

## Spiers Memorial Lecture Quantum and semiclassical theory of chemical reaction rates

William H. Miller

Department of Chemistry, University of California, Berkeley, and Chemical Sciences  
Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460 USA

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Transition state theory (TST) has provided the qualitative picture of chemical reaction rates for over sixty years. Recent theoretical developments, however, have made it possible to calculate rate constants fully quantum mechanically and efficiently, at least for small molecular systems; vestiges of TST can be seen both in the resulting flux correlation functions and in the algorithmic structure of the methodology itself. One approach for dealing with more complex molecular systems is the semiclassical (SC) initial value representation (IVR), which is essentially a way of generalizing classical molecular dynamics simulations to include quantum interference; electronic degrees of freedom in an electronically non-adiabatic process can also be included on a dynamically equivalent basis. Application of the SC-IVR to models of unimolecular isomerization and of electronically non-adiabatic transitions, both coupled to an infinite bath of harmonic oscillators, gives excellent agreement with (essentially exact) quantum path integral calculations for these systems over the entire range of coupling strength.

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### I Reaction rate theory: Retrospective and present directions

In mid-September of 1937 the 67th General Discussion<sup>1</sup> of the Faraday Society was held at the University of Manchester on the subject *Reaction Kinetics*, the purpose being ‘... to clarify certain aspects of the reaction velocity problem’. That clarification was needed is evidenced by the President’s opening remarks: ‘As to whether these methods are fundamentally sound or unsound is a question the consideration of which belongs rather to the domain of philosophy than to that of chemistry ...’!

‘These methods’, of course, refers to the theory of reaction rates ( $\equiv$  ‘velocities’) that had evolved over the preceding five years or so, variously called the transition state (TS) method, activated complex theory, or the theory of absolute reaction rates, and now usually referred to as ‘transition state theory’ (TST). The founding Trinity of TST—M. Polanyi, Eyring and Wigner—were there, as were most of the other notables in the field of kinetics. The excitement, even passion of the moment still comes through on reading the discussion comments. One participant, for example, felt that ‘... arguments used by Evans and Polanyi ... seem to us particularly dangerous, because their logical significance is concealed by the method of presentation,’ and of Eyring’s paper that ‘... I do not believe the treatment described can be of any use,’ while another more experimentally inclined participant felt the entire matter of dubious merit since ‘... it would take much longer to estimate the partition function of the cluster (if at all possible) than to find new and enlightening experimental information on the mechanism of reaction’.

Eyring opened the Discussion with a paper<sup>2</sup> on calculating potential energy surfaces (PESs)—just as our Discussion begins—and their centrality was especially clear to Wigner, who noted that ‘... every calculation of reaction rates is bound to founder

unless we have more detailed energy surfaces than are available at present ...'. Some participants were pessimistic on this issue, one noting that 'Not even for the simplest bimolecular process is it possible to calculate the interaction between two molecules with an accuracy adequate to give even a useful approximation to the energy of activation', but Polanyi had a more philosophical attitude, 'Personally I attach no importance at the present stage to a precise numerical agreement between theory and experiment ...', being content with the qualitative insight TST provided.

Eyring's second paper,<sup>3</sup> and one by Evans,<sup>4</sup> dealt with the thermodynamic version of TST and some applications, but the most perceptive paper was Wigner's.<sup>5</sup> His 'three threes' (*cf.* Table 1) gave a clear outline of the whole subject. First were the three 'steps' in the theory of kinetics: (1) constructing the PESs, (2) calculating the rates of the elementary reactions, and (3) combining the many elementary reactions into a complex reaction mechanism. Next were the three 'groups' of elementary reactions: (1) vibrationally/rotationally inelastic collisions, (2) reactive collisions on a single PES, and (3) electronically non-adiabatic ( $\equiv$  'diabatic' in Polanyi's<sup>6</sup> terminology) reactions involving several PESs. And finally were the three 'assumptions' of TST [which he noted was only applicable to reactions of type (2) above]: (1) no electronically non-adiabatic transitions, (2) validity of classical mechanics for the nuclear motion (with perhaps small quantum corrections), and (3) the existence of a dividing surface, separating reactants and products, that no classical trajectory passes through more than once. This overall picture of reaction dynamics is still quite appropriate today.

Wigner then discussed the three assumptions of TST in some detail, particularly (2) and (3). He noted that it is '... much more difficult to apply the transition state method in quantum theory than it is in classical theory ...' and concluded that 'All that appears to be possible, in general, is to start out from the classical expression and develop the quantum corrections into a power series in  $\hbar$  ...'. He noted that assumption (3) of no re-crossing trajectories (*i.e.*, a transmission coefficient  $\kappa = 1$ ) '... will lead, in general, to too high values of the reaction rate ...' (from which follows the variational aspect of classical TST), though the assumption does in fact become exact at sufficiently low temperature. 'However at higher temperature  $\kappa$  will decrease, ... [and in general] it may be quite difficult to find its accurate value.'

What has happened since 1937? First, with regard to Wigner's 'first step' in Table 1, one is finally beginning to have reliable PESs for a wide variety of molecular systems. The increase in computational power<sup>7</sup> (a factor of *ca.*  $10^6$ ) in only my *ca.* 30 year scientific lifetime has been staggering, and together with the methodological and algorithmic advances<sup>8</sup> over this same period (maybe a factor of  $10^2$ ), the pessimism of 1937 is

**Table 1** Wigner's 'three threes' of reaction kinetics

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Three steps in theory of kinetics
(1) Determine potential energy surfaces
(2) Determine elementary reaction rates*
(3) Solve rate equations for complex reaction mechanism
*Three groups of elementary reactions
(1) Vibrationally/rotationally inelastic collisions
(2) Reactive collisions on a single PES**
(3) Electronically non-adiabatic reactive collisions
**Three assumptions of TST
(1) Electronic adiabaticity
(2) Validity of classical mechanics
(3) Existence of a dividing surface that trajectories do not re-cross

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abating. One is even beginning to think of being able routinely to evaluate the PES ‘on the fly’ during a classical trajectory or quantum dynamics calculation. This will finally eliminate the dreadful task of having to fit some complicated algebraic function to a small number of *ab initio* electronic structure calculations in order to obtain a global PES.

Another major change since 1937 is that one can now study the dynamics of chemical reactions at a much greater level of detail than just *via* their thermal rate constant. Beginning in the late 1950s, molecular beam (and later a host of laser-based) methods<sup>9</sup> made it possible to determine the dependence of reaction cross-sections on collision energy, scattering angle, and initial/final quantum states of reactants/products, and most recently ultrafast laser technology has made it possible to study chemical reactions in real time<sup>10</sup> by various pump–probe schemes. These experimental advances in turn stimulated an explosion of theoretical development,<sup>11</sup> starting in the early 1960s and continuing to the present, as one tries to develop new models and theoretical methods to describe these new experimental phenomena. Indeed some of the most significant advances in reactive scattering theory have taken place in only the last decade.<sup>12</sup> Several contributions to this Discussion are excellent examples of the state-of-the-art in state-to-state reactive scattering calculations for small molecular systems. Reactive scattering methodology has also been adapted to the scattering of small molecules from solid surfaces, and this area is also well represented at this meeting.

Finally, the original goal of theoretical reaction kinetics—the determination of the thermal rate constant, which is the average of the reactive cross-section over energy, scattering angle, and initial/final quantum states—had a re-birth of interest and focus in the 1970s that has continued to the present. This is due in part to practical considerations—a realistic modeling of combustion and of atmospheric phenomena requires rate constants for thousands of elementary gas-phase reactions—and also due to the intellectual challenge, *i.e.*, is it possible even in principle to obtain the thermal rate constant, absolutely correctly, without first calculating the state-to-state reactive cross-sections explicitly and then averaging them appropriately? Also, for reactions in complex environments (*e.g.*, solution) it is still often the case that only the rate constant (or some other highly averaged quantity) is of relevance.

