DISCUSSIONS

Fundamentals: general discussion

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Timothy J. H. Hele, Hannes Jónsson, Johannes Kästner, Nancy Makri,
David E. Manolopoulos, Laura K. McKemmish, Georg Menzl,
Thomas F. Miller III, William H. Miller, Eli Pollak, Sergio Rampino,
Jeremy O. Richardson, Martin Richter, Priyadarshi Roy Chowdhury,
Dmitry Shalashilin, Jonathan Tennyson and Ralph Welsch

Laura McKemmish opened discussion of the introductory lecture by William Miller: Can you please elaborate on the relationship between the classical and quantum Hamiltonian, and between the classical and quantum methods of solving Hamiltonians.

William Miller responded: The quantum Hamiltonian (operator), where the coordinates and momentum variables are the usual quantum coordinate and momentum operators, is exact; *i.e.*, if it were used in the Schrödinger equation it would generate the exact quantum dynamics. The classical Meyer–Miller (MM) Hamiltonian is this same quantity with the coordinate and momentum operators now classical coordinate and momentum variables, whose time evolution is determined by integrating Hamilton's equations (that are generated from the classical Hamiltonian in the usual way).

Jeremy Richardson asked: Your results for the time dependence of the electronic states are excellent. However, can such good information be obtained about the nuclear dynamics using your method? In particular there might be difficulties associated with inverted potentials, caused when the state population becomes less than 0. Will this cause problems when you apply the method to more realistic systems?

William Miller answered: In the published version of my introductory lecture (DOI: 10.1039/c6fd00181e) the issue you mention is discussed, *i.e.*, when some of the nuclear potential energy surfaces (PESs) have very harsh repulsive walls (an infinitely hard wall would be the most dramatic case) and the state populations become less than 0. We saw this in earlier work[1] when the MM Hamiltonian was implemented semiclassically (using the initial value representation). Here some classical trajectories diverged ('ran away') because of the situation you describe, but in that case this was ~10% or fewer of them, so they were simply discarded

from the Monte Carlo sample, thus causing minimal problems. For a recent model problem (two coupled Morse potentials) treated by Subotnik *et al.*,[2] however, almost all the trajectories have this divergent behavior, so something else must be done. One very primitive way that we have tried (unpublished) is simply to cut off the nuclear potentials when they exceed some cutoff value, V_{cut}, that is well above any energy that is relevant for the process of interest; *i.e.*, the nuclear potentials $V(R)$ are modified by

$$V(R) \Rightarrow V(R) \times h[V_{cut} - V(R)] + V_{cut} \times h[V(R) - V_{cut}], \qquad (1)$$

where $h[x]$ is the usual Heaviside function (= 1 for $x > 0$, and = 0 for $x < 0$).

1 E. A. Coronado, J. Xing and W. H. Miller, *Chem. Phys. Lett.*, 2001, **349**, 521.
2 N. Bellonzi, A. Jain and J. E. Subotnik, *J. Chem. Phys.*, 2016, **144**, 154110.

Thomas Miller remarked: You showed results for classical nuclei. Can you comment on the prospects for including nuclear quantum effects within this framework?

William Miller replied: The SQC/MM model we have been developing is a direct extension of classical molecular dynamics (MD) that incorporates the electronic degrees of freedom (DOF) classically. As such, therefore, it makes no contribution toward including nuclear quantum effects, taking them to be classical in exactly the same way as classical MD approaches (even for a single electronic state). As we have discussed privately, though, it may be possible to implement the ring-polymer molecular dynamics (RPMD) approaches, that you and others have been developing, with the Meyer–Miller vibronic Hamiltonian and thus include nuclear and electronic quantum effects (*e.g.*, zero point energy in the latter) *via* the RPMD model.

David Manolopoulos asked: The results you have obtained with the triangular window functions are very impressive. You fleetingly showed some results for a 3 electronic state problem using these windows. For 2 electronic states, the windows are triangles in (n_1, n_2) space. What are they for 3 electronic states? Polyhedra in (n_1, n_2, n_3) space? Is there a general prescription for N electronic states?

William Miller responded: The 3-state example with the new triangle window functions is the first version that Steve Cotton has come up with for more than two states, and the N-state generalization is something he is pursuing. (I have a hard time visualizing this beyond two dimensions, but he is very good at it!) So you are right, it is the next step we need to take.

Dmitry Shalashilin asked: You have shown beautiful results when your approach agrees with the spin–boson model benchmark. Are there cases of spin–boson which are not reproduced so well? This may help to understand better how the technique works and its limitations.

William Miller replied: We have applied the SQC/MM approach to a variety of spin–boson-like models, especially when there have been benchmark quantum

results available for comparison. In all cases thus treated we have found excellent results for the electronic transitions probabilities, and also in the few cases we have treated for obtaining the off-diagonal elements of the electronic density matrix. The model is so simple, however, that there will surely be cases for which the present version of it will fail to give good results, and then the challenge will be to see if we can find a variation on the approach to cover such cases. The case of very weak transitions that I discussed in the introductory lecture is one example of this, where use of our standard square histogram window functions did not work well, but the new triangle windows worked extremely well, and also even better for moderate and strong coupling than our previous 'standard' square histogram windows.

Ralph Welsch asked: Can you transfer what you have learned about windowing in the mapping scheme back to the initialization and analysis of vibrational and rotational modes in the study of reactive scattering using quasi-classical trajectories?

William Miller replied: I think that use of 'symmetrical' quasi-classical (SQC) window functions would be an improvement on the standard quasi-classical trajectory (QCT) model, but we have not explored this except in the first paper[1] with Steve Cotton on the collinear $H + H_2$ reaction, a 'proof of principle' of the SQC approach, which did indeed give much better results than the old QCT approach.

1 S. J. Cotton and W. H. Miller, *J. Phys. Chem. A*, 2013, **117**, 7190.

Timothy Hele enquired: Which distribution (if any) does the symmetrical quasi-classical model with mapping variables conserve? Put another way, if one were to calculate a quantum thermal time-correlation function one would expect a time-evolved expectation value such as $\langle x(t) \rangle$ to fluctuate because the classical dynamics of the method would not generally be expected to conserve the quantum Boltzmann distribution. However, would there be a different distribution that would be conserved, such as one based on the classical-like Hamiltonian used to propagate trajectories?

William Miller replied: The MM Hamiltonian is a classical Hamiltonian for all degrees of freedom (DOF), nuclear and electronic, and the dynamics for all the DOF are determined by integrating Hamilton's equations. The dynamics will thus preserve the classical Boltzmann distribution, which is what is relevant classically.

Priyadarshi Roy Chowdhury communicated: What are the challenges faced during simulations of semi-classical molecular systems?

William Miller communicated in reply: The greatest challenge for treating 'real' molecular systems is obtaining sufficiently accurate potential energy surfaces and their couplings (either diabatic or adiabatic).

Priyadarshi Roy Chowdhury communicated: What boundary conditions did you set during the simulations of semi-classical molecular systems?

William Miller communicated in reply: The boundary conditions for the nuclear degrees of freedom (DOF) are whatever are appropriate to the process being simulated; this is often a Boltzmann distribution on the initial electronic potential surface, but this need not be the case. The initial conditions for the electronic DOF are those determined by the 'window function' for the initial electronic state, and the probabilities to all possible final electronic states at time t are determined by how many trajectories have their action variables in the various 'windows' at time t.

Priyadarshi Roy Chowdhury communicated: In the event of the ground state possessing some amount of zero point energy, what would be the trend in variation of the trajectories, during the transformation of the vibrational modes from ground state to excited state?

William Miller communicated in reply: It would be whatever the classical mechanics of the nuclear–electronic trajectory gives; *e.g.*, if the ground and excited electronic states have a significantly different equilibrium position in a particular nuclear (vibrational) mode, then one would have significant vibrational excitation of this mode accompanying the electronic transition. This would be described by a Franck–Condon factor quantum mechanically, it is also described by the classical mechanics.

Priyadarshi Roy Chowdhury communicated: What would be the benefits of considering smaller windows for performing Gaussian distributions, mentioned in your work?

William Miller communicated in reply: We have experimented with using Gaussian window functions and find that they, and histogram windows, give essentially equivalent results if their widths are comparable. Histogram windows, however, are more consistent with incorporating the zero point energy constraint (in the 'electronic oscillators'), and so we have used them in all application of the SQC/MM approach. We have experimented with various widths of the window functions, but taking them too narrow gives very poor results. The 'Goldilocks' value of the gamma parameter, 0.366, has given excellent results for a number of applications, though the more recent 'triangle windows' have performed even better.

David Clary opened discussion of the paper by Jonathan Tennyson: There have been a large number of quantum scattering calculations published over the years on realistic reactions in 3D.[1] There is a problem of coordinates, and having coordinates that go smoothly from reactants to products is crucial. I do not think the coordinate problem has been referred to in any detail in your paper. One coordinate system used for three and four atom reactions is hyperspherical coordinates (see ref. 2–4 as examples). This set of coordinates has been used successfully for calculating reactive probabilities and resonances very accurately using either the R-matrix propagator or log derivative methods. I am not sure what advantages the method you describe will have over these existing and well-established methods if applied to real chemical reactions in many dimensions.

1 S. C. Althorpe and D. C. Clary, *Annu. Rev. Phys. Chem.*, 2003, **54**, 493–529.
2 D. Skouteris, J. F. Castillo and D. E. Manolopoulos, *Comput. Phys. Commun.*, 2000, **133**, 128–135.
3 D. C. Clary, *J. Chem. Phys.*, 1991, **95**, 7298–7310.
4 B. Kerkeni and D. C. Clary, *J. Chem. Phys.*, 2004, **120**, 2308–2318.

Jonathan Tennyson answered: The use of hyperspherical coordinates is explicitly discussed in the paper. Procedures based on the hyperspherical-coordinate theories of Pack and Parker,[1] and Launay and Le Dourneuf[2] are currently being used to consider low-energy collisions, see for example Honvault *et al.*,[3] and Pradhan *et al.*[4] Ultra-low energy collisions introduce features not present in the higher temperature studies quoted in the question. These include the need to consider weak interactions out to very large distances, the need to characterise very complicated resonance structures as function of energy, the need to consider effects usually considered too small to be important such as hyperfine and spin–orbit effects and possibility of studying chemical reactions with something approaching spectroscopic accuracy. Treatment of magnetic field effects in these collisions would also be highly desirable, especially given the prominent use of magnetic fields to control Feshbach resonances in current experiments.[5] All of these raise specific issues which require development of methods beyond those quoted.

