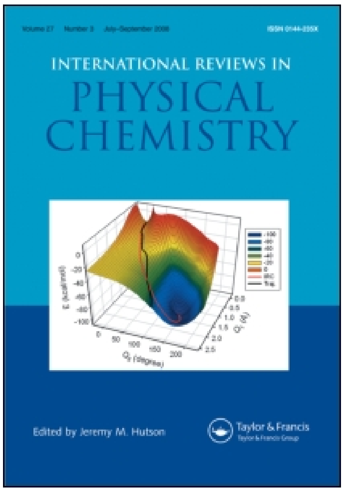

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# Practical methods for calculating rates of unimolecular reactions

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This review focuses on practical methods for calculating rates for unimolecular reactions in large molecules. We describe methods based on classical and semiclassical approximations for which realistic full-dimensional calculations using global potential energy surfaces are feasible. We describe a set of methods that can be used to treat unimolecular processes over the entire energy range: for statistical and non-statistical dynamics, for random and mode selected initial conditions, and when tunnelling effects are important. Standard classical trajectory simulations can be used when the classical approximation is valid but are limited to high energies since the long numerical integration times required at low energies are not feasible. Monte Carlo variational transition-state theory can be used at energies near threshold where the dynamics are usually statistical. The rates in the energy range above the statistical limit and yet below that accessible by straightforward classical simulations can be computed using intramolecular dynamics diffusion theory. Semiclassical approaches can be used to include tunnelling effects in classical trajectory simulations.

## 1. Introduction

Efforts to predict the rates of chemical reactions began in the 1880s [1, 2] with attempts to explain the temperature dependence of reactions. These efforts resulted in not much more than empirical relationships with some underpinnings of simple primitive ideas of their meaning. The application of statistical mechanics and collision theory to reactions [3] provided the first significant steps towards actual theories. The idea that colliding molecules form an activated complex in the region of a potential barrier between reactants and products, with a quasi-equilibrium existing between the reactants and activated complex [4] was the basis for the thermodynamic formulation of transition-state theory (TST) [5, 6]; 'Eyring's TST' dominated the field for more than three decades owing in large part to the ease with which calculations could be performed without digital computers.

Wigner [7(a)] proposed a more general, and dynamically based, version of TST in 1938, which has served as the basis for the modern development of statistical theories (for example [8]). (The classical TST was first proposed by Marcelin [7(b)]; Horiuti [7(c)] also contributed to the development of the theory at about the same time as Wigner.) Wigner assumed that the rate constant is an ensemble average of the flux $v_{\perp}$ of classical trajectories across a critical surface $q_c$ that separates the reactants the reactants and products:

$$k(T) = \langle \delta(q - q_c) |v_{\perp}| \rangle. \tag{1}$$

Keck [9] used this idea to formulate a variational 'phase-space theory' (PST) of reactions providing a link between TST and classical trajectories [10]. Keck's PST ideas were used by Anderson [11] to simulate reactions with classical trajectories originating at the transition state, providing a method for simulations of reactions that are too slow to be treated by straightforward quasiclassical trajectory methods, which

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had, with the advent of modern computers, come to play a central role in theoretical studies of reactions. Following a brief period in which much of the emphasis was on applications on classical trajectory simulations, there was a renewed focus on TST and it is again widely used. The return to TST ideas came about with a better understanding of the dynamical basis of the assumptions on which it was based. Pechukas and McLatterty [12], Pechukus [13] and Miller [14, 15] examined the TST assumptions within the context of classical dynamics and developed a more explicit formalism that reveals the exact nature of the statistical assumptions and their relationships to the dynamics. For an excellent succinct discussion of the dynamical foundations of TST, see [16].

Much of the development of TST has focused on bimolecular reactions, resulting in variational transition-state theory (VTST) [17]; however, the ideas are applied to unimolecular reactions in the Rice–Ramsperger–Kassel–Marcus (RRKM) theory (for example [18]).

The basic mechanism for unimolecular reactions involving collisional energization was proposed by Lindemann [19], and the important idea that the energy is distributed among the normal modes of the energized molecule was suggested by Hinshelwood [20]. According to the Lindemann–Hinshelwood mechanism, molecules gain internal energy in collisions until they possess sufficient energy to react and then, unless they experience deactivating collisions, intramolecular vibrational energy redistribution (IVR) leads to molecules with enough energy in the reaction coordinate mode to traverse the barrier to the products and, finally, if the molecules attain *critical configurations* (i.e. arrive at the transition state moving in the direction of the product valley), reaction occurs. Under these conditions the rate of reaction is usually slow compared with that for the energy flow to the reaction coordinate, and the dynamics that determine the reaction are statistical. When this is true, the rate can be calculated by using a statistical theory.

The simplest theoretical treatment of statistical unimolecular reactions is the classical Rice–Ramsperger–Kassel (RRK) [21, 22] theory, which is based on the assumption that the microcanonical rate coefficient is determined by the probability of the energy needed for reaction is located in the critical mode. The RRK expression for the unimolecular reaction rate is

$$k^{\mathrm{RRK}}(E) = \nu\left(1 - \frac{E^*}{E}\right)^{s-1}, \tag{2}$$

where $\nu$ is a frequency factor, $E^*$ is the energy required for reaction and $s$ is the number of effective degrees of freedom. Theoretically $s = 3N - 6$ if the dynamics are truly statistical, but less than that if they are not. While the RRK theory predicts the correct energy dependence in the statistical limit, it does not yield quantitative predictions of the rates. One must turn to a treatment with less severe approximations for that.

The RRKM theory is much more accurate and is widely applicable. It is a microcanonical TST based on the assumption of statistical distributions of energy among quantum states. It also yields a simple expression

$$k(E) = \frac{N^{\dagger}(E)}{h\rho(E)}. \tag{3}$$

The sum of states $N^{\dagger}(E)$ for the activated complex with energy $E$ and the density of states $\rho(E)$ for the reactants at total energy $E$ are commonly evaluated by using a direct count of quantum states for a set of independent harmonic oscillators [18]. This, of course, ignores the anharmonicity of the potential in favour of accounting for the quantized energy levels of the molecules (for example [23]). However, methods exist for state counting for anharmonic potentials [18].

These theoretical approaches based on TST ideas were of enormous importance in the evolution of our understanding of thermal chemical kinetics and remain valuable methods for calculating rates. However, they were developed before the general availability of digital computers and the advent of experimental techniques (e.g. molecular beams and lasers) that probe the details of reactions. These changed the emphasis of theoretical studies of chemical reactions. Classical trajectory simulations and time-dependent quantum calculations became more relevant. Semiclassical methods [24–26] were used to augment these by providing ways of treating quantum effects when rigorous quantum-mechanical treatments were not possible.

Thus, we now have available a variety of practical methods, based on classical, semiclassical and quantum mechanics, that can be used to perform explicit realistic simulations and accurate rate calculations. Our interest here is on unimolecular reactions in large molecules, and more specifically on methods that allow for the explicit treatment of the multidimensional effects. Thus, the methods of practical interest are based on classical and semiclassical mechanics. The underlying ideas derive from classical trajectory simulations, although the methods incorporate approximations and other methods to attain the pragmatic goal of accurately predicting the rates of realistic models.

Bunker [27] published the first classical trajectory studies of unimolecular reactions and laid much of the groundwork for the focus on the chemical dynamics of unimolecular reactions. Prior to Bunker's work, the most significant attempt to treat explicitly the dynamics was made by Slater [28]. Slater's theory, although not accurate enough for practical applications, provides a useful simple way of thinking about unimolecular reactions. The rate is defined as the frequency of ' up-zeros' in a reaction coordinate function defined as a linear combination of normal modes. Since the modes are separable, the time evolution (and thus the rate) can be calculated using the analytical solutions for harmonic or anharmonic oscillators.

