

Zero-point energy correction for trajectory rate data

Kieran F. Lim†

School of Biological and Chemical Sciences, Deakin University, Geelong, Victoria 3217, Australia

Classical trajectory simulations are often used to calculate rate coefficients and other dynamical properties. Such calculations have a systemic error arising from leakage of zero-point energy into the reaction coordinate. Shen and Pritchard (*J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4357) have recently proposed a method to correct the rate coefficient. This paper shows that the Shen–Pritchard correction factor is applicable to ergodic systems and can be derived from transition-state theory. The relationship to the quantum-mechanical threshold method of Varandas and co-workers is shown and the implications for rate and product-distribution calculations are discussed.

It is often desirable to use (quasi-)classical trajectories¹ to calculate rate coefficients as quantum and semiclassical dynamics can be cost-prohibitive. Trajectory studies can determine if a system will be chaotic (enabling the use of transition state theories²) and in many cases can also identify the location of transition states,³ especially in reactions without a barrier. However, since the quantum zero-point energy (ZPE) is free to contribute to motions along the reaction coordinate, (quasi-)classical trajectory studies will overestimate rate coefficients,^{4,5} for reactions with negligible tunnelling. Over the last few years many research groups have proposed methods to correct this ‘ZPE problem’ while maintaining the computational practicality of classical mechanics.^{6–11}

Varandas and co-workers have advocated a quantum-mechanical threshold (QMT) method.⁶ This is a ‘passive’ method whereby trajectories are calculated without ZPE correction. Trajectories which have final configurations with less than ZPE are removed from the analysis and replaced by new trajectories with similar initial configurations to ensure appropriate sampling of the reactant ensemble.

Recently, Shen and Pritchard proposed a ZPE correction proportional to transition-state sums-of-state.⁷ Other workers (including our own research group) have proposed ‘active’ methods whereby the dynamics during the trajectory are adjusted to ensure conservation of ZPE at all times.^{8–12}

Here, the Shen–Pritchard ZPE correction is derived from Rice–Ramsperger–Kassel–Marcus (RRKM) transition-state theory,² and its relationship to Varandas’ QMT method⁶ demonstrated. The implications for rate and product-distribution calculations, for which more complicated schemes are required,^{11c} are considered.

Relationship between trajectory calculations and RRKM theory

Excellent reviews of the (quasi-)classical trajectory method for microcanonical rate coefficients, RRKM theory and their

relationship have been published.^{1,2} Nevertheless, it is instructive to review the relationship between the two methods here.

The following steps are typical for a trajectory calculation of the rate coefficient: (i) initial positions and momenta (\mathbf{q}, \mathbf{p}) are chosen from the reactant microcanonical ensemble at energy E ; (ii) the equations of motion are integrated for a pre-determined number of time steps, or until reaction occurs; (iii) the trajectory is termed ‘reactive’ if some interatomic distance (bond length) or bond angle passes a critical value, otherwise the trajectory is ‘unreactive’ (the time taken for a jectory to become ‘reactive’ is the trajectory reaction lifetime); (iv) initial positions and momenta (\mathbf{q}, \mathbf{p}) are chosen for a new trajectory and the process repeated until there are sufficient trajectories for statistical analysis.

Analysis of $N(t)$, the number of unreacted trajectories (molecules) at time t , gives the unimolecular rate coefficient $k(E, t)$ at energy E

$$k(E, t) = \frac{d}{dt} \log[N(t)] \quad (1)$$

$k(E, t)$ can be time-dependent since there is no assumption about RRKM or other behaviour.

Let $\Gamma = (\mathbf{q}, \mathbf{p})$ be a point in phase space. $T(\Gamma)$ is the trajectory (molecule) reaction lifetime for a trajectory which has initial configuration Γ :

$T(\Gamma) > t$; trajectory (molecule) has not reacted at time t

$T(\Gamma) = t$; trajectory (molecule) reacts at time t

The number of points (molecules) in reactant space with initial distribution $f(\Gamma)$ at time t is

$$N(t) = \int \cdots \int f(\Gamma) \delta(H - E) S[T(\Gamma) - t] d\Gamma \quad (2)$$

where $\delta(x)$ denotes a delta function and $S(x)$ is a step function. Hence

$$k(E, t) = \frac{\int \cdots \int f(\Gamma) \delta(H - E) \delta[T(\Gamma) - t] d\Gamma}{\int \cdots \int f(\Gamma) \delta(H - E) S[T(\Gamma) - t] d\Gamma} \quad (3)$$

For a microcanonical ensemble, every point Γ will be equally probable and $f(\Gamma)$ is a constant.