Hyperspherical approaches have proved successful but are not without their problems. For example they make an adiabatic separation between the angular and the one radial coordinate which is motivated by computational convenience rather than physics; this separation is likely to ultimately limit the accuracy of these methods. Hyperspherical coordinates are efficient in the reaction region but are increasingly inefficient asymptotically: this means either that they cannot be used to treat ultra-low energy collisions as lower energy collisions are sensitive to a much larger region of the potential energy surface or they require a transformation to a more judicious choice of coordinates for treating the asymptotic problem. Very recently some progress has been made on extending the hyperspherical treatments to very large interaction regions for $D^+ + H_2$ by Lara *et al.*[6] who found that it was necessary to distances of about 10^5 a_0. The other issues remain to be addressed in the hyperspherical methodologies. The inefficiency of hyperspherical coordinate treatments remains a stumbling block to further extension of methods based on them.

The R-matrix procedure we are developing provides a natural solution to many of these issues and one which, in principle, can be extended to systems of arbitrary size and coordinate system. The methodology is being designed not to make an *a priori* choice of coordinates so could in practice be used with hyperspherical coordinates. However our own experience of bound states calculation on the H_3^+ system has shown that hyperspherical treatments of the nuclear motion problem are computationally very much less efficient than other coordinate choices, notably Jacobi coordinates.[7,8]

The use of the R-matrix method allows the choice of appropriate coordinate systems for each of (a) the inner or reaction region, (b) the asymptotic region defined by the reactants and (c) the asymptotic region defined by the products. This is done without the need to include interaction terms between different coordinates by making the coordinate changes on the R-matrix boundary. To do this it is necessary to project the wavefunctions computed in the inner-region

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coordinate system to produce amplitudes in the reactant/product coordinates. Projections of this fashion (from hyperspherical to more physical coordinates) have already been successfully employed in studies of very low-energy collisions.[4] We believe that the inherent flexibility and increased physical content of our RmatReact approach will prove to be much more powerful than the current hyperspherical procedures. In addition implementation of weak effects, such as hyperfine coupling, in the outer region where they are most important should be straightforward.

1 R. T. Pack and G. A. Parker, *J. Chem. Phys.*, 1987, **87**, 3888–3921.
2 J. M. Launay and M. Le Dourneuf, *Chem. Phys. Lett.*, 1989, **163**, 178–188.
3 P. Honvault, M. Jorfi, T. González-Lezana, A. Faure and L. Pagani, *Phys. Rev. Lett.*, 2011, **107**, 023201.
4 G. B. Pradhan, N. Balakrishnan and B. K. Kendrick, *J. Phys. B: At., Mol. Opt. Phys.*, 2014, **47**, 135202.
5 T. Köhler, K. Góral and P. S. Julienne, *Rev. Mod. Phys.*, 2006, **78**, 1311.
6 M. Lara, P. G. Jambrina, F. J. Aoiz and J.-M. Launay, *J. Chem. Phys.*, 2015, **143**, 204305.
7 L. G. Diniz, J. R. Mohallem, A. Alijah, M. Pavanello, L. Adamowicz, O. L. Polyansky and J. Tennyson, *Phys. Rev. A*, 2013, **88**, 032506.
8 I. I. Mizus, A. Alijah, N. F. Zobov, A. A. Kyuberis, S. N. Yurchenko, J. Tennyson and O. L. Polyansky, ExoMol Molecular linelists – XXI. A comprehensive line list for H_3^+, *Mon. Not. R. Astron. Soc.*, 2017.

Stuart Althorpe asked: How critically does the efficiency of the calculation depend on the R-matrix boundary position, and are you able to give rules of thumb for estimating where the optimal boundary should be located?

João Brandão also enquired: Just a practical question; how far is the transition between the inner and outer regions? This seems to be very large for Ar_2, ~15 Å as shown in Fig. 2 of your paper.

Jonathan Tennyson replied: In response to both of these questions, the placement of the R-matrix boundary should, in theory, have no effect on the final results of the computation. This is something that, of course, can be tested by performing calculations with different boundaries. The choice is therefore dictated by a combination of physics and computational efficiency.

With that in mind, an ideal placement for the boundary would be sufficiently far out that the majority (perhaps >90%) of the well depth is captured by the inner region, and most of the bound states have zero amplitude on the boundary. This means that the (sometimes quite costly) calculation of these strongly bound states can be neglected since they make no contribution to the R-matrix constructed on the boundary. In general the R-matrix should be placed close in as this will avoid needlessly using large basis sets to represent the (discretised) continuum and hence increasing the computation time for the inner-region diagonalisation without an equivalent gain in efficiency of the outer region section of the code.

At present we do not have a final answer to where the boundary should be placed but experience with complex absorbing potentials (CAPs) for H_3^+ (ref. 1) and water (ref. 2) found that stable results were obtained with CAPs that started at 13.58 a_0 and 8 a_0, respectively. Given that the inner region in an R-matrix calculation does not need to contain all the bound state wavefunctions, these values should provide upper limits to the value of the coordinate boundary. We note that for these systems, both of which support about 1000 bound vibrational states, it

proved possible to obtain converged (inner-region) wavefunctions well above the dissociation limit.

The placement of the boundary at about 15 Å, see Fig. 2 of our paper, was selected for diagnostic and testing purposes related to our implementation of the method. It was chosen to be sufficiently far out that propagation of the R-matrix would not be necessary, and the outer region could be treated as asymptotic. We have confirmed that we obtain the same results with the boundary closer in and when we propagate the outer-region R-matrix. $a = 15$ Å is further out than we would anticipate using for most practical applications of our method. For the Ar–Ar problem, placing the wall at about 6 Å, which places most of the well in the inner region, and then propagating to an asymptotic distance using a Light–Walker propagator or similar would probably be the best option. This choice should give very accurate results and minimise computation time.

1 B. C. Silva, P. Barletta, J. J. Munro and J. Tennyson, *J. Chem. Phys.*, 2008, **128**, 244312.
2 N. F. Zobov, S. V. Shirin, L. Lodi, B. C. Silva, J. Tennyson, A. G. Császár and O. L. Polyansky, *Chem. Phys. Lett.*, 2011, **507**, 48–51.

David Manolopoulos commented: You mentioned a technical problem in which all of your wavefunctions had zero derivatives on the R-matrix boundary. To fix this, as you know, one has to combine a Bloch boundary value operator with a basis that is complete on the R-matrix boundary. The neatest way I know of to do this is to use a basis of Lobatto shape functions,[1] as Bob Wyatt and I did many years ago in the context of the log derivative Kohn method.[2] Perhaps this basis would be useful for your problem too.

1 D. E. Manolopoulos, Lobatto shape functions, in *Numerical Grid Methods and their Application to Schrödinger's Equation*, ed. C. Cerjan, Kluwer, Dordrecht, 1993.
2 D. E. Manolopoulos and R. E. Wyatt, Quantum scattering *via* the log derivative version of the Kohn variational principle, *Chem. Phys. Lett.*, 1988, **152**, 23–32.

Jonathan Tennyson replied: Thank you for this suggestion. Thus far we have tested the sinc-DVR functions used in the diatomic code DUO,[1] which do indeed seem to give zero derivatives on the boundary, as well as various model vibrational functions based on Laguerre polynomials.[2,3] We will certainly test Lobatto shape functions.

1 S. N. Yurchenko, L. Lodi, J. Tennyson and A. V. Stolyarov, *Comput. Phys. Commun.*, 2016, **202**, 262–275.
2 J. Tennyson and B. T. Sutcliffe, *J. Chem. Phys.*, 1982, **77**, 4061–4072.
3 J. Tennyson and B. T. Sutcliffe, *J. Mol. Spectrosc.*, 1983, **101**, 71–82.

Laura McKemmish asked: Given the prominence of non-adiabatic theories in today's session, can you comment on how the RmatReact method can be used to treat this problem?

Jonathan Tennyson answered: The RmatReact methodology is designed to work with any inner region variational nuclear motion package. Therefore, if the inner region package can treat the non-adiabatic problem, then the RmatReact methodology can be used to calculate the associated scattering properties of the system. The ExoMol group at University College London has recently published a general purpose diatomic code, DUO,[1] that can find the rovibronic energies and

wavefunctions from a set of input potential energy surfaces and coupling curves (including non-adiabatic effects). We are in the process of generalising this approach to higher dimensional systems (triatomics and polyatomics).

1 S. N. Yurchenko, L. Lodi, J. Tennyson and A. V. Stolyarov, *Comput. Phys. Commun.*, 2016, **202**, 262–275.

Stuart Althorpe remarked: R-matrix codes have also proved very powerful for treating electron–molecule scattering. Will it soon be computationally feasible to combine electron and heavy-particle scattering in one efficient R-matrix code, capable of treating dissociative recombination?

Jonathan Tennyson responded: This is an interesting idea. Schneider *et al.*[1] proposed a non-adiabatic implementation of R-matrix theory which used R-matrix treatments of both the nuclear and (scattering) electron coordinates. This method was used to treat dissociative recombination (DR) in HeH^+ (ref. 2) as well as electron impact vibrational excitation.[3,4] However, the method proved to be quite technically challenging to use due to the need to track coefficients of the configuration interaction (CI) calculations as a function of geometry. More recent treatments have concentrated using R-matrix curves as input to a multi-channel quantum defect theory (MQDT) treatment of DR.[5–7] However so far such MQDT treatments have only been applied to diatomics. Combining the RmatReact approach with electron impact R-matrix codes[8] to study DR of polyatomic systems could well be a good way forward.