Classical trajectories have been used extensively to study unimolecular reactions over the past three decades and have provided a practical means of computing rates as well as a great deal of insight into the fundamental nature of the underlying dynamics, IVR and reactions. Obviously, there are some disadvantages to using classical simulations to compute unimolecular reaction rates. First, the simulations are expensive; they are often not feasible at energies near threshold since the time required for reaction can be far greater than that for which it is possible to perform accurate numerical integration of the equations of motion. More important, there can be significant quantum effects. Classical trajectories have the advantages, when valid, however, in that they yield detailed pictures of the dynamics and are relatively easy to carry out. If the system of interest behaves classically and the numerical integration is feasible for the time scale of the processes of interest, then the classical trajectory approach is naturally preferred. However, we need to turn to other methods when these conditions are not met.

In this review we describe practical methods that can be used to compute accurately the rates of unimolecular reactions in large molecules for all ranges of total energy for realistic potential energy surfaces. The underlying dynamics responsible for isomerization and decomposition reactions of polyatomic molecules can change from statistical to non-statistical with increasing energy and, while they are essentially classical, they can be dominated by quantum effects under certain conditions. Thus, it is necessary to select the appropriate method based on the conditions. We discuss the nature of dynamics for the various energy regimes and describe practical methods that can be used to simulate unimolecular dynamics and to compute rates of reactions. We discuss the limitations of practical applications of classical trajectory simulations. We describe how to take advantage of the ease of applying TST when the dynamics are statistical and do so by using Monte Carlo methods to account for realistic forces among all the modes of the system. We show how diffusion theory can be used when these other methods are not applicable. Finally, we describe a multidimensional semiclassical approach that can be used to incorporate tunnelling corrections into classical simulations.

## 2. The classical approximation

The main reason for the widespread use of classical simulations is pragmatism rather than their fundamental correctness; it is the only practical way to treat many problems. However, it should be noted that comparisons of the results of classical simulations with those for quantum mechanics, semiclassical approaches and experiments have shown the approximation to be valid for a wide range of chemical problems. Nevertheless, it is appropriate to keep in mind the limitations of the validity of the classical approximation. The neglect of quantum interference effects is the most significant approximation in classical trajectory simulations. When they are important, as in tunnelling, non-adiabatic processes or the basic behaviour of the dynamics (e.g. resonances or other 'quasi stationary state' characteristics of a system, and the proper behaviour of zero-point energy (ZPE)), one must turn to a quantum-mechanical or semiclassical approach.

Since interference effects are most important at low energies and for light atoms, they can dominate at energies in the region of the reaction threshold and for motions of hydrogen atoms. The neglect of interference effects can lead to significant underestimation of the probability of passage over a potential barrier when the energy is near the barrier height. Of course, reaction is forbidden when the energy is below the barrier although, in reality, quantum-mechanical tunnelling occurs (with negligible probability in most cases, but significant in some cases). Interference effects are most evident at the microscopic level but tend to be 'averaged out' in macroscopic properties. The differences in classical and quantum-mechanical results are much greater for one-dimensional systems, particular at low energies, than for three-dimensional systems, and interference effects may be manifested in state-to-state cross-sections but not evident in thermal rates. Since chemists are often interested in highly averaged properties, the classical approximation is usually good enough.

The aphysical behaviour of the ZPE can be a problem in classical simulations of polyatomic molecules [29]. The ZPE of a large molecule can be significantly greater than the energy needed for reaction, and thus classical trajectories with initial conditions selected using a quasiclassical approximation can result in reaction below the true threshold or even lead to products for energies below ZPE levels. The ZPE in a real system is constrained by interference effects; however, in a classical simulation it flows without these restrictions and can potentially lead to aphysical behaviour, rendering the classical approximation invalid. Unfortunately, there is not a satisfactory way to correct this [29], except by using semiclassical corrections (which can be difficult to apply in some cases).

Some of the ZPE problem may be due to how the classical–quantum correspondence is interpreted, that is to how the trajectory results are analysed. The interpretation is clear in the case of semiclassical eigenvalues, where the correspondence of the invariant tori in classical phase space with the quantum-mechanical eigenvalues $n$ is defined by the Einstein–Brillouin–Keller (EBK) condition

$$\oint p \, \mathrm{d}q = h(n + \tfrac{1}{2}). \tag{4}$$

However, this is rigorous only for bound systems. For unbound systems (e.g. chemical reactions), the appropriate correspondence is between the quantum-mechanical expectation value of the observable and the proper ensemble average of its classical analog, which are expected to be equal only in the limit of high energy. Thus, in applications of classical mechanics to processes such as chemical reactions, it is ensemble averages that have physical meaning. Individual trajectories of a quasibound system must be interpreted only within the context of the ensemble average.

In the quasiclassical approximation, the system is initially specified by a set of quantum numbers for the normal modes; thus the wavefunction is represented by an ensemble of classical trajectories with the appropriate action integrals and uniformly distributed initial phases. The expectation value of an observable for a given set of quantum states corresponds to the ensemble average of the trajectories on the corresponding tori. The system begins in accordance with quantum mechanics but evolves according to classical mechanics. The proper interpretation of the results is in terms of the correspondence of the ensemble average and the expectation value. It is not clear how to improve upon this. Furthermore, it is important to note that the correspondence of wavefunctions with phase space applies to the high-energy limit, while at low energies, where the uncertainty principle precludes defining probability density functions, the quantum effects are most significant. Thus, it is not theoretically justified to assume that regions of phase space where the energies are less than the zero point values are aphysical. On the other hand, ensembles of classical trajectories on a torus do not correspond exactly to wavefunctions, thus indicating a problem.

Classical trajectories should be used with proper consideration of these points, the most fundamental being that it is only the ensemble average that has physical meaning. Properly correcting classical behaviour for quantum effects can only be done on a valid theoretical basis by semiclassical approaches.

## 3. Statistical and dynamical regimes

The basic assumption of statistical theories of unimolecular reactions such as the RRK and RRKM theories is that IVR is rapid compared with the rate of reaction, and that the rate constant $k(E)$ corresponds to a microcanonical ensemble [18]. This is certainly the case when the dynamics are chaotic. The dynamics of large molecules tend to display quasiperiodic behaviour at energies well in excess of the reaction threshold [30]. Nevertheless, there is sufficient mode mixing that 'statistical' reaction rates are commonly observed. That is, at energies near the reaction threshold, the rates of reaction tend to be slower than the rates of IVR, and the rate constant can be predicted by statistical theories such as RRKM and VTST. However, at high energies, the rate of reaction can become much faster than the rate of IVR, and the reaction rate must be calculated by a method that takes into account the non-statistical dynamics. This is illustrated in figure 1. In the region of the reaction threshold energy the energy dependence of the rate generally obeys the RRK equation; that is, a plot of $\ln k$ against $\ln(1 - E^*/E)$ is linear as shown by the solid line in figure 1. This behaviour extends well