Phase space can be divided into the reaction coordinate s (and momentum p_s along s) and all other positions u and momenta p_u , orthogonal to s and p_s :

$$\mathbf{q} = (s, \mathbf{u}); \quad \mathbf{p} = (p_s, \mathbf{p}_u)$$

The transition state is defined as a critical surface dividing reactant space from product space. Hence the delta function $\delta[T(\Gamma) - t]$ in the numerator of eqn. (3) selects points lying on the transition state surface $s = s^\ddagger$ at the instant of passing (in the forward direction: $p_s > 0$) from reactant space to

† E-mail: lim@deakin.edu.au
http://www.deakin.edu.au/-lim/

product space, and can be replaced by a flux integral:²

$$k(E, t) = \frac{\int \cdots \int \delta(H - E) \frac{p_s}{m} S(p_s) \delta(s - s^\ddagger) \chi(\Gamma, t) ds dp_s du dp_u}{\int \cdots \int \delta(H - E) S[T(\Gamma) - t] d\Gamma} \quad (4)$$

The characteristic function $\chi(\Gamma, t) = 1$ if the point belongs to a reacting trajectory (molecule) and $\chi(\Gamma, t) = 0$ if the point arises from a trajectory that has (or will) (re-)cross from product to reactant space.

The transition-state assumption states that every trajectory (molecule) reaching the transition state reacts irreversibly:

$$\chi(\Gamma^\ddagger, t) = 1 \quad (5)$$

Further, in an ergodic system, every point is equally likely to react. Hence the ensemble decays exponentially, and $k(E, t)$ is independent of time. Without loss of generality, eqn. (4) can be evaluated at $t = 0$:

$$S[T - 0] = 1; \text{ for all } T \geq 0 \quad (6)$$

$$k(E) = \frac{\int S(E - \varepsilon) \left[\int \cdots \int \delta(H - \varepsilon) \delta(s - s^\ddagger) ds du dp_u \right] d\varepsilon}{\int \cdots \int \delta(H - E) d\Gamma} \quad (7)$$

Using the result

$$\rho(E) = h^{-n} \int \cdots \int \delta(H - E) dq dp \quad (8)$$

where $n = \text{dimension}(\mathbf{q}) = \text{dimension}(\mathbf{p})$, the usual RRKM formula is obtained (full details can be found elsewhere):²

$$k(E) = \frac{\int \rho^\ddagger(\varepsilon) d\varepsilon}{h\rho(E)} \quad (9)$$

where $\rho(E)$ is the density of states at energy E and $\rho^\ddagger(E)$ is the density of states orthogonal to the reaction coordinate, evaluated at the transition state.

Shen–Pritchard ZPE correction

In RRKM theory, the numerator in eqn. (9) is a sum over all allowed states at the transition state since:

$$\rho^\ddagger(E < E^\ddagger + E_z^\ddagger) \equiv 0$$

where E^\ddagger is the barrier height and E_z^\ddagger is the ZPE of the transition-state motions orthogonal to the reaction coordinate (see Fig. 1):

$$k_{\text{RRKM}}(E) = \frac{\int_{E^\ddagger + E_z^\ddagger}^E \rho^\ddagger(\varepsilon) d\varepsilon}{h\rho(E)} \quad (11)$$

However, when calculated from (quasi-)classical trajectories, the same numerator [eqn. (9)] includes regions of classical phase space (orthogonal to the reaction coordinate) with energy less than ZPE:

$$\rho_{\text{cl}}^\ddagger(\varepsilon) = \int \cdots \int \delta(H' - \varepsilon) \delta(s - s^\ddagger) ds du dp_u; \quad \varepsilon < E \quad (12)$$

$$k_{\text{CT}}(E) = \frac{\int_{E^\ddagger}^{E^\ddagger + E_z^\ddagger} \rho_{\text{cl}}^\ddagger(\varepsilon) d\varepsilon + \int_{E^\ddagger + E_z^\ddagger}^E \rho_{\text{cl}}^\ddagger(\varepsilon) d\varepsilon}{h\rho_{\text{cl}}(E)} \quad (13)$$

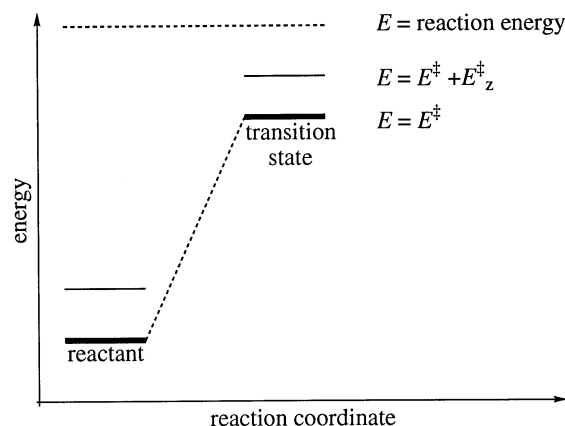


Fig. 1 Potential-energy diagram for a general reaction. The lower energy levels are the electrostatic energies; the higher levels are the lowest quantum state. The product energies are not shown.