1 B. I. Schneider, M. Le Dourneuf and P. G. Burke, *J. Phys. B: At. Mol. Phys.*, 1979, **40**, L365–369.
2 B. K. Sarpal, J. Tennyson and L. A. Morgan, *J. Phys. B: At. Mol. Opt. Phys.*, 1994, **27**, 5943–5953.
3 B. K. Sarpal, J. Tennyson and L. A. Morgan, *J. Phys. B: At. Mol. Opt. Phys.*, 1991, **24**, 1851–1866.
4 I. Rabadán and J. Tennyson, *J. Phys. B: At. Mol. Opt. Phys.*, 1999, **32**, 4753–4762.
5 I. F. Schneider, I. Rabadán, L. Carata, J. Tennyson, L. H. Andersen and A. Suzor-Weiner, *J. Phys. B: At. Mol. Opt. Phys.*, 2000, **33**, 4849–4861.
6 D. A. Little, K. Chakrabarti, I. F. Schneider and J. Tennyson, *Phys. Rev. A*, 2014, **90**, 052705.
7 J. Z. Mezei, R. D. Backodissa-Kiminou, D. E. Tudorache, V. Morel, K. Chakrabarti, O. Motapon, O. Dulieu, J. Robert, L. Tchang-Brillet, A. Bultel, X. Urbain, J. Tennyson, K. Hassouni and I. F. Schneider, *Plasma Sources Sci. Technol.*, 2015, **24**, 035005.
8 J. M. Carr, P. G. Galiatsatos, J. D. Gornkiel, A. G. Harvey, M. A. Lysaght, D. Madden, Z. Mašín, M. Plummer and J. Tennyson, *Eur. Phys. J. D*, 2012, **66**, 58.

Priyadarshi Roy Chowdhury communicated: How would the Jacobi co-ordinates $r(H_2)$, $R(H_2–D)$ and θ vary in the inner regions for DVR3D (*e.g.* H_2D^+) when the R-matrix boundary is increased beyond the limits, as mentioned in this work?

Jonathan Tennyson communicated in reply: The coordinates employed in the inner and outer regions do not need to be the same; indeed, it is our belief that it will often be better if they are not. The inner region coordinates should be chosen to allow the best representation of the inner region wavefunctions with a given size basis set. For the outer region, it is important to identify an appropriate asymptotic coordinate representation by, for example, selecting an appropriate scattering coordinate. Coordinate changes can be made at the R-matrix boundary.

Vijay Beniwal communicated: The paper describes a methodology in the form of the R-matrix method to study low temperature chemistry. However, one of the limitations of collision theory of reactions states that an increase in the number of collisions from 200–300% results in an increment of a mere 2–3% in the rate enhancements of the simple reactions. The collisions are a translational mode of energy whereas most of the energy of reactant molecules lies in the form of vibration motions. In this regard, which type of energy is more important for such reactions? Should there be simultaneous consideration of the vibration energy of reactants or must a separate study be carried out for the same?

Jonathan Tennyson communicated in reply: The RmatReact method provides a fully quantum-mechanical treatment designed for the study of highly controlled cold and ultra-cold collisions. We are working in a regime where one needs to know precisely both the initial reactant states and the collision energy. At very low energies, the colliding species will generally be in their ground states and therefore contain little or no internal energy. These internal states are fully represented by the proposed treatment. The translational energy of the reactants is present in the calculations as the energy of collisions in the reference frame of the reactants. Frame transformations to laboratory frames are possible on the R-matrix boundary; it should be possible, for example, to use these to deal with external magnetic and electric fields. The precise treatment of the vibrational (and rotational) degrees of freedom in the inner (interaction) region of the molecular system under study is a key advantage of our method.

Timothy Hele opened discussion of the paper by Jeremy Richardson: I was very interested in your paper, particularly the part discussing the relative accuracy of QTST and instanton theory. When you state "the quantum transition-state theory approximation which leads to RPTST is not exact, even in the limiting case of a high and wide barrier", should that read "the quantum transition-state theory approximation which leads to RPTST is not exact in the limiting case of a high and wide barrier", since it has been proven to be exact where there is no recrossing? Could it be that these (rather similar) theories have different regimes of applicability and are exact in different limits?

Jeremy Richardson answered: It seems that instanton theory is more accurate than QTST for describing at least certain deep-tunnelling rates as is shown by the example of a high and wide Eckart barrier where instanton is exact and QTST is not. This implies that there must be a certain amount of quantum recrossing occurring below the barrier which is neglected by QTST but obviously included by the instanton approach. This quantum recrossing cannot be described by RPMD either as it gives practically the same result as QTST for simple one-dimensional barriers.

Nonetheless the effect of this quantum recrossing is often quite small—it is the cause of the commonly observed case that RPMD underestimates low-temperature rates by about a factor of 2—and thus QTST and RPMD continue to be used for describing deep tunnelling. Their major advantages over the instanton approach are that they do not involve a steepest-descent integration in the position coordinates and will thus be more accurate when the modes become

more anharmonic. In particular, this allows RPMD to be applied to liquid systems where the instanton is not valid.

Eli Pollak addressed Timothy Hele: You stated in your question that there is THE Quantum Transition State Theory. It is not clear to me what you mean by that as there are many different versions of a quantum TST all of which are exact for parabolic barriers.

Timothy Hele responded: Quantum transition-state theory is the instantaneous thermal flux through a position-dependent dividing surface, which as stated by Eyring[1] produces the exact rate in the absence of recrossing (in Eyring's language, the transmission coefficient being unity). Strictly speaking, this does not uniquely define a QTST because there is a choice of where and how to put the dividing surface along the imaginary-time path-integral. However, if one enforces the physically sensible criterion that the rate is positive-definite at any finite temperature, there is only one known QTST, and that is ring-polymer molecular dynamics transition-state theory (RPMD-TST).[2–4]

1 H. Eyring, *Chem. Rev.*, 1935, **17**, 65.
2 T. J. H. Hele and S. C. Althorpe, *J. Chem. Phys.*, 2013, **138**, 084108.
3 S. C. Althorpe and T. J. H. Hele, *J. Chem. Phys.*, 2013, **139**, 084115.
4 T. J. H. Hele and S. C. Althorpe, *J. Chem. Phys.*, 2013, **139**, 084116.

Eli Pollak remarked: To the best of my knowledge, the first to bridge the crossover regime was in the paper of Peter Hänggi and Waldemar Hontscha.[1] They did this by expanding the energy dependent action beyond linear and this prevents the divergence at the crossover point. Their theory, as also described in the review by P. Hänggi, P. Talkner and M. Borkovec,[2] is essentially the same as proposed in the paper by Richardson.

1 P. Hänggi and W. Hontscha, Unified approach to the quantum Kramers reaction rate, *J. Chem. Phys.*, 1988, **88**, 4904.
2 P. Hänggi, P. Talkner and M. Borkovec, *Rev. Mod. Phys.*, 1990, **62**, 251.

Jeremy Richardson responded: Hänggi and Hontscha also solve the problem with the crossover regime by using the tunnelling expression for the parabolic barrier. At low temperatures, where this approximation will not hold, they recommend using the traditional instanton formulation. In my paper, the microcanonical instanton expression is used for all energies below the barrier and integrated explicitly to provide a unified formula for all temperatures. This is therefore not only able to treat the crossover regime but also to treat problems where the steepest-descent integration is no longer valid at all, such as for reactions with pre-reactive complexes as shown by Prof. Kästner.

David Glowacki enquired: There are a lot of systems where microcanonical rate coefficients are important – *e.g.*, in the atmosphere and in combustion. One thing that was unclear to me from your paper is whether you can back out transmission coefficients? I ask because in, *e.g.* atmospheric and combustion systems, the things you often want are the microcanonical rate coefficients, calculated from microcanonical transition state theory. In microcanonical transition state theory, the $k(E)$ is calculated as $W(E)/[h\rho(E)]$, where $W(E)$ is the sum of states at the

transition state at a particular energy E, and $\rho(E)$ is the density of states of the reactant. The conventional way of folding in transmission probabilities is to calculate the convolution of $W(E)$ and the transmission coefficients, and use that as the numerator instead. Bill Miller showed how to do this awhile back. For a large class of important practical problems, this is often a really useful thing to be able to do. I'm curious whether this approach and/or the quantities required would come out of what you've shown?

Jeremy Richardson replied: No, the instanton method is like a quantum-mechanical version of transition-state theory and will neglect ordinary above-the-barrier recrossing. It should be possible to combine the microcanonical instanton approach with a transmission coefficient computed from classical dynamics in the way you have described. This would have the advantage of including tunnelling effects more rigorously into the rate.

David Glowacki asked: I'm curious how the approach mapped out in your paper maps into microcanonical versions of variational transition state theories, which attempt to minimize $k(E)$ as a function of geometry?

Jeremy Richardson answered: The instanton method does not include a variational approach. Instead the algorithms automatically place the instanton near the top of the barrier in a unique way such that there is no user-defined dividing surface.

David Glowacki asked: When you calculate transmission coefficients for a quantum mechanical system, you see non-classical reflection above the barrier. Is this something which also arises from the method outlined in your paper?

Jeremy Richardson replied: The instanton approach includes quantum recrossings below the barrier and is thus able for instance to calculate the exact rate for a high and wide Eckart barrier. However, as no instanton exists above the barrier, my approach outlined in this paper utilizes the exact expression for the parabolic-barrier rate which does include such non-classical reflections. These effects do not therefore arise from the instanton approach, but are included when following this procedure.