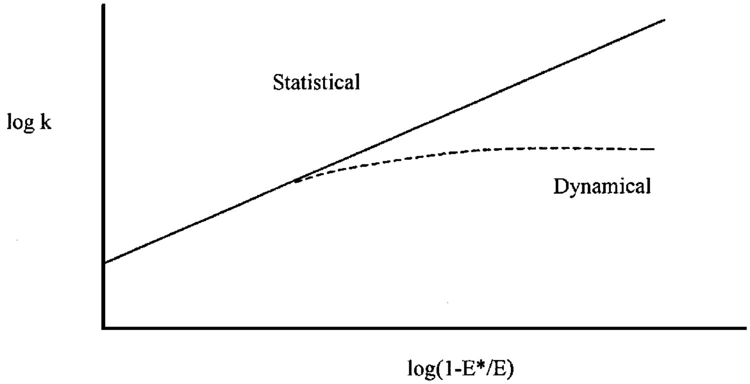

Figure 1. Illustration of the divergence of 'statistical' and 'dynamical' unimolecular reaction rate constants with increasing energy. The solid line shows the statistical rate extending down to the reaction threshold. The broken curve illustrate the effects of IVR-limited reaction, where the rate of reaction is sufficiently fast to deplete the population of phase space near the transition state and thus the observed rate of reaction corresponds to the rate of energy diffusion into the 'reaction coordinate'. ('Recrossings' of the dividing surface in TST would account for some of the difference; however, it is mainly due to what Bunker and Hase called intrinsic non-RRKM behaviour.)

above the threshold; however, at energies well in excess of the threshold the true rate deviates from this linear behaviour, as illustrated by the broken curve in figure 1.

We have demonstrated the behaviours shown in figure 1 for realistic models of various kinds of molecules by comparing the Monte Carlo variational transition-state theory (MCVTST) and classical trajectory stimulation results [31]. At higher energies, the statistical rate is always greater than the true rate, which is controlled by the IVR rate. The behaviour at high energies is the result of weak coupling between the vibrational 'bath' and reaction coordinate modes (or, more precisely, vibrational states) of the molecule. (This is sometimes attributed to 'bottlenecks' in phase space.) This is the intramolecular equivalent to the low-pressure behaviour in gas-phase unimolecular dissociation reactions where the rate of intermolecular energy transfer to the molecules limits the reaction rate. Bunker and Hase [32] categorized the various kinds of behaviour of unimolecular reaction in terms of lifetime distributions. They referred to the case of IVR-limited unimolecular reactions as 'intrinsic non-RRKM' to distinguish it from the non-statistical behaviour when the collisional energy transfer is slower than the rate of reaction. These behaviours are usually discussed in qualitative terms [33–35], although quantitative models have been presented [36, 37].

In the standard classical trajectory approach, an ensemble of initial phase space points are selected by a Monte Carlo procedure and propagated in time by numerically integrating Hamilton's equations of motion. The reaction rate constant can be obtained from the computed lifetimes of the molecules [38]. Even when initial conditions are randomly selected according to a microcanonical distribution, the computed rate constant can be lower than that predicted by a statistical theory, particularly at high energies [31]. In fact, non-statistical behaviour can be most clearly distinguished by comparing classical trajectory rates with those computed using a classical TST, particularly if the calculations use the same potential energy surface (PES) [31]. Comparisons are usually made between trajectory and experimental results or those predicted by RRKM or RRK. Since these statistical theories are based on harmonic vibrations, the causes of any disagreements are not clear. The RRK

Table 1. Comparison of values of the RRK parameter $s$ computed from classical trajectories and the theoretical number of degrees of freedom $3N-6$ for unimolecular reactions of silicon compounds.

| Reaction | $s$ | | Reference |
|---|---|---|---|
| | $3N-6$ | Trajectory | |
| $SiH_2 \rightarrow Si + H_2$ | 3 | 2.24 | [39] |
| $SiH_2 \rightarrow Si + H_2$ | 3 | 3.10 | [40] |
| $Si_3 \rightarrow Si_2 + Si$ | 3 | 2.67 | [41] |
| $SiH_4 \rightarrow$ products | 9 | 2.3–2.8[a] | [42] |
| $H_2Si{=}SiH_2 \rightarrow SiH_2$ | 12 | 8.15 | [43] |
| $H_2Si{=}SiH_2 \rightarrow H_2Si{=}Si + H_2$ | 12 | 11.2 | [43] |
| $H_2Si{=}SiH_2 \rightarrow HSi{=}SiH + H_2$ | 12 | 5.45–6.38[b] | [43] |
| $Si_2H_6 \rightarrow 2SiH_3$ | 18 | 8.10 | [44] |
| $Si_2H_6 \rightarrow Si_2H_5 + H$ | 18 | 8.03 | [44] |
| $Si_2H_6 \rightarrow SiH_4 + SiH_2$ | 18 | 10.26 | [44] |
| $Si_2H_6 \rightarrow 2SiH_3$ | 18 | 8.49 | [44] |
| $Si_2H_6 \rightarrow H_3Si{-}SiH + H_2$ | 18 | 13.69 | [44] |
| $Si_2H_6 \rightarrow H_3Si{-}SiH_2 + H$ | 18 | 8.06 | [44] |

[a] Fits were done for a range of $E^*$ values.

[b] Trajectory calculations were done for three different PESs. The range of $n$ values are for RRK fits to the trajectory results for the three surfaces, which differ mainly in the barrier height for the ring fission reaction.

equation (2) is often used as a convenient analytical function for fitting the energy dependence of unimolecular rates. The value of $s$, the number of effective degrees of freedom, then indicates the extent of the statistical behaviour of the dynamics if the harmonic approximation is valid (which it can be for experiments since the average energy per mode is small). Theoretically $s = 3N - 6$, but the values obtained by fitting trajectory results are often significantly smaller. The RRK theory usually fits the energy dependences of rates in the reaction threshold region; however, trajectory results are usually for much higher energies, and there the fits are not so good. The fits are often good for small molecules, where all the bonds are identical, but large molecules composed of different types of bond show greater non-statistical behaviour and thus the fits are usually not good. This is illustrated by the results in table 1 for several silicon compounds.

What this means in practice is that one needs to use different methods for different energy regimes for computing the decay rates of large molecules. The rates near threshold can be computed using a statistical theory and those at high energies by classical trajectory simulations. We have shown that the rates in the intermediate region can be computed using an energy diffusion theory.

## 4. Classical trajectory simulations

Monte Carlo classical trajectory approaches are well understood and widely used; thus we shall only briefly describe the methods (mainly for completeness) as we have been using them. For further details, we refer the reader to a recent, more thorough review [45].

Classical trajectory simulations of large systems are performed by integrating

Hamilton's equations of motion in laboratory-fixed Cartesian coordinates. For $N$ atoms, the $6N$ coupled first-order equations are

$$\dot{q}_i = \frac{\partial H(\mathbf{q}, \mathbf{p})}{\partial p_i}, \quad \dot{p}_i = \frac{\partial H(\mathbf{q}, \mathbf{p})}{\partial q_i} \quad (i = 1, 2, \ldots, 3N), \tag{5}$$

where $q_i$ and $p_i$ are the positions and conjugate momenta respectively. The Born–Oppenheimer separation is assumed:

$$H(\mathbf{q}, \mathbf{p}) = T(\mathbf{p}) + V(\mathbf{q}). \tag{6}$$

In laboratory fixed Cartesian coordinates, the kinetic energy is quadratic and diagonal:

$$T(\mathbf{p}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i}. \tag{7}$$

The potential energy $V$ is usually written in terms of valence coordinates for convenience, and the chain rule is used to transform to Cartesian coordinates.

The initial conditions are selected to correspond to the experimental conditions of interest. Usually, they are selected to yield either a quasiclassical or a classical microcanonical distribution. The quasiclassical procedure assigns energies to the normal modes in accordance with quantum rules (thus, including the ZPE); this is particularly useful for studying low-energy and state-selected initial conditions. The assignment of classical microcanonical initial conditions is based on Metropolis [47] Monte Carlo sampling [46, 48–52].