The subscript ‘cl’ emphasises that classical sums- and densities-of-state are used in eqn. (12) and (13), while H' indicates that the Hamiltonian in eqn. (12) does not include terms corresponding to motion along the reaction coordinate,

$$H' = H'(\mathbf{u}, \mathbf{p}_u)$$

rather than the full Hamiltonian

$$H = H(s, \mathbf{u}, \mathbf{p}_s, \mathbf{p}_u)$$

A comparison of eqn. (9)–(13) shows that the Shen–Pritchard ZPE correction factor $F(E)$

$$k_{\text{corrected}}(E) = F(E)k_{\text{CT}}(E) \quad (14a)$$

$$F(E) = \frac{\int \rho_{\text{cl}}^\ddagger(\varepsilon) d\varepsilon - \int_{E^\ddagger + E_z^\ddagger}^{E^\ddagger + E_z^\ddagger} \rho_{\text{cl}}^\ddagger(\varepsilon) d\varepsilon}{\int \rho_{\text{cl}}^\ddagger(\varepsilon) d\varepsilon - \int_{E^\ddagger}^{E^\ddagger} \rho_{\text{cl}}^\ddagger(\varepsilon) d\varepsilon} = \frac{G(E) - G(E^\ddagger + E_z^\ddagger)}{G(E) - G(E^\ddagger)} \quad (14b)$$

is exact for ergodic systems. (Shen and Pritchard had previously argued that this result was correct, but without formal proof.⁷) Combining eqn. (1) and (14)

$$k_{\text{corrected}}(E) = F(E) \frac{d}{dt} \log[N(t)] \quad (15)$$

Comparison with the QMT method of Varandas

The QMT method of Varandas and Marques⁶ is similar in spirit to the Shen–Pritchard correction,⁷ but with two important differences: (i) the QMT method discards with replacement trajectories that do not preserve product ZPE, whereas the Shen–Pritchard proportion method retains all trajectories, but applies a correction factor; (ii) the QMT correction of Varandas and coworkers is evaluated at the product configuration, not the transition state.

The Shen–Pritchard proportion method is exact if the system is ergodic. Since the system is ergodic, every initial reactant configuration with sufficient energy will eventually lead to reaction, *i.e.* every reactant configuration Γ is eventually mapped to some point Γ^\ddagger in the transition-state surface

$$\Gamma^\ddagger = (s = s^\ddagger, p_s > 0, \mathbf{u}, \mathbf{p}_u)$$

by the equations of motion:

$$\text{trajectory: } \Gamma \rightarrow \Gamma^\ddagger$$

The transition state assumption states that this mapping is unique since every trajectory crosses the transition-state surface once and once only.

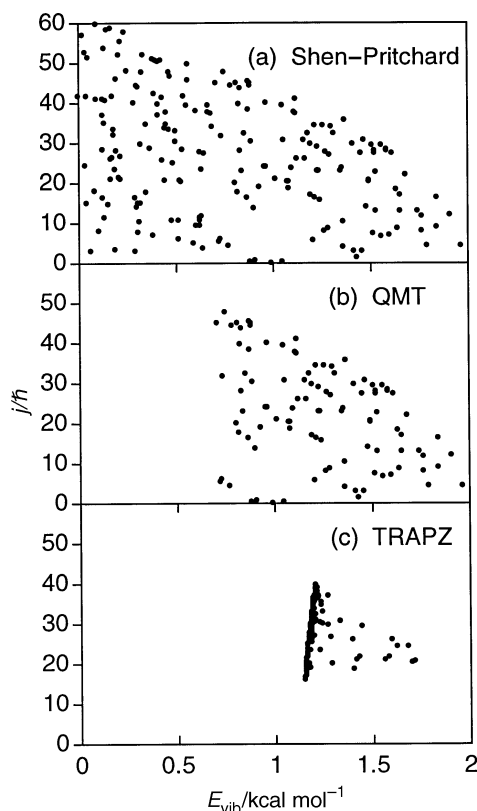


Fig. 2 Diatomic product distribution correlation between vibrational energy and molecular angular momentum for $\text{Al}_3 \rightarrow \text{Al} + \text{Al}_2$.¹² (a) The Shen–Pritchard method⁷ which has the same product distribution as a ‘normal’ trajectory calculation; (b) a simulated QMT method distribution,⁶ obtained by discarding (without replacement) all trajectories with vibrational energy less than the product ZPE; (c) the TRAPZ method.^{11,12} Note that the ‘active’ TRAPZ method has converted the reactant bending vibrational zero-point energy into non-zero product molecular angular momentum.

