters for each of five integration schemes and determined the computer time requirements for various accuracies. The most efficient integration scheme was the Bulirsch–Stoer extrapolation method[42] with automatic error control applied to the second-order (Newtonian) equations of motion.[33] The other schemes evaluated, in order of decreasing efficiency for five-significant-figure accuracy were: the Bulirsch–Stoer extrapolation method with automatic error control applied to the first-order (Hamiltonian) equations of motion, the fixed-step-size, fourth-order Adams–Moulton predictor–corrector method used in QCPE program No. 273,* the fixed-step-size eleventh-order Adams–Mouton predictor–corrector routine used in QCPE program No. 229, and the variable-order, variable-step-size, automatic-error-control Adams method of Shampine and Gordon.[43] Their results are summarized in more detail in Table 1. Of course these results are not indicative of the efficiencies of the various schemes in general, but they do show the kinds of differences in computing times that may occur. And they show that higher-order and variable-step-size methods are not always more efficient than lower-order, fixed-step-size methods.

Other comparisons of the efficiencies of various integration schemes have been made by Parr[44] and Brumer.[45,46] Parr tested an Adams–Moulton eleventh-order predictor/eleventh-order corrector (AM11), an Adams–Moulton fifth-order predictor/sixth-order corrector (AM6), and a Runga–Kutta–Gill fourth-order integrator (RKG4) for the unimolecular dissociation of a triatomic molecule with a pairwise Morse potential. The first two integrators gave comparable results in his tests and both were superior to the RKG4 scheme. Brumer was particularly concerned with trajectories involving long-lived collision complexes. He found that Nord-

---

* The QCPE programs are discussed in Section 2.7.

Table 1. Relative Computing Times for Two $F + H_2$ Trajectories[a]

Integration scheme	Computing time		
	3 s.f.[b]	5 s.f.	6 s.f.
Bulirsch–Stoer, second-order equations	1.0	1.3	1.5
Bulirsch–Stoer, first-order equations	1.4	2.0	2.4
QCPE 273	1.1	2.0[c]	2.4[c]
QCPE 229	2.2	2.3	2.4
Shampine–Gordon (ODE)	1.9	3.2	3.8[c]

[a] The results in this table are based on unpublished calculations by M. K. Matzen and M. E. Riley. They are the average for two trajectories of the minimum computing time necessary to get a specified number of significant figures correct in all of the following final-state properties: positions, momenta, translational energy, vibrational energy, and rotational energy.

[b] s.f. = significant figures.

[c] Extrapolated.

sieck's sixth-order variable-step-size Adams method led to a serious error buildup for long-lived trajectories. Hamming's fourth-order variable-step-size predictor–corrector method suffered from considerable roundoff error propagation and unreliability of the step-size changing algorithm. He was able to integrate long-lived trajectories accurately with the RKG4 scheme and with Gear's sixth-order hybrid method (G6).[47] Since Parr[44] was able to integrate long-lived trajectories using the AM6 scheme, Brumer tested the latter three schemes by integrating a NaCl oscillator for 125 periods. The G6 method was the most efficient. In the range of five to eight significant figures of accuracy, the AM6 scheme gave errors six times larger for the same number of function evaluations. The RKG4 method gave errors 4500 times larger than the G6 method with twice as many function evaluations as the G6 method used to obtain eight significant figures. For problems involving short-lived trajectories, Brumer expected that the Gear method will be competitive with other variable-step-size predictor–corrector schemes of the same order but that the improvement should not be significant.

Once a method has been chosen one must find a step size (for methods with fixed step sizes) or a value of the error control parameter (for methods with variable step sizes and/or variable orders) which yields results of sufficient accuracy for the given problem. This should always be determined carefully for a new problem and rechecked when the problem, energy range, or initial conditions are varied significantly. There are several ways to determine what step size (or step-size control parameter) is needed. One is to integrate a few trajectories with very small step sizes and then increase the step size until the error in the quantities of interest (see Section 2.5) reaches its maximum allowable limit. This is the safest method but it is not always the most convenient. Necessary but not sufficient checks for accuracy are conservation of total energy and angular momentum. Some-

times these are conserved to more significant figures than the accuracy of the trajectory. Another check is back integration of trajectories, i.e., starting a new integration with final coordinates and with reversed final momenta of the original integration to try to recover initial conditions. This is one of the best checks, but sometimes the initial conditions are recovered to more significant figures than the accuracy of the original forward integration.[44] Another danger in performing checks is that some trajectories, especially those for collisions of long duration, are harder to integrate than others. Thus one must be sure that accuracy checks are really performed on a representative sample. It is a good practice to monitor energy and angular momentum conservation on all trajectories and routinely to back-integrate a reasonable fraction of trajectories on all computer runs. If any change in the parameters of the problem causes the errors in these checks to increase, then one should again recheck the results against trajectories integrated with smaller step-sizes.

Each trajectory is integrated in time until the chemical species produced by the collision, either the reactants (A + BC) or some set of products, have separated beyond the "collision shell" distance ρ_0'. As soon as one or another such end test is satisfied, the integration may be stopped and the identity of the products determined. Care must be taken not to stop the trajectory as the reactants are approaching one another, but otherwise a good end test consists of finding two of the R_i larger than ρ_0'. This allows a tentative assignment of the products. The pair of atoms with the smallest internuclear separation may be a stable molecule or a quasibound molecule, but might also have dissociated if the trajectory had been integrated for a longer time. Analysis of the tentative diatomic molecule's internal energy and angular momentum allows a definitive assignment.

The end test procedure just described has the advantages that (i) comparing the various R_i to ρ_0' is very fast computationally and (ii) there is no possible misassignment of products. The end tests used in Reference 5 (comparing to ρ_0' the relative separation of each atom from the center of mass of the other two atoms) can for certain mass combinations (e.g., F + HD) incorrectly identify the product diatomic molecule.

Of course one must be sure that ρ_0' is large enough. It must be large enough not only to insure that the trajectory can be judged reactive or not but also to insure that properties of the reactive collision, such as discussed in Section 2.5, are accurate to the desired number of significant figures. This, like step size, has to be determined numerically.

2.4. Sampling and Averaging over the Initial Conditions

If one can identify some maximum impact parameter such that collisions with impact parameter b greater than b_{max} cannot possibly react according to classical mechanics, then the reaction cross section can be

expressed classically as the product of a geometrical cross section πb_{max}^2 and an average probability of reaction over all possible collisions with $b < b_{max}$, i.e.,

$$\sigma_r = \pi b_{max}^2 \langle \mathscr{P}_r \rangle \tag{24}$$

where $\mathscr{P}_r$ is the reaction probability as a function of all the collision parameters as defined in Section 2.2. The average of $\mathscr{P}_r$ is taken over all possible collisions with the impact parameter $b < b_{max}$ and all possible values of all other variables. If we seek a reactive scattering cross section at some fixed center-of-mass collision energy for atom A with some selected state (n, j) of the molecule BC, then

$$\sigma_r(E_{rel}, n, j) = \pi b_{max}^2 \langle \mathscr{P}_r(E_{rel}, n, j) \rangle \tag{25a}$$

and

$$\langle \mathscr{P}_r(E_{rel}, n, j) \rangle = \frac{1}{(2\pi)^3 b_{max}^2}$$

$$\times \int_{b=0}^{b_{max}} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{\eta=0}^{2\pi} \int_{\xi=0}^{2\pi} \mathscr{P}_r(b, \theta, \phi, \eta, \xi; E_{rel}, n, j)\, b$$

$$\times \sin\theta\, db\, d\theta\, d\phi\, d\eta\, d\xi \tag{25b}$$

where the normalization constant is determined by the definite integral of the volume element. Should we desire to average $\mathscr{P}_r$ over some distribution of collision energies, equation (25) can be appropriately modified. For example, a state-selected thermal rate constant for the reaction of A with the state (n, j) of BC is defined as

$$k_r^{n,j}(T) = \langle v_{rel}\sigma_r(E_{rel}, n, j) \rangle_T \tag{26a}$$

$$= \left(\frac{8kT}{\pi\mu_{A,BC}} \right)^{1/2} \pi b_{max}^2 \left[(2\pi)^3 b_{max}^2 (kT)^2 \right]^{-1}$$

$$\times \int_{E_{rel}=0}^{\infty} \int_{b=0}^{b_{max}} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{\eta=0}^{2\pi} \int_{\xi=0}^{2\pi} \mathscr{P}_r(E_{rel}, b, \theta, \phi, \eta, \xi; n, j)$$

$$\times E_{rel}\, e^{-E_{rel}/kT}\, b \sin\theta\, dE_{rel}\, db\, d\theta\, d\phi\, d\eta\, d\xi \tag{26b}$$

where k is the Boltzmann constant, T is the temperature, and v_{rel} is the initial relative speed given by

$$v_{rel} = P^0/\mu_{A,BC} \tag{26c}$$

One may further obtain the completely thermally averaged rate constant $k_r(T)$ by averaging over Boltzmann distributions of n and j.

The function $\mathscr{P}_r$ in equations (25b) and (26b) is the probability of reaction for a collision specified by some set of collision parameters. In equation (25) it is specified by $(b, \theta, \phi, \eta, \xi)$ at fixed E_{rel}, n, and j. As all classical tra-

jectories with the same set of collision parameters (initial conditions) are identical and either do or do not lead to reaction, the function $\mathscr{P}_r$ is a Boolean function which takes on one of two possible values: zero for no reaction, one for reaction. To determine whether $\mathscr{P}_r$ is zero or one for some particular set of collision parameters, one must compute a trajectory and examine the collision products to see if a reaction has occurred. Selecting initial values of the collision parameters for each trajectory is nothing more or less than selecting points in the collision parameter space for the numerical evaluation of the multidimensional integral in equation (25) or (26). The values of initial collision parameters, therefore, depend upon the numerical integration method chosen.

The two methods in current use in trajectory calculations for evaluation of multidimensional integrals of the form

$$I = \int_0^1 \int_0^1 \cdots \int_0^1 f(\boldsymbol{\beta}) \, d\boldsymbol{\beta} \tag{27}$$

are the *Monte Carlo method*[48-50] and the method of "fixed lattice points" (a so-called *diophantine method*).[17] In the former the selection of points in the unit hypercube is completely random, while in the latter the selection is predetermined by a set of "good" or "optimum" lattice points which depend upon the dimensionality of the hypercube and the total number of points at which the function is to be evaluated. Although there is evidence that the latter method may often converge more rapidly than the Monte Carlo method as the number of points is increased[17] and that practical error estimates are possible, the method allows no rigorous estimate of the error, and none of the previously computed function values can be used to obtain an improved estimate of the integral using a larger number of points. We recommend the use of the Monte Carlo method because it allows a rigorous estimate of the error and because *all previously computed function values are used along with additional points computed to obtain convergence*. We will accordingly restrict our discussion of selection of initial values of collision parameters to that method.

In the Monte Carlo method the integral in equation (27) is approximated by the average value of the function $f(\boldsymbol{\beta})$ over N randomly selected values $\boldsymbol{\beta}^{[i]}$ from a uniform distribution in the unit hypercube, i.e.,

$$I \approx \varepsilon(I) = \frac{1}{N} \sum_{i=1}^{N} f(\boldsymbol{\beta}^{[i]}) \tag{28}$$

where $\varepsilon(I)$ is the Monte Carlo estimator of the integral I.[48-50] In the limit of a sufficiently large number of points, N, the variance of the estimator $\varepsilon(I)$ about the value I is

$$\text{var}\left[\varepsilon(I)\right] \underset{N \to \infty}{\sim} \frac{\text{var}\left[f\right]}{N} \tag{29}$$

where the $\mathrm{var}[f]$ is the variance of the function $f(\boldsymbol{\beta})$ over the unit hypercube and is some constant. The standard deviation of the estimator is then

$$s = \{\mathrm{var}[\varepsilon(I)]\}^{1/2} \underset{N \to \infty}{\sim} \frac{\{\mathrm{var}[f]\}^{1/2}}{N^{1/2}} \tag{30}$$

The estimated error in $\varepsilon(I)$ is usually taken to be some multiple of the standard deviation, the exact multiple being determined by the desired confidence limits, so that for a sufficiently large number of points

$$\Delta\varepsilon(I) \propto \frac{1}{N^{1/2}} \tag{31}$$

The probability that the estimator $\varepsilon(I)$ is within $\Delta\varepsilon(I)$ of I is 0.6826 if $\Delta\varepsilon(I)$ is taken as one standard deviation and 0.9554 if it is taken as two standard deviations. Confidence limits for the case when N is not very large can be obtained from standard statistical tables.[51]

Now the variance of the function $f(\boldsymbol{\beta})$ is defined as

$$\mathrm{var}[f] = \langle f^2 \rangle - \langle f \rangle^2 \tag{32}$$

where the average values are taken over the unit hypercube. In the *special case* in which f is a Boolean function (see above), $\langle f^2 \rangle = \langle f \rangle$ so that

$$\mathrm{var}[f_{\mathrm{Boolean}}] = \langle f_{\mathrm{Boolean}} \rangle (1 - \langle f_{\mathrm{Boolean}} \rangle) \tag{33}$$

Further, $\langle f \rangle = I$ so that $\varepsilon(I)$ is an estimator of $\langle f \rangle$. For a Boolean function

$$\varepsilon(I) = \frac{N_r}{N} \tag{34}$$

where N_r is the number of nonzero values of f_{Boolean} sampled (i.e., the number of reactive trajectories or the number of different trajectories for which $f_{\mathrm{Boolean}} = 1$). Therefore

$$\mathrm{var}[f_{\mathrm{Boolean}}] \cong \frac{N_r}{N}\left(1 - \frac{N_r}{N}\right) = \frac{N_r(N - N_r)}{N^2} \tag{35}$$

and from equation (29)

$$\mathrm{var}[\varepsilon(I)] \approx \frac{N_r(N - N_r)}{N^3} = \frac{N_r^2}{N^2}\frac{N - N_r}{N_r N} \tag{36}$$

Using a one standard deviation rule (68 % confidence level), we obtain the result for the error in $\varepsilon(I)$,[5]

$$\Delta\varepsilon(I) \approx \frac{N_r}{N}\left(\frac{N - N_r}{N_r N}\right)^{1/2} \tag{37a}$$

for the case of a Boolean function. In many practical applications one has $N_r \ll N$. In this case equations (34) and (35) may be combined to yield

the useful limiting form

$$\frac{\Delta\varepsilon(I)}{\varepsilon(I)} \underset{\substack{N\to\infty \\ N\gg N_r}}{\sim} \frac{1}{N_r^{1/2}} \tag{37b}$$

It is apparent from the $N^{-1/2}$ dependence of the estimated error in equation (31) that the Monte Carlo method converges very rapidly at first but then very slowly as the number of points N is increased. In other words not too many points are required to obtain a moderately accurate estimate of the integral, but very many points are required to obtain high accuracy.

To put the integral in equation (25) in the form of equation (27) we must transform variables according to

$$d\beta_1 = \frac{1}{c_1} b\, db \tag{38a}$$

$$d\beta_2 = \frac{1}{c_2} \sin\theta\, d\theta \tag{38b}$$

$$d\beta_3 = \frac{1}{c_3} d\phi \tag{38c}$$

$$d\beta_4 = \frac{1}{c_4} d\eta \tag{38d}$$

$$d\beta_5 = \frac{1}{c_5} d\xi \tag{38e}$$

This implies that

$$\langle \mathscr{P}_r \rangle \equiv \frac{c_1 c_2 c_3 c_4 c_5}{(2\pi)^3\, b_{\max}^2}$$

$$\times \int_{\beta_1=0}^{1} \int_{\beta_2=0}^{1} \int_{\beta_3=0}^{1} \int_{\beta_4=0}^{1} \int_{\beta_5=0}^{1} \mathscr{P}_r(\boldsymbol{\beta})\, d\beta_1\, d\beta_2\, d\beta_3\, d\beta_4\, d\beta_5 \tag{38f}$$

The relationships of the new variables to the old are then obtained straightforwardly by integration:

$$\beta_1 = \int_0^{\beta_1} d\beta_1 = \frac{1}{c_1} \int_0^b b\, db = \frac{1}{c_1} \frac{b^2}{2} \tag{39a}$$

$$\beta_2 = \int_0^{\beta_2} d\beta_2 = \frac{1}{c_2} \int_0^\theta \sin\theta\, d\phi = \frac{1}{c_2}(1 - \cos\theta) \tag{39b}$$

$$\beta_3 = \int_0^{\beta_3} d\beta_3 = \frac{1}{c_3} \int_0^\phi d\phi = \frac{1}{c_3}\phi \tag{39c}$$

$$\beta_4 = \int_0^{\beta_4} d\beta_4 = \frac{1}{c_4} \int_0^\eta d\eta = \frac{1}{c_4} \eta \tag{39d}$$

$$\beta_5 = \int_0^{\beta_5} d\beta_5 = \frac{1}{c_5} \int_0^\xi d\xi = \frac{1}{c_5} \xi \tag{39e}$$

The normalization constants c_i are determined from the conditions $\beta_i = 1$ at the upper limit of the corresponding variable. The result is

$$\beta_1 = \left(\frac{b}{b_{max}} \right)^2 \tag{40a}$$

$$\beta_2 = \tfrac{1}{2}(1 - \cos\theta) \tag{40b}$$

$$\beta_3 = \frac{1}{2\pi} \phi \tag{40c}$$

$$\beta_4 = \frac{1}{2\pi} \eta \tag{40d}$$

$$\beta_5 = \frac{1}{2\pi} \xi \tag{40e}$$

and the expression for $\langle \mathscr{P}_r \rangle$ becomes a special case of equation (27) as follows:

$$\langle \mathscr{P}_r \rangle = \int_0^1 \int_0^1 \int_0^1 \int_0^1 \int_0^1 \mathscr{P}_r(\boldsymbol{\beta}) \, d\boldsymbol{\beta} \tag{41}$$

The procedure for selecting appropriate values of the collision parameters over which to average the reaction probability $\mathscr{P}_r$ is as follows.