Quasiclassical initial conditions are based on the normal mode approximation and thus the energy levels are given by

$$E_i = (n_i + \tfrac{1}{2}) h\nu_i = \tfrac{1}{2}\dot{Q}_i^2 + \tfrac{1}{2}\lambda_i Q_i^2 \tag{8}$$

where $n_i$ is the quantum state of mode $i$ corresponding to energy $E_i$, $Q_i$ is the normal mode coordinate and $\lambda_i = 4\pi^2\nu_i^2$ is the force constant. The vibrational phase for the harmonic oscillator is randomly selected for the distribution function [53]:

$$F(Q) = \frac{1}{[\pi(Q_0^2 - Q^2)]^{1/2}}, \tag{9}$$

where $Q_0$ is the maximum classical displacement for the oscillator in the specified quantum state. Details of how the Monte Carlo selections are made, as well as how to do so for anharmonic modes [54], have been given elsewhere [45, 55]. Since the actual potential used in a simulation is usually anharmonic and coupled while the Monte Carlo selections are based on the normal mode approximation, it is necessary to scale the coordinates and momenta to give a fixed total energy [45].

Angular momentum can be assigned by adding velocities due to rotation to each atom (for example [56]). The initial rotational energy is precisely defined by this procedure since the angular momentum is exactly zero in the assignment of the vibrational energy.

This procedure, however, does not precisely define fixed initial vibrational energies for each mode because of the scaling of the harmonic assignments to give a precise value of the total energy. The accuracy of the quasiclassical initial conditions then depends on the degree of anharmonicity and coupling.

Adiabatic switching [57, 58] can be used to define initial states precisely. A useful application of adiabatic switching is in the calculation of semiclassical eigenvalues (for example [59]). Adiabatic switching is based on the assumption that a multidimensional

Hamiltonian can be written as separable zeroth-order terms plus higher-order terms that couple them and, based on Einstein's adiabatic hypothesis, for example [60] (i.e. the classical actions are conserved in an adiabatic slow process) that the zeroth-order Hamiltonian is approximately conserved as the perturbing interactions are slowly turned on (about $10^2$ vibrational periods in practice). This obviously assumes regular motion. Various time-dependent switching functions are used to introduce the coupling; Johnson [58] suggested and tested several. Huang *et al.* [61] have used adiabatic switching to generate semiclassical initial conditions for a trajectory study of the bimolecular reaction $H + CD_4 \rightarrow HD + CD_3$. Adiabatic switching is difficult to apply for many degrees of freedom and at high energies owing to crossing resonance zones and irregular dynamics; thus it is not particularly useful for studies of unimolecular reactions. Furthermore, many of the problems of interest do not depend on sampling good action angle variables, even if they exist.

Metropolis Monte Carlo sampling [47] is well suited to averaging over the phase space of a multidimensional system, for example highly excited polyatomic molecules. It is efficient, practical and easily implemented. Since there are excellent thorough descriptions of Monte Carlo methods already available [62–67], it is not appropriate for us to go into details here. Thus, we provide only a brief introduction with references to relevant reviews.

Metropolis Monte Carlo sampling is a convenient way to compute estimates for integrals of the type:

$$\langle G \rangle = \frac{\int_V G(\mathbf{x}) F(\mathbf{x})\, d\mathbf{x}}{\int_V F(\mathbf{x})\, d\mathbf{x}}, \tag{10}$$

where $F(\mathbf{x})$ is the probability density. The Monte Carlo approximant is

$$\langle G \rangle = \frac{\Sigma_{i=1}^{N} G(x_i)\, F(x_i)}{\Sigma_{i=1}^{N} F(x_i)}, \tag{11}$$

where the points $\{x_i\}$ are randomly chosen with uniform probability over the region $V$. A Markov walk is generated with the function $F$ determining the probability of accepting or rejecting attempted steps. These are the kinds of integral that must be evaluated to compute ensemble averages. The probability density for the canonical ensemble is

$$F(\mathbf{q}, \mathbf{p}) = \frac{\exp[-H(\mathbf{q}, \mathbf{p})/\kappa T]}{\int_V \exp[-H(\mathbf{q}, \mathbf{p})/\kappa T]\, d\mathbf{q}\, d\mathbf{p}}; \tag{12}$$

where $H(\mathbf{q}, \mathbf{p})$ is the system Hamiltonian, $\mathbf{q}$ and $\mathbf{p}$ are the position coordinates and conjugate momenta respectively. Although the Metropolis Monte Carlo methods were developed, and mostly widely used, for canonical ensemble sampling, they are easily applied to the microcanonical ensemble, which is appropriate in unimolecular reaction rate constant calculations. The probability density for the microcanonical ensemble is

$$F(\mathbf{q}, \mathbf{p}) = \frac{\delta[E - H(\mathbf{q}, \mathbf{p})]}{\int_V \delta[E - H(\mathbf{q}, \mathbf{p})]\, d\mathbf{q}\, d\mathbf{p}}, \tag{13}$$

where $\delta$ is the Dirac delta function.

Bradly *et al.* [48] originally suggested a procedure using Metropolis sampling to generate initial conditions for classical trajectories. A sequence of phase-space configurations are randomly generated to give a Markov chain, with some of these configurations, picked at arbitrary points along the walk, providing starting conditions for classical trajectories. For the microcanonical ensemble, the probability density is

$$P(\mathbf{q}, \mathbf{p}) = \delta[H(\mathbf{q}, \mathbf{p}) - E]; \tag{14}$$

all phase space points with energy $E$ have equal weights. The random walk is begun at an arbitrary point in phase space, usually the equilibrium geometry (for convenience) with the momenta assigned to give the desired total energy $E$. A Markov chain is generated by attempting random changes of $(0.5\text{-}\xi_1)\,\Delta q$ and $(0.5\text{-}\xi_2)\,\Delta p$ in the coordinates and momenta respectively of one or more of the atoms; the $\xi_i$ are pseudorandom numbers uniformly distributed on (0, 1), and $\Delta q$ and $\Delta p$ are the maximum step sizes. The coordinates and momenta of other atoms are changed to conserve the centre of mass of the system. The walk is arbitrarily restricted to the configuration space of the reactants. The Markov walk is restricted to an energy shell about $E$ by using a prelimit delta function to accept attempted steps:

$$P(\mathbf{q}, \mathbf{p}) = \frac{\varepsilon}{\varepsilon^2 + [H(\mathbf{q}, \mathbf{p}) - E]^2}, \quad \text{if} \left| H(\mathbf{q}, \mathbf{p}) - E \right| \leqslant f\varepsilon, \tag{15}$$

$$P(\mathbf{q}, \mathbf{p}) = 0, \quad \text{if} \left| H(\mathbf{q}, \mathbf{p}) - E \right| > f\varepsilon, \tag{16}$$

when $f > 0$ and $\varepsilon$ is a parameter that determines the width of the delta function. The trial configuration is accepted if

$$\frac{P(\mathbf{q}^{\mathrm{trial}}, \mathbf{p}^{\mathrm{trial}})}{P(\mathbf{q}^{\mathrm{old}}, \mathbf{p}^{\mathrm{old}})} \geqslant \xi_3, \tag{17}$$

where $\xi_3$ is a pseudorandom number; otherwise the attempted move is rejected and the 'old' configuration is taken as the 'new' configuration. This procedure is repeated until the computed properties converge. It has been found empirically that the convergence is fastest when the acceptance-to-rejection ratio is about 0.5. The values of the parameter $\varepsilon$ and the step sizes $\Delta q$ and $\Delta p$, as well as the number of variables randomly adjusted for each move, are chosen to optimize the rate of convergence.