Let B_+ be the set of initial configurations which eventually lead to reaction but with more than ZPE (orthogonal to the reaction coordinate) at the transition state and, similarly, let B_- be the set of initial configurations which eventually lead to reaction but with less than ZPE:

$$B_+ = \left\{ \Gamma \left| \int \cdots \int \varepsilon \delta[H'(\Gamma^\ddagger) - \varepsilon] \delta(s - s^\ddagger) ds d\mathbf{u} d\mathbf{p}_u \right. \right. \\ \left. \left. > E^\ddagger + E_z^\ddagger \right\} \quad (16)$$

$$B_- = \left\{ \Gamma \left| \int \cdots \int \varepsilon \delta[H'(\Gamma^\ddagger) - \varepsilon] \delta(s - s^\ddagger) ds d\mathbf{u} d\mathbf{p}_u \right. \right. \\ \left. \left. < E^\ddagger + E_z^\ddagger \right\} \quad (17)$$

A consequence of ergodicity is that each initial configuration Γ has equal likelihood of reacting. The distributions of reaction lifetimes in both sets will be identical and hence the calculated rate coefficients are also identical.

Suppose those trajectories in the Shen–Pritchard method which had less than ZPE (orthogonal to the reaction coordinate) at the transition state were discarded and replaced. There would be no change to the calculated trajectory rate coefficient, $k_{\text{CT}}(E)$ for ergodic systems. However, $k_{\text{CT}}(E)$ overestimates the true rate coefficients since, in reality, B_+ must be an empty set and is corrected by counting trajectories in B_- as non-reactive: eqn. (13)–(15). This proportion correction is equivalent to discarding without replacement B_- trajectories from the count of reactive trajectories, but including such trajectories in the count of total trajectories.

The Varandas QMT method is more general and does not depend on the assumption of ergodicity.⁶ Hence to maintain a uniform (random) sampling of reactant phase space, discarded trajectories must be replaced. The QMT method effectively uses analogues of eqn. (13)–(17), but evaluated at the product configurations, not at the transition state: this is a good approximation in the late (product-like) transition-state limit. On the other hand, Varandas and Marques have studied systems such as $\text{H} + \text{O}_2$ and $\text{O} + \text{OH}$, which have variational transition states. It would be extremely difficult to use the QMT criterion for zero-point preservation on each trajectory at the transition state since its location varies. Our own ‘TRAPZ’ studies,^{11,12} and those using the ‘momentum reversal’ method of Bowman, Miller and Hase^{8,9,13} have shown that it is possible to require zero-point preservation at all times during the trajectory, but at much greater computational expense.

Product distributions

The rate coefficient from trajectories will be overestimated from trajectory calculations as ZPE can leak into the reaction coordinate. RRKM transition-state theory has been used to show that simple procedures can be used to correct these rate coefficients,^{6,7} and will be exact (in the context of classical mechanics) when the system is ergodic or if the transition state is product-like.

However, transition-state theory makes no predictions about product distributions,² which may also be adversely affected by non-preservation of the ZPE. For example, dissociation of a triatomic ($J = 0$) results in a rotationally excited ($j \neq 0$) diatomic product. This is most clearly seen in the dissociation of a non-linear triatomic which will have non-zero product orbital angular momentum, $L \neq 0$. By the conservation of angular momentum

$$J_{\text{reactant}} = 0 = L + j_{\text{diatomic}}$$

$$j_{\text{diatomic}} = -L \neq 0$$

the diatomic is formed with non-zero molecular angular momentum j_{diatomic} .