(i) Select a set of five random numbers $\beta_1, \beta_2, \ldots, \beta_5$ uniformly distributed in the interval $(0, 1)$. Most modern computing centers now have system libraries which include programs for random number or pseudo-random number generation. These are always or almost always good enough for our purposes so this step will not be discussed in detail.

(ii) Obtain the corresponding values of the collision parameters by inverting equations (39). This gives

$$b = \beta_1^{1/2} b_{max} \tag{42a}$$

$$\theta = \cos^{-1}(1 - 2\beta_2) \tag{42b}$$

$$\phi = 2\pi\beta_3 \tag{42c}$$

$$\eta = 2\pi\beta_4 \tag{42d}$$

$$\xi = 2\pi\beta_5 \tag{42e}$$

These values of the collision parameters are then used in equations (10), (11), (12), and (19) to define the initial values of the generalized coordinates

and momenta for a trajectory, and the trajectory is computed to determine whether $\mathscr{P}_r(b(\beta_1), \theta(\beta_2), \phi(\beta_3), \eta(\beta_4), \xi(\beta_5); E_{rel}, n, j)$ is one or zero. If this procedure is repeated N times and N_r nonzero values of $\mathscr{P}_r$ are obtained, then from equations (25), (28), (34), (37), and (41) we have

$$\sigma_r(E_{rel}, n, j) = \pi b_{max} \langle \mathscr{P}_r \rangle \tag{43a}$$

$$\cong \pi b_{max}^2 N_r / N \tag{43b}$$

and

$$\Delta \sigma_r \approx \pi b_{max}^2 \frac{N_r}{N} \left(\frac{N - N_r}{N_r N} \right)^{1/2} \tag{44}$$

Similarly, an expression for the state-selected rate constant $k_r^{n,j}$ is obtained by the Monte Carlo integration of equation (26). The result is

$$k_r^{n,j} \cong \left(\frac{8kT}{\pi \mu_{A,BC}} \right)^{1/2} \pi b_{max}^2 \frac{N_r}{N} \tag{45}$$

and

$$\Delta k_r^{n,j} \approx \left(\frac{8kT}{\pi \mu_{A,BC}} \right)^{1/2} \pi b_{max}^2 \frac{N_r}{N} \left(\frac{N - N_r}{N_r N} \right)^{1/2} \tag{46}$$

The collision energy may be selected in the following manner. A new transformed variable

$$d\beta_6 = ue^{-u} du \tag{47}$$

where $u = E_{rel}/kT$ is defined analogous to those in equation (38). Integrating equation (47) to obtain $\beta_6(u)$ we have

$$\beta_6 = \int_0^{\beta_6} d\beta_6 = \int_0^u ue^{-u} du = 1 - (u + 1) e^{-u} \tag{48}$$

which, unfortunately, cannot be inverted to obtain a closed-form expression for $u(\beta_6)$. Successive approximations to u, however, may be obtained using the relation

$$u_{i+1} = u_i + \frac{u_i + 1 - (1 - \beta_6) e^{u_i}}{u_i} \tag{49}$$

which is derived using the Newton–Raphson iteration method. The sequence of partial sums, u_i, is absolutely convergent for all values of β_6 in the (open) interval $(0, 1)$ when $u_1 = 1$, the inflection point of $\beta_6(u)$, is used as the initial guess. Once a converged value $u(\beta_6)$ is obtained using equation (49), the collision energy is given by $E_{rel} = ukT$. Alternatively the initial relative translational energy may be selected by a rejection method.[8]

To compute the completely thermally averaged rate constant one must

also average over discrete distributions of n and j. When the number of internal states is not too large this can be done in the following manner.[27] Pick a number $N_{\text{select}}^{\text{total}}$ much larger than the number of trajectories to be run. For example, let $N_{\text{select}}^{\text{total}}$ be 10^7. Compute the energies of all states with a probability of occurrence greater than $1/N_{\text{select}}^{\text{total}}$ by using equation (20) and compute the number $N_{\text{select}}(n, j)$ of times each such state should be sampled in 10^7 collisions. If the total probability of occurrence of states with probabilities less than $1/N_{\text{select}}^{\text{total}}$ is nonnegligible, then $N_{\text{select}}^{\text{total}}$ is too small. Arrange the states in order and store the subtotals of the $N_{\text{select}}(n, j)$. Then, for each trajectory, pick a random number in the range $(0, 1)$, multiply by $N_{\text{select}}^{\text{total}}$, and compare efficiently to the table of subtotals to decide what n and j should be used. If the number of states of the reactant is too large for this scheme to be practical it can be modified as necessary, e.g., by analytic approximations for $\varepsilon_{n,j}$.

The transformed variables defined by equations (38) and (47) are those appropriate for so-called *crude Monte Carlo sampling*. Crude Monte Carlo sampling is a completely "safe" and unbiased sampling technique (so long as b_{max} is chosen properly), but it is not necessarily optimum in the sense of yielding the most precise results for a particular reaction attribute for a given number of trajectories computed. The goal of the alternative sampling methods is variance reduction, i.e., by biasing the selection process for initial conditions we attempt to accelerate the convergence of the Monte Carlo evaluation of unbiased reaction attributes. This is the most important area for research in the theory of Monte Carlo integration, and the newcomer to the field of Monte Carlo trajectory calculations of chemical dynamics might be surprised to find how little such variance-reducing techniques have been used in this area. This, however, is not without a good reason. Simply stated, a nonuniform selection procedure which reduces the variance of one computed reaction attribute will generally increase the variance of one or more other interesting attributes. Since we are typically interested in several such reaction attributes (as discussed in later sections), we often adopt the compromise of using no nonuniformity at all. As an example, some workers prefer to skew their sample in favor of low impact parameters. This does not produce biased estimates of reaction attributes if trajectories with high impact parameters are weighted relatively more highly than trajectories with low impact parameters. And it may lead to a smaller Monte Carlo uncertainty (variance) in the estimated reaction cross section if, as is often the case, the probability of reaction is a decreasing function of impact parameter. But it will also generally lead to much poorer statistics for the differential cross section in the forward direction if, as is usually also the case, the forward-scattered trajectories tend to come from large impact parameters. However, if one is really interested in only one or a few reaction attributes, e.g., in only the thermal rate coefficient, it may be possible to use variance-reducing techniques quite profitably. In general

the use of any variance-reducing technique requires knowledge of the dependence of the trajectory results (which are the integrand of an integral being evaluated by the Monte Carlo method) on the independent variable whose distribution is to be sampled nonuniformly. Thus we usually have no grounds for biasing the selection of initial variables like the vibrational phase or the orientation of the BC angular momentum, but we may be able to bias the selection of initial energy quantities or impact parameters. Two alternative sampling methods—importance sampling and stratified sampling—will now be discussed and illustrated by applying each to the selection of the impact parameter.

Consider the *opacity function* (this is one of the *reactivity functions* discussed in Section 2.6.1),

$$\mathscr{P}_r(b; E_{rel}, n, j) = \frac{1}{2(2\pi)^3}$$

$$\times \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{\eta=0}^{2\pi} \int_{\xi=0}^{2\pi} \mathscr{P}_r(b, \theta, \phi, \eta, \xi; E_{rel}, n, j)$$

$$\times \sin\theta \, d\theta \, d\phi \, d\eta \, d\xi \tag{50}$$

denoted simply by $\mathscr{P}_r(b)$ in the following discussion, which has the properties

$$\langle \mathscr{P}_r \rangle = \frac{2}{b_{max}^2} \int_0^{b_{max}} \mathscr{P}_r(b) \, b \, db \tag{51}$$

$$\sigma_r = 2\pi \int_0^{b_{max}} \mathscr{P}_r(b) \, b \, db \tag{52}$$

and

$$\frac{d\sigma_r}{db} = 2\pi b \mathscr{P}_r(b) \tag{53}$$

where

$$\sigma_r = \int_0^{b_{max}} \frac{d\sigma_r}{db} db \tag{54}$$

If an *expected* opacity function $\mathscr{P}_r^0(b)$ is defined, then equation (51) may always be rewritten as[52]

$$\langle \mathscr{P}_r \rangle = \frac{2}{b_{max}^2} \int_0^{b_{max}} \frac{\mathscr{P}_r(b)}{\mathscr{P}_r^0(b)} \mathscr{P}_r^0(b) \, b \, db \tag{55}$$

$$= \int_0^1 \frac{\mathscr{P}_r(\beta_1)}{\mathscr{P}_r^0(\beta_1)} d\beta_1 \tag{56}$$

where

$$d\beta_1 = \frac{2}{b_{\max}^2} \mathscr{P}_r^0(b)\, b\, db \tag{57}$$

If the *actual* opacity function resembles the *expected* function, the ratio $\mathscr{P}_r(b)/\mathscr{P}_r^0(b)$ should vary quite slowly with impact parameter (or equivalently, with β_1). The more slowly varying this ratio can be made, the smaller the variance of the integrand becomes, and the smaller the estimated error for a given number of trajectories computed. The function $\mathscr{P}_r^0(b)$ is an *importance-sampling* function.

It is clear from equation (57) that use of the crude Monte Carlo selection of the impact parameter defined by equations (38a) or (40a) corresponds to taking the expected opacity function (importance-sampling function) as a step function, i.e.,

$$\mathscr{P}_r^0(b) = \begin{cases} 1, & b \le b_{\max} \\ 0, & b > b_{\max} \end{cases} \tag{58}$$

If the step function in equation (58) is not expected to have the same shape as the actual $\mathscr{P}_r(b)$, then crude Monte Carlo sampling might not be the method of choice for the calculation of the reaction cross section or reaction rate constant. One alternative is to use the following importance-sampling function[52]:

$$\mathscr{P}_r^0(b) = \begin{cases} 3\left(1 - \dfrac{b}{b_{\max}}\right), & b \le b_{\max} \\ 0, & b > b_{\max} \end{cases} \tag{59}$$

in which case

$$d\beta_1 = \frac{6}{b_{\max}^2}\left(1 - \frac{b}{b_{\max}}\right) b\, db \tag{60}$$

$$\beta_1 = \int_0^{\beta_1} d\beta_1 = 3\left(\frac{b}{b_{\max}}\right)^2 - 2\left(\frac{b}{b_{\max}}\right)^3 \tag{61}$$

$$\langle \mathscr{P}_r \rangle = \int_0^1 \frac{\mathscr{P}_r(\beta_1)}{\mathscr{P}_r^0(\beta_1)}\, d\beta_1 \tag{62}$$

and

$$b = b_{\max}\left\{\cos\left[\tfrac{1}{3}\cos^{-1}(1 - 2\beta_1) + \tfrac{4}{3}\pi\right] + \tfrac{1}{2}\right\} \tag{63}$$

Notice that the factor of 3 in equation (59) was chosen so that $\beta_1(b = b_{\max}) = 1$, and in deriving equation (61) we used the fact that $\beta_1(b = 0) = 0$. When using an importance-sampling function for the selection of the impact

parameter. equation (41) becomes

$$\langle \mathscr{P}_r \rangle = \int_0^1 \int_0^1 \int_0^1 \int_0^1 \int_0^1 \frac{\mathscr{P}_r(\boldsymbol{\beta})}{\mathscr{P}_r^0(\beta_1)} \, d\beta_1 \, d\beta_2 \, d\beta_3 \, d\beta_4 \, d\beta_5 \tag{64}$$

and its Monte Carlo estimator becomes

$$\langle \mathscr{P}_r \rangle \cong \frac{1}{N} \sum_{i=1}^{N} \frac{\mathscr{P}_r(\boldsymbol{\beta}^{[i]})}{\mathscr{P}_r^0(\beta_1^{[i]})} = \frac{1}{N} \sum_{i=1}^{N_r} \frac{1}{\mathscr{P}_r^0(\beta_1^{[i]})} \tag{65}$$

where the N computed trajectories are for β_1 selected at random uniformly on the interval $(0, 1)$. It is evident from equation (65) that each trajectory is *weighted* by

$$w_i \equiv \frac{1}{\mathscr{P}_r^0(\beta_1^{[i]})} \tag{66a}$$

when importance sampling is used. Note that $w_i = 1$ for each trajectory when $\mathscr{P}_r^0$ is given by equation (58). Because we have required that $\mathscr{P}_r^0(b)$ be normalized so that $\beta_1(b = b_{\max}) - \beta_1(b = 0)$ is unity, one will find in general that

$$\sum_{i=1}^{N} w_i \underset{\text{large } N}{\sim} N \tag{66b}$$

The importance-sampling estimator for the reaction cross section is

$$\sigma_r \cong \pi b_{\max}^2 \frac{1}{N} \sum_{i=1}^{N_r} w_i \tag{67}$$

with estimated error (for sufficiently large N)

$$\Delta\sigma_r \approx \pi b_{\max}^2 \frac{1}{N} \left[\sum_{i=1}^{N_r} w_i^2 - \frac{1}{N} \left(\sum_{i=1}^{N_r} w_i \right)^2 \right]^{1/2} \tag{68}$$

It should be pointed out that the above procedure for importance sampling always results in an unbiased estimator for the cross section but is advantageous only if $\mathscr{P}_r/\mathscr{P}_r^0$ has a smaller variance than $\mathscr{P}_r$ itself. For example, the importance-sampling function $\mathscr{P}_r^0(b) = b_{\max}/2b$ is a poor choice because of its unphysical behavior near $b = 0$. This leads to extremely large weights for some trajectories and thus to a very uneven approach of the calculated results to convergence. This sampling function leads to a flat b distribution, i.e., equal probability of sampling any b rather than the probability being proportional to b. In practice, when flat b sampling has been employed it has usually been combined[12,13,19,20,22] with a discrete selection of the corresponding angular momentum J_{rel}, given by $\mu_{\text{A,BC}} v_{\text{rel}} b/\hbar$, but this does not eliminate the problems. We recommend that equation (59) is generally a better way to give higher weights to small-b collisions when that is appropriate.

Equations (64)–(66) are easily generalized for the importance sampling of variables other than (or in addition to) the impact parameter.

Another type of sampling which is often quite useful is *stratified sampling*. In stratified sampling the unit hypercube is divided into subvolumes (usually by hyperplanes perpendicular to the edges). Sampling is carried out within each subvolume exactly as in crude Monte Carlo sampling, but all subvolumes are not sampled equally densely.

As an example of stratified sampling consider partitioning the impact parameter interval $(0, b_{max})$ into k_{strat} subintervals (b_{k-1}, b_k) where k goes from 1 to k_{strat} and $b_0 = 0$. This partition corresponds to a division of the unit hypercube by the $(k_{strat} - 1)$ hyperplanes $\beta_1 = \beta_{1,k} \equiv (b_k/b_{max})^{1/2}$. Let subvolume k, denoted by $\mathscr{V}_k$, be defined as the subvolume characterized by β_1 in the interval $\beta_{1,k-1} \leq \beta_1 \leq \beta_{1,k}$. By design,

$$\sum_{k=1}^{k_{strat}} \mathscr{V}_k = 1 \tag{69}$$

The stratified-sampling analog of equation (41) is

$$\langle \mathscr{P}_r \rangle = \sum_{k=1}^{k_{strat}} \mathscr{V}_k \langle \mathscr{P}_r \rangle_k \tag{70a}$$

$$\cong \sum_{k=1}^{k_{strat}} \mathscr{V}_k \frac{N_{rk}}{N_k} \tag{70b}$$

with estimated error

$$\Delta \langle \mathscr{P}_r \rangle \approx \left\{ \sum_{k=1}^{k_{strat}} \mathscr{V}_k^2 \frac{N_{rk}(N_k - N_{rk})}{N_k^3} \right\}^{1/2} \tag{71}$$

where N_{rk} and N_k are subtotals of N_r and N for the kth subvolume. Any number of trajectories N_k may be computed at random in the kth stratum, but the estimated error in equation (71) is minimized for a fixed total number of trajectories

$$N = \sum_{k=1}^{k_{strat}} N_k$$

when for each stratum k,[53]*

$$N_k \propto \mathscr{V}_k \frac{N_{rk}}{N_k} \left(\frac{N_k - N_{rk}}{N_{rk}N_k} \right)^{1/2} \tag{72}$$

Alternatively we may ask: what is the optimum allocation of stratification boundaries in the sense that all N_k are equal for the optimum boundaries? Clearly, for impact parameter strata, the answer is that the bounda-

---

* This is a consequence of the Tschuprow–Neyman theorem.

ries should correspond to an equipartition of the variable β_1 (b) as computed by integrating equation (57) with the optimum $\mathscr{P}_r^0$ (b). The generalization to boundaries for the other β_i is straightforward. Allocating trajectories to the various strata according to equation (72) or using the strata which are optimum for $\langle \mathscr{P}_r \rangle$ may, however, defeat one of the very useful applications of stratified sampling. As will be discussed in Section 2.6, stratified sampling can be used to obtain greatly improved statistics on cross sections for producing *minor products* or final-state distributions of any products in regions of their final-state parameter space that are lightly populated if the region of initial conditions leading to that product or that region of product space can be identified. Equation (72) applies only to minimizing the error of $\langle \mathscr{P}_r \rangle$ or of the cross section related to it by equation (25).