A paper by Pechukas and McLafferty<sup>13</sup> was particularly influential in this revival of interest in TST. Though dealing only with classical TST, they emphasized the Wignerian dynamical perspective (*i.e.*, no re-crossing trajectories) that had essentially been buried by the enormous number of applications using Eyring’s thermodynamic picture. The thermodynamic picture does of course lead to useful phenomenology (entropy of activation, *etc.*), but it masks the dynamical understanding of TST that is necessary to extend and generalize the theory. In particular, this re-focus on the dynamical perspective of TST stimulated the search<sup>14,15</sup> for a rigorous quantum version of TST, *i.e.*, a way to implement the assumption of no re-crossing dynamics quantum mechanically, without incorporating any further approximations (such as assuming separability of a reaction coordinate from the other degrees of freedom of the molecular system). The rationale was that since the TST assumption (of no re-crossing dynamics) is accurate at low energy, which is the most important region for determining thermal rate constants, but at low energies tunneling and other quantum effects become more important, a quantum theory built on the TST assumption would be quite accurate for thermal rate constants (at least those with a simple activation barrier).

Nature turned out to be not quite so simple. Though some very interesting and useful approaches have emerged from this quest for a quantum TST (QTST)—*e.g.*, the instanton model<sup>15b</sup> (a periodic orbit in pure imaginary time that describes tunneling through the TS region of the PES), a semiclassical TST involving the conserved classical action variables at the TS,<sup>15f</sup> path integral centroid approaches,<sup>16,17</sup> and a variety of other semiclassical models for including the effects of reaction path curvature on TS

tunneling probabilities<sup>18–20</sup>—the conclusion of it all is that there is no uniquely well defined quantum version of TST in the sense that there is in classical mechanics. This is because tunneling along the reaction coordinate necessarily requires one to solve the (quantum) dynamics for some finite region about the TS dividing surface, and if one does this fully quantum mechanically there is no ‘theory’ left, *i.e.*, one has a full dimensional quantum dynamics treatment which is *ipso facto* exact, a quantum simulation.

The frustrated quest for a rigorous QTST was not for naught, however, for the theoretical formulation it engendered has led in recent years to a very useful procedure for calculating rate constants ‘directly’, *i.e.*, without having to solve the state-to-state reactive scattering problem explicitly, but also ‘correctly’, *i.e.*, without any inherent dynamical approximations. This approach is summarized briefly in the next section, with some illustrative examples presented in Section III. A more comprehensive review of this work has recently been published elsewhere.<sup>21</sup>

Though this ‘direct’ and ‘correct’ approach is a significant step in reaction rate theory, it can at present be applied without approximation only for relatively small molecular systems. It is of course possible—and often quite useful—to divide a complex molecular system of many degrees of freedom into a few that are most central to the reaction and treat them by rigorous quantum methods, with the remaining degrees of freedom treated approximately. Particularly useful in this regard are the ‘reduced dimensionality’ models that Bowman and co-workers<sup>22</sup> have described and applied, the time-dependent self-consistent field approximation<sup>23</sup> that Gerber and others have used extensively, and the multi-configuration time-dependent Hartree (MC-TDH) methodology<sup>24</sup> that Manthe *et al.* have applied to this problem. The many semiclassical approximations<sup>18–20</sup> for making tunneling corrections to TST can also be thought of as approximate versions of this strategy, as can the many kinds of ‘mixed quantum-classical’ approaches<sup>25</sup> that treat the (many) less important degrees of freedom by classical mechanics.

Another approach for dealing with more complex molecular systems is to use the semiclassical (SC) initial value representation (IVR)<sup>26–30</sup> to evaluate the rigorous quantum rate expressions. This has the advantage that all degrees of freedom—even the electronic degrees of freedom in electronically non-adiabatic processes<sup>31–32</sup>—are treated equivalently. The goal here is to generalize classical molecular dynamics (MD) simulation methods to include quantum interference and tunneling effects. Section IV describes this approach and some of its applications that have been carried out to date. Since classical trajectory simulations can be performed for truly complex molecular systems—*e.g.*, reactions in solution, clusters, biomolecular environments, or on surfaces—these SC-IVR approaches have the potential of extending rigorous quantum rate theory into such areas.

## II Rigorous quantum rate theory

I have reviewed this topic in several places<sup>21,33</sup> and thus give only a brief synopsis here. Assuming that the reactants are in Boltzmann equilibrium (and the validity of non-relativistic quantum mechanics), one can show<sup>15a</sup> that the proper average of the state-to-state reactive scattering cross-section over energy, scattering angle, and initial/final quantum states gives the following relatively simple trace expression for the rate constant of a bimolecular reaction

$$k(T) = \lim_{t \rightarrow \infty} C_{fs}(t) \quad (1)$$

where the flux-side correlation function  $C_{fs}$  is

$$C_{fs}(t) = Q_r(T)^{-1} \text{tr} [e^{-\beta \hat{H}} \hat{F} \hat{P}(t)] \quad (2)$$

Here  $\hat{H}$  is the Hamiltonian operator of the molecular system,  $\hat{F}$  the flux operator with respect to a dividing surface that separates reactants and products,  $\hat{\mathbb{P}}(t)$  the projector onto all states that are in the product region at time  $t$ , and  $\beta = (k_B T)^{-1}$ ;  $Q_r(T)$  is the reactant partition function per unit volume. If  $s(\mathbf{q}) = 0$  is the equation which defines the dividing surface— $s(\mathbf{q}) > 0$  being the product region and  $s(\mathbf{q}) < 0$  the reactant region—then the projection operator  $\hat{\mathbb{P}}(t)$  can be expressed as<sup>34</sup>

$$\hat{\mathbb{P}}(t) = e^{i\hat{H}t/\hbar} h[s(\mathbf{q})] e^{-i\hat{H}t/\hbar} \quad (3)$$

where  $h(s)$  is the standard Heaviside function,

$$h(s) = \begin{cases} 1, & s > 0 \\ 0, & s < 0 \end{cases} \quad (4)$$

This makes the classical limit of eqn. (2) transparent: a classical phase space average replaces the trace, giving

$$C_{fs}^{CL}(t) = Q_r(T)^{-1} (2\pi\hbar)^{-F} \int d\mathbf{p}_0 \int d\mathbf{q}_0 e^{-\beta H(\mathbf{p}_0, \mathbf{q}_0)} F(\mathbf{p}_0, \mathbf{q}_0) h[s(\mathbf{q}_t)] \quad (5)$$

where  $\mathbf{q}_t \equiv \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$  is the  $F$ -dimensional coordinate at time  $t$  that has evolved from initial conditions  $(\mathbf{p}_0, \mathbf{q}_0)$ .

Sometimes it is useful to differentiate eqn. (2) and then integrate the result to obtain the rate,<sup>34</sup>

$$k(T) = \int_0^\infty dt C_f(t) \quad (6a)$$

where

$$C_f(t) = \frac{d}{dt} C_{fs}(t) = Q_r(T)^{-1} \text{tr} [e^{-\beta\hat{H}} \hat{F} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar}] \quad (6b)$$

the fact having been used that

$$\frac{d}{dt} e^{i\hat{H}t/\hbar} h(s) e^{-i\hat{H}t/\hbar} = e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar} \quad (7)$$

$C_f(t)$  is a flux–flux autocorrelation function; whether one expresses the rate as the long time limit of  $C_{fs}(t)$ , or as the time integral of  $C_f(t)$ , is a matter of convenience. It has also been noted<sup>34</sup> that the rate constant (though not the correlation functions) is unchanged if one makes the following modification to the above expressions,

$$e^{-\beta\hat{H}} \hat{F} \rightarrow e^{-\lambda\hat{H}} \hat{F} e^{-(\beta-\lambda)\hat{H}} \quad (8)$$

for any value of  $\lambda$  between 0 and  $\beta$ . In most applications we have made the choice  $\lambda = \beta/2$ , initially so that the Boltzmann operator could be combined with the time evolution operators and have just one (complex time) propagator, *i.e.*,

$$C_f(t) = Q_r(T)^{-1} \text{tr} [\hat{F} e^{i\hat{H}t_c/\hbar} \hat{F} e^{-i\hat{H}t_c/\hbar}] \quad (9)$$

where  $t_c = t - i\hbar\beta/2$ . [This was particularly useful in trying to compute  $C_f(t)$  by analytic continuation methods;<sup>35,36</sup> *i.e.*, one computes

$$C_f(-i\tau) \equiv Q_r(T)^{-1} \text{tr} [\hat{F} e^{-(\beta/2 - \tau/\hbar)\hat{H}} \hat{F} e^{-(\beta/2 + \tau/\hbar)\hat{H}}] \quad (10)$$

for a range of real  $\tau$  values in the interval  $-\hbar\beta/2 < \tau < \hbar\beta/2$ , and then analytically continues  $C_f(-i\tau)$  to the complex value  $\tau = it$  to obtain  $C_f(t)$ .] Much earlier Yamamoto,<sup>37</sup> using Kubo linear response theory, expressed the rate as the time integral of a

flux–flux autocorrelation function that corresponds to averaging eqn. (8) over  $\lambda$ . Though the rate constant is formally the same as that given by eqn. (9), this is less useful in practice because the resulting correlation function is singular at  $t = 0$ .