Very long Markov walks are usually required to sample phase space adequately. One could, of course, calculate a classical trajectory at every step in the walk; however, this is not necessary. Following a long 'warm-up' sequence, small batches of trajectories (say, five) can be computed periodically for short sequences of phase space points along the walk [48]. This is an arbitrary scheme to select appropriately weighted initial conditions. It is relatively inefficient since it is necessary to balance the width of the prelimit delta function and step size to realize a reasonable acceptance-to-rejection ratio.

There are various ways to improve upon this basic approach. For example, jump–walk sampling schemes can be used to increase the rate of exploration of the phase space [68]. In a simple Markov chain it is possible for the walk to become 'trapped' for long sequences of steps in local regions of phase space. Thus, schemes in which 'jumps' are interspersed with walk sequences can improve the rate of convergence. Since it is possible to separate the kinetic and potential energies, it is not necessary to sample momentum space. The kinetic energy can be obtained analytically [69, 70]. This is useful in applications of Monte Carlo averaging to compute reaction rates (as described in Section 5).

Nordholm and co-workers [49, 50] have developed a method, which they call efficient microcanonical sampling, which is a refinement of the methods just described. The delta function is replaced by the exact configurational statistical weight determined by the momentum density of states. This allows for sampling on an exact energy surface rather than an energy shell of finite width. Dumont [51, 52] has developed a similar method and provided a mathematical proof for it.

The momenta in the microcanonical ensemble depends on the molecular coordinates $\mathbf{q}$:

$$\sum_{i=1}^{3N} \frac{p_i^2}{2m_i} = E - V(\mathbf{q}), \tag{18}$$

where $m_i$ is mass corresponding to the $i$th momentum. The probability density function is written as the product:

$$P(\mathbf{q}, \mathbf{p}) = \delta[E - H(\mathbf{q}, \mathbf{p})] = P_{\mathbf{q}}(\mathbf{q})\, P_{\mathbf{p}}(\mathbf{p}), \tag{19}$$

where $P_{\mathbf{q}}$ is the probability density for $\mathbf{q}$ and $P_{\mathbf{p}}$ is the conditional probability density for the conjugate momenta $\mathbf{p}$ given $\mathbf{q}$. The configuration space probability density is proportional to

$$[E - V(\mathbf{q})]^{(3N-5)1/2} \tag{20}$$

for an $N$-atom molecule. This weight function can be used in the same way as the prelimit delta function as described above.

Unimolecular rate constants can be calculated from microcanonical distributions of lifetimes of the trajectories. This requires that a definition of the reactant and product phase spaces (often it is sufficient to consider only configuration space) be used. The 'dividing surface' need not be as rigorously determined as in VTST since the rate is based on lifetimes. When spatial criteria are used for the 'end tests' for dissociation, it is convenient to define the lifetime as the time up to the last inner turning point in the reaction coordinate; this eliminates the variations in the lifetimes due to the different times resulting from variations in the final translational velocities of the separating products [38].

The distribution of lifetimes, assuming a single decay rate, can be fitted to

$$\ln \left( \frac{N_t}{N_0} \right) = - k(E)t, \tag{21}$$

where $N_0$ is the total number of molecules in the ensemble and $N_t$ is the number of unreacted molecules at time $t$. The decay lifetime is

$$\tau(E) = \frac{1}{k(E)}. \tag{22}$$

This assumes only that the molecules decay with random lifetimes, not that there is rapid energy redistribution (as is assumed in the RRKM theory).

## 5. Monte Carlo methods for computing rates

Doll [71] pointed out that Metropolis Monte Carlo sampling can be used to evaluate the corresponding classical phase space integrals to determine the sums and densities of states for the RRKM expression. While the quantum features of the RRKM theory are given up, this approach allows the use of realistic PESs. A benefit of this is that the Monte Carlo RRKM calculations can be performed for exactly the same PES used in a classical trajectory simulation, thus allowing a direct comparison of the results and a clear evaluation of the statistical against non-statistical effects.

Classically, $G^\dagger(E)$ is written as a $6n$-dimensional phase-space integral

$$G^\dagger(E) = \frac{1}{h^n} \int_{H=E} \dots \int \prod_{i=1}^{n} \mathrm{d}\mathbf{q}_i \, \mathrm{d}\mathbf{p}_i, \tag{23}$$

where $H$ is the system Hamiltonian; the integration is over the configuration space of the activated complex. The density of states is given by

$$N(E) = \frac{\mathrm{d}S(E)}{\mathrm{d}E}, \tag{24}$$

where

$$S(E) = \frac{1}{h^n} \int_{0 \leqslant H \leqslant E} \dots \int \prod_{i=1}^{n} \mathrm{d}\mathbf{q}_i \, \mathrm{d}\mathbf{p}_i. \tag{25}$$

The integration is over the configuration space of the reactants [63]. This reduces the RRKM theory to a classical microcanonical TST.

There have been a number of applications of this approach. Some of the early studies were for model systems; most of these were done to investigate the effects of anharmonicity and coupling. Noid *et al.* [72] showed that the classical phase-space integrals calculated by the Monte Carlo method are in excellent agreement with the exact quantal sums for the Henon–Heiles system. Doll [73] showed how the method could be used to calculate unimolecular rates and illustrated it for four-atom argon clusters. Farantos *et al.* [74] applied the method to ozone and formaldehyde for coupled anharmonic PESs; the Monte Carlo rates for $O_3$ were compared with the RRKM theory and are in good agreement. Bhuiyan and Hase [75] used the method to study the influence of stretch–bend coupling on sums and densities of states for model triatomic systems. Viswanathan *et al.* [76] used the method with a variational determination of the transition state to compute $k(E)$ for the unimolecular bond fission reactions in methane and silane. They also extended the procedure to compute the microcanonical rate coefficient $k(E, J)$ for specific angular momentum states [77]. Wardlaw and Marcus [78, 79] used a combination of quantum state counting and Monte Carlo phase-space integrations in RRKM calculations. Smith [80, 81] and Klippenstein and co-workers [82–85] have further developed the methods and applied them in various ways for practical RRKM calculations.

A more useful approach, also suggested by Doll [71, 86], is to use Monte Carlo methods to evaluate the integrals in the Wigner [7(a), 87] phase space theory formalism [9]. This requires the calculation of the frequency of crossings into the product region, which in practice is determined by calculating the frequency of the system passing through the ‘critical’ surface (defined by the minimum flux) between reactants and products along the reaction coordinate. A convenient way to develop the formulation is to use concepts from Slater’s [28] theory. In Slater’s theory a ‘critical coordinate’ $q_c$ is followed as a function of time and the reaction rate is assumed to be the frequency with which $q_c$ attains a ‘critical extension’ $q_0$, that is the frequency of up-zeros of the function $q_c(t)$-$q_0$. Slater assumed that the molecule could be represented by normal modes and $q_c$ is a linear combination of normal mode coordinates; we assume that the molecule is described by a coupled anharmonic potential. The number of up-zeros of the function $q_c(t)$-$q_0$ over the time interval $\tau$ is [88]

$$n(\tau) = \tfrac{1}{2} \int_0^\tau \delta[q_c(t) - q_0] \left| \frac{\mathrm{d}q_c}{\mathrm{d}t} \right| \mathrm{d}t, \tag{26}$$

where $\delta$ is the Dirac delta function. The average value,

$$\langle n(\tau)\rangle = \tfrac{1}{2}\left\langle \int_0^\tau \delta[q_c(t) - q_0] \left|\frac{dq_c}{dt}\right| \right\rangle dt, \tag{27}$$

is time independent for a stationary process. In practice, the process is made stationary by imposing a reflecting barrier along $q_c$ at $q_0$. The unimolecular rate coefficient is

$$k(E) = \tfrac{1}{2}\left\langle \delta[q_c(t) - q_0] \left|\frac{dq_c}{dt}\right| \right\rangle. \tag{28}$$