We conclude our discussion of stratified sampling by noting that from equation (70)

$$\langle \mathscr{P}_r \rangle \cong \frac{1}{N} \sum_{k=1}^{k_{strat}} \frac{\mathscr{V}_k N}{N_k} N_{rk} \tag{73a}$$

$$= \frac{1}{N} \sum_{k=1}^{k_{strat}} \sum_{i=1}^{N_k} \frac{\mathscr{V}_k N}{N_k} \mathscr{P}_{rk}(\beta^{[i]}) \tag{73b}$$

This implies that the statistical weight of each trajectory in the kth stratum is $\mathscr{V}_k N / N_k$.

2.5. Product Analysis

Once a trajectory is complete and a product diatomic molecule tentatively identified, it is most convenient to transform to a new set of generalized coordinates and momenta in which the Hamiltonian is asymptotically separable, i.e.,

$$H(\mathbf{q}', \mathbf{Q}', \mathbf{p}', \mathbf{P}') \sim T_{rel}(\mathbf{P}') + H_{int}(\mathbf{q}', \mathbf{p}') \tag{74}$$

Here $\mathbf{q}'$ and $\mathbf{p}'$ are the coordinates and conjugate momenta for the *product diatomic molecule* and $\mathbf{Q}'$ and $\mathbf{P}'$ are those for the *relative motion of the products*. As the trajectory is integrated in the generalized coordinates appropriate for reactants, $\{q_i, Q_i, p_i, P_i; i = 1, 2, 3\}$, it is necessary to derive expressions for the product coordinates $\{q_i', Q_i', p_i', P_i'; i = 1, 2, 3\}$ in terms of those for reactants. (Of course, if the product molecule is BC no transformation is necessary.) This is accomplished in two steps:

(i) Derive expressions analogous to equation (4) for $\mathbf{q}'$ and $\mathbf{Q}'$ in terms of the reference Cartesian coordinates, $\{x_i; i = 1, 9\}$. This defines the transformation matrix $\mathbf{T}'$ in the transformation

$$\begin{bmatrix} \mathbf{q}' \\ \mathbf{Q}' \end{bmatrix} = \mathbf{T}'\mathbf{x} \tag{75}$$

The matrix $\mathbf{T}$ is defined by equation (4) and

$$\begin{bmatrix} \mathbf{q} \\ \mathbf{Q} \\ \mathbf{S} \end{bmatrix} = \mathbf{Tx} \tag{76}$$

Note $\mathbf{T}'$ is 6×9 but $\mathbf{T}$ is 9×9. It should be pointed out that the convention for the *scattering angle* depends upon whether the relative motion coordinate is taken to be the atom with respect to the center of mass of the diatomic, or vice versa. If, as is often the case, the scattering angle is to be defined as the angle between the final relative velocity of the species which contains the (initially free) atom A and the incident direction of A, then the sign of the right-hand side of (4b) should be changed for $\mathbf{T}'$ but not for $\mathbf{T}$.

(ii) Find the inverse of the transformation defined by equation (76), i.e., find the inverse of the square matrix $\mathbf{T}$; then

$$\mathbf{x} = \mathbf{T}^{-1} \begin{bmatrix} \mathbf{p} \\ \mathbf{Q} \\ \mathbf{S} \end{bmatrix} \tag{77a}$$

which upon substitution in equation (75) gives

$$\begin{bmatrix} \mathbf{q}' \\ \mathbf{Q}' \end{bmatrix} = \mathbf{T}'\mathbf{T}^{-1} \begin{bmatrix} \mathbf{q} \\ \mathbf{Q} \\ \mathbf{S} \end{bmatrix} \tag{77b}$$

the desired result. It does not matter that $\mathbf{T}'$ is not a square matrix as its inverse is not required. The new conjugate generalized momenta are obtained from

$$p_i' = m\dot{q}_i' \qquad (i = 1, 2, 3) \tag{78a}$$

$$P_i' = \mu\dot{Q}_i' \qquad (i = 1, 2, 3) \tag{78b}$$

where

$$\begin{bmatrix} \dot{\mathbf{q}}' \\ \dot{\mathbf{Q}}' \end{bmatrix} = \mathbf{T}'\mathbf{T}^{-1} \begin{bmatrix} \dot{\mathbf{q}} \\ \dot{\mathbf{Q}} \\ \dot{\mathbf{S}} \end{bmatrix} \tag{79}$$

and

$$\dot{q}_i = \frac{1}{\mu_{BC}} p_i \qquad (i = 1, 2, 3) \tag{80a}$$

$$\dot{Q}_i = \frac{1}{\mu_{A,BC}} P_i \qquad (i = 1, 2, 3) \tag{80b}$$

$$\dot{S}_i = \frac{1}{M} P_{S_i} \qquad (i = 1, 2, 3) \tag{80c}$$

For the products AB + C, m is μ_{AB} and μ is $\mu_{C,AB}$. For the products AC + B, m is μ_{AC} and μ is $\mu_{B,AC}$. The (6×9) matrix product $\mathbf{T}'\mathbf{T}^{-1}$ appropriate for the transformation to collision products other than reactants is defined by

$$q_i' = -\frac{m_C}{m_B + m_C}q_i - Q_i \qquad (i = 1, 2, 3) \quad (81a)$$

$$Q_i' = -\frac{m_B M}{(m_A + m_B)(m_B + m_C)}q_i + \frac{m_A}{m_A + m_B}Q_i \qquad (i = 1, 2, 3) \quad (81b)$$

for the products AB + C, and by

$$q_i' = \frac{m_B}{m_B + m_C}q_i - Q_i \qquad (i = 1, 2, 3) \quad (82a)$$

$$Q_i' = \frac{m_C M}{(m_A + m_C)(m_B + m_C)}q_i + \frac{m_A}{m_A + m_C}Q_i \qquad (i = 1, 2, 3) \quad (82b)$$

for the products AC + B. Dissociative collisions producing A + B + C may (for convenience) be analyzed in the *reactant* generalized coordinate system.

Expressions for various quantities associated with collision products in terms of the generalized coordinates and momenta appropriate for reactants (the final values of which are known from the calculation of the trajectory) are obtained from the relations given below by substitution of the proper transformation [equations (4) for A + BC or A + B + C, equations (81) for AB + C, or equations (82) for AC + B]. The scalar diatomic internuclear separation is denoted by r $(\equiv [\mathbf{q}' \cdot \mathbf{q}']^{1/2})$ and the diatomic potential energy, defined analogous to equation (14), is represented by $V_D(r)$. A tilde is used to denote a quantity which is continuous according to the expression given, but would be discrete according to quantum mechanics. Expressions derived for the AB + C products may be compared to those given in Reference 5:

Total energy (conserved):

$$H' = \frac{1}{2\mu}\sum_{i=1}^{3} P_i'^2 + \frac{1}{2m}\sum_{i=1}^{3} p_i'^2 + V(\mathbf{R}(\mathbf{Q})) \qquad (83)$$

Internal energy:

$$\tilde{\varepsilon}_{int} = \frac{1}{2m}\sum_{i=1}^{3} p_i'^2 + V_D(r) \qquad (84)$$

Internal angular momentum:

$$\tilde{\mathbf{J}}'_r = \mathbf{q}' \times \mathbf{p}' \tag{85a}$$

$$= (q'_2 p'_3 - q'_3 p'_2)\,\hat{\mathbf{e}}_x + (q'_3 p'_1 - q'_1 p'_3)\,\hat{\mathbf{e}}_y + (q'_1 p'_2 - q'_2 p'_1)\,\hat{\mathbf{e}}_z \tag{85b}$$

Relative angular momentum:

$$\tilde{\mathbf{J}}'_{\text{rel}} = \mathbf{Q}' \times \mathbf{P}' \tag{86}$$

Total angular momentum (conserved):

$$\tilde{\mathbf{J}}'_{\text{tot}} = \tilde{\mathbf{J}}'_r + \tilde{\mathbf{J}}'_{\text{rel}} \tag{87a}$$

$$= \mathbf{q}' \times \mathbf{p}' + \mathbf{Q}' \times \mathbf{P}' \tag{87b}$$

Relative velocity and relative speed:

$$\mathbf{v}'_{\text{rel}} = \frac{1}{\mu}\mathbf{P}' \tag{88a}$$

$$v'_{\text{rel}} = \frac{1}{\mu}(\mathbf{P}' \cdot \mathbf{P}')^{1/2} = \frac{1}{\mu}\left(\sum_{i=1}^{3} P_i'^2\right)^{1/2} \tag{88b}$$

Scattering angle:

$$\theta = \cos^{-1}\frac{\mathbf{v}_{\text{rel}} \cdot \mathbf{v}'_{\text{rel}}}{v_{\text{rel}} v'_{\text{rel}}} \tag{89a}$$

where

$$\mathbf{v}_{\text{rel}} = \frac{P^0}{\mu_{\text{A,BC}}}\hat{\mathbf{e}}_z \tag{89b}$$

and $\mathbf{v}_{\text{rel}}$ is the initial relative velocity.

Diatomic vibrational and rotational energies:

$$\tilde{\varepsilon}'_{\text{rot}} = \min\left\{ V_D(r) + \frac{\tilde{\mathbf{J}}'_r \cdot \tilde{\mathbf{J}}'_r}{2mr^2} \right\} - V_D(r_e) \tag{90a}$$

$$\tilde{\varepsilon}'_{\text{vib}} = \tilde{\varepsilon}'_{\text{int}} - \tilde{\varepsilon}'_{\text{rot}} \tag{90b}$$

where r_e is the internuclear separation at the minimum of V_D, $V_D(r_e)$ is the classical zero of internal energy for the product molecule, and the minimum of the effective potential $V_D(r) + \tilde{\mathbf{J}}'_r \cdot \tilde{\mathbf{J}}'_r/2mr^2$ may be determined, for example, using the Newton–Raphson iteration technique.

Diatomic rotational "quantum number" (continuous):

$$\tilde{j}' = -\tfrac{1}{2} + \tfrac{1}{2}[1 + 4\,\tilde{\mathbf{J}}'_r \cdot \tilde{\mathbf{J}}'_r/h^2]^{1/2} \tag{91}$$

Diatomic vibrational "quantum number" (continuous):

$$\tilde{n}' = -\frac{1}{2} + \frac{1}{\pi h} \int_{r_-}^{r_+} \left\{ 2m \left[\varepsilon'_{\text{int}} - V_D(r) - \frac{J'_r \cdot J'_r}{2mr^2} \right] \right\}^{1/2} dr \qquad (92)$$

where $r_\pm$ are the diatomic turning points of the effective potential at the energy $\varepsilon'_{\text{int}}$ and are determined using the Newton–Raphson iteration technique as in equations (13) and (20). The integral is evaluated using equations (21).

The definitions of the quantities in equations (83)–(88) are unambiguous. We have already mentioned the arbitrary choice of direction for $\mathbf{v}_{\text{rel}}$ which affects the definition of scattering angle. Diatomic vibrational and rotational energies cannot be unambiguously defined. Various definitions that make them sum to $\tilde{\varepsilon}'_{\text{int}}$ are acceptable in various circumstances; the choice given in equations (90) seems reasonable for many purposes.* The correspondence principle for rotational quantum number is also not unique; the choice given in equation (91) is equivalent to $\tilde{J}_r'^2 = j(j + 1)\hbar^2$ as opposed to $\tilde{J}_r'^2 = (j + 1/2)^2 \hbar^2$. The continuous "quantum numbers" j' and $\tilde{n}'$ are often rounded to the nearest integer value in making the correspondence between the result of a trajectory calculation and the discrete nature of the quantum-mechanical states of the product molecule. While this is an extremely powerful procedure it should be exercised with caution, especially in cases where rounding to a higher value places the product in a "closed" (energetically forbidden) state.

After calculating each trajectory and analyzing the collision products, it is quite useful to store certain information about that trajectory on some mass storage device (tape, disk, etc.). Having the pertinent information about each trajectory in such a form greatly facilitates the calculation of reaction attributes (see the following section, 2.6) through the analysis of a large number of trajectories. In fact, it is sometimes more convenient to create *two data files*: one to be used in most of the data analysis which contains only the more commonly used information (e.g., channel designation, impact parameter, scattering angle, product internal state, final relative velocity, etc.) and another which contains the initial and final coordinates of each trajectory from which any additional information may be computed at a later time if desired.

---

* Often it is best to define the rotational and vibrational energies in terms of the quantum-mechanical eigenenergies of the states with discrete quantum numbers n and j as assigned by the histogram method. Then $\tilde{\varepsilon}_{\text{int}}$ will be one of the allowed discrete product internal energies. Optionally, v'_{rel} can then be adjusted for energy conservation but it is difficult and almost always unnecessary to readjust all product variables in a consistent fashion this way.

2.6. Calculation of Reaction Attributes

Having completed the calculation of a statistically significant sample of trajectories and calculated a reactive scattering cross section using equations (43) and (44), or a state-selected rate constant using equations (45) and (46), one is faced with the realization of having calculated far more information than is represented by $\sigma_r \pm \Delta\sigma_r$, or $k_r \pm \Delta k_r$. The following discussion focuses on extracting this additional information, calculated for individual trajectories using the above formulas, from the trajectory data in a form amenable to comparison with experiment.

2.6.1. Reactivity Functions

We use the term *reactivity function* to denote the probability of reaction, or any other quantity derived from the reaction probability, as a function of some *reactant* collision parameter. The *opacity function*, or probability of reaction as a function of impact parameter, defined by equation (50), is one example of a reactivity function. Another (closely related) example is $d\sigma_r/db$, defined by equation (53). Still another example is the *excitation function* $\sigma_r(E_{rel})$. We will limit our discussion to a few of the more commonly used reactivity functions involving the impact parameter and collision energy. Other reactivity functions (e.g., the dependence of reactivity upon reactant orientation or vibrational phase) may be obtained in an analogous manner.

In constructing *histogrammic* representations of reactivity functions, the proper specification of the "bins" into which the trajectory results are to be sorted is intimately coupled to the manner in which initial values of the collision parameters were selected. For reactivity as a function of initial collision parameters, there is an *a priori* "best method" for specifying the bins assuming the initial conditions were selected optimally. We note that the choice of sampling method implies some knowledge about the reaction probability function $\mathscr{P}_r$. This same knowledge should be brought to bear on the presentation of results; reactivity function histograms should be constructed in a manner consistent with the sampling method.[52]

Consider the histogrammic representation of the opacity function $\mathscr{P}_r(b)$. The initial selection of $b(\beta_1)$ according to equation (42a) or (63) implies some *expected* opacity function $\mathscr{P}_r^0$, either equation (58) or (59), respectively. To the extent that the choice of $\mathscr{P}_r^0(b)$ was optimal, the bins of the histogrammic representation of $\mathscr{P}_r(b)$ should correspond to an equipartition of the variable $\beta_1(b)$.[52] The following considerations will make the meaning of this statement more clear. If $\mathscr{P}_r^0(b)$ is defined by equation (58), the values of the impact parameter corresponding to the boundaries of the k_{max} bins are given by

$$b_k = (k/k_{max})^{1/2} b_{max} \qquad (k = 0, \ldots, k_{max}) \qquad (93a)$$

In general, they are given by

$$b_k = b(\beta_1 = \beta_{1,k}) = b\left(\beta_1 = \frac{k}{k_{max}}\right) \qquad (k = 0, \dots, k_{max}) \qquad (93b)$$

The value of the opacity function in each bin may be calculated more than one way. First one may use

$$\mathscr{P}_{rk} \cong \sum_{i=1}^{N_{rk}} w_i \bigg/ \sum_{i=1}^{N_k} w_i \qquad (94a)$$

where $\mathscr{P}_{rk}$ is the average value of $\mathscr{P}_{rk}(b)$ for b in the kth bin (i.e., $b_{k-1} < b \leq b_k$) when impact parameters in this range are properly sampled at random from a distribution uniform in b^2, and where N_{rk} and N_k are the number of reactive and total collisions, respectively, with impact parameter b in the kth bin. The estimated error for each $\mathscr{P}_{rk}$ is

$$\Delta\mathscr{P}_{rk} \approx \left[\frac{1}{N_k}(\mathscr{P}_{rk} - \mathscr{P}_{rk}^2)\right]^{1/2} \qquad [\text{with } \mathscr{P}_{rk} \text{ from (94a)}] \qquad (94b)$$

Note that if the expected opacity function is within a constant factor of the true opacity function, each of the numerators on the right-hand side of equation (94a) is approximately equal to $N\langle\mathscr{P}_r\rangle/k_{max}$. In this case each bin accounts for roughly an equal fraction of the reactive cross section. This is the sense in which the equipartition of the variable $\beta_1(b)$ was optimum. Furthermore, we see that the optimum allocation of bins for reactivity functions of collision parameters is closely related to the optimum allocation of strata for stratified sampling of collision parameters.