William Miller commented: The correct (and usually very accurate) semi-classical result for the transmission probability through a one dimensional barrier is given by the uniform barrier connection formula of WKB theory as

$$P = \exp(-2t)/[1 + \exp(-2t)] \tag{2}$$

where t is the (imaginary time) action integral through the barrier. Expanding the denominator in a Taylor (here, geometric) series gives

$$P = \exp(-2t) - \exp(-4t) + \exp(-6t) - \exp(-8t) + \dots \tag{3}$$

a very simple result which suggests that it could be obtained by adding up contributions from multiple bounces back and forth inside the barrier. For

a number of years I tried to find such a simple approach, without success. For example, semiclassical scattering theory first obtains the amplitude, *i.e.*, S-matrix for the process (the 'classical S-matrix'), the square modulus of which then gives the probability, $P = |S|^2$. The WKB uniform barrier connection formula gives the S-matrix as

$$S = \frac{\exp(-t)}{\sqrt{[1 + \exp(-2t)]}} \tag{4}$$

which obviously gives the correct P of eqn (2). (There are WKB phase factors describing classical motion on both sides of the barrier, but these do not contribute to P.) The Taylor series expansion of the denominator of eqn (4) gives something analogous to eqn (3)

$$S = \exp(-t) - (1/2)\exp(-3t) + (3/8)\exp(-5t) - (5/16)\exp(-7t) + \dots \tag{5}$$

which is qualitatively correct: the first term is the amplitude for the direct transition through the barrier, left (L) to right (R); the second term that for making an extra pass back and forth inside the barrier (L ⇒ R ⇒ L ⇒ R); the next term that for two passes back and forth inside the barrier; *etc.* [The alternating signs of the terms arise because there is a phase factor of $\exp(i \times \pi/2)$ for each (imaginary) time the trajectory inside the barrier reverses its velocity at a classical turning point.] *i.e.*, the net amplitude is the sum of contributions from all trajectories that go from 'reactants' (L) to 'products' (R). The problem is with the pre-exponential coefficients in eqn (5); I know of no simple way to obtain these from standard semiclassical theory; maybe someone else does. I was thus very surprised (and pleased) when it turned out that eqn (3) [and thus eqn (2)] was found to result from a semiclassical approximation to the quantum flux-side correlation function, as developed in a 1975 paper,[1] which gave a result later called the 'instanton'. The key is that this semiclassical approximation to the quantum reactive flux yields the transmission probability, not the amplitude, and the correlation function has a contribution from all trajectories that cross the 'dividing surface', not only the 'reactive' ones that go L to R. The first term in eqn (2) is thus the probability for the direct, L ⇒ R, passage through the barrier. The second term is the probability for the non-reactive trajectory that 're-crosses' the dividing surface and goes back to reactants, L ⇒ R ⇒ L, and this is the origin of the minus sign—it subtracts from the reactive flux. The third term is that for the reactive trajectory L ⇒ R ⇒ L ⇒ R, and so forth. The alternating signs of the terms in eqn (2) and eqn (4) thus have a very different origin, something that I had not previously appreciated.

1 W. H. Miller, *J. Chem. Phys.*, 1975, **62**, 1899.

Priyadarshi Roy Chowdhury communicated: What are the boundary conditions that you have set in the case of microcanonical as well as thermal instanton rate theory for the purpose of understanding the barriers of both the temperature regimes?

Jeremy Richardson communicated in reply: Chemical reaction rate theory is rigorously derived using scattering boundary conditions. However, it is often the

case that the same rate expressions can also be applied in the condensed phase when there is a sufficient separation of timescales. The advantage of integrating explicitly over the microcanonical rates is that energies below the reactant asymptote can be excluded as these should not contribute to the rate of a bimolecular collision.

Eli Pollak opened discussion of the paper by Johannes Kästner: You spoke about the effect of the pre-reaction well and the problems with the instanton picture, since the instanton is found at an energy which is lower than the asymptotic energy. Two questions related to this. One, wouldn't the way to solve this problem be to use RPMD at the temperature of the reaction instead of using instantons? As a follow up, is it really that crucial that the instanton energy is lower then the threshold energy? After all there are also zero point effects and couplings between modes which are difficult to assess, so why isn't the direct way of simply using the instanton without worrying about its energy valid?

Johannes Kästner replied: RPMD at the temperature of the reaction is probably an accurate solution, but it requires much more energy and gradient evaluations than instanton calculations. For bimolecular cases with pre-reactive minima instanton theory results in rate constants which increase with lowering of the temperature. The slope corresponds to the vibrationally-adiabatic energy difference between the reactants and the pre-reactive minimum. You are right, a better criterion than the energy of the instanton would be the zero-point-corrected energy of the instanton *vs.* the zero-point energy of the reactants. The former, however, is non-trivial to calculate.

David Glowacki asked: In the comparison that you showed with the experimental numbers, I noticed that the experimental measurements were for bimolecular reactions? I was under the impression that it's rather difficult to calculate instantons for an A + B type reaction. Can you clarify how you are doing your instanton sampling for this particular bimolecular reaction?

Johannes Kästner replied: In fact, in this work, we report instanton rate constants only for the unimolecular case due to the difficulties mentioned in section 3.2.2 of our paper. In general, however, it is possible to calculate bimolecular rate constants with instanton theory as long as the barrier is not submerged. The instanton and its fluctuations are the same as in the unimolecular case. Only the partition function of the reactant state is different. In a bimolecular case, the translational and rotational partition functions of both reactants need to be considered.

David Glowacki remarked: As far as I know, instanton theory is a method for sampling thermal reaction pathways. So in using instantons to sample the reaction pathway from the pre-reactive complex, it seems that this amounts to an assumption that the complex is thermalised. Is that a reasonable thing to assume in an astrochemical context? It would be easy to run some quick master equation calculations (*e.g.*, using the open-source MESMER package[1]) and verify whether or not this is the case.

1 D. R. Glowacki, C.-H. Liang, C. Morley, M. J. Pilling and S. H. Robertson, *J. Phys. Chem. A*, 2012, **116**, 9545.

Johannes Kästner answered: At low pressure (like in the interstellar medium) in the gas phase the pre-reactive complex will not equilibrate. Therefore, as soon as the instanton spreads into the pre-reactive minimum, the obtained rates are not reliable. This is one reason why we don't report any, see section 3.2.2 in the paper. On a surface, *e.g.* of dust grains, thermal equilibration will occur fast and efficiently. There, a Langmuir–Hinshelwood process originates from a pre-reactive minimum and the corresponding unimolecular rates are physically meaningful.

David Clary said: The reaction you study has quite a complicated rate constant as a function of temperature. Your paper only describes rate constants calculated using somewhat simplified theories. Is this reaction a good example where a full dimensional quantum reactive scattering calculation would be useful as a benchmark?

Johannes Kästner replied: Yes, certainly full quantum dynamics calculations would be very useful here. Ideally on the same potential energy surface as our calculations. This way we would learn about the accuracy of the rate theory in that complicated potential as well as get physical insight into the system. Our calculations were performed with energies, gradients and Hessians calculated on the fly, however. So the transfer of a potential energy surface is not trivial.

William Miller commented: One way that could be useful in treating a bifurcating reaction path is not to follow one of the two minimum energy paths, but rather to follow a 'reference' path that follows the crest between the two minimum energy paths. One of the vibrational modes perpendicular to this reaction coordinate will then have an imaginary frequency, and one would thus need to treat it beyond the harmonic approximation (*e.g.*, to quartic order) in order to describe its double-well character. Such an approach was described in ref. 1.

1 W. H. Miller, *J. Phys. Chem.*, 1983, **87**, 21.

Ralph Welsch remarked: As you have energies, gradients and Hessians from your instanton calculations you can easily obtain a potential energy surface of the transition state region using Shepard interpolation. Using this potential you can calculate exact thermal rate constants using the quantum transition state concept and MCTDH without doing full scattering calculations. The exact calculation will be challenging for the very low temperature region, but might still be an interesting way forward as it provides a good basis for comparison of the different approximate methods.

Wei Fang asked: You mentioned a pre-reactive minimum exists in the reaction you studied, why is that minimum not used as the initial state in the rate calculations? If in some other reaction, a more deep pre-reactive minimum exists, will you consider using that minimum as the initial state?

Johannes Kästner responded: That depends on the type of rate constant to be calculated. In unimolecular rate constants, the pre-reactive minimum is used as the reactant state. For bimolecular rate constants, the separated reactants are used as the reactant state, but the pre-reactive minimum influences the rate constants *via* the shape of the potential energy surface.

Jeremy Richardson enquired: You have shown that at low temperatures the instanton pathway varies considerably from the minimum-energy path. How accurate can we therefore assume that the semiclassical tunnelling calculations are, if they are based on the small-curvature approximation?

Johannes Kästner replied: Since the small-curvature tunneling correction is based on the minimum-energy path and its close environment, significant inaccuracies can be expected. However, the large-curvature transmission probabilities turned out to be even smaller.

William Miller commented: If you are dealing with two transition states (*e.g.*, one long range one that is due to a centrifugal barrier, and a short range 'chemical' barrier), with a minimum between them, there is a 'unified statistical model' that describes this situation; *cf.* ref. 1. It treats the transitional behavior between one transition state (and thus a 'direct' reaction), and two transition states (with a short-lived complex between them) for which TST would fail (because of re-crossing trajectories).

1 W. H. Miller, *J. Chem. Phys.*, 1976, **65**, 2216.

Sergio Rampino communicated: Thermal rate coefficients for use in astrochemical kinetic networks are often stored in dedicated databases (such as the KIDA and UMIST ones mentioned in the paper) in the form of a set of parameters expressing their temperature dependence *via*, for example, the popular Arrhenius–Kooij equation. In our recent works on the astrochemical reaction $C + CH^+ \rightarrow C_2^+ + H$ (ref. 1) we have found that the Arrhenius–Kooij equation might be not flexible enough[2] and that a better parametrization might be provided by the so called 'deformed Arrhenius' law proposed by Aquilanti and Mundim.[3,4] Have the authors made any attempt to fit the computed thermal rate coefficients with parametrized formulations for inclusion in astrochemical kinetic databases?

1 L. Pacifici, M. Pastore, E. Garcia, A. Laganà and S. Rampino, *J. Phys. Chem. A*, 2016, **120**, 5125–5135.
2 S. Rampino, M. Pastore, E. Garcia, L. Pacifici, A. Laganà, *Mon. Not. R. Astron. Soc.*, 2016, **460**, 2368–2375.
3 V. Aquilanti, K. C. Mundim, M. Elango, S. Kleijn, T. Kasai, *Chem. Phys. Lett.*, 2010, **498**, 209–213.
4 V. Aquilanti, K. C. Mundim, S. Cavalli, D. De Fazio, A. Aguilar, J. M. Lucas, *Chem. Phys.*, 2012, **398**, 186–191.

Johannes Kästner communicated in reply: In most cases, we fit our calculated rate constants to parametrized forms. However, in this particular case, Fig. 2 in our paper makes it clear that both the UMIST and the KIDA parameters describe the system sufficiently well. So we did not make another attempt to fit new parameters.

Thomas Miller opened discussion of the paper by Nancy Makri: Can you clarify the situations in which the blip-summation approach can be used to gain improved efficiency? Is it most effective for system-bath models or can it also be employed to accelerate the simulation of all-atom models?