The microcanonical average can be written in terms of phase-space integrals; thus the rate is

$$k(E) = \frac{(1/h^{3N}) \int dq \int \frac{1}{2} \delta(E - H)\, \delta(q_c - q_0)\, \dot{q}_c}{(1/h^{3N}) \int dq \int \delta(E - H)}, \tag{29}$$

where $N$ is the number of degrees of freedom and $H$ is the Hamiltonian. In the Monte Carlo approximation, the integrals are replaced by sums:

$$k(E) = \frac{1}{2N_{\text{steps}}} \sum_{i=1}^{N_{\text{steps}}} \delta(E - H)\, \delta(q_c - q_0)\, |\dot{q}_c|, \tag{30}$$

where $N_{\text{steps}}$ is the number of phase-space points in the Markov walk. An analogous expression can be written for the thermal rate coefficient (for example [89]):

$$k(T) = \frac{\frac{1}{2}\int \exp[-\beta V(\mathbf{q})]\, \delta(q_c - q_0)\, |\dot{q}_c|\, d\mathbf{q}\, d\mathbf{p}}{\int \exp[-\beta V(\mathbf{q})]\, d\mathbf{q}\, d\mathbf{p}}. \tag{31}$$

This method is usually referred to as the MCVTST. Since the averaging is done using Monte Carlo procedures, realistic PESs can be used, thus eliminating the usual approximations of the PESs in TST calculations. Furthermore, it includes 'multi-dimensional effects' since the averaging is done for all the phase space; this can provide information, as well as improved predictions, not available with traditional TST approaches; that is, it explicitly includes the contributions to the rate for barrier transmission off the minimum-energy path (MEP).

The integrals over momentum space can be done analytically; thus the Markov walk is needed only for the configuration space [69, 70]. The Monte Carlo procedure developed by Severin *et al.* [46] provides an efficient means of performing the Markov walk restricted to a fixed energy value [63].

These methods are based on random uniform sampling of the phase space relevant to the process of interest, that is the reactant phase space extending through the transition state to products. The rate of convergence can be greatly increased by importance sampling. With importance sampling the Markov walk is biased so that the phase space in the region of the transition state is sampled more frequently, thus increasing the rate of convergence (for example [90]).

The MCVTST method is generally applicable to rate processes [63] however, most applications have been for unimolecular reactions, and similar processes that occur at gas–surface interfaces [40, 69, 70, 76, 91–98]. Variations of it have also been used to compute rates for proton tunnelling [99] and electronically non-adiabatic processes [100].

## 6. Intramolecular dynamics diffusion theory

As we discussed above, there is a range of energies starting at the upper limit of statistical behaviour and extending up to the high-energy region at which classical trajectory simulations become feasible where it is necessary to resort to a method such as diffusion theory to compute the non-statistical unimolecular decay rates. We have developed methods and shown them to be accurate, which can be used in conjunction with TST and classical trajectories to predict the energy dependence of unimolecular reaction rates over the entire energy range.

Kramers [101] formulated a theory of chemical reactions in which reaction is treated as crossings of a potential barrier by one-dimensional particles under the influence of a heat bath. The process is driven by the diffusion of energy from the heat bath to the 'reacting particle', and reaction corresponds to the diffusion of phase-space points from the reactant to the product region. Kramers' theory has its most obvious applications to reactions occurring in condensed phases (for example [102]); however, diffusion theory is also applicable to unimolecular reactions. The most direct application is the description of the thermal excitation of molecules by collisions, Nikitin [103] has given a thorough discussion of the 'diffusion theory of chemical reactions' (DTCR). Kramers [101] pointed out in his original paper that the theory could also be applied to the intramolecular dynamics of polyatomic molecules. The molecule is considered to consist of a bath of vibrational modes that exert Brownian forces upon the reaction coordinate mode (the 'single particle'). This provides a means of calculating the rates of unimolecular reactions for IVR-limited conditions. The accuracy, of course, depends on the validity of the assumption that the dynamics that determine the flow of energy from the bath to the reaction coordinate are chaotic.

We have shown that classical diffusion theory can be used to compute rates of unimolecular reactions, and how the parameters in the theory can be determined from classical trajectory results [104, 105]. We refer to this approach as *intramolecular dynamics diffusion theory* (IDDT). The critical parameter, the rate of energy flow into the reaction coordinate, can be determined in one of two ways. In one approach, short-time dynamics can be used to compute the rate of energy flow from the bath modes to the reaction coordinate. Alternatively, the required parameter can be determined by using the rate at a single total energy. Once the diffusion rate parameter is determined, it can be used to predict the energy dependence of the rate over the entire energy range. Thus, IDDT provides considerable practical benefits since it can be used to compute rates for energies where it is not practical to perform direct classical trajectory simulations of the reactions and where statistical treatments are not appropriate. The calculations require much less computer time than do standard classical trajectory direct simulations of reactions.

The 'parameterization' of IDDT using short-time classical trajectory simulations to determine the rate of energy flow into the reaction coordinate not only is of practical use but also illustrates the fundamental nature of intramolecular dynamics underlying unimolecular reactions (and supports the basic assumptions of approaches such as reaction-path Hamiltonian theory [106–108]).

The reaction rate constant $k(E)$ can be written in terms of the flux of phase space points through the critical surface $S^*$ that divides the reactants from the products:

$$k(E) = \frac{\int_{S^*} f(p, q, t)\, v_\perp \,\mathrm{d}S^*}{\int_V f(p, q, t)\,\mathrm{d}\Gamma}, \tag{32}$$

where $v_\perp$ is the velocity perpendicular to the critical surface. The integral in the numerator is over the critical surface and that in the denominator over the phase space of the reactants. If we assume that the initial distribution $f(p, q, t = 0)$ is microcanonical, the evolution of the ensemble of phase space points is given by the Liouville equation

$$\frac{\partial f}{\partial t} = -\sum_i \left( \frac{\partial H}{\partial p_i}\frac{\partial f}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial f}{\partial p_i} \right), \tag{33}$$

where $H$ is the system Hamiltonian. Since it is not practical to solve this equation, Monte Carlo classical trajectory methods are commonly used in practical applications. However, replacing the exact Liouville equation by the approximate Fokker–Planck equation (for example [109]) provides a viable alternative to classical trajectories, which can be prohibitively expensive at low energies.