Rather than computing these time correlation functions, in some applications it is useful rather to compute the cumulative reaction probability<sup>15b,34,38</sup> (CRP)  $N(E)$  as a function of total energy  $E$ , in terms of which the thermal rate constant is given by

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE e^{-\beta E} N(E) \quad (11)$$

Furthermore, in some applications the microcanonical rate constant  $k(E)$  is the object of interest (typically for unimolecular reactions), and it is given in terms of the CRP,

$$k(E) = [2\pi\hbar \rho_r(E)]^{-1} N(E) \quad (12)$$

where  $\rho_r(E)$  is the reactant density of states per unit energy. The ‘direct’ and ‘correct’ expression for  $N(E)$  that corresponds to the above time correlation functions is<sup>34</sup>

$$N(E) = \frac{1}{2}(2\pi\hbar)^2 \text{tr} [\hat{F} \delta(E - \hat{H}) \hat{F} \delta(E - \hat{H})] \quad (13)$$

where  $\delta(E - \hat{H})$  is the microcanonical density operator that can be represented in terms of the outgoing wave Green’s function

$$\delta(E - \hat{H}) = \frac{-1}{\pi} \text{Im} \hat{G}^{(+)}(E) \quad (14a)$$

$$\hat{G}^{(+)}(E) = (E + i\varepsilon - \hat{H})^{-1} \quad (14b)$$

or in terms of the time evolution operator,

$$\delta(E - \hat{H}) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} e^{-i\hat{H}t/\hbar} \quad (15)$$

Note that eqn. (12) looks superficially like the RRKM expression for the microcanonical rate constant, with the CRP replacing the ‘integral density of states of the activated complex’ of the RRKM ( $\equiv$  microcanonical TST) approximation.

Though some of these formally exact expressions for the rate constant have been known for many years, it was less than ten years ago that practical ways began to be developed for evaluating them. The work of my research group in this regard is reviewed elsewhere,<sup>21,33</sup> and I also want to note especially the important contributions of Light and co-workers<sup>39</sup> and Manthe and co-workers<sup>40</sup> in developing the methodology for these calculations. Applications have been made to a number of reactions, all in their full dimensionality:  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ ,<sup>38b,39a</sup>  $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ ,<sup>39a</sup>  $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ ,<sup>39a</sup>  $\text{O} + \text{HD} \rightarrow \text{OD} + \text{H}$ ,<sup>41</sup>  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ ,<sup>42</sup>  $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ ,<sup>43</sup>  $\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$ ,<sup>44</sup>  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ ,<sup>45</sup>  $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ ,<sup>39d,40c,46</sup>  $\text{D}_2 + \text{OH} \rightarrow \text{HOD} + \text{D}$ ,<sup>40c</sup> and  $\text{H}_2 + \text{CN} \rightarrow \text{HCN} + \text{H}$ .<sup>40b,39e</sup> The methodology is now sufficiently well developed that it should be applicable to essentially any small molecular system.

To close this summary of formal rate expressions, I note another that has not yet found practical use but has interesting possibilities. The derivation (omitted here) is a rather straight-forward route from eqn. (9): the canonical and microcanonical rate constants can be expressed in terms of the following correlation function

$$C(t) = \lim_{t' \rightarrow \infty} \text{tr} [\hat{F} e^{i\hat{H}(t'+t/2)\hbar} h(s) e^{-i\hat{H}(t'-t/2)\hbar}] \quad (16)$$

which is a function neither of  $E$  nor  $T$ . The CRP is the Fourier transform of this correlation function,

$$N(E) = \int_{-\infty}^{\infty} dt e^{-iEt/\hbar} C(t) \quad (17)$$

and the thermal constant given by its analytic continuation to the imaginary value  $t = i\hbar\beta$ ,

$$k(T) = Q_r(T)^{-1} C(i\hbar\beta) \quad (18)$$

Calculation of this one correlation function would thus allow one to obtain  $N(E)$  and  $k(T)$  for all (or at least some range of) values of  $E$  and  $T$ , respectively. It remains to be seen if this will lead to practically useful approaches.

### III Some examples

In the classical limit, if the TST assumption of no re-crossing trajectories is correct—*i.e.*, a direct reaction—it is not hard to show that the classical flux–flux autocorrelation function is proportional to a Dirac delta function at  $t = 0$ , *i.e.*,

$$C_f(t) = 2 \delta(t) \frac{k_B T}{h} \frac{Q^\ddagger(T)}{Q_r(T)} \quad (19)$$

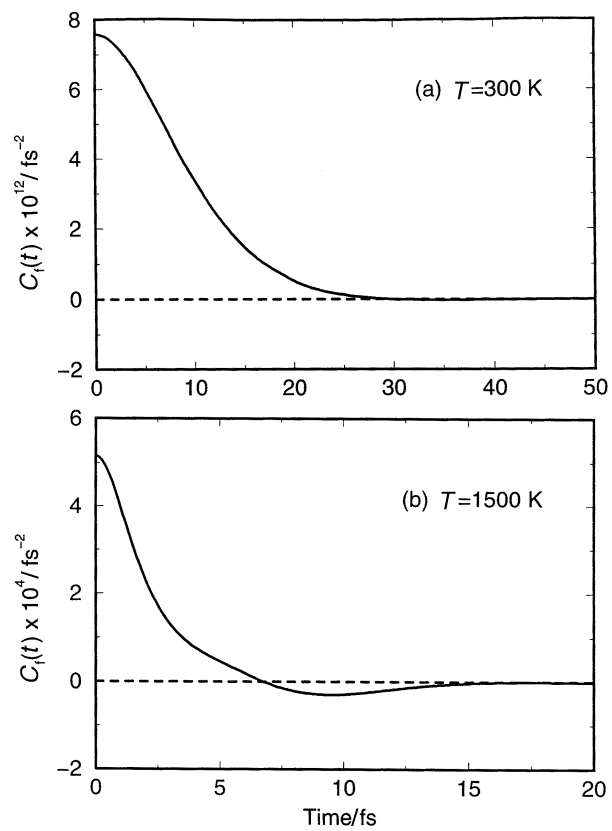
Since  $\int_0^\infty dt \delta(t) = \frac{1}{2}$ , this integrates [*cf.* eqn. (6a)] to give the TST rate constant, and it also shows that one needs to evaluate  $C_f(t)$  only for very short (in fact, infinitesimal) times in order to be able to integrate it to obtain the rate constant.

Quantum mechanics is not quite so simple, even for a direct reaction. This can be seen explicitly for the case of a one dimensional reaction coordinate separable from the other  $(F - 1)$  degrees of freedom; if the reaction coordinate is treated as a free particle, eqn. (19) is modified as follows<sup>34</sup>

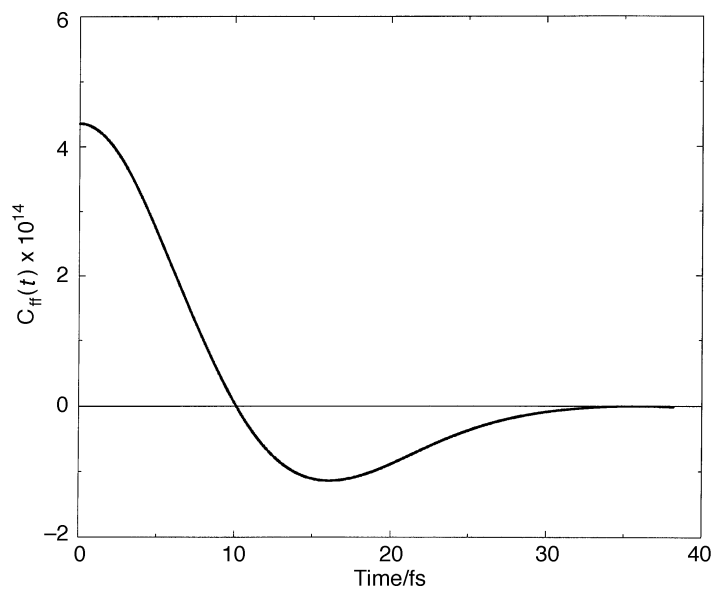
$$2 \delta(t) \rightarrow \frac{\left(\frac{\hbar\beta}{2}\right)^2}{\left[t^2 + \left(\frac{\hbar\beta}{2}\right)^2\right]^{3/2}} \quad (20)$$