Nancy Makri answered: The blip decomposition of the path integral (where paths with many blips are omitted because their contribution is exponentially small) is not restricted to system-bath models. It allows elimination of a large number of terms and can be used in QCPI simulations where the atoms of the quantum system's environment interact *via* anharmonic potentials without any simplification. The savings achieved through the blip truncation depend on the parameters and are described in detail in ref. 1. (Note that ref. 1 deals with harmonic baths, but the number of terms is independent of the specific nature of the system's environment.) In the case of a harmonic bath, the cumulative/iterative treatment of quantum memory leads to a very substantial additional acceleration, reducing the number of trajectories to those that would be required in an ordinary molecular dynamics (MD) simulation. It may be possible to take advantage of this additional acceleration in the general case of an anharmonic environment, however we are still exploring this possibility.

1 N. Makri, *J. Chem. Phys.*, 2014, **141**, 134117.

Dmitry Shalashilin added: This question is a follow up to the previous question. In the paper you consider the case of coupling, which is linear with respect to the bath coordinate. Why is it important to have such coupling? Is it essential or simply helps to converge faster?

Nancy Makri replied: The quantum–classical path integral (QCPI) methodology is completely general and requires no particular form of potential interactions. The QCPI simulation of the ferrocene–ferrocenium charge transfer in liquid hexane treated explicitly 1320 atoms with CHARMM force fields. The blip sum acceleration I discuss in the *Faraday Discussions* paper also applies to the most general case. In the *Faraday Discussions* paper I also show that in the special case of a harmonic bath linearly coupled to the quantum system (for which the QCPI treatment is fully equivalent to the Feynman–Vernon influence functional), a cumulative treatment of the quantum memory leads to dramatic computational savings, and argue that the same code acceleration should be realizable in the most general case of a complex, anharmonic environment if the quantum memory, which arises from the vacuum, is treated within the quadratic approximation. (Note, of course, that what distinguishes QCPI from other methods is the lack of any assumptions or approximations, so one may prefer to refrain from introducing this approximate treatment of the quantum memory. Nevertheless, the validity of such a treatment could be tested on select trajectories prior to performing the full QCPI run.)

Martin Richter asked: You presented numerical converged results of the blip-summed QCPI method for a symmetric two-level Hamiltonian employing 60 discretized harmonic modes for the representation of an Ohmic spectral density and 120 000 trajectories in total (Fig. 1 in the paper). Could you comment on the

scaling behaviour of the blip-summed QCPI method with respect to system size and complexity of the spectral density.

Nancy Makri responded: QCPI is not restricted to harmonic baths, and the blip sum version is just a way of accelerating convergence. However, the cumulative treatment of the quantum memory is at the moment specific to harmonic baths, and I understand your question pertains to this situation. This method requires a single trajectory from each initial condition, regardless of the complexity of the spectral density.

The scaling of QCPI with system size is related to the number of system paths that span the quantum memory. (All classical memory is automatically accounted for without truncation in our formulation.) For example, in the case of a general two-level system (TLS), the number of trajectory initial conditions would be multiplied by 3^L, where L is the number of path integral time steps required to saturate the quantum memory. By incorporating as much of the decoherence as possible in effective propagators and using a judicious memory truncation algorithm,[1] L typically has small values. For example, in the cases we have studied, $L \approx 4$–5. This means that the cost of a TLS calculation would be 3^4–3^5 times higher than the cost of an ordinary molecular dynamics (MD) simulation. If, in addition, one implements the blip decomposition, this factor is reduced very significantly, and this reduction is more dramatic in cases of sluggish solvents with large reorganization energies, where larger values of L may be required for convergence. (See ref. 2 for a detailed description of the rapid convergence of the blip decomposition.) I emphasize again that these numbers apply to the most general situation of a condensed phase environment consisting of hundreds or thousands of interacting atoms. The QCPI simulation will surely be more expensive than a MD simulation, often by one or two orders of magnitude, but this cost is not prohibitive (especially given that QCPI is easily parallelizable), and the confidence of obtaining results free of *ad hoc* assumptions or adjustable parameters, justifies the effort. Again, if the cumulative quantum memory treatment is also implemented, only a single trajectory from each initial condition is needed. If the cumulative quantum memory treatment can be extended (without noticeable loss of accuracy) to a complex polyatomic environment, the cost of QCPI will become comparable to that of an ordinary MD simulation. We are currently investigating this possibility.

1 P. L. Walters and N. Makri, *J. Chem. Phys.*, 2016, **144**, 044108.
2 N. Makri, *J. Chem. Phys.*, 2014, **141**, 134117.

Stuart Althorpe said: You mention (ref. 41, currently unpublished) that you are able to obtain directly the parameters needed to construct the influence functional for a harmonic bath, without first computing the spectral density. Could you please give some details of this procedure?

Nancy Makri answered: The influence functional coefficients within the quasi-adiabatic propagator path integral (QuAPI) discretization that we introduced in the 1990s involve double integrals of the bath correlation function,[1] thus the numerical construction of the spectral density is not necessary. The practical

issue is that the solvent correlation function is usually obtained *via* molecular dynamics simulations which yield a real-valued quantity. Still, the imaginary part of the correlation function can be extracted from knowledge of the real part within the harmonic bath assumption. This allows us to compute the influence functional coefficients directly from the molecular dynamics data. Besides its simplicity, an additional advantage of the direct procedure[2] is higher accuracy. Similar ideas can also be applied to the discretization of the bath,[3] to yield discrete modes that can be used in a quantum–classical treatment of the system-bath dynamics, if this is desired.

1 N. Makri, *J. Math. Phys.*, 1995, **36**, 2430–2457.
2 T. C. Allen, P. L. Walters and N. Makri, *J. Chem. Theory Comput.*, 2016, **12**, 4169–4177.
3 P. L. Walters, T. C. Allen and N. Makri, *J. Comput. Chem.*, 2017, **38**, 110–115.

Priyadarshi Roy Chowdhury communicated: What are the primary advantages of using QCPI formulation of system-bath models in studying the dynamics of chemically reactive processes?

Nancy Makri communicated in reply: The main advantage of QCPI is that it is not restricted to system-bath models and can be used to simulate reactive processes in complex polyatomic environments (*e.g.* liquids or biological molecules). When applied to system-bath models, it allows larger time steps than influence functional based methods and a faster convergence with respect to memory in some regimes, because QCPI captures the entire classical memory without truncation.

Jeremy Richardson opened discussion of the paper by Hannes Jónsson: Could you please describe how this approach could be applied to study spin flips in a magnetic solid? It will surely not be possible to flip a large number of spins simultaneously as this would have a negligible probability.

Hannes Jónsson responded: In an extended magnetic solid spin flips or magnetization reversal needs to be nucleated in a finite volume and then proceed from there. This is analogous to the nucleation of a phase transformation. We have, for example, estimated the size of such a nucleus in quantitative analysis of a hysteresis loop using transition state theory.[1] Often, however, such a transition nucleates from a free surface or a defect and then propagates through the system. A nice example of this is provided by magnetic iron islands on a surface. For a small enough island, all the spins rotate in a uniform way, but the energy barrier for this mechanism grows in proportion to the size of the island. Once the island becomes larger than a certain critical size, it is more likely that the spins at the edge of the island rotate first, creating a temporary domain wall which then propagates through the island until all spins have been reversed. The largest pre-exponential factor in the rate expression is indeed found to be at the critical size where both mechanisms, uniform rotation and temporary domain wall, are active. In recent calculations we could explain an experimentally observed maximum in the pre-exponential factor for magnetization reversal in Fe islands on a W(110) surface in this way.[2]

1 M. Moskalenko, P. F. Bessarab, V. M. Uzdin and H. Jónsson, Qualitative Insight and Quantitative Analysis of the Effect of Temperature on the Coercivity of a Magnetic System, *AIP Adv.*, 2016, **6**, 025213.
2 P. F. Bessarab, V. M. Uzdin and H. Jónsson, Size and Shape Dependence of Thermal Spin Transitions in Nanoislands, *Phys. Rev. Lett.*, 2013, **110**, 020604.

Stuart Althorpe asked: So far you have calculated the instanton cross-over temperature, and the transition-state theory rate above this temperature. What further steps would be required to calculate the instanton rate?

Hannes Jónsson answered: The expression for the instanton rate at a finite temperature has yet to be derived. We are working on this using the coherent state path integral approach, but there are several complications that come up and this work has not been completed yet. The magnetic instantons are found in a way similar to what we have presented for atomic systems.[1]

1 D. M. Einarsdóttir, A. Arnaldsson, F. Óskarsson and H. Jónsson, Path Optimization with Application to Tunneling, *Lect. Notes Comput. Sci.*, 2012, **7134**, 45.

David Glowacki enquired: Coming back to Jeremy Richardson's question, I was wondering if you could clarify how you selected your collective variables? You show 1d projections of the barrier height in the paper, but how do you know what the collective variables should be in these cases?

Hannes Jónsson replied: The reaction coordinate is taken to be the minimum energy path for the transition. Given the initial state (magnetization pointing in a direction along the anisotropy axis) and the final state (magnetization pointing in the opposite direction), the minimum energy path is obtained using the geodesic nudged elastic band (GNEB) method, an adaptation of the NEB method to magnetic systems. Within the harmonic approximation to transition state theory, the activation energy is given by the highest energy along the minimum energy path. For magnetic transitions where a temporary domain wall (sometimes referred to as a soliton) is formed and translates through the system, the energy remains practically constant along the minimum energy path in the vicinity of the maximum. In principle there can be more than one minimum energy path connecting the given initial and final states. Then, the GNEB method converges most likely on the path closest to the initial path from which the iterative optimization is started. Here, the initial path was just a straight line interpolation between the endpoints. We have not seen evidence of multiple minimum energy paths in the systems presented here, but this is always something to look out for.

**Peter Bolhuis** asked: Do you need to know where this saddle point is located?

Hannes Jónsson responded: Yes, in order to estimate the crossover temperature, we first find the minimum energy path using GNEB and locate the energy maximum(a) along the path, *i.e.* saddle point(s) on the energy surface. Above the crossover temperature, the Feynman path is collapsed at the saddle point, but at the crossover temperature, an additional unstable mode (with negative eigenvalue) appears, corresponding to the images of the system in the Feynman path

spreading out. If more than one saddle point is present, then there can be more than one crossover temperature. This analysis is done within a harmonic approximation, which assumes the energy surface is smooth enough.