Fig. 2 shows some trajectory data on the $\text{Al}_3 \rightarrow \text{Al} + \text{Al}_2$ reaction.¹² Correlations between the Al_2 vibrational energy and molecular angular momentum are plotted. The product ZPE is *ca.* $0.7 \text{ kcal mol}^{-1}$. The uppermost panel shows the product distribution for the Shen–Pritchard method: since all trajectories are retained (only the resultant rate coefficient is corrected) there are many trajectories with near-zero product vibrational energy (less than ZPE). The middle panel shows a simulated QMT distribution⁶ which has discarded (without replacement) all trajectories with Al_2 vibrational energy less than the product ZPE. However, since the reactant is allowed to have energy less than ZPE in the reactant bending mode, it is possible to form product Al_2 in $J \simeq 0$ states.

The lowest panel of Fig. 2 shows the result of a TRAPZ calculation which requires zero-point preservation at all times during the trajectory.^{11,12} Instead of using the true ZPE at each point along the reaction coordinate, TRAPZ uses a harmonic expansion of the potential surface about each instantaneous geometry to approximate the ZPE. This has moved the reaction threshold to higher product vibrational energy. More importantly, the reactant bending ZPE has been preserved during the early part of each trajectory, and then converted into non-zero Al_2 angular momentum.

Summary and Conclusions

The use of quantum or semiclassical dynamics is often impractical in calculations. Classical mechanics offers a partial remedy but (*inter alia*) cannot preserve the quantum ZPE. The trajectory technique¹ can be used to calculate rate coefficients

which are: (i) corrected using ratios of transition-state sums-of-state after the completion of the trajectory simulation;⁷ or (ii) corrected by adjusting the ensemble at the end of each set of trajectories.⁶ Since each individual trajectory is permitted to run without perturbation, these are known as 'passive' corrections to the ZPE problem and will predict rate coefficients that are exact in the limits discussed above. However, the prediction of product distributions and other dynamical properties using trajectories may require 'active' correction methods which perturb the classical mechanical motions to preserve the ZPE at all times during each trajectory.^{8–12} these methods also have some shortcomings.

Careful consideration must be given to the choice of computational technique for the calculation at hand as no single method will be able to predict every quantity of interest.

This work was funded by an Australian Research Council Large Grant. The author thanks Mr. Drew A. McCormack (University of Melbourne) for the Al₃ results; Professor Huw O. Pritchard (York University) for a preprint of ref. 7, and Ms. Jeanne Lee (ICI Polyurethanes, Asia Pacific RDC) for helpful and encouraging discussions.

References

- 1 R. N. Porter and L. M. Raff, in *Dynamics of Molecular Collisions*, ed. W. H. Miller, Plenum Press, New York, 1976, vol. B, p. 1;

- J. I. Steinfeld, J. S. Francisco and W. L. Hase, *Chemical Kinetics and Dynamics*, Prentice Hall, Englewood Cliffs, NJ, 1989; J. N. Murrell and S. D. Bosanac, *Introduction to the Theory of Atomic and Molecular Collisions*, Wiley, Chichester, 1989.
- 2 R. G. Gilbert and S. C. Smith, *Theory of Unimolecular and Recombination Reactions*, Blackwells Scientific, Oxford, 1990.
- 3 K. F. Lim and J. I. Brauman, *J. Chem. Phys.*, 1991, **94**, 7164, and references therein.
- 4 L. L. Gibson, G. C. Schatz, M. A. Ratner and M. J. Davis, *J. Chem. Phys.*, 1987, **86**, 3263.
- 5 J. Davidsson and G. Nyman, *J. Chem. Phys.*, 1990, **92**, 2407.
- 6 A. J. C. Varandas and J. M. C. Marques, *J. Chem. Phys.*, 1994, **100**, 1908, and references therein.
- 7 D. L. Shen and H. O. Pritchard, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4357.
- 8 J. M. Bowman, B. Gazdy and Q. Sun, *J. Chem. Phys.*, 1989, **91**, 2859; W. H. Miller, W. L. Hase and C. L. Darling, *J. Chem. Phys.*, 1989, **91**, 2863.
- 9 G. H. Peslherbe and W. L. Hase, *J. Chem. Phys.*, 1994, **100**, 1179; 1996, **104**, 9445.
- 10 M. Ben-Nun and R. D. Levine, *J. Chem. Phys.*, 1994, **101**, 8768.
- 11 (a) K. F. Lim and D. A. McCormack, *J. Chem. Phys.*, 1995, **102**, 1705; (b) D. A. McCormack and K. F. Lim, *J. Chem. Phys.*, 1995, **103**, 1991; (c) 1997, in the press.
- 12 D. A. McCormack and K. F. Lim, in preparation.
- 13 F. E. Budenholzer, M. Y. Chang and K. C. Huang, *J. Phys. Chem.*, 1994, **98**, 12501.

Communication 6/08119C; Received 2nd December, 1996