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Perspective

Perspective on "Exchange reactions with activation energy. I. Simple barrier potential for (H, H_2)"

Karplus M, Porter RN, Sharma RD (1965) J Chem Phys 43: 3259–3287

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Abstract. This paper provides an overview of the title paper by Karplus, Porter and Sharma, including a description of the history that led to this work, some details of the calculation and the results, and a discussion of subsequent developments in the field which were stimulated by this work.

Key words: Quasiclassical trajectory method – Reactive cross section – Thermal rate coefficient – Potential-energy surface – Quantum scattering

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The paper by Karplus, Porter and Sharma (KPS) [1] is, from my perspective, the most important early (pre-1970) piece of computational work in gas-phase chemical reaction dynamics. In it, the commonly used quasiclassical trajectory (QCT) method was described for three-dimensional atom–diatom reactive collisions (i.e., $A + BC \rightarrow AB + C$), and was applied to the $H + H_2$ reaction to determine cross sections and thermal rate constants. In 35 years of subsequent work on gas-phase reaction dynamics, the QCT method has remained largely the same, and it continues to be a standard tool for studying quantum state-resolved dynamical processes.

This paper also provided much of the early stimulus for developing semiclassical and quantum mechanical theories of chemical reaction dynamics, which is a research field that continues to be active. In addition, this paper provided the foundation for molecular dynamics studies of chemical reactions in condensed phases, including applications to gas–surface scattering and biomolecular simulation.

To understand the importance of this paper, let me give some background. The possibility of using first-principles theoretical methods to determine the rate constants for simple gas-phase bimolecular reactions became of interest shortly after the discovery of quantum mechanics in the 1920s. The reaction $H + H_2$ was a focal point of much of this work, due to the simplicity of the electronic Schrödinger equation (just three electrons), the simplicity of the nuclear motion (just three nuclei), and the fact that measurements of the thermal rate constant were available from studies of the conversion of para hydrogen into ortho hydrogen, and from studies of isotopic labeled reactions such as $D + H_2$ and $H + D_2$.

One important accomplishment of work on $H + H_2$ during the 1920s and 1930s was the development of a potential surface that determines the forces between the atoms during reaction. This was done for $H + H_2$ initially by London, Eyring and Polanyi (LEP) [2] using valence-bond methods. The resulting surface was not very accurate, but it was good enough to give useful qualitative information about the nature of nuclear motions during reactive collisions. In fact, in the mid 1930s, Hirschfelder, Eyring, and Topley [3] attempted to do the first classical molecular dynamics study of $H + H_2$ using this LEP surface. This required numerical computations to solve the classical equations of motion, and at the time these had to be done by hand and thus were very tedious. As a result, only a short segment of one trajectory was determined, and no results that could be compared with experiment were obtained.

Further developments in this field waited until computers were developed. In the late 1950s and early 1960s computer programs were developed to perform trajectory studies of several atom–diatom chemical reactions [4]. For the most part these calculations were simplified in important ways to make them feasible, such as by reducing the motions to one or two rather than three dimensions, or by greatly restricting the number of trajectories integrated so that only a coarse-grained description of the reaction was obtained. In addition, many of the early studies used inaccurate potential-energy surfaces, and so the results were of only qualitative use for interpreting experiments.

By the mid 1960s, computers had advanced to the point where a detailed three-dimensional classical molecular dynamics study of an atom–diatom reaction was feasible (although still requiring a substantial amount of programming and data processing). In addition the potential-energy surface for H + H_2 had been improved by Porter and Karplus [5] and others, such that it was now quite realistic (though still not chemically accurate). This set the stage for the work of KPS [1].

The KPS calculation was based on integrating Hamilton's equations of motion for the time evolution of the Cartesian components of the Jacobi coordinates that describe the three-atom system. A fourth-order Runge–Kutta method was used for the numerical integration, and the computations were done using an IBM 7090-4 computer at the IBM Watson Research Center and the Columbia Computing Center. The computation time per trajectory was listed as 10 s using a time step of 0.025 fs.