Peter Bolhuis opened discussion of the paper by Eli Pollak: You showed in the presentation that for Langevin dynamics with low friction the effective diffusion constant on a periodic potential does not follow the Arrhenius Law any more at high temperature. What is exactly the cause of the breakdown? Is it due to the slow velocity decorrelation for low friction, leading to multiple correlated hops? Second, is this observation limited to periodic smooth potentials? Or does this apply generally for arbitrary potentials, and even for very rough energy landscapes?

Eli Pollak answered: One of the outcomes of the recently developed theory for finite barrier corrections for both diffusion on a periodic potential and the rate of escape from a potential well is that it enables one to assess the limits of the Arrhenius theory which predicts that a plot of the logarithm of rates *versus* the inverse temperature should be linear with a negative slope. The deviation from such a linear Arrhenius plot when the barrier is low (in units of kT) and the friction is low (see Fig. 1) is a result of the competition between the temperature dependent prefactor which expresses the slow energy exchange mechanism with the bath, which is then the rate limiting step and the Arrhenius exponential factor which is under these conditions comparable or even larger in magnitude. This is not limited to diffusion, it happens also for the escape rate, as may be deduced from our numerical studies on the rate of escape of a cubic oscillator[1] and as shown in Fig. 1 here.

1 E. Pollak and R. Ianconescu, *J. Phys. Chem. A*, 2016, **120**, 3155–3164.
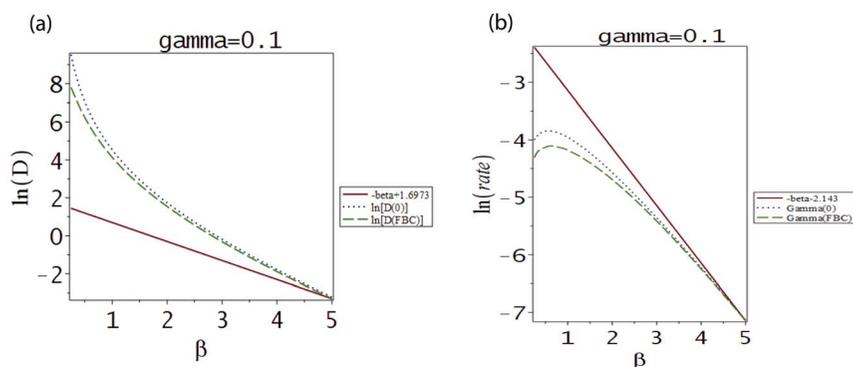
Fig. 1 (a) The logarithm of the diffusion coefficient is plotted *vs.* the inverse temperature for motion on a periodic cosine potential at low reduced friction. The solid line shows the expected Arrhenius behavior, the dotted line the result from the turnover theory without finite barrier corrections, and the dashed line with FBCs. (b) The logarithm of the escape rate from the well of a cubic potential is plotted *vs.* the inverse temperature. The solid line shows the expected Arrhenius behavior, the dotted line the result from the turnover theory without finite barrier corrections, and the dashed line with FBCs.

Peter Bolhuis added: For very high temperature, the system becomes effectively diffusive as the potential barriers become very small with respect to the thermal energy. Do you recover the free diffusion result for this limit? (If I am correct, the diffusion constant even decreases with temperature for high temperature. Can you explain this?)

Eli Pollak answered: The free diffusion limit is recovered in the sense that the diffusion coefficient diverges as $1/\gamma$ (with γ the friction coefficient) when the friction goes to zero. However, the derivation presented in the paper is no longer valid and the leading order correction term is not sufficient when the barrier height (in terms of kT) is less than the order of unity.

Peter Bolhuis continued: Is that also the reason why you say your simple model is applicable to more complex systems like proteins?

Eli Pollak responded: The simple Langevin model is applicable to proteins, since motion over the microstates bridging between folded and unfolded states, for example, may be described in the continuum limit in terms of a Smoluchowski equation, as shown by van Kampen[1] and as detailed in a more recent paper[2] where we studied the properties of a Markov chain and a Smoluchowski continuum limit description.

1 N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North Holland, Amsterdam, NY, 1981.
2 E. Pollak, A. Auerbach and P. Talkner, *Biophys. J.*, 2008, **95**, 4258.

David Glowacki asked: An open question for people that work on huge master equation simulations – *e.g.* for proteins, or for large combustion/atmospheric systems – is how many wells the system skips as it explores the system configuration space? More generally, this is an interesting question: if I have dynamics on some complex topology with an array of minima in a hyperdimensional space, I'm curious whether your analysis can tell us the average number of wells that are skipped as a function of energy transfer efficiency?

Eli Pollak responded: For the diffusion on a periodic potential the turnover theory gives explicit expressions for the hopping distributions, so yes, the theory provides answers. The essential parameter is the energy loss parameter, if it is unity or greater, the hopping distribution is exponential and long hops are not very important. If the energy loss is much smaller than unity, multiple hops dominate. In the case of proteins, the assumption is that the residence times in any of the microstates are very long compared to vibration time periods and, in this case, only nearest neighbor hops must be considered.

David Glowacki enquired: There has been lots of work in the last few years by people that do combustion modelling to calculate potential energy surface stationary points for molecules with 10–20 atoms. They typically uncover hundreds of microstates, for which they then solve a master equation in some temperature–pressure regime. A key parameter of these models is the energy transfer probability which I saw was also in your model. There's an open question

in that community: how much resolution does one require in mapping out stationary points? Is it necessary to characterize every microfeature on that topology? I'm curious whether your analysis provides any 'rules-of-thumb' that might prove useful here?

Eli Pollak replied: I have not addressed these very practical and important questions. However, I would guess that the rule of thumb would be that a microstate which is separated from other microstates with a barrier which is 2 or more (in units of kT) should be considered as an element in the master equation.

Georg Menzl asked: You study to which extent the depth of the free energetic well, *i.e.*, the height of the free energy barrier preventing the escape of a particle, determines the applicability of Kramers' theory. In a simple model, where the choice of the reaction coordinate is clear, these quantities are well defined. However, if you are looking at complex processes such as protein folding and unfolding, the collective variables used as reaction coordinates are typically not unique. Does the depth of the well have physical significance in such systems if one considers that a change in the choice of reaction coordinate can change the estimated value of the well-depth considerably?

Eli Pollak answered: There is a difference between theory and experiment. From a measured temperature dependence one may extract an activation energy which is meaningful provided that the temperature range is not too small or that the experimental error bars are not too large. From theory you are of course right, different coordinates may give different results. But suppose that the experiment gives an activation energy of the order of unity in terms of kT, the question remains whether rate theory is applicable. This was answered to a certain extent in the finite barrier corrections analysis of Kramers' turnover theory.

Peter Bolhuis said: I wanted to continue in that direction, especially on the difference between the simple one dimensional models that appear in your theory, employing *e.g.* a periodic cosine potential, and a much more complex biomolecule or other high dimensional systems. When you are looking at kinetics on a one dimensional surface you can define a hopping rate that can show non-Arrhenius behaviour and memory effects, but as soon as the system becomes very high dimensional with a rugged energy landscape, in many cases memory is lost, and the system effectively Markovian, with no correlations between hopping. In that sense the hopping picture is pretty accurate for such systems.

Eli Pollak responded: That is correct, in the Smoluchowski limit applicable to proteins. The multiple hops considered in the paper are more applicable for example to surface diffusion, where in many cases the friction felt by a diffusing particle is rather low.[1]

1 Y. Georgievskii, M. A. Kozhushner and E. Pollak, *J. Chem. Phys.*, 1995, **102**, 6908.

Priyadarshi Roy Chowdhury communicated: What are the restrictions that need to be maintained throughout for derivation of finite barrier corrections?

Eli Pollak communicated in reply: The finite barrier corrections are a first term in an asymptotic series. They will fail when the small parameter $-kT/V$ (where V is the barrier height) is no longer small. Of course, underlying it all is the assumption of the existence of a generalized Langevin equation. If the memory in the memory friction is too long the theory will fail, since in this case, one traversal in the well may no longer be independent of the previous one.

John Ellis opened a general discussion: In the previous session we have had a number of mentions of quantum transition state theory and the use of instantons in calculating tunnelling rates, and it seemed perhaps useful to give an example in which experimental measurements of hydrogen diffusion, both activated and tunnelling, are compared with QTST and instanton predictions. The experimental technique used is helium spin echo. A beam of spin polarised ^{3}He is scattered from a moving surface adsorbed species and the precession of the nuclear spins in magnetic fields aligned along the beam axis before and after scattering is used to measure the quantum mechanical Doppler shift caused by scattering from the mobile species – and from this the motion of the atoms can be inferred on an Ångström and 0.3–10 000 ps time scale. The measurements are highly accurate and are made on such a fast timescale that relatively little extrapolation is needed to get pre-exponential values for activated processes which are typically accurate to 5–10%, making meaningful comparisons with rate theory possible. By contrast, as illustrated in Fig. 2, extrapolating more traditional diffusion measurements (made on millisecond to hour timescales) over the 12–14 orders of magnitude gives such errors in the pre-exponential factor as to make comparisons with rate theory impossible.[1]

The measurements presented here are for the diffusion of hydrogen on the Ru(0001) surface[2] between the non-degenerate fcc and hcp hollow sites with the bridge site being the 'transition state' (Fig. 3).
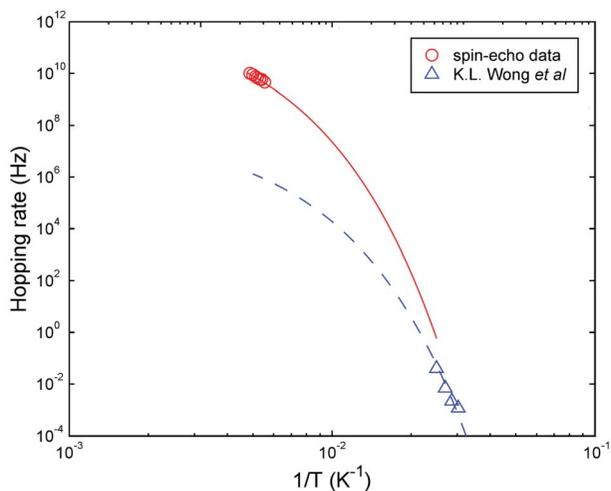

Fig. 2 A comparison of measurements of the temperature dependence of the hopping rate of CO on Cu(111) made by the spin echo (circles) and STM techniques (triangles) (from ref. 1).
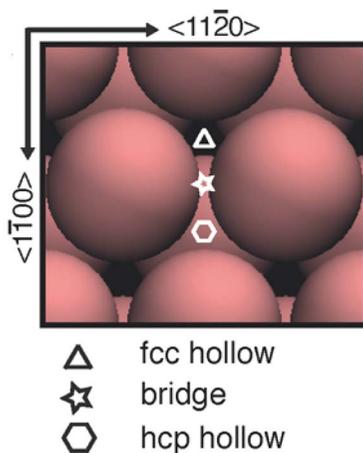
Fig. 3 Schematic of the adsorption sites for H on Ru(001). (Taken from ref. 2.)