The right hand side of eqn. (20) also integrates to unity, so that the TST rate expression is maintained (though with quantum partition functions), but here it is necessary to integrate  $C_f(t)$  from 0 to a time of at least *ca.*  $\hbar\beta$  in order to obtain the quantum rate constant. This is still a short time ( $\hbar\beta \approx 27$  fs at  $T = 300$  K), but not zero. One sees this same qualitative behaviour in the quantum correlation function for direct reactions of real molecular systems—for which all the degrees of freedom are coupled—*i.e.*,  $C_f(t)$  falls effectively to zero in a time of *ca.*  $\hbar\beta$ . This is the ultimate source of the efficiency and usefulness of this ‘direct’ and ‘correct’ way of computing rate constants: it is necessary to generate the full quantum dynamics of the coupled system, but only for short time. It is during this time from 0 to  $\hbar\beta$  that all the tunneling, corner-cutting, *etc.*, phenomena take place.

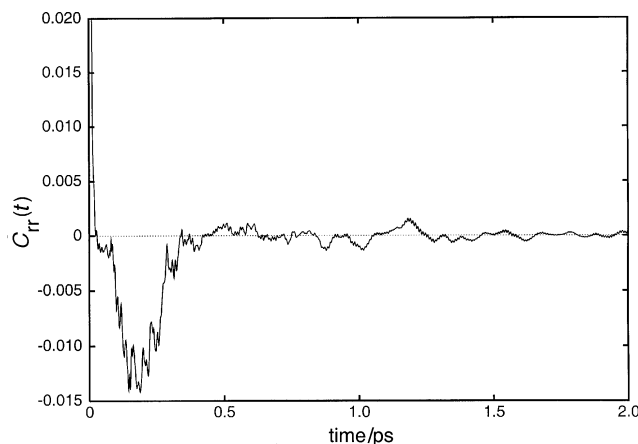
Fig. 1 shows the flux correlation function for a prototypical direct reaction,<sup>42</sup>  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ . The lower temperature (300 K) in Fig. 1(a) shows the classic behaviour for a direct reaction, but at the higher temperature ( $T = 1500$  K,  $\hbar\beta \approx 5$  fs) in Fig. 1(b) one sees a small negative region of  $C_f(t)$  at longer time; this is the manifestation of re-crossing dynamics, *i.e.*, a breakdown of the no re-crossing trajectory TST picture that Wigner noted would arise at high temperature/energy. Fig. 2 shows  $C_f(t)$  for a



**Fig. 1** Flux-flux autocorrelation function for the  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$  reaction (in 3D,  $J = 0$ ) for (a)  $T = 300 \text{ K}$  and (b)  $T = 1500 \text{ K}$



**Fig. 2** Flux-flux autocorrelation function for the  $\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$  reaction, for  $T = 300 \text{ K}$



**Fig. 3** Flux-flux autocorrelation functions for the  $\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$  reaction at  $T = 1200$  K

heavy + light-heavy reaction,<sup>44</sup>  $\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$ , for which it is well known that re-crossing dynamics is common.

Fig. 3 shows  $C_f(t)$  for the reaction<sup>45b</sup>  $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ , which involves the formation and decay of a long lived collision complex. The peak in  $C_f(t)$  at  $t = 0$  is barely discernible in the figure since  $\hbar\beta \approx 7$  fs = 0.007 ps at  $T = 1200$  K, and the negative lobe of re-crossing flux extends to *ca.* 0.5 ps. The area under the negative lobe is about 70% of that under the positive peak, so that the transmission coefficient in TST language is *ca.* 0.3. This example illustrates the fact that complex-forming reactions are more difficult to treat without approximation, since one must follow the quantum dynamics for long enough time for the quantum wavepackets to ‘decide’ whether they will be products or reactants (analogous to the situation in a classical trajectory calculation). Other aspects of these examples, and others, are discussed more fully elsewhere.<sup>21</sup>

Even with this very brief discussion of the nature of flux correlation functions and their applications, one sees how vestiges of TST emerge in these rigorous calculations. This is also evident in the algorithmic details of the methodology.<sup>38</sup> Thus the TST picture survives as an important tool for understanding the qualitative behaviour of flux correlation functions even when they are computed by rigorous quantum simulation methods.

## IV Semiclassical approximations for complex systems

### a The semiclassical initial value representation

The rigorous quantum approaches summarized in the previous section are at present only feasible, without introducing approximations, for small molecular systems. For more complex systems most approximations involve dividing the overall molecular system into two parts and treating the (small) most relevant part rigorously and the remainder approximately, as discussed in the Introduction. Here I describe another approach, one which treats all degrees of freedom equivalently; it is based on using the semiclassical (SC) initial value representation (IVR)<sup>26–30</sup> to evaluate the quantum rate expressions of the previous section. The SC-IVR is a classical trajectory-based theory that had its origins in the early 1970s but which has recently had a re-birth of interest as a way of building quantum interference and tunneling effects into classical molecular dynamics (MD) simulations. The primary difference in the recent IVR approaches from the original version is that they are now implemented in the cartesian coordinate (or

coherent state) representation, rather than in action-angle variables, and this is more general, better behaved numerically, and also more accurate.

The coordinate space IVR for the time evolution operator involves a phase space average over initial conditions for classical trajectories:

$$e^{-i\hat{H}t/\hbar} = \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{q}_t\rangle \langle \mathbf{q}_0| \quad (21a)$$

where  $\mathbf{q}_t \equiv \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$  is the coordinate at time  $t$  that evolves from these initial conditions, and  $S_t$  is the classical action integral (the time integral of the Lagrangian) along the trajectory. The pre-exponential factor involves the Jacobian relating the coordinates at time  $t$  to the initial momenta,

$$C_t(\mathbf{p}_0, \mathbf{q}_0) = \left[ \frac{\partial \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)}{\partial \mathbf{p}_0} \right] / (2\pi i \hbar)^F \Big]^{1/2} \quad (21b)$$

The states  $\{|\mathbf{q}\rangle\}$  in eqn. (21a) are the usual Dirac coordinate eigenstates. The momentum space IVR is similar to eqn. (21) but different. Herman and Kluk (HK)<sup>29</sup> introduced a hybrid IVR that effectively interpolates between the coordinate and momentum versions using coherent states (minimum uncertainty wavepackets). The HK expression for the propagator is the same as eqn. (21a) with the Dirac states replaced by coherent states,

$$\begin{aligned} |\mathbf{q}_0\rangle &\rightarrow |\mathbf{p}_0, \mathbf{q}_0\rangle \\ |\mathbf{q}_t\rangle &\rightarrow |\mathbf{p}_t, \mathbf{q}_t\rangle \end{aligned} \quad (22a)$$

whose coordinate space wavefunction is

$$\langle \mathbf{q}' | \mathbf{p}, \mathbf{q} \rangle = \left( \frac{\gamma}{\pi} \right)^{F/4} \exp \left[ -\frac{\gamma}{2} |\mathbf{q}' - \mathbf{q}|^2 + i\mathbf{p} \cdot (\mathbf{q}' - \mathbf{q})/\hbar \right] \quad (22b)$$

and with a modified pre-exponential factor

$$C_t^{\text{HK}}(\mathbf{p}_0, \mathbf{q}_0) = (2\pi\hbar)^{-F} \left[ \det \frac{1}{2} \left( \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} + \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} + \frac{i}{\hbar\gamma} \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0} + \frac{\hbar\gamma}{i} \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \right]^{1/2} \quad (22c)$$

If the coherent state parameter  $\gamma \rightarrow \infty$ , the coordinate space IVR, eqn. (21), is recovered, and  $\gamma \rightarrow 0$  gives the momentum space IVR.