The QCT approach that was used by KPS involves choosing the initial H_2 vibrational energy to equal the quantum energy for the initial state of interest. The H_2 rotational angular momentum was correspondingly chosen to be an integer multiple of $\hbar$. The other variables such as vibrational and rotational phases, and the impact parameter were sampled by Monte Carlo methods, which means that they are chosen randomly from the appropriate probability distributions. The QCT procedure thus has the feature that it mimics quantum mechanics as far as the initial conditions are concerned but the collisions themselves are purely classical. No attempt was made in the KPS study to assign quantum numbers to the final conditions of the reactive trajectories, but this is now frequently done, and the term “QCT” commonly refers to calculations in which final quantum numbers are assigned based on the vibrational and/or rotational states of the products of the trajectory calculations [6].

The results presented by KPS were mostly in the form of integral cross sections as a function of collision velocity and thermal rate constants as a function of temperature. There were no experimental cross sections to compare with back then, so most of the analysis was concerned with the comparison of thermal rate constants with either experiment, or with other theories such as transition-state theory. The comparisons with experiment were actually quite good, but KPS included many “cautions” towards the end of their paper to note the many uncertainties associated with these comparisons. These uncertainties include errors in the potential surface used, uncertainties in the experimental results, and errors due to the use of classical mechanics. They conclude by saying that “no unequivocal answer [could] be given concerning ... the direct applicability of the present study to specific chemical reactions.” The authors were, in retrospect, far too pessimistic about the accuracy and usefulness of their results, as I now discuss.

There have been numerous tests since the KPS study of the QCT approach, mostly based on comparisons of QCT results with those from quantum scattering theory (QST) calculations for the same potential-energy surface. These scattering calculations involve solving the Schrödinger equation for the collision dynamics, which is the quantum mechanical analog of what KPS did with classical mechanics, and thus should provide rigorously correct results.

Many of the early comparisons between QCT and QST results suggested that there were serious errors in the QCT cross sections [7], but eventually it was discovered that the errors were actually in the quantum dynamics results. Once this problem was corrected [8], the comparisons of QCT and QST results were much better, with essentially quantitative agreement in the total reactive cross sections except at very low energies where barrier tunneling is important. Even more-detailed comparisons of QCT and QST results have been made more recently [9] using more-accurate potential-energy surfaces. These studies also include extensive comparison with recently measured experimental cross sections and thermal rate constant data [10]. These comparisons show unequivocally that the QCT method is capable of describing most aspects of the reaction dynamics with sufficient accuracy to match experimental data. Alternative algorithms to the QCT method have been proposed and tested (such as schemes for constraining zero-point energy throughout the collision event [11], and schemes for imposing constraints on final state energies (so as to correct for the lack of microscopic reversibility in the QCT method) [12]); however, the QCT method developed by KPS generally gives the best agreement with quantum cross sections [13].

The KPS paper stimulated research in several new directions, and ultimately spawned new fields. Many researchers, including Karplus, got interested in the development of QST of chemical reactions, and this led to accurate quantum descriptions of the H + H_2 reaction [8] a decade after the KPS paper. There was also significant interest in the application of QCT methods to gas-phase reactions other than H + H_2, and in fact this approach is now considered to be a standard research tool for studying gas-phase reaction dynamics of relevance to laser chemistry, combustion chemistry, atmospheric chemistry, and other applications.

Another direction of research that was fostered by the KPS work was the development of semiclassical theories of chemical reactions. This development arose because the QCT method is an ad hoc procedure for mimicking quantum effects in chemical reaction dynamics wherein quantization is imposed initially and finally but not in-between. In semiclassical methods, one imposes the $\hbar \to 0$ limit of quantum mechanics in a consistent way throughout the reactive collision process. The search for a consistent semiclassical theory eventually produced classical S-matrix theory [14], which is a topic of continuing interest in gas-phase dynamics [15], and it also led to the development of Gaussian wave-packet methods for simulating chemical reactions [16].

Finally, we should note that the success of the KPS work in describing gas-phase chemical reaction dynamics has stimulated continuing research aimed at using first-principles methods to describe reaction dynamics in gas–surface scattering, in biomolecular processes, and in other processes taking place in condensed phases [17].

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