The formalism for describing the energy diffusion within a molecule for the microcanonical distribution can be obtained by using a different interpretation of the physical meanings of the parameters in Nikitin's DTCR equations [104, 105]. The kinetic Fokker–Planck equation that needs to be solved is

$$\frac{\partial F(E_{\mathrm{RC}}, t)}{\partial t} = -\frac{\partial}{\partial E_{\mathrm{RC}}}\left[ \beta \frac{1}{2}\frac{\partial}{\partial t}(\Delta E^2_{\mathrm{RC}}) \left( F(E_{\mathrm{RC}}, \mathrm{t}) + \frac{1}{\beta}\frac{\partial F(E_{\mathrm{RC}}, t)}{\partial E_{\mathrm{RC}}} \right) \right] - \frac{F(E_{\mathrm{RC}}, t)}{\tau_{\mathrm{rxn}}(E_{\mathrm{RC}})}, \tag{34}$$

where the reaction rate constant is $k(E) = 1/\tau_{\mathrm{rxn}}$. For a thermal distribution, $\beta = 1/\kappa T$; however, for the microcanonical distribution this parameter can be treated as the effective temperature $T_{\mathrm{eff}}$ and $\beta \approx 1/\kappa T_{\mathrm{eff}} = n/E$, where $E$ is the total energy and $n$ is the number of molecular modes. The term

$$b(E_{\mathrm{rxn}}) = \beta \frac{1}{2}\frac{\partial}{\partial t}(\Delta E^2_{\mathrm{RC}}) = \beta D(E), \tag{35}$$

where $D(E)$ is the diffusion coefficient, characterizes the time dependence of the energy flow into the reaction coordinate from the bath modes and thus is the dynamical variable that defines the reaction rate in IDDT.

We assume that the reaction coordinate experiences a random force due to the bath modes. This, of course, is an approximation in the case of intramolecular dynamics, but an acceptable one in practice as we have demonstrated with calculations [31, 104, 105].

We are interested in long-time non-statistical reactions, where the reaction time is fast compared with that for the energy transfer into the reaction coordinate. (On short times the initial rate of reaction will be statistical even at very high energies since the reactions are directly due to an initial microcanonical distribution). If the coupling is weak (corresponding to the weak-collision limit), the energy flow to the reaction coordinate will be sufficiently slow that $D(E) \ll k(E)$. Thus, we can assume that, when the energy in the reaction coordinate attains sufficient energy $E_{\mathrm{b}}$ for crossing the critical surface to products, the molecule immediately reacts, and the long-time non-statistical behaviour of the reaction can be taken into account by assuming an absorbing boundary condition. The reaction rate coefficient is then

$$k(E) = \tau^{-1}_{\mathrm{rxn}} = 2\int_0^{E_{\mathrm{b}}} \rho(E)\exp(-\beta E_{\mathrm{RC}}) \left( \int_{E_{\mathrm{RC}}}^{E_{\mathrm{b}}} \frac{\exp(\beta \tilde{E}_{\mathrm{RC}})}{(\partial/\partial t)\langle \Delta \tilde{E}_{\mathrm{RC}} \rangle} \mathrm{d}\tilde{E}_{\mathrm{RC}} \right) \mathrm{d}E_{\mathrm{RC}}. \tag{36}$$

We have shown that the ensemble average $(\partial/\partial t)\langle \Delta E^2_{\mathrm{RC}} \rangle$ can be computed by using short-time classical trajectory simulations [104, 105]. Ensembles of trajectories for various values of $E_{\mathrm{RC}}$ are computed at a given total energy $E$. The rate of energy flow in the reaction coordinate is determined by calculating the energy in it at fixed intervals. That is, the rates of spreading of initially narrow distributions of energy in the reaction coordinate are determined for ensembles of trajectories integrated for short times (about a few femtoseconds) at a fixed total energy $E$.

We have shown that this approach can be used to predict accurately, based on comparisons to direct classical trajectory simulations of the reactions, rates for the unimolecular dissociation reactions in disilane [104] and dimethylnitramine [105].

The Si–Si bond fission in disilane, $H_3Si{-}SiH_3 \rightarrow 2SiH_3$, is a case where one would expect IDDT to be most applicable since the reaction coordinate mode (the Si−Si stretching motion) is relatively isolated from the remaining molecular modes and, indeed, we find that the theory works well. The value of the rate constant for Si−Si bond fission in disilane computed by direct classical trajectory simulations of the reaction at a total energy of 400 kcal $\mathrm{mol}^{-1}$ is $5.1\times 10^{11}$ $\mathrm{s}^{-1}$ and the corresponding IDDT value is $4.6\times 10^{11}$ $\mathrm{s}^{-1}$ [104]. However, we also find that IDDT is accurate in cases, for example N−N bond rupture in dimethylnitramine, $(CH_3)_2N{-}NO_2 \rightarrow (CH_3)_2N + NO_2$, where the reaction coordinate mode is not separable [105]. The IDDT predicts the same energy dependence as predicted by classical trajectory simulations, and we have shown how it can be used to interpolate qualitatively between the IVR-limited regime and the statistical regime near the reaction threshold [31].

In practice the direct determination of the diffusion coefficient from short-time dynamics calculations can be complicated by the quasiperiodic behaviour of the molecular vibrations that is commonly observed in large polyatomic molecules, even at relatively high energies [30]. As Shalashilin and Thompson [31] have shown, accurate predictions can be made by properly selecting computational parameters such as the sizes of histogram boxes.

The advantages of determining the diffusion coefficient from short-time dynamics are obvious. Not only does it greatly reduce the computer time needed to determine the rates, but also it permits predictions to made on the basis of less than the full global PES. The aspects of the potential that determine the intramolecular dynamics responsible for the exchange of energy between the reaction coordinate modes and the bath modes are all that is required (much in the spirit of reaction-path Hamiltonian theory [107, 110, 111]). Of course, a completely realistic potential can also be used if available.

Kramers' energy diffusion theory is the basis for an alternative approach for predicting reaction rates over the full dynamic energy range by determining the diffusion coefficient from a single value of $k(E)$ [112]. It is useful to rewrite the Fokker–Planck equation in terms of the density of states $\rho(E)$ and the diffusion coefficient $D(E)$:

$$\frac{\partial P(E,t)}{\partial t} = -\rho^{-1}\frac{\partial}{\partial E}\left[D(E)\,\rho(E)\left(\beta + \frac{\partial}{\partial E}\right)P(E,t)\right] - k(E)\,P(E,t). \tag{37}$$

This gives the time evolution of the energy distribution of a single particle in contact with a heat bath, which is characterized by the diffusion coefficient $D(E)$.

Kramers showed, assuming constant friction, that the distribution $P(E,t)$ evolves according to

$$\frac{\partial P(E,t)}{\partial t} = \xi\nu\frac{\partial}{\partial E}I\left(1 + \beta^{-1}\frac{\partial}{\partial E}\right)P(E,t), \tag{38}$$

where $\xi$ is the friction constant, $I$ is the action and $\nu = \partial E / \partial I$. Then the diffusion coefficient is

$$D(E) = \xi \beta^{-1} \nu(E)\, I(E). \tag{39}$$

The reaction time can be written as

$$\tau_{\mathrm{rxn}} = \frac{1}{k_{\mathrm{rxn}}} = \int_0^{E_\mathrm{b}} \frac{\beta \exp(\beta E)}{\xi \nu(E)\, I(E)\, \rho(E)} \mathrm{d}E \int_0^{E_\mathrm{b}} \rho(\tilde{E}) \exp(-\beta \tilde{E})\, \mathrm{d}\tilde{E}. \tag{40}$$

The friction constant $\xi$ can be fitted to a known value of the microcanonical rate coefficient $k$ and, assuming a simple functional form for the reaction coordinate potential, for example the Morse potential, the action and density of states can be readily calculated. We have demonstrated this approach for the unimolecular decompositions of disilane, dimethylnitramine [112] and hexahydro-1,3,5-trinitro-1,3,5-*s*-triazine [113].

## 7. Semiclassical tunnelling

Fortunately, many of the processes of interest to chemists can be described classically; however, phenomena due to interference effects, such as tunnelling, can be important in isomerization, dissociation and bimolecular reactions (for example [114]). Proper treatment of both the multidimensional dynamics and the quantum effects in large systems usually requires the use of a semiclassical approach. We have developed a practical approach for including semiclassical tunnelling corrections in classical trajectory simulations. Since we have recently reviewed these methods [115], only a brief discussion of them will be given here.