Since eqn. (21) and (22) provide a way to evaluate the time evolution operator, an SC approximation can be immediately written down for any formal quantum expression involving it. A number of applications<sup>27-30,47-51</sup> have shown the SC-IVR to be capable of providing an accurate description of quantum effects in a variety of molecular phenomena. Our present interest is to use it to obtain an SC approximation for the correlation function  $C_{\text{fs}}(t)$  of eqn. (2)–(4); with the SC-IVR of eqn. (21) for the propagators this becomes

$$\begin{aligned} C_{\text{fs}}(t) &= Q_r(T)^{-1} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \int d\mathbf{p}'_0 h[s(\mathbf{q}_0)] \langle \mathbf{q}_t | \hat{F}(\beta) | \mathbf{q}'_t \rangle C_t(\mathbf{p}_0, \mathbf{q}_0) C_t(\mathbf{p}'_0, \mathbf{q}_0)^* \\ &\quad \times e^{i[S_t(\mathbf{p}_0, \mathbf{q}_0) - S_t(\mathbf{p}'_0, \mathbf{q}_0)]/\hbar} \end{aligned} \quad (23)$$

where  $\mathbf{q}_t = \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$  and  $\mathbf{q}'_t = \mathbf{q}_t(\mathbf{p}'_0, \mathbf{q}_0)$ , and  $\hat{F}(\beta)$  is the Boltzmannized flux operator

$$\hat{F}(\beta) = e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2} \quad (24)$$

Here there is a double phase space average (the initial coordinates for the two trajectories are the same because  $h[s(\mathbf{q})]$  is a local operator) in contrast to the single phase space average of the classical expression, eqn. (5). More troublesome, however, is the oscillatory character of the integrand in eqn. (23) which arises from the interference

between the two trajectories and makes the phase space integrals considerably more difficult to carry out than in the classical case. Applications to date have used various filtering methods<sup>27a,52–54</sup> to dampen the oscillatory character and make Monte Carlo calculations feasible for simple systems, but a more general solution to this problem is a matter of intense research activity.

### b The linearization approximation

In lieu of carrying out the full SC-IVR evaluation in eqn. (23) we have considered a rather drastic approximation that leads to a much simplified approach and, rather surprisingly (at least to me), has been seen to give very good results for some non-trivial applications. The idea is to expand the integrand of eqn. (23) to first order in the difference between  $\mathbf{p}_0$  and  $\mathbf{p}'_0$ , which linearizes the difference in the actions,<sup>55–58</sup>

$$S_i(\mathbf{p}_0, \mathbf{q}_0) - S_i(\mathbf{p}'_0, \mathbf{q}_0) \approx \frac{\partial S_i(\bar{\mathbf{p}}_0, \mathbf{q}_0)}{\partial \bar{\mathbf{p}}_0} \cdot (\mathbf{p}_0 - \mathbf{p}'_0) \quad (25)$$

with  $\bar{\mathbf{p}}_0 = \frac{1}{2}(\mathbf{p}_0 + \mathbf{p}'_0)$ . Carrying out this approximation leads (after some manipulation) to the following very simple result<sup>59,60</sup>

$$C_{fs}(t) = Q_r(T)^{-1} \int d\mathbf{p}_0 \int d\mathbf{q}_0 F_W^\beta(\mathbf{p}_0, \mathbf{q}_0) h[s(\mathbf{q}_t)] \quad (26a)$$

where  $F_W^\beta$  is the Wigner transform<sup>61</sup> of the operator  $\hat{F}(\beta)$ ,

$$F_W^\beta(\mathbf{p}_0, \mathbf{q}_0) = (2\pi\hbar)^{-F} \int d\mathbf{q} e^{-i\mathbf{p}_0 \cdot \mathbf{q}/\hbar} \langle \mathbf{q}_0 + \mathbf{q}/2 | \hat{F}(\beta) | \mathbf{q}_0 - \mathbf{q}/2 \rangle \quad (26b)$$

Eqn. (26a) is seen to be effectively the same as the classical expression [eqn. (5)] with the Wigner transform of  $\hat{F}(\beta)$  replacing the classical Boltzmann-flux function; one thus computes classical trajectories—to see if  $h[s(\mathbf{q}_t)]$  is 1 or 0, *i.e.*, on the product or reactant side of the dividing surface at time  $t$ —simply with a modified distribution of initial conditions.

This linearized SC-IVR (LSC-IVR) has been applied<sup>59</sup> to a popular model for chemical reactions in a condensed phase environment, namely a double well potential coupled to an infinite bath of harmonic oscillators, for which the Hamiltonian is

$$H(p_s, s, \mathbf{P}, \mathbf{Q}) = \frac{p_s^2}{2m} + V_0(s) + \sum_j \frac{P_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left( Q_j - \frac{c_j s}{m_j \omega_j^2} \right)^2 \quad (27a)$$

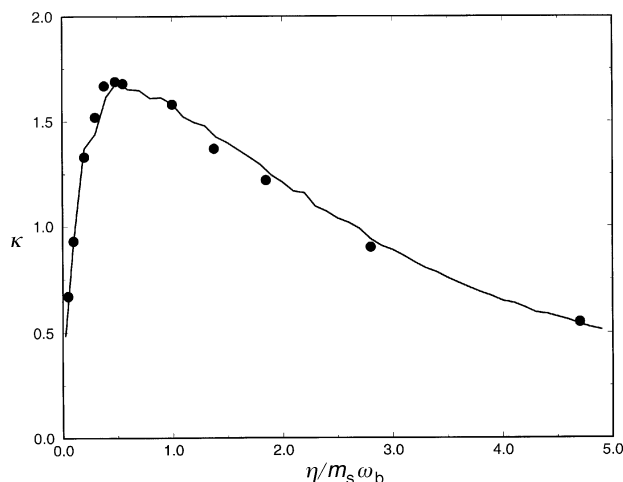
The mass  $m$  is that of an H atom, the barrier height of the double well potential  $V_0(s)$  is *ca.* 6 kcal mol<sup>-1</sup> (typical of H atom transfer reactions), and the spectral density of the harmonic bath is of the usual Ohmic form with an exponential cut-off,

$$J(\omega) \equiv \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) \quad (27b)$$

$$= \eta \omega e^{-\omega/\omega_c} \quad (27c)$$

the same model for which Topaler and Makri<sup>62</sup> have carried out (numerically exact) Feynman path integral calculations.

Fig. 4 shows the rate constant (at  $T = 300$  K) as a function of the coupling strength  $\eta$ , and one sees that the results of the LSC-IVR approximation are in essentially quantitative agreement with the accurate quantum values over the entire range. More insight into the dynamics is revealed by examining the correlation function  $C_{fs}(t)$  itself to see how the  $t \rightarrow \infty$  limit—the rate constant—is approached. Fig. 5(a) shows  $C_{fs}(t)$  for a case of strong coupling (large  $\eta$ ), and it is seen to behave just as for the direct reaction in Fig. 1 [remember that  $C_{fs}(t) = \int_0^t dt' C_f(t')$ ], reaching its ‘plateau’ value in a time of *ca.*



**Fig. 4** Rate constant for isomerization in a double well potential coupled to a harmonic bath; *cf.* eqn. (27). The quantity shown is the rate  $k(T)$  relative to the classical TST rate, *i.e.*, the transmission coefficient  $\kappa \equiv k(T)/k_{\text{CLTST}}$ , for  $T = 300$  K, as a function of the coupling strength to the bath. The solid line is the result of the linearized SC-IVR approximation described in Section IVb, and the solid points the accurate quantum path integral calculations of Topaler and Makri, *ref.* 62.