A second expression for $\mathscr{P}_{rk}$ may be obtained by replacing the denominator of equation (94a) by its converged value (which is *not* generally N_k when the weights are not all unity):

$$\sum_{i=1}^{N_k} w_i \underset{N \text{ large}}{\sim} N_k \frac{\beta_{1,k}^{original} - \beta_{1,k-1}^{original}}{\beta_{1,k}^{new} - \beta_{1,k-1}^{new}} \qquad (95a)$$

$$\underset{N \text{ large}}{\sim} N(\beta_{1,k}^{original} - \beta_{1,k-1}^{original}) \qquad (95b)$$

where $\beta_{1,k}^{original}$ and $\beta_{1,k}^{new}$ are defined by equations (38a) and (57), respectively. Thus

$$\mathscr{P}_{rk} \cong \frac{b_{max}^2 \sum_{i=1}^{N_{rk}} w_i}{N(b_k^2 - b_{k-1}^2)} \qquad (96a)$$

with error estimate

$$\Delta\mathscr{P}_{rk} \approx \frac{b_{max}^2}{N(b_k^2 - b_{k-1}^2)}\left[\sum_{i=1}^{N_{rk}} w_i^2 - \frac{1}{N}\left(\sum_{i=1}^{N_{rk}} w_i\right)^2\right]^{1/2} \qquad (96b)$$

Although equations (94a) and (96a) give the same results for infinite N,

one or the other may be more useful or more accurate in different calculations with finite N. Notice that if we take $k_{max} = 1$, then $\mathscr{P}_{rk}$ becomes $\langle \mathscr{P}_r \rangle$. In this case equations (96a) and (96b) reduce to equations (67) and (68), but equations (94a) and (94b) provide an alternative method of calculation. In general it requires some judgment or a comparison of error estimates to decide which formula to use in a specific case.

Consider now the histogrammic representation of the related function $d\sigma_r/db$, as defined by equation (54). We may define the expected function [cf. equation (53)]

$$\left(\frac{d\sigma_r}{db} \right)^0 = 2\pi b \mathscr{P}_r^0(b) \tag{97}$$

which, for $\mathscr{P}_r^0$ defined by equation (58), is

$$\left(\frac{d\sigma_r}{db} \right)^0 = \begin{cases} 2\pi b, & b \leq b_{max} \\ 0, & b > b_{max} \end{cases} \tag{98}$$

Equation (54) may always be rewritten as

$$\sigma_r = \int_0^{b_{max}} \frac{(d\sigma_r/db)}{(d\sigma_r/db)^0} \left(\frac{d\sigma_r}{db} \right)^0 db \tag{99}$$

which upon substitution of equations (57) and (97) becomes

$$\sigma_r = \pi b_{max}^2 \int_0^1 \frac{d\sigma_r/db}{(d\sigma_r/db)^0} d\beta_1 \tag{100}$$

Again it is clear that, if the expected function $(d\sigma_r/db)^0$ is an accurate one, the "best" impact parameter bins, in the sense that each bin contains an equal fraction of the cross section, correspond to an equipartition of the variable β_1. The histogrammic representation of $d\sigma_r/db$ is derived from equation (54) as follows. We write

$$\sigma_r = \sum_{k=1}^{k_{max}} \int_{b_{k-1}}^{b_k} \frac{d\sigma_r}{db} db \tag{101a}$$

$$= \sum_{k=1}^{k_{max}} (b_k - b_{k-1}) \left(\frac{d\sigma_r}{db} \right)_k \tag{101b}$$

$$\cong \pi b_{max}^2 \frac{1}{N} \sum_{k=1}^{k_{max}} \sum_{i=1}^{N_{rk}} w_i \tag{102}$$

where $(d\sigma_r/db)_k$ is the average value of $d\sigma_r/db$ in the kth interval of b (i.e., in $[b_{k-1}, b_k]$). Equating equations (101) and (102) term by term gives[52,54]

$$\left(\frac{d\sigma_r}{db} \right)_k \cong \frac{\pi b_{max}^2}{b_k - b_{k-1}} \frac{1}{N} \sum_{i=1}^{N_{rk}} w_i \tag{103}$$

Clearly, if one substitutes each $(d\sigma_r/db)_k$ into equation (101a) for

$b_{k-1} < b \leq b_k$ and integrates, one obtains the correct value of the integral as given by equation (67). The estimated error in each bin is given by

$$\Delta\left(\frac{d\sigma_r}{db}\right) \approx \frac{\pi b_{\max}^2}{(b_k - b_{k-1})} \frac{1}{N}\left[\sum_{i=1}^{N_{rk}} w_i^2 - \frac{1}{N}\left(\sum_{i=1}^{N_{rk}} w_i\right)^2\right]^{1/2} \quad (104)$$

Other histogrammic distributions as functions of initial collision parameters can be constructed in a similar fashion. Of course in some cases one does not necessarily desire an equal contribution to the cross section from each bin of a reactivity function, and then one should adjust the boundaries according to some alternative criterion.[52]

Another reactivity parameter of interest when calculating $k_r^{n,j}$ is the *activation energy*

$$E_a^{n,j}(T) = \frac{d\log k_r^{n,j}}{d(-1/RT)} \quad (105)$$

This is the activation energy for a state-selected rate constant. By analogy to the derivations for completely thermally averaged rate constants,[55-57] it can be shown to be[54,58]

$$E_a^{n,j}(T) = \langle E_{\rm rel}\rangle_{\rm rc;T} - \langle E_{\rm rel}\rangle_{\rm ap;T} \quad (106a)$$

$$= \langle E_{\rm rel}\rangle_{\rm rc;T} - \langle E_{\rm rel}\rangle_{\rm ac;T} + \tfrac{1}{2}kT \quad (106b)$$

where the subscripts rc, ap, and ac mean reactive collisions, all pairs, and all collisions, respectively. The use of this definition of the activation energy will be called the Tolman method. It yields a far more precise estimate of that quantity than any algorithm involving differences in $k_a^{n,j}$ at different temperatures.[56-58] To apply equation (106) to a set of trajectory data at some fixed temperature, the average values are evaluated by the Monte Carlo method,

$$E_a^{n,j} \cong \frac{\sum_{i=1}^{N_r} w_i E_{{\rm rel},i}}{\sum_{i=1}^{N_r} w_i} - \frac{\sum_{i=1}^{N} w_i E_{{\rm rel},i}}{\sum_{i=1}^{N} w_i} + \tfrac{1}{2}kT \quad (107a)$$

$$\cong \frac{\sum_{i=1}^{N_r} w_i E_{{\rm rel},i}}{\sum_{i=1}^{N_r} w_i} - \frac{\sum_{i=1}^{N} w_i E_{{\rm rel},i}}{N} + \tfrac{1}{2}kT \quad (107b)$$

For a sufficiently large number N of trajectories, the second term in both equations (107a) and (107b) becomes $2kT$. For the activation energy of completely thermally averaged rate constants one must also compute the average value of the internal energy for all reactions minus that for all collisions. For N sufficiently large one will obtain the same results for the averages over all collisions using $\sum_{i=1}^{N} w_i$ as using N. But if importance sampling is being used there may be a significant difference. This illustrates the general principle that if importance sampling is used to accelerate the convergence of one reaction attribute, e.g., $\langle \mathscr{P}_r\rangle$, the convergence of others,

in these examples $\langle E_{rel} \rangle_{ac; T}$ or $\langle \varepsilon_{int} \rangle_{ac; T}$, may be decelerated. The user of these algorithms must therefore use discretion in deciding which results are reliable and which are not.

2.6.2. Final-State Distributions

We subdivide the discussion of the analysis of final-state distributions according to the number and type of variables involved, i.e., according to whether the distribution is a function of one or two variables, and whether the variables take on discrete values quantum mechanically or are really continuous. More than two variables may be considered but such distributions are difficult to plot and usually suffer from poor statistics.

2.6.2.1. One Variable—Discrete. The discrete variables of interest in product distributions are those corresponding to the quantized internal states of the product molecule. It is of interest to calculate a reactive scattering cross section for collisions of some fixed vibrational–rotational state (n, j) of the BC molecule producing some specific product state (n', j') or group of product states (e.g., all states with a specific n' irrespective of j'). For fixed E_{rel}, this is called a *state-to-state cross section* and for a thermal distribution of E_{rel} it is called a *state-to-state rate constant*. We will explicitly discuss state-to-state cross sections but the methods are also applicable to state-to-state rate constants and to final-state distributions when the reactant states are completely thermal. The total reaction cross section for producing arrangement α' may be decomposed as

$$\sigma_{r\alpha'}(E_{rel}, n, j) = \sum_{n'} \sum_{j'} \sigma_r(n, j \rightarrow \alpha', n', j'; E_{rel}) \tag{108a}$$

$$= \sum_{n'} \sigma_r(n, j \rightarrow \alpha', n'; E_{rel}) \tag{108b}$$

$$= \sum_{j'} \sigma_r(n, j \rightarrow \alpha', j'; E_{rel}) \tag{108c}$$

where the index α' refers to the chemically distinct product molecules (AB or AC). To calculate a histogrammic representation of $\sigma_r(n, j \rightarrow n', j')$, $\sigma_r(n, j \rightarrow n')$, or $\sigma_r(n, j \rightarrow j')$ for a given product, the continuous values of $\tilde{n}'$ and $\tilde{j}'$ from equations (91) and (92) for each trajectory are first rounded to the nearest integer value (as discussed above). The Boolean reaction probability function $\mathscr{P}_r$ is then redefined (for each trajectory) such that

$$\mathscr{P}_r = \begin{cases} 1, & \text{for } (\alpha', n', j'), (\alpha', n'), \text{ or } (\alpha', j') \text{ equal to some} \\ & \text{preselected values} \\ 0, & \text{otherwise} \end{cases} \tag{109}$$

The state-to-state cross section and estimated error are then computed using the same equations as for the total reaction cross section [e.g., using

equations (43) and (44) for crude Monte Carlo sampling] except that N_r now represents the number of trajectories with $\mathscr{P}_r = 1$ as defined by equation (109). N is still the total number of trajectories calculated. Estimated relative errors, $\Delta\sigma_r(n, j \rightarrow \alpha', n', j')/\sigma_r(n, j \rightarrow \alpha', n', j')$, for state-to-state cross sections are generally much larger than those for the total reactive scattering cross section because N_r is generally much smaller.

As an example, if we wish to compute the way in which the products are distributed in their various vibrational states, we would "bin" the product states generated from a set of N trajectories according to the identity of the products (α'), and within each of these arrangement bins we would further "bin" the trajectories according to the value of $\tilde{n}'$ rounded to the nearest integer. The result would be a one-variable (n') histogram for each distinct product molecule.

Another method for calculating final-state distributions of variables which quantum mechanically take on discrete values is classical P matrix theory.[59-64] Because quantal rotational energies are more closely spaced than vibrational energies, the histogram method is more justified for assigning j' than for assigning n'. It may be useful to use the histogram method for assigning j' and classical P matrix theory to assign n'. To do this we write the state-to-state cross section as (suppressing the index α')

$$\sigma_r(n, j \rightarrow n', j'; E_{rel}) = \sigma_r(n, j \rightarrow j'; E_{rel}) P_{n'}(n, j \rightarrow j'; E_{rel}) \qquad (110)$$

where $\sigma_r(n, j \rightarrow j'; E_{rel})$ is computed by the histogram method as described above and $P_{n'}(n, j \rightarrow j'; E_{rel})$ is the probability that collisions with initial conditions n, j, and E_{rel} and final rotational quantum number j' should be assigned final vibrational quantum number n'. Define moments of the final vibrational quantum number n' for such collisions by

$$\langle (n')^m \rangle (n, j \rightarrow j'; E_{rel}) = \frac{\sum_{n'=0}^{n'_{max}} (n')^m \sigma_r(n, j \rightarrow n', j'; E_{rel})}{\sum_{n'=0}^{n'_{max}} \sigma_r(n, j \rightarrow n', j'; E_{rel})} \qquad (111)$$

$$= \frac{\sum_{n'=0}^{n'_{max}} (n')^m P_{n'}(n, j \rightarrow j'; E_{rel})}{\sum_{n'=0}^{n'_{max}} P_{n'}(n, j \rightarrow j'; E_{rel})} \qquad (112)$$

where n'_{max} is the maximum value allowed by conservation of total energy. These moments may be approximated from the trajectories as an average over the $N_{rj'}$ trajectories which are assigned final rotational quantum number j' as follows:

$$\langle (\tilde{n}')^m \rangle (n, j \rightarrow j'; E_{rel}) \cong \frac{\sum_{i=0}^{N_{rj'}} (\tilde{n}'_i)^m w_i}{\sum_{i=0}^{N_{rj'}} w_i} \qquad (113)$$

Then the classical P matrix theory prescribes that the quantities $P_{n'}(n, j \rightarrow j'; E_{rel})$ be given by the least-biased estimate in the information-theory sense consistent with the constraints that the probabilities sum to one and that the first N_{mom} moments $(m = 1, 2, \ldots, N_{mom})$ of equation (112) are equal to the first N_{mom} moments of equation (113). A least-biased estimate in the

information-theory sense is one that maximizes the information-theory entropy of the distribution. For a probability distribution $P_{n'}$ the information-theory entropy is[65]

$$I = -K \sum_{n'=0}^{n'_{\max}} P_{n'} \ln \left(\frac{P_{n'}}{P_{n'}^0} \right) \tag{114}$$

where $P_{n'}^0$ is an *a priori* probability and where K is a constant. For the present problem, maximization of the information-theory entropy subject to the constraints yields

$$P_{n'} = \frac{P_{n'}^0 \exp\left[-\sum_{m=1}^{N_{\mathrm{mom}}} \lambda_m (n')^m \right]}{\sum_{n'=0}^{n'_{\max}} P_{n'}^0 \exp\left[-\sum_{m=1}^{N_{\mathrm{mom}}} \lambda_m (n')^m \right]} \tag{115}$$

where the arguments $(n, j \to j'; E_{\mathrm{rel}})$ have been suppressed on $P_{n'}$, $P_{n'}^0$, and λ_m. The quantities λ_m are Lagrange multipliers whose values are found by using the trajectory results [equation (113)] on the left side of equation (112) and substituting equation (115) on the right side of equation (112). This gives N_{mom} simultaneous nonlinear equations for N_{mom} Lagrange multipliers.

The above description shows that a complete specification of the algorithm requires specifying N_{mom} and the prior probabilities $P_{n'}^0$. There are three approaches to each of these choices. For N_{mom} one might try to use (i) the value that would make the classical P matrix predictions be most accurate as compared to a quantum-mechanical calculation,[59,60] (ii) the minimum value required to reach a region of stability of the information-theory entropy with respect to increasing N_{mom},[62,63] or (iii) some fixed small value such as 1, 2, or 3.[61,64] Choice (i) requires theoretical considerations of how many classical moments might be accurate as compared to quantum-mechanical ones.[60] The other choices have the disadvantage that inaccurate classical moments might be used or accurate classical moments might be unused. The choice of N_{mom} is not independent of the choice of *a priori* probabilities. There are four approaches to this choice. The original one was to use the statistical phase-space theory[66,67] predictions as the *a priori* probability.[59,60] This has the advantage that every individual quantum state allowed by energy and angular momentum conservation has the same weight. Including angular momentum conservation requires a model so it might be neglected. Then for the present problem $P_{n'}^0$ is proportional to the sum of the degeneracies of all energetically allowed rotational states of vibrational level n'. The second choice is $P_{n'}^0 = 1$,[61,63] which coincides with the first choice for collinear collisions. The third choice of *a priori* probabilities is the microcanonical statistical thermodynamic one[68,69] which allows information-theory entropy to be treated like statistical mechanical entropy.[62] Fourthly, we might use a model for $P_{n'}^0$.[62,63] Atabek and Lefebvre used N_{mom} in the range 1–3 and two sets of $P_{n'}^0$ to predict the final vibrational distribution of CN in the photodissociation of

ICN. They found for that problem that for $N_{mom} \geq 2$, the results are fairly insensitive to either the *a priori* probabilities or N_{mom}; the information-theory entropy and the larger probabilities become invariant to varying either. The classical P matrix approach is recommended for consideration because it is capable of much better accuracy than the histogram method for final vibrational state distributions. But the optimal choices for N_{mom} and the *a priori* probabilities are not clear at this time and are subjects for further research.