From the measured ratio of forward/backward jumps between the two adsorption sites, the ground state energy difference between them is determined to be 22.2 ± 0.6 meV. DFT calculations predict the ground state energy in the hcp site to be ~50 meV above that of the fcc site,[2] with the bridge site 150 meV above the fcc site. The H-surface parallel vibrational mode is measured with HREELS to be 84 meV,[3] and solving the Schrödinger equation for the full 3D H-frozen surface DFT potential[2,4] gives 79 meV for this mode. Fig. 4 compares the measured fcc to
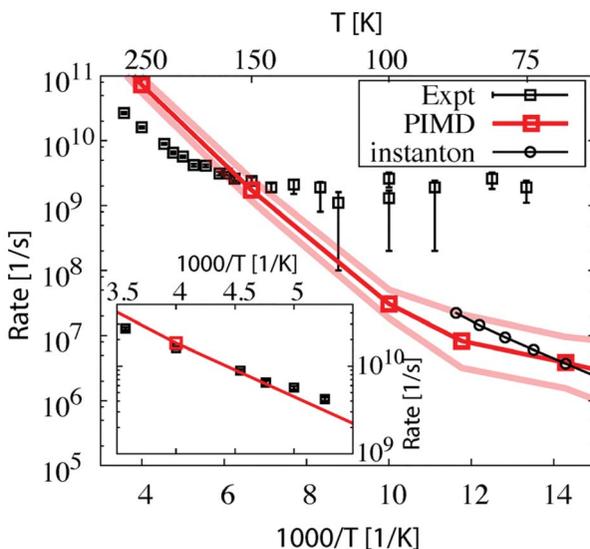

Fig. 4 Experimental rates (black squares), calculated jump rates from PIMD (red line with squares, error bars denoted by thick shaded lines), and instanton calculations on a 1D potential (black line with circles). The inset shows a comparison of the measured jump rate with high temperature PIMD rates scaled by 0.25. (Derived from figure in ref. 2.)

hcp hopping rate with QTST predictions derived from path integral molecular dynamics (PIMD) simulations based on DFT potential calculations with a fully mobile substrate,[2] which will therefore include the interactions of the diffusing H atom with the substrate phonons. Fig. 4 also includes 1D instanton calculations of the H atom tunnelling rate from fcc to hcp sites across the bridge site, which are seen to be in good agreement with the QTST/PIMD rates, indicating that the coupling to the phonons is weak in this context. Whilst, as can be seen from the inset to Fig. 4, the QTST/PIMD rates show the correct activation energy in the activated regime (above about 200 K), they overestimate the rate by a factor of 4, which was ascribed to the use of classical H atom velocities in the QTST formalism used to derive the jump rate from the free energy of the transition state determined from PIMD calculations with the H ring centroid frozen at various values of the reaction coordinate.

An alternative approach which makes no attempt at including connections to the heat bath provided by either the phonons or the electrons of the substrate is to calculate the full 3D dispersion of the vibrational/translational modes of the adsorbed H atoms, moving in a 'frozen surface' 3D H-surface potential[4,5] calculated using DFT[2] and then use the actual density of H states at all energies instead of a free atom density of states in the 'over the barrier' regime as in traditional TST, and use the actual (group) velocity of the states derived from the band structure instead of the classical free atom velocities. Fig. 5 shows that the rate calculated in this way from the simulated band structure (smooth black line) is in remarkable agreement with the measurements, and also with the QTST results (red line with point markers) reduced by a factor of 4. This confirms that the discrepancy between the QTST results and the data arises from the use of the properties of classical H states rather than the actual quantum H states to convert
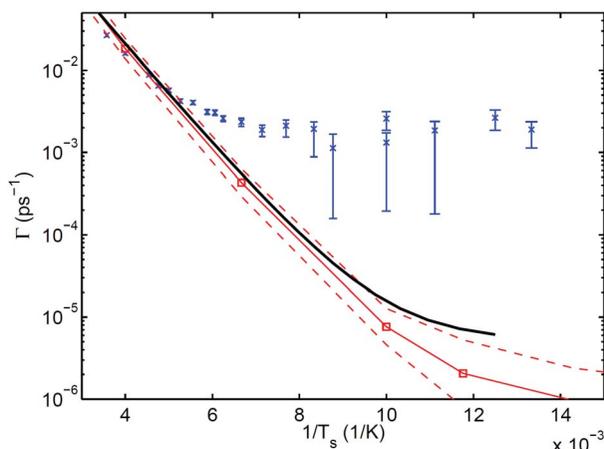

Fig. 5 Arrhenius plot for 0.2 ML H on Ru(0001) (blue crosses) showing the temperature dependence of the hopping rate. Rates calculated using the band structure method are shown with a black line. Jump rates calculated from PIMD are shown with red squares, with errors at the 66% confidence interval shown with dashed red lines. The PIMD rates have been scaled by 0.25 to match the experimental data at high temperatures. (From ref. 6.)

the PIMD 'frozen centroid' free energies to a rate, and also confirms that the phonons (which are not included in the band structure approach) are having little effect on the QTST results.

For the deep tunnelling regime, however, all three approaches give similar results, but, as can be seen from Fig. 4 and 5, all give tunnelling rates 2–3 orders of magnitude less than that observed.

The agreement of the band structure results (which take full account of the extended periodicity of the substrate) with the QTST/instanton results that focus on the local fcc–bridge–hcp path segment is curious since the band structure results relate to tunnelling from a state in one well to an identical state in another one – so the deep tunnelling is from one fcc well across the hcp well to the next fcc well – and it is no surprise that its rate is therefore low. The QTST/instanton results, however, model inelastic tunnelling from the fcc site to a neighbouring, and different energy, hcp site. The obvious omission from all these models is the coupling to the free electron heat bath of the substrate – but this would only be expected to slow the tunnelling in the QTST/instanton simulations in the deep tunnelling regime, though might increase the rate in the band structure model as it would supply the energy needed for the H atom to tunnel from fcc to the non-degenerate hcp site (Fig. 6 shows a schematic of the energies at neighbouring fcc and hcp sites).

Given the reasonable agreement between the DFT based predictions and the measured jump rates in the activated regime, and the good agreement between the predicted and measured H vibrational frequencies, it does seem that the DFT is giving a reasonably realistic representation of the H-surface potential energy surface. The good agreement of the bandstructure derived TST rates for the activated regime suggests strongly that the real system must have a 'friction' (i.e. rate of energy exchange with the substrate) of such a magnitude that the mean free path of the propagating H atoms is roughly the distance from the fcc to hcp sites i.e. the system is roughly in the 'TST limit'. As is illustrated in Fig 7, if the friction is lower (dashed lines) then the moving species will 'roller coaster' so some of the atoms in the transition state will have come from further away, reducing the number in the transition state that have just left the neighbouring well and thus reducing the number jumping from one site to a neighbouring one, meaning that the actual jump rate is lower then the TST prediction. At high frictions (dotted line) since one atom may re-cross the transition state, the
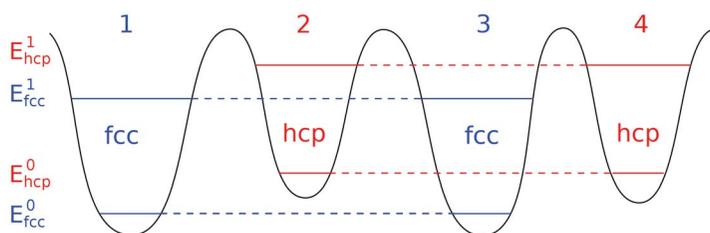

Fig. 6 Schematic of the energy dependence of an adsorbed H atom along the fcc–bridge–hcp–bridge–fcc path, and of the ground and first excited (surface parallel) vibrational states.
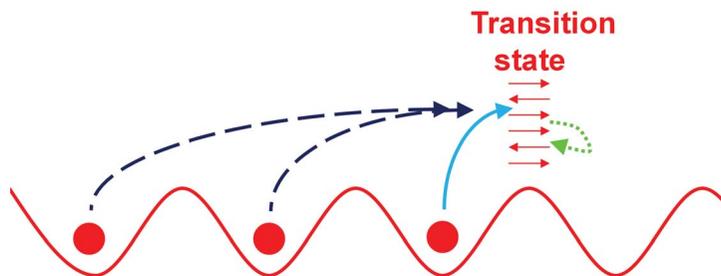
Fig. 7 Schematic of the contributions to the population of the transition state arising from (a) 'roller coasting' from distant adsorption wells in the case of low adatom–surface friction (dashed dark blue lines) and (b) recrossing (dotted green line) that both result in an actual jump rate (rate of leaving a particular site – blue solid line) that is lower than the TST prediction.

number of atoms in the transition state will overestimate the number jumping between neighbouring sites.

This work highlights the limitations of the prefactors used in QTST, shows the relative unimportance of the phonon–H atom coupling meaning that most of the coupling must be to the electrons of the substrate, and shows a clear failure of QTST and this implementation of the instanton method to deal with deep tunnelling.