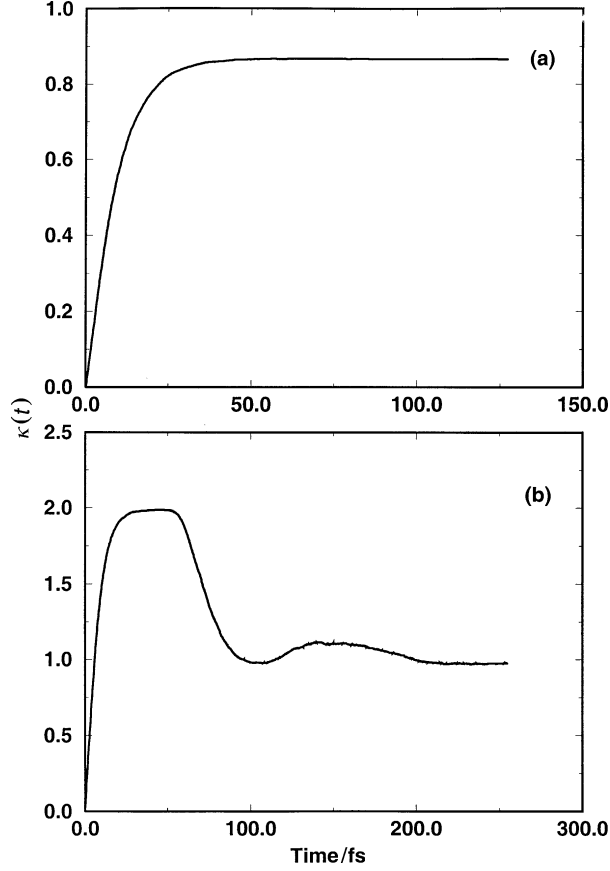
$\hbar\beta = 27$  fs; *i.e.*, this is a case of TST-like dynamics: trajectories leave the region of the dividing surface and do not re-cross it because they rapidly lose energy to the bath and are trapped in one of the potential wells. In contrast, for a weak coupling (small  $\eta$ ) case shown in Fig. 5(b),  $C_{\text{fs}}(t)$  still reaches its TST plateau value in a time of *ca.* 27 fs, but now coupling to the bath is too weak to prevent re-crossings, which cause  $C_{\text{fs}}(t)$  to decrease, then increase, *etc.*; one can identify an average of about three re-crossings before it reaches its final value (which gives the rate constant). The ‘transmission coefficient’ in this case—the ratio  $C_{\text{fs}}(\infty)/C_{\text{fs}}^{\text{TST}}$ —is seen to be about 1/2.

### c Electronically non-adiabatic dynamics

It is also possible to treat electronically non-adiabatic processes *via* the SC-IVR by using the Meyer–Miller (MM) approach<sup>63</sup> to model the electronic degrees of freedom. In the Cartesian representation this gives the following classical Hamiltonian for the nuclear ( $\mathbf{P}, \mathbf{Q}$ ) and ‘electronic’ ( $\mathbf{p}, \mathbf{x}$ ) degrees of freedom,<sup>31,32</sup>

$$H(\mathbf{P}, \mathbf{Q}, \mathbf{p}, \mathbf{x}) = \frac{\mathbf{P}^2}{2\mu} + \sum_{i=1}^N \frac{1}{2} (p_i^2 + x_i^2 - 1) H_{ii}(\mathbf{Q}) + \sum_{i < j=1}^N (p_i p_j + x_i x_j) H_{ij}(\mathbf{Q}) \quad (28)$$

where  $\{H_{ij}(\mathbf{Q})\}$  is an  $N \times N$  diabatic electronic PES provided, for example, by *ab initio* electronic structure calculations. (There is also an adiabatic electronic representation of similar form.<sup>63,31</sup>) A number of applications were made some years ago<sup>64</sup> using this Hamiltonian to carry out quasiclassical trajectory calculations (sampling initial conditions *via* action-angle variables, histogramming final action variables, *etc.*), treating electronic and nuclear degrees of freedom equivalently, but it is clear that one can ‘up-grade’ the treatment to the SC level by using the IVR. (MM also discussed the semiclassical implementation of the model.) If one up-grades the description to the quantum level—*i.e.*, takes eqn. (28) to be a Hamiltonian operator and solves the Schrödinger equation with it—then one has an exact treatment of the nuclear-electronic dynamics.



**Fig. 5** Flux-side correlation function  $C_{fs}(t)$  corresponding to the rate constants of Fig. 4. The quantity shown is  $\kappa(t) \equiv C_{fs}(t)/k_{CLTST}$ , so that the  $t \rightarrow \infty$  limit is  $\kappa$  of Fig. 4. (a) Strong coupling ( $\eta/m\omega_b = 2.8$ ), (b) weak coupling ( $\eta/m\omega_b = 0.2$ ).

Application of the SC-IVR to the MM Hamiltonian [eqn. (28)] has been made<sup>31</sup> to the suite of two-state one (nuclear) dimensional scattering problems used by Tully<sup>65</sup> for testing surface-hopping approximations for non-adiabatic dynamics, and yielded very good agreement with the correct quantum results for these examples. Stock and Thoss<sup>32</sup> also applied it to the two-state problem coupled to a harmonic oscillator, also with excellent results. Perhaps more impressive is recent work<sup>66</sup> applying the linearized (LSC-IVR) version of the SC-IVR (described in Section IVb above) to the popular spin-boson problem.<sup>67</sup> This is a two-electronic state model often used to describe radiationless transitions, electron transfer, *etc.*, in large polyatomic molecules or to model the effect of condensed phase environments. The two diabatic PESs are infinite dimensional harmonic oscillators with shifted equilibrium positions, and the off-diagonal PES is constant; eqn. (28) becomes

$$\begin{aligned}
 H(\mathbf{P}, \mathbf{Q}, \mathbf{p}, \mathbf{x}) = & \sum_j \left( \frac{P_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 Q_j^2 \right) + \frac{1}{2} (p_1^2 + x_1^2 - p_2^2 - x_2^2) \sum_j c_j Q_j \\
 & + \Delta(p_1 p_2 + x_1 x_2)
 \end{aligned} \tag{29}$$

where  $\Delta \equiv H_{12}(\mathbf{Q})$  is constant. The spectral density of the harmonic bath is the same as in eqn. (27) above.

Fig. 6 shows the population relaxation from electronic state 1 [with the bath initially in a Boltzmann distribution on PES  $H_{11}(\mathbf{Q})$ ] as a function of time,

$$D(t) \equiv \bar{P}_{1 \leftarrow 1}(T) - \bar{P}_{2 \leftarrow 1}(T) = Q_1(T)^{-1} \text{tr} [e^{-\beta \hat{H}_{11}} |1\rangle\langle 1| e^{i\hat{H}t/\hbar} \hat{\sigma}_z e^{-i\hat{H}t/\hbar}] \quad (30a)$$

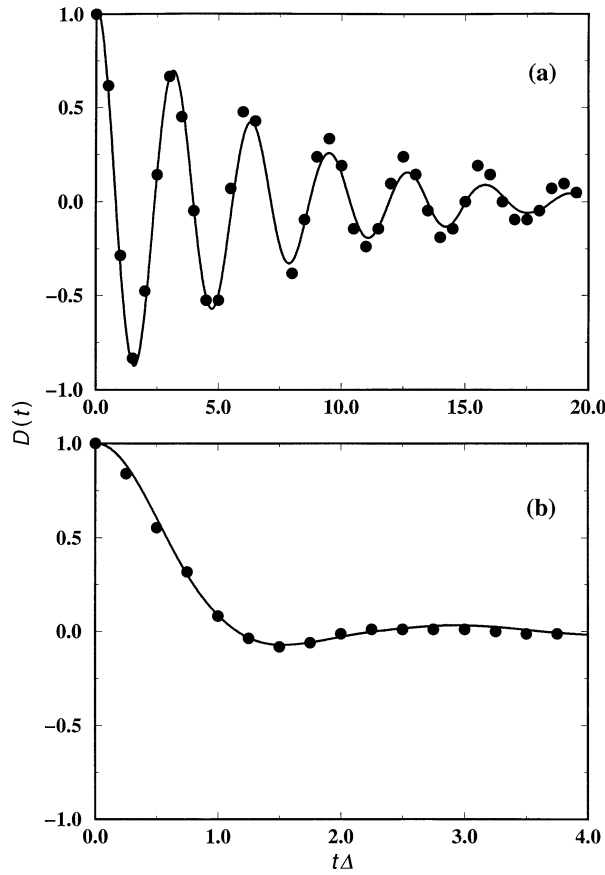
where

$$Q_1(T) = \text{tr} [|1\rangle\langle 1| e^{-\beta \hat{H}_{11}}] \quad (30b)$$

and

$$\hat{\sigma}_z = |1\rangle\langle 1| - |2\rangle\langle 2| \quad (30c)$$

One sees excellent agreement with (numerically exact) Feynmann path integral calculations by Makarov and Makri<sup>68</sup> for both large electronic coupling [Fig. 6(a)], which