2.6.2.2. One Variable—Continuous. As the choice of sampling method for initial conditions does not necessarily imply any knowledge of distributions of product state variables (e.g., scattering angle, final relative velocity, etc.), there is no *a priori* method for binning the final values of these variables to achieve the maximum resolution of their distributions. However, one extremely useful technique for obtaining histogrammic representations of product state distributions is to construct "bins" such that each bin contains an equal volume of phase space.[70] This uniform phase space (UPS) method for constructing histograms is applicable to any number of discrete and/or continuous variables. The basic premise of the UPS method is that having no *a priori* knowledge of a distribution is equivalent to "expecting" the distribution to be uniformly spread over all the available phase space, and that in the absence of such knowledge the histogrammic representation should be constructed according to this expectation.[70] Of course as soon as some trajectories have been computed one can make a more knowledgeable estimate of the shape of the distribution, and one may find that it differs significantly from the uniform distribution. If so, then the UPS prescription for binning may be inappropriate. For example, because of vibrational population inversion in the products, the distribution of final relative velocities for an exoergic reaction is often peaked at a value corresponding to a low fraction of the total available energy being in translation; but a uniform phase-space distribution is peaked at high final relative velocity. Thus the UPS prescription corresponds to large bins at low v'_{rel} and small bins at high v'_{rel}, but a more optimum presentation of the results would involve small bins at low v'_{rel} and large bins at high v'_{rel}. The systematics of choosing bin sizes so that all bins contain the same number of reactive trajectories or so that all bins contain the same fraction of the total cross section are presented elsewhere.[52] In this chapter we present a detailed treatment only for the UPS prescription for binning trajectories. This illustrates the general techniques, but as just discussed it is not always the preferred method for binning.

Consider the distribution $g(\gamma)$, where γ is some continuous product variable, which is related to the total reaction cross section by

$$g(\gamma) = \frac{d\sigma_r}{d\gamma} \qquad (116a)$$

i.e.,

$$\sigma_r = \int_{\gamma_{min}}^{\gamma_{max}} g(\gamma)\, d\gamma \tag{116b}$$

$$= \int_{\gamma_{min}}^{\gamma_{max}} \frac{g(\gamma)}{\rho(\gamma)} \rho(\gamma)\, d\gamma \tag{116c}$$

Here $\rho(\gamma)$ is the density of phase space along the γ coordinate[70] and is assumed to have the normalization

$$\int_{\gamma_{min}}^{\gamma_{max}} \rho(\gamma)\, d\gamma = 1 \tag{117}$$

Equation (116c) may be rewritten as

$$\sigma_r = \int_0^1 g(u)\, du \tag{118}$$

where

$$g(u) \equiv \frac{g(\gamma)}{\rho(\gamma)} \tag{119}$$

and

$$du = \rho(\gamma)\, d\gamma \tag{120}$$

Equal increments of the transformed variable

$$u = \int_0^u du = \int_{\gamma_{min}}^{\gamma} \rho(\gamma)\, d\gamma \tag{121}$$

contain equal volumes of phase space. If the density of products were uniformly distributed over all allowed phase space, the distribution $g(u)$ would be a constant. In such a case, if the variable $\gamma(u)$ were binned in equal increments of u, then $g_k \Delta \gamma_k$, where $g_k \equiv \langle g(\gamma) \rangle_k$, would be identical for each (in general, nonuniform) interval $\Delta \gamma_k$. In fact, any deviation from a uniform (flat) distribution $g(u)$, or equal volumes (areas) in the bars of the histogram g_k vs. γ, reflects a dynamical preference for certain regions of phase space and is directly related to the dynamical information contained in the distribution.[70,71] The UPS method will now be used to derive expressions for histogrammic representations of several common product state distributions.

The solid-angle differential reaction cross section $d^2\sigma_r/d\Omega$ is related

to the integral reaction cross section by

$$\sigma_r = \int_0^{4\pi} \frac{d^2\sigma_r}{d\Omega} d\Omega \tag{122a}$$

$$= \int_0^{4\pi} \frac{(d^2\sigma_r/d\Omega)}{\rho(\Omega)} \rho(\Omega) d\Omega \tag{122b}$$

Taking $\rho(\Omega) = 1/4\pi$ yields

$$\sigma_r = 4\pi \int_0^1 \frac{d^2\sigma_r}{d\Omega} du \tag{123}$$

where (using the cylindrically symmetric $d\Omega = 2\pi \sin\theta \, d\theta$)

$$du = \rho(\Omega) \, d\Omega = \rho(\theta) \, d\theta \tag{124}$$

$$= \tfrac{1}{2} \sin\theta \, d\theta \tag{125}$$

Therefore,

$$u = \tfrac{1}{2}(1 - \cos\theta) \tag{126}$$

The UPS partition of θ is then given by

$$\theta_k = \cos^{-1} \frac{k_{max} - 2k}{k_{max}} \qquad (k = 0, \ldots, k_{max}) \tag{127}$$

An expression for $d^2\sigma_r/d\Omega_k$ is derived as follows. Equation (123) is rewritten over the partition of θ given by equation (127) and equated to the Monte Carlo expression for the integral reaction cross section over the same partition,

$$\sigma_r = 4\pi \sum_{k=1}^{k_{max}} \int_{(k-1)/k_{max}}^{k/k_{max}} \frac{d^2\sigma_r}{d\Omega} du \tag{128a}$$

$$= \frac{4\pi}{k_{max}} \sum_{k=1}^{k_{max}} \left\langle \frac{d^2\sigma_r}{d\Omega} \right\rangle_k \tag{128b}$$

$$\cong \pi b_{max}^2 \frac{1}{N} \sum_{k=1}^{k_{max}} \sum_{i=1}^{N_{rk}} w_i \tag{128c}$$

where $\langle d^2\sigma_r/d\Omega \rangle_k$ is the average value of $(d^2\sigma_r/d\Omega)$ in the kth interval of u. Equating equations (128b) and (128c) term by term gives the desired result[52,72]

$$\left\langle \frac{d^2\sigma_r}{d\Omega} \right\rangle_k \cong \frac{k_{max} b_{max}^2}{4} \frac{1}{N} \sum_{i=1}^{N_{rk}} w_i \tag{129}$$

The estimated error is given by

$$\Delta \left\langle \frac{d^2\sigma_r}{d\Omega} \right\rangle_k \approx \frac{k_{max}b_{max}^2}{4} \frac{1}{N} \left[\sum_{i=1}^{N_{rk}} w_i^2 - \frac{1}{N} \left(\sum_{i=1}^{N_{rk}} w_i \right)^2 \right]^{1/2} \quad (130)$$

The polar differential reactive scattering cross section, $(d\sigma_r/d\theta)$, is related to σ_r and $d^2\sigma_r/d\Omega$ by

$$\sigma_r = \int_0^\pi \frac{d\sigma_r}{d\theta} d\theta \quad (131)$$

and

$$\frac{d\sigma_r}{d\theta} = 2\pi \sin\theta \frac{d^2\sigma_r}{d\Omega} \quad (132)$$

As indicated by equation (122b), the density of phase space is not uniform along the θ coordinate. If the integral in equation (131) is partitioned according to equation (127), then each interval of θ will contain the same volume of phase space. Hence

$$\sigma_r = \sum_{k=1}^{k_{max}} \int_{\theta_{k-1}}^{\theta_k} \frac{d\sigma_r}{d\theta} d\theta \quad (133)$$

$$= \sum_{k=1}^{k_{max}} (\theta_k - \theta_{k-1}) \left\langle \frac{d\sigma_r}{d\theta} \right\rangle_k \quad (134)$$

$$\cong \pi b_{max}^2 \sum_{k=1}^{k_{max}} \sum_{i=1}^{N_{rk}} w_i \quad (135)$$

where $\langle d\sigma_r/d\theta \rangle_k$ is the average value of $d\sigma_r/d\theta$ in the interval $[\theta_{k-1}, \theta_k]$. Equating equations (134) and (135) term by term yields[52]

$$\left\langle \frac{d\sigma_r}{d\theta} \right\rangle_k \cong \frac{\pi b_{max}^2}{\theta_k - \theta_{k-1}} \frac{1}{N} \sum_{i=1}^{N_{rk}} w_i \quad (136)$$

The estimated error is given by

$$\Delta \left\langle \frac{d\sigma_r}{d\theta} \right\rangle_k \approx \frac{\pi b_{max}^2}{\theta_k - \theta_{k-1}} \frac{1}{N} \left[\sum_{i=1}^{N_{rk}} w_i^2 - \frac{1}{N} \left(\sum_{i=1}^{N_{rk}} w_i \right)^2 \right]^{1/2} \quad (137)$$

For differential scattering cross sections we have just seen that the UPS criterion suggests that histogrammic boundaries should correspond to equal intervals of $\cos\theta$ rather than equal intervals of θ. The use of equal intervals of $\cos\theta$ rather than θ has also been suggested [72] on the grounds that such bins contain equal fractions of the available 4π sr of solid angle. But the argument involving equal fractions of the available phase space is more general and can also be applied to other kinds of product distributions. For example, consider the relative translational degree of free-

dom of the products. The continuous variable under consideration here could be the final relative translational energy E'_{rel} or final relative speed v'_{rel}. We may define $f_{E'} \equiv E'_{rel}/E'_{max}$ and $f_{v'} \equiv v'_{rel}/v'_{max}$ as the fractions of could be the final relative translational energy E'_{rel} or final relative speed respectively, which are related by $f_{E'} = f_{v'}^2$. The densities of phase space along the coordinates $f_{E'}$ and $f_{v'}$ are rather complicated to specify exactly, but in the limit of classical (continuous) vibrational and rotational energies for a rigid-rotor harmonic oscillator (RRHO), which should resemble a real system well enough for the purpose of constructing bins of a histogram, the phase-space densities are[65,70]

$$\rho(f_{E'}) = \tfrac{15}{4} f_{E'}^{1/2}(1 - f_{E'}) \tag{138}$$

$$\rho(f_{v'}) = \tfrac{15}{2} f_{v'}^{2}(1 - f_{v'}^{2}) \tag{139}$$

It is easily shown that[70]

$$z_{E'} = z_{v'} \equiv z \tag{140}$$

where

$$z_{E'} = \int_0^{f_{E'}} \rho(f_{E'}) \, df_{E'} \tag{141}$$

$$z_{v'} = \int_0^{f_{v'}} \rho(f_{v'}) \, df_{v'} \tag{142}$$

This unique translational variable, along which equal increments represent equal volumes of phase space, may be written in terms of either $f_{E'}$ or $f_{v'}$ as

$$z = \tfrac{5}{2} f_{E'}^{3/2}(1 - \tfrac{3}{5} f_{E'}) \tag{143}$$

or

$$z = \tfrac{5}{2} f_{v'}^{3}(1 - \tfrac{3}{5} f_{v'}^{2}) \tag{144}$$

To calculate a UPS histogrammic representation of, say, $d\sigma_r/dv'_{rel}$ one constructs an equipartition of the uniform variable z and finds by interpolation of equation (144) the value of $f_{v',k}$ corresponding to each z_k. As the function $z(f_{v'})$ has an inflection point at $f_{v'} = 1/2^{1/2}$, this point is a good initial guess when using the Newton–Raphson method for the interpolation. The final-relative-speed bins are then defined by $v'_{rel,k} = v'_{max}f_{v',k}$. The desired result is then obtained by analyzing

$$\sigma_r = \int_0^{v'_{max}} \frac{d\sigma_r}{dv'_{rel}} \, dv'_{rel} \tag{145}$$

analogous to the way equations (134) and (135) were analyzed. The result is[52]

$$\left(\frac{d\sigma_r}{dv'_{rel}} \right)_k \cong \frac{\pi b_{max}^2}{v'_{rel,k} - v'_{rel,k-1}} \frac{1}{N} \sum_{i=1}^{N_{rk}} w_i \tag{146}$$

with estimated error

$$\Delta \left(\frac{d\sigma_r}{dv'_{\rm rel}} \right)_k \approx \frac{\pi b^2_{\max}}{v'_{{\rm rel},k} - v'_{{\rm rel},k-1}} \frac{1}{N} \left[\sum_{i=1}^{N_{rk}} w_i^2 - \frac{1}{N} \left(\sum_{i=1}^{N_{rk}} w_i \right)^2 \right]^{1/2} \quad (147)$$

It is also possible (and, in some cases, more appropriate) to treat $v'_{\rm rel}$ as a discrete variable resulting from the quantized (n', j') internal states of the product diatomic molecule.[70,71]

Other histogrammic distributions as functions of a single continuous variable may be derived in a similar fashion. In addition, if one has some knowledge of the product distribution (on general grounds or by having already calculated some trajectories) one may generalize the treatment given above by replacing $\rho(\gamma)$ by a more appropriate function.

An alternative way to calculate continuous distributions of product variables is to expand them in a set of functions and determine the expansion coefficients by moment methods.[29,72,73] The most convenient functions are the natural orthogonal functions for the interval involved. We present here the details only for final angular distributions; extension of the method to other continuous distributions proceeds analogously. In addition the extension to recoil velocity distributions will be clear from the treatment of joint distributions.

Just as for histogram methods, it is recommended first to transform to an appropriate variable u such that, e.g., equal increments of u correspond to equal volumes of phase space. For angular distributions the variable u is given by equation (126). Angular distributions are defined on a finite interval so the convenient orthogonal polynomials are the Legendre polynomials. They are usually defined on the interval $-1 < \tilde{u} < 1$ so we make a linear transformation

$$\tilde{u} = Au + B \quad (148)$$

to a variable $\tilde{u}$ which has this range and is therefore a more convenient argument for Legendre polynomials but, since the transformation is linear, still provides a UPS representation. This yields

$$\tilde{u} = \cos \theta \quad (149)$$

We recall the following important properties of the Legendre polynomials:

$$P_0(\tilde{u}) = 1 \quad (150)$$

$$P_1(\tilde{u}) = \tilde{u} \quad (151)$$

$$P_{l+1}(\tilde{u}) = (2l + 1)\tilde{u}P_l(\tilde{u}) - lP_{l-1}(\tilde{u}) \quad (152)$$

$$\int_{-1}^{1} P_l(\tilde{u}) P_{l'}(\tilde{u}) = \frac{2\delta_{ll'}}{2l + 1} \quad (153)$$

So it is convenient to define normalized Legendre polynomials by

$$\tilde{P}_l(\tilde{u}) = [(2l + 1)/2]^{1/2} P_l(\tilde{u}) \quad (154)$$

Then the differential reaction cross section per unit solid angle is expanded as

$$\frac{d^2\sigma_r}{d\Omega} = \frac{\sigma_r}{2\pi} \sum_l d_{rl} \tilde{P}_l(\tilde{u}) \tag{155}$$

and the expansion coefficients are determined by the usual method of multiplying both sides by one normalized Legendre polynomial and integrating. This gives

$$d_{rl} = \frac{2\pi}{\sigma_r} \int_{-1}^{1} \frac{d^2\sigma_r}{d\Omega} \tilde{P}_l(\tilde{u}) \, d\tilde{u} \tag{156}$$

$$= \frac{1}{\sigma_r} \int_{-1}^{1} \frac{d\sigma_r}{d\tilde{u}} \tilde{P}_l(\tilde{u}) \, d\tilde{u} \tag{157}$$

$$= \frac{1}{\sigma_r} \int \tilde{P}_l(\tilde{u}) \, d\sigma_r \tag{158}$$

If σ_r and the last integral are both evaluated from the same sample of trajectories, this becomes

$$d_{rl} \cong \sum_{i=1}^{N_r} P_l(\tilde{u}_i) \, w_i \, \Big/ \, \sum_{i=1}^{N_r} w_i \tag{159}$$

where the sums are over the N_r trajectories which yield the product of interest. Substitution of equation (159) into equation (155) yields the desired result except that one must decide what upper limit to use in equation (155). For exact values of the d_{rl}, the limits should be 0 to ∞. But for the Monte Carlo values of d_{rl} given by equation (159) it is best not to include the highest l values in the sum. If the values of l used are too high, the computed differential cross section will exhibit meaningless statistical noise. It is recommended for working purposes to use only those terms for which d_{rl} is reasonably well converged with respect to increasing the number N of trajectories run. This provides an appropriately smoothed analytic representation of $d^2\sigma_r/d\Omega$. If desired, the differential reaction cross section per unit polar angle may then be obtained from it by equation (132) as before.

When using the moment method one does not get as convenient an error estimate for the differential cross section as one gets for the differential cross section averaged over a bin width in the histogram method. But one does get an analytic smoothed result as a compensating advantage. The differential cross section computed by the moment method must be checked both with respect to increasing l_{max} and increasing N. If l_{max} is increased indefinitely for fixed N, the result will tend to a sequence of delta functions at the set of N_r scattering angles. But for large enough N, there should be a region of stability where the result is insensitive to increasing l_{max}. This result is the actual differential cross section. Distributions computed with

smaller l_{max} and smaller N are approximate smoothed versions of this converged result. It is not possible to give a universal recommendation for how far the result should be converged with respect to increasing l_{max} (always including only terms reasonably well converged with respect to increasing N) and increasing N (to converge better the individual terms). These decisions depend on the use to which the calculation will be put.