1 P. R. Kole, H. Hedgeland, A. P. Jardine, W. Allison, J. Ellis and G. Alexandrowicz, *J. Phys.: Condens. Matter*, 2012, **24**, 104016.
2 E. M. McIntosh, K. T. Wikfeldt, J. Ellis, A. Michaelides and W. Allison, *J. Phys. Chem. Lett.*, 2013, **4**, 1565.
3 K. L. Kostov, W. Widdra and D. Menzel, *Surf. Sci.*, 2004, **560**, 130.
4 J. Ellis, unpublished.
5 J. Zhu, PhD thesis, University of Cambridge, 2016.
6 E. M. McIntosh, PhD thesis, University of Cambridge, 2013.

Eli Pollak commented: It seems that the real challenge is understanding the low temperature limit of the rate for diffusion on Ru where the transition state theory like approximations fail by three orders of magnitude. One of the difficulties which is typically ignored in these theories is the question of coherences induced by band structures in the periodic potentials. Motion in such a band is coherent and may significantly increase the tunneling rate. The TST method cannot account for such coherences. As far as the semiclassical and classical turnover theories are concerned, low friction in itself does not create any difficulty. In practice, even though the reduced friction coefficient is typically smaller than one, the parameter which really defines the dynamics is the energy loss parameter which is proportional to the product of the friction coefficient and the barrier height in units of kT. This is typically of order unity or more, leading to the exponential hopping regime[1] where the probability for many multiple hops is exponentially small. In this regime, recrossing of the barrier is a small correction to the rate and may be ignored.

1 E. Hershkovitz, P. Talkner, E. Pollak and Y. Georgievskii, *Surf. Sci.*, 1998, **421**, 73.

David Manolopoulos asked John Ellis: Can you measure a tunneling splitting for that?

John Ellis responded: The fcc site is the global ground state and has a calculated bandwidth of 9.5 neV, and the next state in the calculated band structure is located as the vibrational ground state at the hcp site and this has a bandwidth of 2.5 μeV around an energy 53 meV about the global ground state. Experimentally we cannot infer the splitting from the jump rate as the tunneling from it is dominated by inelastic effects and the technique does not enable direct spectroscopy of the H states as the splitting of the fcc ground state is too small to be resolved experimentally and the hcp ground state is inferred to be 22 meV above the fcc state from the relative forward and backward fcc–hcp jump rates, but the He beam energy is only 8 meV, so direct spectroscopy on this hcp state and its dispersion is unfortunately not accessible with the He spin echo technique. Even if the beam did have sufficient energy (as would be the case for HREELS) given the fcc and hcp states are essentially located at different sites the matrix element for a scattering induced transition between the states would be in any case very small, again unfortunately rendering direct spectroscopic measurement impossible.

David Manolopoulos added: What would be your explanation for the three orders of magnitude discrepancy that you see between the QTST and instanton results and your measured jump rates in the tunneling regime?

John Ellis responded: We don't have an explanation for the 3 orders of magnitude discrepancy between the QTST and instanton methods and the measured jump rates in the deep tunneling regime. The band structure method can only calculate the rate of tunneling between identical energy states – *i.e.* fcc to fcc tunneling through the hcp site – which will obviously be very slow. The band structure method cannot yield a tunneling rate for the fcc to hcp site as they are of different energies – but the question arises if one can work from the calculated wavefunctions of the fcc and hcp sites to calculate the inelastic tunneling rate.

Timothy Hele remarked: It is very interesting to see an experimental case where QTST appears to break down, another example being the Marcus inverted regime if RPMD is used naively. It could be that the transition-state theory assumptions themselves are failing, namely that there could be significant recrossing of the dividing surface (the hydrogen 'bounces back') and/or the reaction could be diffusive, with hops between different sites being correlated (where the "separation of timescales" between reaction and equilibration would break down). Interestingly, the computed rate underestimates the experimental rate, whereas classical TST is generally an upper bound (QTST is an approximate upper bound). Could there be inaccuracies in the potential energy surface, such as a barrier which is too "fat", meaning that although it may be of the correct height (and reproduce Arrhenius behaviour at high temperature) it would not allow sufficient tunnelling, leading to the observed discrepancies?

John Ellis responded: Whilst inaccuracies in the potential energy surface cannot of course be ruled out (and indeed the fcc/hcp adsorption energy difference predicted by the DFT work is of the order of 50 meV, whereas it is measured

to be 22.2 ± 0.6 meV), the vibrational frequencies and the hopping rate in the 'activated' regime are in remarkable agreement with those predicted by the bandstructure method from the 3D DFT potential. If the barrier was too 'fat' this would impact significantly on the vibrational frequencies. The theory is giving a rate that is too low, but the TST rate is always a maximum rate – effects of friction ('roller coasting' at low friction and 'recrossings' at high friction) always reduce the rate from the TST maximum, *i.e.* would only make matters worse for the QTST/PIMD or instanton calculations.

Jeremy Richardson commented: These results show a very important failure of quantum dynamics calculations to predict low temperature behaviour. It poses many unanswered questions and it will unfortunately not be possible to give a definitive answer now as to the causes of the discrepancies.

As you point out, the coupling to the phonons appears to be weak at low temperatures and thus the rates derived from the band structure model are probably a good description of the dynamics, *i.e.* that fcc sites tunnel directly to the next fcc site without thermalizing in an hcp well. This is predicted to be a slow process and does not agree with the experimental results. However, there must also be a similar pathway where hcp sites tunnel directly to other hcp sites without thermalizing in an fcc well. The activation energy for this process would be lower and thus the rates much faster. Of course the Boltzmann distribution of hydrogens in hcp sites will be lower than those in fcc sites but the dominant effect for the diffusion may still come from the former. Could it be that at low temperatures your spin echo experiments are only observing the moving hcp hydrogens and not the almost stationary fcc hydrogens?

It is for problems such as these that I have been developing a microcanonical instanton approach which could be used in conjunction with a master equation solver to study hopping dynamics without assuming thermal equilibration in each well. I hope that in the future it will be possible to use these methods to simulate the hydrogen diffusion in your system more accurately.

John Ellis responded: The question as to whether the observed rate could be due to tunneling from the more energetic hcp site is indeed a good one, however the bandstructure derived rates do include the propagation rates from all states within the bandstructure – both those located primarily at the hcp and fcc sites as well as the more delocalised higher energy states – all weighted by the appropriate Boltzmann factor to allow for the relative occupation for each state, so is actually already accounted for. I think it likely that the connection to the electron heat bath facilitates the tunneling from fcc to hcp ground states which would otherwise be forbidden on account of their differing energies.

David Manolopoulos enquired: In the plot that you showed, you have alternating deep and shallow wells for the hydrogen on the surface. Is it possible that there is some sort of resonant tunnelling associated with a near degeneracy between the eigenvalues of the hydrogen in the two wells?

John Ellis answered: The ground states in the fcc and hcp sites are actually measured to be 22.2 ± 0.6 meV different in energy, which is probably too great to allow for much of a resonance between the two states, and indeed the 3D H

ground state wavefunctions located in one type of minima show only a very small amplitude in the other minima. Clearly, however, the rate of tunnelling between the two states must relate somehow to the overlap between these two wavefunctions.

David Manolopoulos added: And that's the calculation you do that agrees best with your experiments?

John Ellis replied: Indeed, the band structure based TST method, which calculates the elastic propagation group velocities for all the states, does give the best result for temperatures where rapid activated diffusion is observed, but all fail hopelessly for the deep tunneling temperature range where the tunneling time is 2 or 3 orders of magnitude greater than the reciprocal of the energy transfer rate. In the activated regime, the fact that this calculation reproduces the TST rate so closely suggests the energy transfer rate is such that it corresponds roughly to the time taken to execute a single jump – but whilst the jump is underway energy exchange has not had time to take place, so this elastic band-structure based method can give good results.

David Glowacki asked: On the last slide you showed with the multiple wells, I'm curious whether you think that this sort of picture might qualitatively resolve the discrepancy between experiment and theory? The other question I have is related to one of the previous questions: are the barrier heights relatively consistent all the way through, or do you have any reason to believe that local fluctuations and/or defects might impact the relative barrier heights as the hydrogen hops between sites on the surface?

John Ellis responded: The last figure (Fig. 7) was designed to illustrate Kramers' ideas about the role of friction, in particular that the TST rate is only obtained for an 'intermediate' friction such that the adatom can travel from one site to a neighbouring one, *i.e.* make a single jump, before its energy is changed and it loses the energy to continue 'roller coasting' over the surface.

The issue of how constant the barrier heights are is one on which I have little information. The fact that the bandstructure TST method gives good agreement with the measured values implies that we are in this 'intermediate friction regime' which allows us to make a rough estimate of the friction (which corresponds to the rate at which the adatom's energy is changed/loses memory of what it was) experienced by atoms in the non-ground-state, 'mobile' states (*i.e.* reasonable bandwidth/group velocity states) to be somewhere in the range $0.4 \text{ ps}^{-1} < 4 \text{ ps}^{-1}$ in these systems. For the barrier to diffusion to change significantly one would need the two neighbouring atoms either side of the bridge site to move apart – a motion that would relate to the shortest wavelength surface phonons – which in these systems would have energies in the range 10–20 meV, *i.e.* 2.5 to 5 THz, which is inconveniently within the top end of our friction estimate – *i.e.* the barrier would undergo one complete 'cycle' in around the timescale of the atomic jump – so it is indeed possible that the adatoms' motion is affected by the variations in barrier height. The phonon frequencies are however on the upper range of our friction estimates, so maybe they are fast enough to simply average barrier height variations out during a jump. A contra-indicating piece of information to the notion

that barrier height fluctuations are significant, however, is again the good agreement of the band structure TST results with the experiment: if the adatom had to wait for a favourable phonon phase in order to make the jump this would produce a 'steric factor' that would reduce the jump rate. It is also significant that, as can be seen from Fig. 5, the experimental activation energy in the high temperature limit agrees with the results from both the 'frozen surface' band-structure and the 'fully mobile surface' PIMD methods. So on balance I would say that what evidence we have points to it being more likely that variations in the barrier height induced by phonon fluctuations do not play a major role in these systems. The surfaces are very highly ordered single crystal surfaces with very low defect densities, so the role of structural defects can be ruled out with a high probability. Clearly DFT could be used to see if the magnitude of adatom displacements expected for thermal phonon excitation would induce significant barrier height changes, but I am not aware of such calculations for these systems.