**Fig. 6** Electronic population decay [ $D(t)$  of eqn. (30)] for the two-state system coupled to a harmonic bath (spin-boson system); *cf.* eqn. (29) of Section IVc. The solid line is the result of the linearized SC-IVR approximation, and the points the path integral calculations by Makarov and Makri, ref. 68. (a) Large electronic coupling,  $\beta\Delta = 5$ , leading to oscillatory behaviour, (b) small electronic coupling,  $\beta\Delta = 0.1$ , leading to monotonic decay.

leads to oscillatory (coherent) structure in the decay, and also weak coupling [Fig. 6(b)] that has little coherent structure. Fig. 7 shows the spin–spin correlation function (which is closely related to the ‘side–side’ correlation function<sup>34</sup> for a continuous potential),

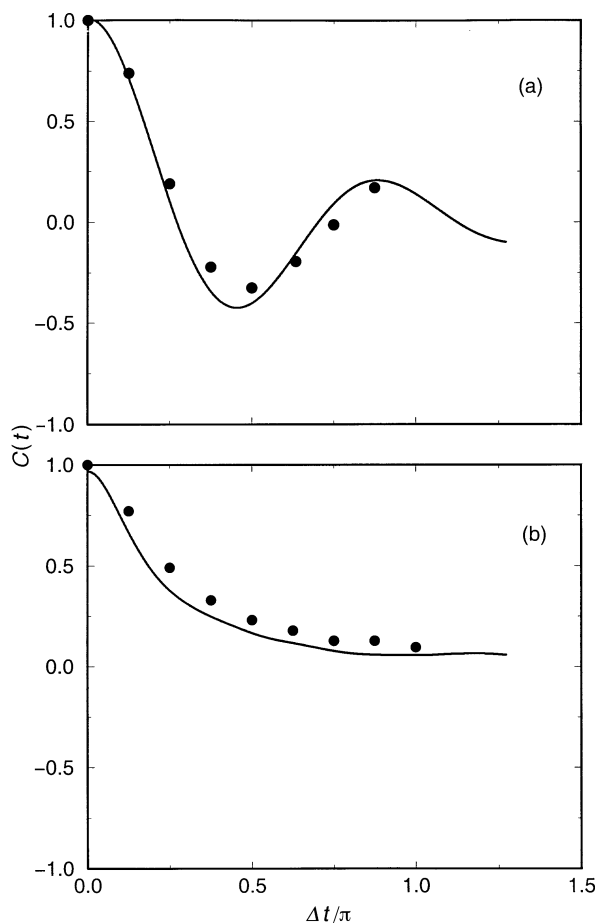
$$C(t) = Q(T)^{-1} \text{tr} [e^{-\beta\hat{H}} \hat{\sigma}_z e^{i\hat{H}t/\hbar} \hat{\sigma}_z e^{-i\hat{H}t/\hbar}] \quad (31a)$$

where here  $Q(T)$  is the total partition function

$$C(t) = \text{tr} [e^{-\beta\hat{H}}] \quad (31b)$$

Again there is excellent agreement with Feynmann path integral calculations (here by Mak and Chandler<sup>69</sup>) for both the coherent and incoherent regimes.

The simple linearized version of the SC-IVR thus captures essentially all of the dynamical features in the ‘condensed phase’ processes here and in Section IVb above. This is surprising, since the real time dynamics in this approximation is essentially that of classical mechanics, the only true quantum aspects of it being the Wigner transform of the Boltzmannized flux operator. This produces the correct quantum dynamics



**Fig. 7** Spin correlation function,  $C(t)$  of eqn. (31), for the spin-boson system of Section IVc. The solid line is the result of the linearized SC-IVR approximation, and the points the path integral calculations by Mak and Chandler, ref. 69. (a) Weak coupling to the bath (the coherent regime), (b) strong coupling to the bath (the incoherent regime).

(within the SC-IVR description) for times of order  $\hbar\beta$ —which is sufficient to describe quantum effects in TST-like dynamics—but the longer time dynamics is basically that of classical mechanics. Other applications<sup>59b</sup> have indeed shown this, namely that the longer time dynamics given by the LSC-IVR, even the coherent features seen in Fig. 5–7, are identical to that of classical mechanics. A full SC-IVR treatment,<sup>59b</sup> without the linearization approximation, is able to describe true quantum effects in the longer time dynamics, but these calculations are considerably more different.

#### d Forward–backward IVR

Though the above results using the linearized approximation to the SC-IVR are very impressive and encouraging, one would like to be able to implement the SC-IVR without having to make this approximation. Otherwise one will never know whether quantum effects are important for  $t \gg \hbar\beta$  or not. Therefore I conclude this section with a suggestion for how to simplify the SC-IVR calculation of time correlation functions,

$$C_{AB}(t) = \text{tr} [\hat{A} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}] \quad (32)$$

which are typically the objects of interest in a complex dynamical system. As noted above, since there are two time evolution operators involved in eqn. (32), straightforward use of the SC-IVR [eqn. (31) or (32)] for each propagator leads to a double phase space integral, which is not only twice the dimensionality of the corresponding classical expression but also has an oscillatory integrand because of the interference between the two trajectories. The basic idea for simplifying matters is to combine the two time evolution operators into one IVR.<sup>70,71</sup>

To do this, suppose first that operator  $\hat{B}$  in eqn. (32) is a multiplicative operator of the form

$$\hat{B} = e^{i\phi(\mathbf{q})/\hbar} \quad (33)$$

where  $\phi(\mathbf{q})$  is a sufficiently smooth function of  $\mathbf{q}$ . The operator  $\hat{U}$ ,

$$\hat{U} \equiv e^{i\hat{H}t/\hbar} e^{i\phi(\mathbf{q})/\hbar} e^{-i\hat{H}t/\hbar} \quad (34a)$$

is unitary and can be thought of as the time evolution operator for a time increment  $0 \rightarrow t$  and then  $t \rightarrow 0$  with the time-dependent Hamiltonian

$$\hat{H}(t') = \hat{H} - \delta(t' - t)\phi(\mathbf{q}) \quad (34b)$$

Since the general SC expression for a time evolution operator has the same form also for a time-dependent potential energy function, the SC-IVR for operator  $\hat{U}$  is given by eqn. (21) or (22) above, with the trajectories (and action integral) computed from the Hamiltonian of eqn. (34b). It is not hard to show that these trajectories are as follows: starting with initial condition  $(\mathbf{p}_0, \mathbf{q}_0)$  at time 0, one integrates to time  $t$  with the molecular Hamiltonian  $H(\mathbf{p}, \mathbf{q})$ , yielding coordinates and momenta  $(\mathbf{p}_t, \mathbf{q}_t)$ ; at this point one makes the following change in the momentum,

$$\mathbf{p}_t \rightarrow \mathbf{p}_t + \left( \frac{\partial \phi(\mathbf{q})}{\partial \mathbf{q}} \right)_{\mathbf{q}=\mathbf{q}_t} \quad (34c)$$

and then integrates from time  $t$  back to 0, yielding the final values  $\mathbf{q}'_0(\mathbf{p}_0, \mathbf{q}_0)$  and  $\mathbf{p}'_0(\mathbf{p}_0, \mathbf{q}_0)$ . The action integral along this trajectory is

$$S_0(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t dt' (\mathbf{p} \cdot \dot{\mathbf{q}} - H) + \phi(\mathbf{q}_t) + \int_t^0 dt' (\mathbf{p} \cdot \dot{\mathbf{q}} - H) \quad (34d)$$

so that eqn. (21) then gives

$$\hat{U} = \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_0(\mathbf{p}_0, \mathbf{q}_0) e^{iS_0(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{q}'_0\rangle \langle \mathbf{q}_0| \quad (35a)$$

with

$$C_0(\mathbf{p}_0, \mathbf{q}_0) = \left[ \left| \frac{\partial \mathbf{q}'_0(\mathbf{p}_0, \mathbf{q}_0)}{\partial \mathbf{p}_0} \right| / (2\pi i \hbar)^F \right]^{1/2} \quad (35b)$$

The HK-IVR indicated by eqn. (22) is obtained similarly.