2.6.2.3. Two Variables—Discrete, Continuous, and Mixed. Provided the two variables are separable, the construction of histogrammic representations of distributions of two variables is an obvious generalization of the one-variable cases discussed above.* Only one example need be given here. Consider the distribution $d^3\sigma_r/d\Omega\, dv'_{rel}$ in velocity–angle space. The defining relation is

$$\sigma_r = 2\pi \int_0^\pi \int_0^{v'_{max}} \frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} \sin\theta\, d\theta\, dv'_{rel} \tag{160}$$

which may be rewritten in terms of the UPS angle variable u as

$$\sigma_r = 4\pi \int_0^1 \int_0^{v'_{max}} \frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} du\, dv'_{rel} \tag{161}$$

If boundaries $\{u_j\}$ are defined by an equipartition of u, and boundaries $\{v'_{rel,k}\}$ are defined by an equipartition of the UPS translational variable z, then

$$\sigma_r = 4\pi \sum_{j=1}^{j_{max}} \sum_{k=1}^{k_{max}} \int_{u_{j-1}}^{u_j} \int_{v'_{rel,k-1}}^{v'_{rel,k}} \frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} du\, dv'_{rel} \tag{162}$$

$$= \frac{4\pi}{j_{max}} \sum_{j=1}^{j_{max}} \sum_{k=1}^{k_{max}} \left\langle \frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} \right\rangle_{j,k} (v'_{rel,k} - v'_{rel,k-1}) \tag{163}$$

$$\cong \frac{\pi b_{max}^2}{N} \sum_{j=1}^{j_{max}} \sum_{k=1}^{k_{max}} \sum_{i=1}^{N_{rjk}} w_i \tag{164}$$

where N_{rjk} is the number of reactive trajectories which produced a product in the jth angle bin *and* the kth velocity bin. The final expresion is[52]

$$\left(\frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} \right)_{j,k} \cong \frac{j_{max} b_{max}^2}{4(v'_{rel,k} - v'_{rel,k-1})} \frac{1}{N} \sum_{i=1}^{N_{rjk}} w_i \tag{165}$$

with estimated error

$$\Delta \frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} \approx \frac{j_{max} b_{max}^2}{4(v'_{rel,k} - v'_{rel,k-1})} \frac{1}{N} \left[\sum_{i=1}^{N_{rjk}} w_i^2 - \frac{1}{N} \left(\sum_{i=1}^{N_{rjk}} w_i \right)^2 \right]^{1/2} \tag{166}$$

Unless a very large sample of trajectories has been computed, the N_{rjk} for

* The case of nonseparable variables is treated elsewhere.[70]

most (j, k) bins will generally be quite small, resulting in large relative errors.

Distributions which are functions of two or more variables can also be calculated by moment methods. We will illustrate this only for one important distribution—molecular-beam, velocity–angle maps. The extension to other cases proceeds analogously. The quantity to be calculated is the double differential reaction cross section $d^3\sigma_r / d\Omega\, dv'_{rel}$, where v'_{rel} is final relative speed. For a fixed initial energy, v'_{rel} is confined to a finite interval from zero to a maximum value determined by conservation of total energy. Just as for histograms of final relative velocity we first transform to the variable which provides a UPS representation. Then, since the conventional finite interval for orthogonal polynomials is $-1 < \tilde{z} < 1$, we transform to a new UPS variable defined on this range. This yields

$$\tilde{z} = 5f_{v'}^3\left(1 - \tfrac{3}{5}f_{v'}^2\right) - 1 \tag{167}$$

Then the triple differential reaction cross section is expanded as

$$\frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} = \frac{\sigma_r}{2\pi} \sum_k \sum_l d_{rkl} \tilde{P}_k(\tilde{z})\, \tilde{P}_l(\tilde{u}) \tag{168}$$

where $\tilde{u}$ is $\cos\theta$ as in Section 2.6.2.2. Multiplying both sides of this equation by a product of normalized Legendre polynomials and integrating yields

$$d_{rkl} = \frac{2\pi}{\sigma_r} \int_{-1}^{1} \int_{-1}^{1} \frac{d^3\sigma_r}{d\Omega\, dv'_{rel}} P_k(\tilde{z})\, \tilde{P}_l(\tilde{u})\, d\tilde{z}\, d\tilde{u} \tag{169}$$

$$= \frac{1}{\sigma_r} \int_{-1}^{1} \int_{-1}^{1} \frac{d^2\sigma_r}{d\tilde{u}\, d\tilde{z}} \tilde{P}_k(\tilde{z})\, \tilde{P}_l(\tilde{u}) \frac{d\tilde{z}}{dv'_{rel}}\, d\tilde{z}\, d\tilde{u} \tag{170}$$

$$= \frac{1}{\sigma_r} \int \tilde{P}_k(\tilde{z})\, \tilde{P}_l(\tilde{u}) \frac{d\tilde{z}}{dv'_{rel}}\, d\sigma \tag{171}$$

If σ_r and the last integral are both evaluated from the same sample of trajectories, this becomes

$$d_{rkl} \cong \frac{\sum_{i=1}^{N_r} \tilde{P}_k(\tilde{z}_i)\, \tilde{P}_l(\tilde{u}_i) \dfrac{d\tilde{z}}{dv'_{rel}}\bigg|_{v'_{rel} = v'_{rel,i}} w_i}{\sum_{i=1}^{N_r} w_i} \tag{172}$$

where the Jacobian will be considered below and the sums are over the N_r trajectories which yield the product of interest. Substitution of equation (172) into equation (168) yields the desired result. As for angular distributions one must decide what upper limits to use in the sums. Again we recommend that only converged coefficients be used in the sums. This automatically smooths out statistical noise.

Equation (172) involves a Jacobian which can be evaluated analytically

for each trajectory. It equals

$$\frac{d\tilde{z}}{dv'_{\text{rel}}} = \frac{15}{v'_{\text{max}}} f_{v'}^2 (1 - f_{v'}^2) \tag{173}$$

where we have used equation (141) and the definitions preceding equation (138).

Finally, we mention that moment methods are also very convenient for calculating quantities such as the mean final relative velocity as a function of scattering angle or the mean component of product rotational angular momentum along some axis as a function of scattering angle. Details are in the literature.[29]

We have explicitly discussed only the case of two continuous final variables. One could also consider two discrete final variables, e.g., n' and j', or a mixed pair. e.g., j' and θ. The application of the above techniques to such cases is straightforward.

2.6.3. Initial-State–Final-State Correlations

Another application of the above techniques is to calculate initial-state–final-state correlations. An example is the average product rotational angular momentum as a function of reactant orbital angular momentum l.[26] Another example is the average value of l as a function of scattering angle.[29] More complicated examples would be the distribution of product rotational angular momentum as a function of l, the distribution of l as a function of scattering angle, or the distribution of scattering angle as a function of b.[27] These kinds of results can all be obtained efficiently by various combinations of the techniques explained above.

2.7. Available Programs

The Quantum Chemistry Program Exchange (QCPE) has four computer programs (QCPE Nos. 229, 248, 273, and 316) for carrying out trajectory calculations on reactive atom–diatom collisions. Although they do not incorporate all the most recommended techniques described in this section, they may be convenient for some trajectory studies where the use of the optimal techniques is not of the utmost importance.

All four programs are written in single-precision FORTRAN IV. Program 248 is an expanded version of program 229. Program 229 is the program used for one of the author's trajectory studies[9,14,74] on the $F + H_2$. HD. and D_2 systems. Program 316 is a version of program 273 that is suitable for use on minicomputers; thus it is less efficient than 273 when used on large computers. Program 273 is, in the words of the manual, a program "expressly intended for easy transferability between computers and for use by people who may be unfamiliar with the numerical techniques involved."

Table 2. QCPE Trajectory Codes

Number	Authors	Name	Number of symbolic cards
229	J. T. Muckerman	CLASTR: Monte Carlo quasiclassical trajectory program	2000
248	D. G. Hopper	CTAMYM: Modification of the atomic–diatomic quasiclassical trajectory program CLASTR	3000
273	S. Chapman, D.L. Bunker, and A. Gelb	A + BC: General trajectory program	1225
316	S. Chapman, K.R. Wright, D. L. Bunker, A. Gelb, and J. Santamaria	MINI A + BC: Minicomputer adapted version of the QCPE #273 general trajectory program	1500

It includes several options and is probably to be most recommended for general purposes. The program writers and the names and sizes of the programs are given in Table 2. Further documentation and/or the programs themselves may be ordered for small fees from QCPE (Chemistry Department, Indiana University, Bloomington, Indiana).

3. Other Trajectory Methods for Single-Surface Reactions

The quasiclassical trajectory method discussed in Section 2 is unsymmetrical in the way it treats initial and final states. Initial vibrational and rotational energies or actions are quantized exactly,* but final states are quantized by histogram or moment methods, if at all. Thus cross sections and rate constants calculated by the quasiclassical trajectory method do not satisfy detailed balance and time-reversal requirements.[75] It has been suggested that more accurate quasiclassical histogram results can be obtained for some state-to-state cross sections by quantizing the actions in the final state rather than the initial one.[76] This involves running trajectories on the reverse reaction using the procedures of Section 2 to calculate the reverse state-to-state cross section. The state-to-state cross section of original interest is calculated from the detailed balance relation which relates the exact forward and reverse state-to-state cross sections. This is called the quasiclassical trajectory reverse histogram (QCTRH) method, and the original method may be called the quasiclassical trajectory forward histogram (QCTFH) method. The QCTRH region may be useful in some cases near thresholds for a given state-to-state process, but

* Some workers also quantize the initial orbital angular momentum l of relative translational motion, but there is usually no good reason to do this.

it is hard to decide for a given case which method is more accurate.[60,77] We recommend that if QCTRH calculations are done they not be considered, without further evidence, as probably more accurate than the QCTFH calculations. Rather any large difference of the QCTRH results from the QCTFH results should be considered as a warning that perhaps neither is reliable.

There are also some techniques which do treat initial and final states more symmetrically. These are discussed in the rest of this section.

3.1. Unquantized Initial and Final Conditions

When one is interested in thermally averaged reaction rates rather than state-to-state rates or cross sections, it may not be necessary to use the quasiclassical quantization procedures of Section 2. In some cases, for example, for all the atoms heavy, equivalent results may be obtained if one treats the initial rotational and vibrational energies purely classically and, for thermal averaging, samples from a classical continuous Boltzmann distribution instead of a quantum discrete one. This may be called the forward classical trajectory method. If the problem of interest allows one to forego the quasiclassical quantization, then one can use the Liouville theorem to make the calculation more efficient by beginning the trajectories in a transition region instead of the reactant region. Liouville's theorem states that probability density is conserved along phase-space trajectories.[78] Therefore, in the absence of transition-region trajectories which never reach reactants or products, a classical equilibrium distribution of reactant and product states implies an equilibrium distribution at the transition region. This is rather obvious, but it has caused some confusion. Some workers have argued that this cannot be true because if a batch of trajectories sampled from an equilibrium distribution in the reactant region (where the reactant atom is not interacting with the molecule) is followed to a dividing surface in the region where all the atoms are interacting, a nonequilibrium distribution is obtained there. But this should be expected because the batch sampled does not contain those interaction-region trajectories which began in the product region. Further, if the trajectories are stopped when they first reach the dividing surface, one will be missing those interaction-region trajectories which started as reactants, have reached the dividing surface at least once previously, and are returning to it. Thus to obtain the thermal reaction rate by sampling in the interaction region, one can sample from an equilibrium distribution along the dividing surface, but one must count only those trajectories which originated from reactants and which proceed directly to products without recrossing the dividing surface. Alternatively, one could count only those trajectories which arrived directly from reactants (without previously crossing the dividing surface) and which eventually proceed to products. But there may be more computational advantage in one formulation than the other. In the formulation given second one must integrate every sampled trajectory forward until it

reaches one of the asymptotic regions, but one needs to integrate trajectories backward only until they recross the dividing surface or reach the reactant region. In the formulation given first one needs to integrate every trajectory backwards until it reaches an asymptotic region, but one can stop the forward integration if a trajectory recrosses the dividing surface. This method is called the combined phase–space–trajectory (CPST) method. It was developed and applied by Keck,[79-81] has been applied most extensively to atom–molecule reactions by Anderson and co-workers,[82-84] and has also been discussed by Mayer[85] and Miller.[86] In this method the equilibrium reaction rate constant $k_r(T)$ is given by the product $k_e(S, T) \xi(S, T)$, where $k_e(S, T)$ is the one-way equilibrium rate constant at temperature T for flow of phase points through the dividing surface S which separates reactants and products, and $\xi(S, T)$ is the fraction of trajectories, sampled from a Boltzmann distribution along the surface S at temperature T, which initiated as reactants and proceed directly to products.* If S is placed in the reactant region this yields the classical trajectory method mentioned in the first two sentences of this paragraph. This has the advantage that $k_e(S, T)$ is very easy to calculate and unweighted sampling may be done by general methods, as in Section 2. If S is in the interaction region, however, one may gain the computational advantage that $\xi(S, T)$ is much larger. But $k_e(S, T)$ and the distributions to be sampled need to be recalculated for every new choice of S. For processes with small rates the calculation may be economically prohibited if trajectories are sampled in the reactant region. But the higher efficiency of the CPST method opens these systems to the possibility of trajectory analysis.

Since the converged results of the CPST method are necessarily identical to the converged results of a classical trajectory calculation with sampling in the reactant region, one may calculate product distributions, using the methods of Section 1. By applying "product analysis" to the reactant end of the trajectory too, one may also calculate reactivity functions and reactant–product correlations. If state-to-state cross sections or rates are not needed and effects of initial- or final-state quantization are not important, the CPST method should be considered whenever the inefficiency of sampling in the reactant region is a serious problem.

3.2. Symmetrically Averaged Initial and Final Conditions

It was mentioned at the end of Section 3.1 that one could sample trajectories in the interaction region, integrate both forward and backward, and apply "product analysis" techniques to both ends of the trajectories.

---

* Alternatively, one may sample from a surface dividing reactants and products, integrate in both directions, and sum the quantity

$$(1/2)(N_c^{[i]} + 1)^{-1}[1 + (-1)^{N_c^{[i]}}]$$

where $N_c^{[i]}$ is the number of additional crossings of the $[i]$th trajectory as time runs in both directions.[79,86]

For example, one could calculate state-to-state rate constants by applying the histogram method to both ends of the trajectory. One could calculate the same kind of approximation to the state-to-state rate constants by starting the trajectories at one end and averaging the initial conditions over a histogram interval instead of fixing them at the center as in the quasi-classical trajectory method. By sampling in the reactant region this way one can also calculate state-to-state cross sections. This is called the symmetrically averaged classical trajectory method.[75,86-88] It has not been applied widely, and the few results have not been encouraging. While this method has the advantage over the quasiclassical trajectory method that it can be carried out in such a way as to satisfy detailed balance, it has the disadvantage that it appears to be less accurate. Apparently quasiclassical quantization of at least one end of the trajectories is an important element in the correspondence of trajectory results with state-to-state cross sections. The symmetrically averaged classical trajectory method is not recommended.

3.3. Exactly Quantized Initial and Final Conditions

Another way to eliminate the asymmetry of the methods of Section 2 is to calculate all results using only trajectories which satisfy the double-ended quantized boundary conditions. If this is done without including any interference effect,† it yields what has variously been called the classical limit or the classical–semiclassical method.[2,60,89-92] The quasiclassical trajectories already satisfy the quantized boundary conditions in the reactant channel, but imposition of such boundary conditions on the products requires a root search. Having found these root trajectories, the state-to-state cross sections may be calculated from the Jacobian determinant D of the final quantized action variables with respect to the initial values of the angle variables conjugate to the corresponding reactant action variables.[2,91,92] However, it has been shown both on general grounds[90] and by computational examples[60] that this method is not more accurate than the quasiclassical trajectory histogram method. Since (because of the root search) it is also more difficult computationally, it is not recommended.

3.4. Classical S Matrix Theory and Other Semiclassical Methods That Include Interference Effects

In this section we discuss a few methods for incorporating more quantum effects into trajectory calculations. In particular the methods discussed here all incorporate some effects due to the phase of the quantum-mechanical wave function, i.e., interference effects, and they also allow for the treatment of multidimensional tunneling effects. They have not been demonstrated to be practical for three-dimensional reactive scattering cal-

† Interference effects are discussed in the following section, 3.4.

Donald G. Truhlar and James T. Muckerman

culations, and we are not recommending them for such. But they provide valuable insight into the reasons for the successes and failures of simpler trajectory techniques, and they provide a language for discussion of semi-classical and quantum corrections to these techniques. For these reasons we recommend the study of these methods.