Many semiclassical methods for treating tunnelling are constrained by their 'rigorousness' and are difficult to apply to systems with many degrees of freedom. These methods include the instanton model [116–119] and Miller's classical **S**-matrix theory [120–124] and are 'rigorous' within the Wentzel–Kramers–Brillouin approximation for one dimension but are not easily applied in many degrees of freedom.

Methods based on tunnelling corrections of TST rates are widely used [125–128]. This approach uses simple models to compute the tunnelling probabilities at turning points along the MEP. As shown in numerous applications [128], these methods provide accurate corrections to classical thermal rates. However, they provide no information about dynamical effects since the tunnelling corrections are based on tunnelling paths originating from the MEP (for an illustration of tunnelling probabilities for paths off the MEP see figure 11 of [129]).

A realistic treatment of the dynamics effects in tunnelling requires explicit consideration of the behaviour of all the degrees of freedom on the global PES. A practical method for doing this is based on tunnelling corrections in classical trajectory simulations. Waite and Miller [130] introduced the basic idea for incorporating tunnelling corrections in standard classical trajectory simulations, much in the spirit of the Tully–Preston [131] surface hopping model, as a way of explicitly treating the multidimensional effects.

The classical trajectory plus tunnelling model is conceptually simple (for example [132]). Classical trajectories with initial conditions selected from the appropriate distributions are propagated in the reactant phase space and, when a trajectory encounters a turning point at the barrier, the Jeffries–Wentzel–Kramers–Brillouin tunnelling probability is computed. The cumulative tunnelling probability is calculated for the ensemble of trajectories. The essence of the problem is the determination of the tunnelling paths. The appropriate paths are those that minimize the action; however, these are difficult to determine exactly for systems with many degrees of freedom. It is necessary to use approximations based on some pragmatically predefined tunnelling coordinate.

Quantum-mechanically, the amplitude for the tunnelling transition from reactant state $\varphi_i$ to product state $\varphi_f$ is $\langle \varphi_i | H | \varphi_f \rangle$. In a semiclassical treatment, one could choose classical trajectories that lie on the invariant torus that corresponds to the quantum state $\varphi_i$. The action integrals can be quantized by using the EBK condition (4) (for example [133]). Adiabatic switching provides a practical way of doing this [58]. The tunnelling paths would extend from caustics along these classical trajectories in the 'reactant' well to caustics in the 'product' phase space. Theoretically, the tunnelling direction is along the path of least action. Makri and Miller [134] have shown how this can be done in low-dimensional models; however, this is difficult to do for multidimensional systems. Also, this assumes stationary states; this is not rigorously correct for tunnelling states.

The practical difficulty in applying this approach, as well as other related applications of this general semiclassical approach, is locating the two ends of the tunnelling paths. However, the 'root search' problem can be avoided by taking advantage of a fundamental property of quantum mechanics. It is most easily understood in terms of resonant tunnelling between symmetric double wells [135]. Quantum-mechanically, tunnelling is the result of interference of the waves in the two wells, with the amplitude damped under the barrier in the classically forbidden region. The damping and penetration are symmetrical, and one needs to consider explicitly only half of the process since the other half is the mirror image of the first. That is, the entire process can be described by explicitly treating the dynamics in the reactant well and the penetration of the particle into the classically forbidden region up to the midpoint of the barrier. Then, the result is simply multiplied by two to obtain the probability of tunnelling between the two identical states. Thus, it is not necessary to locate both ends of the tunnelling paths, obviating the most difficult problem in practical applications of the semiclassical approach to multidimensional systems. It is also important to note again that this is consistent with the fundamental features of quantum mechanics.

We assume that energy levels are widely spaced, as they would be at low energies where tunnelling is most important. Thus, in general, double-well systems can be considered to have only two states that are close in energy and well separated from other states. Thus, there are two eigenvalues $E_1$ and $E_2$:

$$E_{\pm} = \tfrac{1}{2}(E_1 + E_2) \pm \tfrac{1}{2}[(E_1 + E_2)^2 + 4|H_{12}|^2]^{1/2}. \tag{41}$$

where $H_{12}$ is the shift in the energy levels, which, assuming that the two wells are identical, is given by the semiclassical expression

$$|H_{12}| = \hbar\nu \exp\left(-\frac{S}{\hbar}\right) \tag{42}$$

where $\nu$ is the vibrational frequency at energy $E$ in the well and $S$ is the action integral through the barrier:

$$S = \int_{x_1}^{x_2} |p_x| \, \mathrm{d}x. \tag{43}$$

$x_1$ and $x_2$ are the classical turning points on the two sides of the barrier. The basic idea in our approach is that a classical trajectory is propagated in the 'reactant' well, and each time that a turning point is encountered in the predetermined tunnelling direction $x$ the amplitude factor $\exp(-S/\hbar)$ is computed. The energy level splitting is given by

$$\Delta E = 2|H_{12}| = 2\hbar \frac{d}{dt} \langle A(t) \rangle, \tag{44}$$

where

$$A(t) = \Sigma h(t - t_n) \exp\left(-\frac{S}{\hbar}\right) \tag{45}$$

is the accumulated amplitude factor. $t_n$ are the times at which the trajectory is at a turning point and $h$ is the usual step function. The angular brackets imply an average over the initial vibrational phase.

A similar approach can be used to treat tunnelling in asymmetric systems. In the case of tunnelling between asymmetric states, one merely needs to calculate the probability amplitudes for both 'halves' of the processes [115]. That is, one must consider barrier penetrations from both directions and then add the two results to obtain the probability for tunnelling between the two-resonant states. The case of tunnelling into a continuum of states, that is dissociative tunnelling, the problem is greatly simplified since there is always a state available in the product region at the ends of all paths starting at the turning points on the barrier within the reactant well. It is necessary to define the 'tunnelling coordinate'; however, the rate (or splitting) is an ensemble average of tunnelling paths and the arbitrariness of a predefined tunnelling direction as well as the nature of the paths (straight lines or curves) tend not to be critical [136].

Initial conditions are selected using the standard quasiclassical approximation to sample normal mode coordinates and momenta [55]. That is, they are selected for the quantized torus of the zeroth-order harmonic Hamiltonian. This is adequate, even appropriate, for semiclassical tunnelling calculations. We have shown that adiabatic switching and standard quasiclassical initial conditions give comparable tunnelling splittings for a two-dimensional double-well model [136]. The level splitting, which is an ensemble-averaged quantity, is accurately predicted within the quasiclassical approximation because of averaging of the tunnelling paths.

We have applied this approach to the various kinds of tunnelling situation. These applications include tunnelling in malonaldehyde [133], methyl malonaldehyde [137], tropolone [138], aziridine [139], HSiOH [140] and $H + H_2$ [141]. Thus, we have illustrated the method for most types of tunnelling process of interest: simple double-well level splitting, asymmetric double-well intramolecular conversion, tunnelling that includes more than a single coordinate (methyl malonaldehyde), and molecular collisions ($H + H_2$).

## 8. Concluding comments

One of the goals in theoretical chemical dynamics is to develop the capability of computing rates of complex processes by using sufficiently realistic models that the results are comparable with experimental observations. The methods described here can be used to perform practical calculations of rates for unimolecular reactions in large molecules. These methods include straightforward classical trajectory simulations, Monte Carlo variational transition state theory, intramolecular dynamics diffusion theory, and a semiclassical approach for including tunnelling corrections in standard classical trajectory calculations.

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