With the SC-IVR for operator  $\hat{U}$  [eqn. (35)], the expression for the correlation function of eqn. (32) thus becomes

$$C_{AB}(t) = \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_0(\mathbf{p}_0, \mathbf{q}_0) e^{iS_0(\mathbf{p}_0, \mathbf{q}_0)/\hbar} \langle \mathbf{q}_0 | \hat{A} | \mathbf{q}'_0 \rangle \quad (36)$$

which involves only a single phase space integral. Furthermore, since the action integral  $S_0$  [eqn. (34d)] is for a forward and backward time increment—though with a momentum jump [eqn. (34c)] in the middle—one expects the integrand to be much less oscillatory than the double phase space integral. For the same reason, the pre-exponential factor should also be better behaved (*i.e.*, closer to unity).

For the flux-side correlation function  $C_{fs}(t)$  of interest, however, the operator  $\hat{B}$  in eqn. (32) is not of the form of eqn. (33), but rather corresponds to  $\hat{B} = h[s(\mathbf{q})]$ . By using the Fourier transform of the Heaviside function, though, it can be written as a one-dimensional integral over operators of this form,

$$h[s(\mathbf{q})] = \int_{-\infty}^{\infty} dp_s [2\pi i(p_s - i\varepsilon)]^{-1} e^{ip_s s(\mathbf{q})/\hbar} \quad (37)$$

where  $\varepsilon$  is a small positive constant. (In practice one can set  $\varepsilon \equiv 0$  since other factors in the integrand are zero when  $p_s = 0$ .) Thus the forward-backward SC-IVR for  $C_{fs}(t)$  is given by

$$C_{fs}(t) = Q_r(T)^{-1} \int_{-\infty}^{\infty} dp_s (2\pi i p_s)^{-1} \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_0(\mathbf{p}_0, \mathbf{q}_0) e^{iS_0(\mathbf{p}_0, \mathbf{q}_0)/\hbar} \langle \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{q}'_0 \rangle \quad (38a)$$

where the ‘momentum jump’ of eqn. (34c) at time  $t$  is

$$\mathbf{p}_t \rightarrow \mathbf{p}_t + p_s \left( \frac{\partial s(\mathbf{q})}{\partial \mathbf{q}} \right)_{\mathbf{q}=\mathbf{q}_t} \quad (38b)$$

and the action  $S_0$  is

$$S_0(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t dt' (\mathbf{p} \cdot \dot{\mathbf{q}} - H) + p_s s(\mathbf{q}_t) + \int_t^0 dt' (\mathbf{p} \cdot \dot{\mathbf{q}} - H) \quad (38c)$$

Eqn. (38) expresses  $C_{fs}(t)$  as a single phase space integral over initial conditions plus a one-dimensional integral (over the ‘momentum jump’  $p_s$ ), and the oscillatory character of the integrand is expected to be much less than for the double phase space integral. This is therefore only slightly more involved than the corresponding classical expression and probably about as simple and efficient as one can hope for. Preliminary applications indicate that these optimistic features are indeed borne out.<sup>71</sup>

Finally, one can use this forward-backward idea also to simplify applications other than time correlation functions. The SC eigenvalues for a molecular system, for example,

are typically determined by computing a matrix element of the microcanonical density operator with respect to some reference wavefunction  $|\chi\rangle$ ,

$$I(E) \equiv \langle \chi | \delta(E - H) | \chi \rangle = \sum_k |\langle \chi | \psi_k \rangle|^2 \delta(E - E_k) \quad (39a)$$

where  $\{|\psi_k\rangle\}$  and  $\{E_k\}$  are the eigenfunctions and eigenvalues. Using the Fourier representation of the delta function gives the following expression for  $I(E)$ ,

$$I(E) = \frac{\text{Re}}{\pi\hbar} \int_0^\infty dt e^{iEt/\hbar} \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle \quad (39b)$$

and the SC-IVR is used for the matrix element of the propagator,

$$\langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle = \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} \chi(\mathbf{q}_t)^* \chi(\mathbf{q}_0) \quad (39c)$$

(or the HK version). This expression involves only one time evolution operator, and thus only a single phase space integral, but it can nevertheless be difficult to evaluate because of the oscillatory character of the integrand. This can be reduced by taking  $|\chi\rangle$  to be the eigenfunction of some reference Hamiltonian  $\hat{H}_0$  that approximates  $\hat{H}$  as closely as possible. Then, since  $\hat{H}_0 |\chi\rangle = E_0 |\chi\rangle$ , one has

$$|\chi\rangle = e^{-iE_0 t/\hbar} e^{i\hat{H}_0 t/\hbar} |\chi\rangle \quad (40)$$

so that eqn. (39b) can be written as

$$I(E) = \frac{\text{Re}}{\pi\hbar} \int_0^\infty dt e^{i(E - E_0)t/\hbar} \langle \chi | e^{i\hat{H}_0 t/\hbar} e^{-i\hat{H}t/\hbar} | \chi \rangle \quad (41a)$$

One now applies the SC-IVR to the operator  $\hat{U}$

$$\hat{U} \equiv e^{i\hat{H}_0 t/\hbar} e^{-i\hat{H}t/\hbar} \quad (41b)$$

which corresponds to the time evolution operator for the time increment  $0 \rightarrow t$  with Hamiltonian  $\hat{H}$ , and then  $t \rightarrow 0$  with Hamiltonian  $\hat{H}_0$ . The SC-IVR for operator  $\hat{U}$  is therefore of standard form,

$$\hat{U} = \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_0(\mathbf{p}_0, \mathbf{q}_0) e^{iS_0(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{q}'_0\rangle \langle \mathbf{q}_0| \quad (41c)$$

so that

$$\langle \chi | e^{i\hat{H}_0 t/\hbar} e^{-i\hat{H}t/\hbar} | \chi \rangle \equiv \langle \chi | \hat{U} | \chi \rangle = \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_0(\mathbf{p}_0, \mathbf{q}_0) e^{iS_0(\mathbf{p}_0, \mathbf{q}_0)/\hbar} \chi(\mathbf{q}'_0)^* \chi(\mathbf{q}_0) \quad (41d)$$

where  $(\mathbf{p}'_0, \mathbf{q}'_0)$  and the action integral  $S_0$  result from the trajectory that starts with initial conditions  $(\mathbf{p}_0, \mathbf{q}_0)$  and is integrated to time  $t$  with Hamiltonian  $H$ , and then—with  $(\mathbf{q}_t, \mathbf{p}_t)$  continuous—is integrated back to time 0 with Hamiltonian  $H_0$ . Application of eqn. (41) to the vibrational–rotational eigenvalues of  $(\text{HCl})_2$ —treated earlier<sup>72</sup> via eqn. (39)—shows that using the forward–backward IVR with a reference Hamiltonian  $H_0$  does indeed make the calculation better behaved.<sup>73</sup>

## V Concluding remarks

As has often been noted, science makes progress by each generation standing on the shoulders of its predecessors, and nothing could more accurately describe the subject of this Faraday Discussion. Transition state theory provided the essential qualitative picture for understanding thermal reaction rates, and long after more rigorous quantum

methods will have eliminated the need for the specific approximations it entails, the insight it affords will survive.

Yet, the present paradigm of chemical reaction theory is simulation, engendered by the computer revolution. One now fully appreciates that understanding and computing/simulation go hand in hand: understanding a particular process theoretically allows one to carry out calculations to model it quantitatively, and simulation of a complex process often leads to understanding in terms of simple pictures and models. The papers presented at this Discussion are an excellent example of this interaction between computing and understanding.

For the simplest chemical reactions—gas phase reactions of small molecular systems—the theoretical methodology is essentially in hand to permit rigorous quantum calculations for any quantity of interest, from the thermal rate constant to the most detailed state-specific quantity. Yet even here there is a rich variety of dynamical phenomena that continue to surprise us, it seems, with each new system that is studied. At the opposite end of the spectrum, it is not even possible to carry out classical simulations for the most complex biomolecular processes, and in between there are many complex processes that can be treated classically but for which quantum effects are significant and must be included approximately. This range from the simple to the complex is well represented at this Discussion. It is also interesting to see the extent to which the rigorous methodology presently applicable to simple systems is working its way upwards to address more complex reactions. It would be interesting, though unlikely at least for me, to be present at a Faraday Discussion on this topic sixty years hence to see what directions it had taken—and whether (or not) the participants would be musing over any of the comments during this Discussion.

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