The first method is the classical S matrix theory,[2,89-92] also called exact semiclassical theory.[93] Using the root trajectories of Section 3.3, which satisfy double-ended quantized boundary conditions, one calculates a phase along each trajectory. The phase is an action integral computed from the local momenta and is basically the number of de Broglie wave-lenghts in the trajectory divided by 2π. Each root trajectory j contributes an amplitude $D_j^{1/2}e^{i\phi_j}$, where D_j is the Jacobian determinant and ϕ_j the phase. Adding amplitudes of all root trajectories for a given-state-to-state transition and then squaring gives what is called the primitive semiclassical approximation of classical S matrix theory. Because amplitudes are added, interference effects are included. If there are no root trajectories for a given state-to-state process then the state-to-state transition is said to be classi-cally forbidden or classically inaccessible. A state-to-state process for which the quasiclassical trajectory histogram methods, either forward or reverse, yield zero is always classically forbidden. But the converse is not true. If a state-to-state process is classically forbidden, one may still always find solutions to the classical equations of motion which satisfy the double-ended quantized boundary conditions by letting the time step be a complex number in the numerical integration. This causes the coordinates, momenta, and phase to become complex valued (i.e., have a nonzero imaginary part) during the trajectory although, to satisfy physical boundary conditions at the end of the trajectory, the positions and coordinates must all become real valued again at the end of the trajectory. This requirement is sometimes associated with computational instabilities. The instabilities must be re-lieved by judicious choice of path through the complex t plane. This free-dom of choice exists because the final values of coordinates, momenta, and phases are independent of the path chosen as long as no branch lines of the trajectory are crossed.[91] For complex time paths, the phase is complex and the physically interesting solutions have $|e^{i\phi_j}| < 1$, often $\ll 1$. Thus the contribution of complex-valued trajectories to the cross section for a state-to-state process is exponentially small. This procedure is called the analytic continuation of classical mechanics and it provides a multidimen-sional generalization for classically forbidden transitions of the tunneling picture for one-dimensional barrier penetrations. When any real-valued root trajectories contribute to a particular state-to-state cross section, their contributions will often but not always dominate the contributions of complex-valued trajectories. For practical applications to real problems it is difficult to know whether or not one has found all the significant root trajectories, especially the complex ones. Another serious problem is that

usually, and especially in threshold regions for the state-to-state process of interest, accurate numerical results can be obtained only by using a uniformized expression (rather than a simple sum) to add the amplitudes of the root trajectories.[60,90,94-97] The appropriate uniformized expression may be special to each new case, and at this time no straightforward general way to derive the appropriate uniformized expressions for new cases is known. An additional difficulty in applying uniformized expressions is that they require absolute phase differences, including the phase differences coming from $D_j^{1/2}$, but phase differences are easier to calculate modulo π.[96]

Although, as mentioned above, it is generally impractical to apply the classical S matrix theory to real problems, the theory does help one to understand the limitations of the quasiclassical trajectory histogram method. The quasiclassical trajectory histogram method can be derived as a suitable average of the primitive semiclassical method with real-valued trajectories when applied to an observable which does not correspond to a completely specified (including a component of rotational angular momentum) final state or which involves some averaging over initial conditions.[90] But for classically forbidden processes or threshold regions, the analytically continued trajectories and the phase information are crucial aspects of the problem which must be included for quantitative results.

An alternative approach to semiclassical dynamics is the Gaussian wave packet method of Heller.[98-100] In this method the initial states are decomposed into time-dependent localized wave packets, each of which is separately propagated using the assumption that the potential energy may be expanded quadratically around the instantaneous center of the wave packet. Because of this assumption the center of the wave packet in both coordinate and momentum space follows the classical equations of motion. The wave packets carry phase information and must be added coherently in the product region. This method has the advantages that it requires no root searches and in a sense uniformization is automatic. In addition the visualization of the wave packets as quantum trajectories has appeal for intuitive understanding of quantum effects. But the method has the disadvantage that effects of barrier penetration, rapidly varying potential surfaces, and long-lived collisions require wave packet bifurcation or multifurcation to attain good accuracy. There is no simple criterion for how often to bifurcate the wave packet. If the reexpansion of the wave packets is repeated often enough, the method yields the exact quantum-mechanical result in the form of a discrete phase-space path integral. Many of the practical details of application of this new method to semiclassical dynamics have not been thoroughly explored, but the method seems well suited in principle to computational exploitation, and further study is clearly warranted.

Another approach to semiclassical dynamics involves the use of Wigner phase-space densities.[101] It has been suggested that Wigner phase-space

densities might provide semiclassical initial conditions for a trajectory study; the semiclassical phase-space distributions might be more accurate than the quasiclassical ones of Section 1.[102] The Wigner phase-space densities have a high-energy tail which can provide a semiclassical description of multidimensional tunneling effects. Further, they have negative weights in some regions of phase space; this suggests that interference effects might be included. Heller has analyzed some of the errors in classically propagating such phase-space distributions, and he has suggested a revised classical-like dynamics for ameliorating the difficulties.[102] General practical solutions to all the computational difficulties have not yet been obtained. But comparison of the quasiclassical initial phase-space distributions to the Wigner ones does help visualize some of the effects missing in the former approach.

4. Trajectory Methods for Multisurface Reactions

So far in this chapter we have only considered the case where the electronic motion is treated completely adiabatically. Then there are no electronic transitions, and the electronic energy plus internuclear electrostatic interactions provide a potential energy surface for internuclear motion. This is the correct limit if electronic motion is treated by quantum mechanics and nuclear motion is treated classically, i.e., if the wave function is expanded in exact fixed-nuclei electronic states at any time, but the limit $h \to 0$ is taken when considering the changes in the system's wave function due to nuclear motion.[2,103,104] Such a limit is most valid when the spacing between electronic energy states (for fixed nuclei) is large compared to the kinetic energy of internuclear motion. For some chemical reactions, e.g., $H + H_2$ at low energies, this is true for all points on all trajectories. For some other problems, e.g., low-energy collisions of systems with isolated surface crossings or isolated weakly avoided surface crossings, this is true for all except a few isolated regions of configuration space. These regions may be considered as narrow subspaces in the configuration space, and collisions may be considered as electronically adiabatic except when the trajectories enter these subspaces. Other problems of interest involve weak interaction of electronic states with large energy differences, interaction of electronic states which are close in energy over wide regions of configuration space, and interactions of dense (in number of electronic states per unit energy) sets of electronic states where successive surface crossings or avoided surface crossings are not well isolated. For these classes of problems, electronic and internuclear motion are not well separated dynamically. Since electronic motion in bound states must almost always be treated quantum mechanically, its nonseparation from internuclear motion means that internuclear motion must be treated quantum

mechanically and the trajectory concept must be discarded as inapplicable for such collisions. For the former class of problems, involving only narrow regions of nonadiabaticity, we can use the model of trajectory surface hopping. In this model one defines a seam in the nonadiabatic region. The internuclear motion is treated by trajectories everywhere else, and transitions are assumed to be able to occur only when a seam is crossed. At seams it is assumed that there is a certain probability for an electronic transition to occur. If it does the internuclear motion is continued as a new trajectory, starting at the seam and governed by the potential surface corresponding to the new electronic state. If it does not then the original trajectory may be continued as if a single-surface problem were being considered. This is called the trajectory surface-hopping (TSH) model.

The account just given indicates that there are three new elements in a TSH calculation: (i) defining the seam, (ii) calculating the probability of a surface hop, and (iii) determining the momenta to start the trajectory on the new surface. All the other aspects of the calculation are the same as for single-surface calculations discussed in Sections 2 and 3. Element (i) depends on electronic structure considerations and is discussed briefly in Chapter 18. Here we discuss elements (ii) and (iii).

The probability of a surface hop is governed by the nonadiabatic coupling terms in the quantum-mechanical equations[105,106] for coupled electronic and internuclear motion. In an adiabatic representation, transitions are caused by internuclear kinetic energy operators acting on the internuclear parameters in the electronic fixed-nuclei wave functions. The simplest theory of nonadiabatic transitions is the Landau–Zener semiclassical model (see Chapter 13) for transitions caused by the radial kinetic energy in atom–atom collisions. It is natural to try to extend this to treat nonadiabatic transitions in atom–molecule systems as caused by the velocity component perpendicular to the seam. Tully and Preston have shown by classical path calculations (see Chapter 18) that this velocity component is the effective one in causing nonadiabatic transition in some cases.[107] It is clear from its derivation, however, that the Landau–Zener model has serious shortcomings. We recommend instead that the surface-hop probability be calculated by the original method of Tully and Preston,[107] which is to perform classical path semiclassical calculations for the time-dependent probability amplitudes of the coupled electronic states and parametrize an analytic expression to the results for probabilities of a surface hop to be used in the TSH calculations. However, if the conditions for validity of the Landau–Zener approximation are to be assumed to apply, then the parameters of the Landau–Zener expression should be evaluated by the prescription of Stine and one of the authors.[108] This problem is discussed further in Chapters 13 and 18.

The prescription for changing momenta when an electronic transition occurs at a seam can be obtained by solving the classical equations of

motion for the internuclear motion on a potential surface given by the old surface $V_1(R_1, R_2, R_3)$ on one side of the seam and the new surface $V_2(R_1, R_2, R_3)$ on the other side of the seam.[103] In general the location of the seam is given by a function $w(\mathbf{q}, \mathbf{Q})$ of the generalized coordinates of equation (9).* Since $w(\mathbf{q}, \mathbf{Q})$ is independent of time and depends only on relative coordinates $(q_1, q_2, q_3, Q_1, Q_2, Q_3)$ the solution to the equations of motion automatically conserves total energy and total angular momentum. The explicit solution to the equations of motion indicates that the change in the generalized momenta is proportional to the gradient of w evaluated at the point where the trajectory crosses the seam. The final expression is[103,108]

$$p_i^{(2)} = p_i^{(1)} - \left(\frac{\partial w}{\partial q_i}\right)_{\text{seam}} \frac{A}{B}\left[1 - \left(1 - 2\Delta W_{\text{seam}}\frac{B}{A^2}\right)^{1/2}\right] \tag{174}$$

$$P_i^{(2)} = P_i^{(1)} - \left(\frac{\partial w}{\partial Q_i}\right)_{\text{seam}} \frac{A}{B}\left[1 - \left(1 - 2\Delta W_{\text{seam}}\frac{B}{A^2}\right)^{1/2}\right] \tag{175}$$

where

$$A = \sum_{i=1}^{3}\left[\left(\frac{\partial w}{\partial q_i}\right)_{\text{seam}}\frac{1}{\mu_{\text{BC}}}p_i^{(1)} + \left(\frac{\partial w}{\partial Q_i}\right)_{\text{seam}}\frac{1}{\mu_{\text{A,BC}}}P_i^{(1)}\right] \tag{176}$$

and

$$B = \sum_{i=1}^{3}\left[\frac{1}{\mu_{\text{BC}}}\left(\frac{\partial w}{\partial q_i}\right)_{\text{seam}}^2 + \frac{1}{\mu_{\text{A,BC}}}\left(\frac{\partial w}{\partial Q_i}\right)_{\text{seam}}^2\right] \tag{177}$$

where the superscripts (1) and (2) indicate values just before and just after crossing the seam, respectively. In equations (174) and (175)

$$\Delta W_{\text{seam}} \equiv (V_2 - V_1)_{\text{seam}} \tag{178}$$

One final point should be mentioned. It is computationally more efficient to let the trajectory branch rather than hop.[107] In other words, instead of letting the trajectory change surfaces or not based on the probability P, one can continue integrating two trajectories, one on the original surface with weight $(1 - P)$ and one on the final surface with weight P. As each branch reaches additional crossing points it branches further and each branch acquires new reduced weights. This complicates the error analysis but is more efficient. Tully and Preston have named these two techniques the anteater and the ants technique. They found the most efficient procedure was a compromise between the two in which trajectories were allowed to branch at first but when the number of branches became too great they were forced to hop.[107]

---

* For cases where the seam is the locus of intersection of two diabatic surfaces, $w(R_1, R_2, R_3)$ is the energy difference of the two diabatic surfaces.

Just as semiclassical methods are useful for understanding the errors in trajectory studies of single-surface reactions, they are helpful in understanding the errors of trajectory surface-hopping calculations. The classical path method[107] and classical S matrix theory[2,103,109-114] are most useful in this regard. The former shows clearly how TSH calculations must fail when the nonadiabatic regions become too nonlocalized. The latter shows clearly how TSH calculations must fail when successive nonadiabatic regions occur too close to each other or when nonadiabatic regions are too close to classical turning points or in classically forbidden regions of configuration space. The latter regions are regions which are not visited by trajectories starting with the initial conditions of interest.

5. Concluding Remarks

In this chapter we have tried to recommend computationally efficient techniques for carrying out molecular trajectory calculations for atom–diatom reactive collisions. We have discussed different ways of using the trajectories to predict final distributions of both discrete and continuous properties of the products. We have also discussed semiclassical theories which shed some light on the errors due to using classical mechanics.* Despite these errors the trajectory method is ·one of the most powerful computational techniques for studying the details of reactive molecular collisions and we envision its increasing use in the years to come.

References

1. J.L. Powell and B. Craseman, *Quantum Mechanics*, Addison-Wesley, Reading, Massachusetts (1961), pp. 98–100.
2. W.H. Miller, Classical-limit quantum mechanics and the theory of molecular collisions, *Adv. Chem. Phys.* **25**, 69–177 (1974).

* The errors in using classical mechanics for reactive collisions are discussed again in Chapter 18 where some comparisons of classical and quantum calculations are referenced and discussed.

3. M. Karplus and L.M. Raff, Theoretical investigations of reactive collisions in molecular beams: K + CH_3I, *J. Chem. Phys.* **41**, 1267–1277 (1964).

4. D.L. Bunker and N.C. Blais, Monte Carlo calculations. V. Three-dimensional study of a general bimolecular interaction potential, *J. Chem. Phys.* **41**, 2377–2386 (1964).

5. M. Karplus, R.N. Porter, and R.D. Sharma, Exchange reactions with activation energy. I. Simple barrier potential for (H, H_2), *J. Chem. Phys.* **43**, 3259–3287 (1965).

6. P.J. Kuntz, M.H. Mok, and J.C. Polanyi, Distribution of reaction products. V. Reactions forming an ionic bond, M + XC(3D), *J. Chem. Phys.* **50**, 4623–4652 (1969).

7. J.C. Polanyi and W.H. Wong, Location of energy barriers. I. Effect on the dynamics of reactions A + BC, *J. Chem. Phys.* **51**, 1439–1450 (1969).

8. D.L. Bunker, Classical trajectory methods, *Methods Comput. Phys.* **10**, 287–325 (1971).

9. J.T. Muckerman, Monte Carlo calculations of energy partitioning and isotope effects in reactions of fluorine atoms with H_2, HD, and D_2, *J. Chem. Phys.* **54**, 1155–1164 (1971).

10. R.L. Jaffe and J.B. Anderson, Classical trajectory analysis of the reaction F + H_2 → HF + H, *J. Chem. Phys.* **54**, 2224–2236 (1971); Erratum: **56**, 682 (1972).

11. A.G. Clarke and G. Burns, Trajectory studies of atomic recombination reactions, *J. Chem. Phys.* **55**, 4717–4730 (1971).

12. D.L. Thompson, On a classical trajectory study of energy transfer in some atom–diatomic molecule systems, *J. Chem. Phys.* **56**, 3570 (1972); Erratum: **65**, 5031–5032 (1976).

13. L.M. Raff, D.L. Thompson, L.B. Sims, and R.N. Porter, Dynamics of the molecular and atomic mechanisms for the hydrogen–iodine exchange reaction, *J. Chem. Phys.* **56**, 5998–6027 (1972); Erratum: **65**, 4338 (1976).

14. J.T. Muckerman, Classical dynamics of the reaction of fluorine atoms with hydrogen molecules. III. The hot-atom reactions of ^{18}F with HD, *J. Chem. Phys.* **57**, 3388–3396 (1972).

15. C.A. Parr, J.C. Polanyi, and W.H. Wong, Distribution of reaction products (theory). VIII. Cl + HI, Cl + DI, *J. Chem. Phys.* **58**, 5–20 (1973).

16. N.C. Blais and D.G. Truhlar, Monte Carlo trajectories: Dynamics of the reaction F + D_2 on a semiempirical valence-bond potential energy surface, *J. Chem. Phys.* **58**, 1090–1108 (1973).

17. H.H. Suzukawa, Jr., D.L. Thompson, V.B. Cheng, and M. Wolfsberg, Empirical testing of the suitability of a nonrandom integration method for classical trajectory calculations: Comparisons with Monte Carlo techniques, *J. Chem. Phys.* **59**, 4000–4008 (1973).

18. J.C. Polanyi and J.L. Schreiber, The dynamics of bimolecular reactions, in *Physical Chemistry: An Advanced Treatise*, Vol. VIA, *Kinetics of Gas Reactions*, W. Jost, editor, Academic Press, New York (1974), pp. 383–487.

19. J.M. White and D.L. Thompson, Monte Carlo quasiclassical trajectory study of Br + HBr and H + HBr: Effect of reactant vibration and rotation on reaction rates and energy transfer, *J. Chem. Phys.* **61**, 719–732 (1974).

20. N.C. Blais and D.G. Truhlar, Monte Carlo trajectories: The reactions H + Br_2 → HBr + Br, *J. Chem. Phys.* **61**, 4186–4203 (1974); Erratum: **65**, 3803 (1976).

21. P.J. Kuntz, The classical trajectory method, in *Interaction between Ions and Molecules*, P. Ausloos, editor, Plenum Press, New York (1975), pp. 123–137.

22. R.N. Porter, D.L. Thompson, L.M. Raff, and J.M. White, Comparison of the combined phase-space/trajectory and quasiclassical trajectory methods in the study of reaction dynamics: H + I_2 and H + Br_2, *J. Chem. Phys.* **62**, 2429–2445 (1975).

23. D.J. Malcome-Lawes, Dynamics of some hydrogen isotopic exchange reactions at high energies, *J. Chem. Soc. Faraday Trans. II* **71**, 1183–1199 (1975).

24. R.N. Porter, L.M. Raff, and W.H. Miller, Quasiclassical selecton of initial coordinates and momenta for a rotating Morse oscillator, *J. Chem. Phys.* **63**, 2214–2218 (1975).

25. J.C. Polanyi, J.L. Schreiber, and J.J. Sloan, Distribution of reaction products, *Chem. Phys.* **9**, 403–412 (1975).

26. N.H. Hijazi and J.C. Polanyi, Magnitude and orientation of rotation in exchange reactions $A + BC \rightarrow AB + C$. II, *Chem. Phys.* **11**, 1–16 (1975).

27. N.C. Blais and D.G. Truhlar, Monte Carlo trajectory study of $Ar + H_2$ collisions. I. Potential energy surface and cross sections for dissociation, recombination, and inelastic scattering, *J. Chem. Phys.* **65**, 5335–5356 (1976).

28. R.N. Porter and L.M. Raff, Classical trajectory methods in molecular collisions, in *Modern Theoretical Chemistry*, Vol. 2, *Dynamics of Molecular Collisions: Part B*, W.H. Miller, editor, Plenum Press, New York (1976), pp. 1–52.

29. N.C. Blais and D.G. Truhlar, Monte Carlo trajectories: Alignment of HBr rotational angular momentum as a function of scattering angle for the reaction $H + Br_2 \rightarrow HBr + Br$, *J. Chem. Phys.* **67**, 1540–1546 (1977).

30. H. Goldstein, *Classical Mechanics*, Addison-Wesley, Reading, Massachusetts (1950).

31. J.O. Hirschfelder, Coordinates which diagonalize the kinetic energy of relative motion, *Int. J. Quantum Chem. Symp.* **3**, 17–31 (1969).

32. R.A. LaBudde and R.B. Bernstein, Classical study of rotational excitation of a rigid rotor: $Li^+ + H_2$, *J. Chem. Phys.* **55**, 5499–5516 (1971).

33. M.E. Riley and M.K. Matzen, Non-Maxwellian H and F velocity distributions in in an $H_2 - F_2$ reaction, *J. Chem. Phys.* **63**, 4787–4799 (1975).

34. I.C. Percival, Semiclassical theory of bound states, *Adv. Chem. Phys.* **36**, 1–61 (1977).

35. P.J. Davis and I. Polonsky, Numerical interpolation, differentiation, and integration, in *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, M. Abramowitz and I.A. Stegun, editors, U.S. Government Printing Office, Washington, D.C. (1964), pp. 875–924, especially pp. 888–889.

36. J.B. Scarborough, *Numerical Mathematical Analysis*, 4th ed., Johns Hopkins Press, Baltimore, Maryland (1958), pp. 192–198.

37. Z. Kopal, *Numerical Analysis*, Chapman and Hall, London (1955), p. 381.

38. F.J. Smith, The numerical evaluation of the classical angle of deflection and of the J.W.K.B. phase shift, *Physica (Utrecht)* **30**, 497–504 (1964).

39. R.T. Pack, Space-fixed vs. body-fixed axes in atom–diatomic molecule scattering: Sudden approximations, *J. Chem. Phys.* **60**, 633–639 (1974).

40. L. Lapidus and J.H. Seinfeld, *Numerical Solution of Ordinary Differential Equations*, Academic Press, New York (1971).

41. M.K. Matzen and M.E. Riley, private communication.

42. R. Bulirsch and J. Stoer, Numerical treatment of ordinary differential equations by extrapolation methods, *Numer. Math.* **8**, 1–13 (1966).

43. L.F. Shampine and M.K. Gordon, *Computer Solution of Ordinary Differential Equations: The Initial Value Problem*, W.H. Freeman, San Francisco (1975).

44. C.A. Parr, Classical dynamics of triatomic systems, Ph.D. Thesis, California Institute of Technology, Pasadena, California (1968), pp. 47–55, 156–159, 168–176.

45. P.W. Brumer, Structure and collision complex dynamics of alkali halide dimers, Ph.D. Thesis, Harvard University, Cambridge, Massachusetts (1972), pp. IV-39 to IV-61.

46. P. Brumer and M. Karplus, Collision complex dynamics in alkali halide exchange reactions, *Discuss. Faraday Soc.* **55**, 80–92 (1973).

47. C.W. Gear, Hybrid methods for initial value problems in ordinary differential equations, *J. SIAM Numer. Anal. Ser. B* **2**, 69–86 (1964).

48. *Symposium on Monte Carlo Methods Held at the University of Florida*, H.A. Meyer, editor, John Wiley and Sons, New York (1956); see especially the contributions of A.W. Marshall, pp. 1–14, H. Kahn, pp. 146–190, and J.W. Butler, pp. 249–264.

49. J.M. Hammersley and D.C. Handscomb, *Monte Carlo Methods*, Methuen & Co., London (1964, corrected printing 1965).

50. *The Monte Carlo Method: The Method of Statistical Trials*, Yu. A. Schreiber, editor, Pergamon Press, Oxford (1966); see especially the first chapters by Yu. A. Schreiber, pp. 1–90, and I.M. Sobol', pp. 91–130.

51. M. Zelen and N.C. Severo, in *Handbook of Mathematical Functions*, M. Abramowitz and I.A. Stegun, editors, National Bureau of Standards, Washington, D.C. (1964), pp. 925–995; see Table 26.10.

52. M.B. Faist, J.T. Muckerman, and F.E. Schubert, Importance sampling and histo-grammic representations of reactivity functions and product distributions in Monte Carlo quasiclassical trajectory calculations *J. Chem. Phys.* **69**, 4087–4096 (1978).

53. M.H. Hansen, W.N. Hurwitz, and W.G. Madow, *Sample Survey Methods and Theory*, Vols. 1, 2, John Wiley and Sons, New York (1953), p. 209 (Vol. 1) and pp. 132–134 (Vol. 2.)

54. N.C. Blais and D.G. Truhlar, Monte Carlo trajectory study of $Ar + H_2$: Vibrational selectivity of dissociative collisions at 4500°K, *J. Chem. Phys.*, in press.

55. R.C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, Chemical Catalog Company, New York (1927), pp. 260–270.

56. D.G. Truhlar, Interpretation of the activation energy, *J. Chem. Educ.* **55**, 309–311 (1978).

57. D.G. Truhlar and N.C. Blais, Direct calculation of the equilibrium value of the energy of activation for dissociation of H_2 by Ar and evidence for the important contribution of collisional dissociation from low vibrational quantum numbers at shock-tube tem-peratures, *J. Am. Chem. Soc.* **99**, 8108–8109 (1977).

58. D.G. Truhlar and J.C. Gray, Interpretation and temperature dependence of the energy of activation for the reactions $H + Cl_2, H_2 + I, H + H_2$, and isotopic analogues, *Chem. Phys. Lett.* **57**, 93–99 (1978).

59. D.G. Truhlar and J.W. Duff, Classical probability matrix: Prediction of quantum-state distributions by a moment analysis of classical trajectories, *Chem. Phys. Lett.* **36**, 551–554 (1975).

60. D.G. Truhlar, Quasiclassical predictions of final vibrational state distributions in reactive and nonreactive collisions, *Int. J. Quantum Chem. Symp.* **10**, 239–250 (1976).

61. R.J. Gordon, A comparison of exact classical and quantum mechanical calculations of vibrational energy transfer, *J. Chem. Phys.* **65**, 4945–4957 (1976).

62. U. Halavee and R.D. Levine, Quantal transition probabilities from classical trajec-tories: Application to the collinear reactive $H + Cl_2$ system, *Chem. Phys. Lett.* **46**, 35–41 (1977).

63. O. Atabek and R. Lefebvre, Moment analysis of dynamics of photodissociation of linear triatomics, *Chem. Phys. Lett.* **52**, 29–33 (1977).

64. R.J. Gordon, A comparison of exact classical and quantum mechanical calculations of vibrational energy transfer. II. The effect of long-lived collision complexes, *J. Chem. Phys.* **67**, 5923–5929 (1977).

65. A. Ben-Shaul, R.D. Levine, and R.B. Bernstein, Entropy and chemical change. II. Analysis of product energy distributions: Temperature and entropy deficiency, *J. Chem. Phys.* **57**, 5427–5447 (1972).

66. J.C. Light, Statistical theory of bimolecular exchange reactions, *Discuss. Faraday Soc.* **44**, 14–29 (1968).

67. D.G. Truhlar and A. Kuppermann, Exact and approximate quantum mechanical reaction probabilities and rate constants for the collinear $H + H_2$ reaction, *J. Chem. Phys.* **56**, 2232–2252 (1972).

68. A. Ben-Shaul, R.D. Levine, and R.B. Bernstein, Prior-expectation distribution func-tions for energy disposal and energy consuption in reactive molecular collisions, *J. Chem. Phys.* **61**, 4937–4938 (1974).

69. A. Ben-Shaul, On statistical models and prior distributions in the theory of chemical reactions, *Chem. Phys.* **22**, 341–366 (1977).

70. M.B. Faist, The uniform phase space representation of product state distributions of elementary chemical reactions, *J. Chem. Phys.* **65**, 5427–5435 (1976).

71. R.B. Bernstein and M.B. Faist, Information content of detailed differential cross sections (molecular beam scattering velocity-angle maps) vs. resolved product state distributions, *J. Chem. Phys.* **65**, 5436–5444 (1976).

72. D.G. Truhlar and N.C. Blais, Legendre moment method for calculating differential scattering cross sections from classical trajectories with Monte Carlo initial conditions, *J. Chem. Phys.* **67**, 1532–1539 (1977).

73. E.A. Gislason and J.G. Sachs, Expansion of differential cross sections determined from classical trajectory studies in a series of Legendre polynomials, *Chem. Phys. Lett.* **52**, 270–275 (1977).

74. J.T. Muckerman, Classical dynamics of the reaction of fluorine atoms with hydrogen molecules. II. Dependence on the potential surface, *J. Chem. Phys.* **56**, 2997–3006 (1972).

75. J.L. Schreiber, Discussion, *Faraday Discuss. Chem. Soc.* **55**, 72–73 (1973).

76. S.C. Leasure and J.M. Bowman, A dynamic threshold in the $F + H_2$ reaction as determined from three-dimensional quasiclassical-reverse trajectory calculations, *Chem. Phys. Lett.* **39**, 462–467 (1976).

77. D.G. Truhlar, J.A. Merrick, and J.W. Duff, Comparison of trajectory calculations, transition state theory, quantum mechanical reaction probabilities, and rate constants for the collinear reaction $H + Cl_2 \rightarrow HCl + Cl$, *J. Am. Chem. Soc.* **98**, 6771–6783 (1976).

78. R.C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, London (1938), pp. 48–52.

79. J. Keck, Statistical investigation of dissociation cross-sections for diatoms, *Discuss. Faraday Soc.* **33**, 173–182 (1962).

80. J. Keck, Variational theory of reaction rates, *Adv. Chem. Phys.* **13**, 85–121 (1967).

81. J.C. Keck, Monte Carlo trajectory calculations of atomic and molecular excitation in thermal systems, *Adv. At. Molec. Phys.* **8**, 39–69 (1972).

82. J.B. Anderson, Statistical theories of chemical reactions: Distributions in the transition region, *J. Chem. Phys.* **58**, 4684–4692 (1973).

83. R.L. Jaffe, J.M. Henry, and J.B. Anderson, Variation theory of reaction rates: Application to $F + H_2 \leftrightarrows HF + H$, *J. Chem. Phys.* **59**, 1128–1141 (1973).

84. J.B. Anderson, A test of the validity of the combined phase-space trajectory method, *J. Chem. Phys.* **62**, 2446–2453 (1975).

85. I. Mayer, Some remarks on "Statistical theories of chemical reactions. Distribution in the transition region," *J. Chem. Phys.* **60**, 2564–2565 (1974).

86. W.H. Miller, Quantum mechanical transition state theory and a new semiclassical model for reaction rate constants, *J. Chem. Phys.* **61**, 1823–1834 (1974).

87. W.H. Miller, Discussion, *Faraday Discuss. Chem. Soc.* **55**, 71–72 (1973).

88. H. Essén, G.D. Billing, and M. Baer, Comparison of quantum mechanical and quasiclassical calculations of collinear reaction rate constants for the $H + Cl_2$ and $D + Cl_2$ systems, *Chem. Phys.* **17**, 443–449 (1976).

89. W.H. Miller, The semiclassical nature of atomic and molecular collisions, *Acc. Chem. Res.* **4**, 161–167 (1971).

90. W.H. Miller, Classical S matrix for rotational excitation: Quenching of quantum effects in molecular collisions, *J. Chem. Phys.* **54**, 5386–5397 (1971).

91. J.D. Doll, T.F. George, and W.H. Miller, Complex-valued classical trajectories for reactive tunneling in three-dimensional collisions of H with H_2, *J. Chem. Phys.* **58**, 1343–1351 (1973).

92. A.W. Raczkowski and W.H. Miller, Classical S matrix calculation for vibrationally inelastic transitions in three-dimensional collisions of Li^+ with H_2, *J. Chem. Phys.* **61**, 5413–5420 (1974).

93. R.A. Marcus, The theoretical approach, *Faraday Discuss. Chem. Soc.* **55**, 9–21 (1973).

94. H. Kreek, R.L. Ellis, and R.A. Marcus, Semiclassical collision theory: Multidimensional Bessel uniform approximation, *J. Chem. Phys.* **61**, 4540–4544 (1974).

95. H. Kreek, R.L. Ellis, and R.A. Marcus, Semiclassical collision theory: Application of multidimensional uniform approximations to atom–rigid rotor system, *J. Chem. Phys.* **62**, 913–926 (1975).

96. J.W. Duff and D.G. Truhlar, Classical S matrix: Numerical applications to classically allowed chemical reactions, *Chem. Phys.* **4**, 1–23 (1974).

97. J.W. Duff and D.G. Truhlar, Classical S matrix: Application of the Bessel uniform approximation to a chemical reaction, *Chem. Phys. Lett.* **40**, 251–256 (1976).

98. E.J. Heller, Time dependent approach to semiclassical dynamics, *J. Chem. Phys.* **62**, 1544–1555 (1975).

99. E.J. Heller, Wavepacket path integral formulation of semiclassical dynamics, *Chem. Phys. Lett.* **34**, 321–325 (1975).

100. E.J. Heller, Classical S matrix limit of wavepacket dynamics, *J. Chem. Phys.* **65**, 4979–4989 (1976).

101. E. Wigner, On the quantum correction for thermodynamic equilibrium, *Phys. Rev.* **40**, 749–759 (1932).

102. E.J. Heller, Wigner phase space method: Analysis for semiclassical applications, *J. Chem. Phys.* **65**, 1289–1298 (1976).

103. W.H. Miller and T.F. George, Semiclassical theory of electronic transitions in low energy atomic and molecular collisions involving several nuclear degrees of freedom, *J. Chem. Phys.* **56**, 5637–5652 (1972).

104. J.-T. Hwang and P. Pechukas, The adiabatic theorem in the complex plane and the semiclassical calculation of nonadiabatic transition amplitudes, *J. Chem. Phys.* **67**, 4640–4653 (1977).

105. J.O. Hirschfelder and W.J. Meath, The nature of intermolecular forces, *Adv. Chem. Phys.* **12**, 3–106 (1967).

106. H. Eyring and S.H. Lin, Potential energy surfaces, in *Physical Chemistry: An Advanced Treatise,* Vol. VIA, *Kinetics of Gas Reactions,* W. Jost, editor, Academic Press, New York (1974), pp. 121–186.

107. J.C. Tully and R.K. Preston, Trajectory surface hopping approach to nonadiabatic molecular collisions: The reaction of H^+ with D_2, *J. Chem. Phys.* **55**, 562–572 (1971).

108. J.R. Stine and J.T. Muckerman, On the multidimensional surface intersection problem and classical trajectory "surface hopping," *J. Chem. Phys.* **65**, 3975–3984 (1976).

109. T.F. George and Y.-W. Lin, Multiple transition points in a semiclassical treatment of electronic transitions in atom(ion)–diatom collisions, *J. Chem. Phys.* **60**, 2340–2349 (1974).

110. Y.-W. Lin, T.F. George, and K. Morokuma, Semiclassical treatment of electronic transitions in molecular collisions: Collinear $H^+ + D_2 \rightarrow HD^+ + D$, *J. Chem. Phys.* **60**, 4311–4322 (1974).

111. Y.-W. Lin, T.F. George, and K. Morokuma, Semiclassical treatment of electronic transitions in molecular collisions: Three-dimensional $H^+ + D_2 \rightarrow HD^+ + D$, *Chem. Phys. Lett.* **30**, 49–53 (1975).

112. A. Komornicki, T.F. George, and K. Morokuma, Decoupling scheme for a semiclassical treatment of electronic transitions in atom–diatom collisions: Real-valued trajectories and local analytic continuation, *J. Chem. Phys.* **65**, 48–54 (1976).

113. J.R. Stine and J.T. Muckerman, Conditions for the equivalence of the "surface hopping" and complex-valued-time methods to effect nonadiabatic transitions, *Chem. Phys. Lett.* **44**, 46–49 (1976).

114. G.L. Bendazzolli, M. Raimondi, B.A. Garetz, T.F. George, and K. Morokuma, Semiclassical study of collision-induced predissociation: Comparison of the Landau–Zener model with the method of analytic continuation, *Theor. Chim. Acta* **44**, 341–350 (1977).