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Perspective

Perspective on "Quantum mechanical reactive scattering for three-dimensional atom plus diatom systems. II. Accurate cross sections for H + H_2"

Schatz GC, Kuppermann A (1976) J Chem Phys 65: 4668–4692

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Abstract. An overview is given of the impact of the title paper on the field of quantum reactive scattering.

Key words: Quantum reactive scattering – Chemical reactions

In quantum reactive scattering the aim is to solve the Schrödinger equation for the nuclei involved in a chemical reaction. If the potential-energy surface or surfaces used in such calculations are accurate, and if the scattering calculations are performed with no approximations, then these computations should yield a variety of highly useful and reliable results. These include differential and integral cross sections selected in initial and final quantum states, and reaction rate constants. Application of the Born–Oppenheimer approximation separates the treatment of a reaction into solutions of two Schrödinger equations: first for the electrons at fixed nuclear positions, and then for the nuclei. Methods for calculating the potential-energy surface have been improved over many years but it was not until the 1976 paper by Schatz and Kuppermann on the simplest chemical reaction,

$$H + H_2 \rightarrow H_2 + H \ ,$$

that converged cross sections were reported from a quantum scattering calculation on a chemical reaction in three dimensions. This paper, therefore, set the scene for the modern theory of chemical reaction dynamics.

Prior to 1976 there had been several quantum scattering calculations on nonreactive molecular collisions [1] and on chemical reactions constrained to move in one dimension [2]. In addition there had been many classical trajectory calculations on chemical reactions in three dimensions [3] and a small number of quantum scattering calculations that modeled the three-dimensional $H + H_2$ reaction with approximations or with incomplete convergence [4–6].

The difficulty in performing quantum scattering calculations on chemical reactions in three dimensions is in obtaining a solution for the scattering wavefunction that is continuous from reactants to products and is also a function of all the energetically available ro–vibrational quantum states. In addition, to compute converged integral or differential cross sections to compare with the results of molecular beam experiments it is necessary to repeat the calculations for a range of total angular momenta, and the computations also have to be done for several different energies to average over the cross sections to obtain rate constants.

The $H + H_2 \rightarrow H_2 + H$ reaction problem was solved by Schatz and Kuppermann by using natural collision coordinates [7] that exploited the symmetry of the reaction to ensure the continuity of the scattering wavefunction between the three different arrangement channels of the reaction [8]. They also exploited the use of body-fixed coordinate systems [9] and a close-coupling expansion of the time-independent wavefunction that was first developed and applied to nonreactive scattering problems [10]. The potential-energy surface used in the scattering computations was a semiempirical one due to Porter and Karplus [11] as an accurate potential-energy surface based on high-quality ab initio computations was not available at that time. Thus, despite the convergence of the three-dimensional quantum scattering calculations, the cross sections and rate constants obtained were not expected to give very accurate comparisons with experiment; however, the results obtained served as benchmarks for the field of reactive scattering calculations and did much to stimulate the development of new methods of quantum reactive scattering and more accurate computations of potential-energy surfaces.

The Schatz-Kuppermann paper also produced new insight into chemical reactions that derived from the detail and reliability of their results. For example, a surprisingly strong sensitivity of the reaction cross section on the j and m_j rotational states of the reactants and products was discovered. In addition, the benchmark results demonstrated the importance of tunneling at low temperatures and provided the first rigorous test of the widely used quasiclassical trajectory [3], reduced dimensionality [12] and transition-state [13] methods for a three-dimensional reaction. The paper also gave the first rigorous quantum scattering calculation of a differential cross section for a reaction and the predicted strong backward peaking of the angular distributions agreed with experiment [14].

It was not long before other calculations followed on from the pioneering work of Schatz and Kuppermann. Their work stimulated the ab initio computation of a highly accurate potential-energy surface for the $H + H_2 \rightarrow H_2 + H$ reaction [15] that enabled reactive cross sections of a very high accuracy to be calculated [16]. However, despite intensive work by several groups, it took some time to go beyond $H + H_2$, even to the $D + H_2 \rightarrow HD + H$ reaction. The natural collision coordinate technique used by Schatz and Kuppermann proved difficult to extend to nonsymmetric reactions in three dimensions and, eventually, different coordinate systems and new methods were developed. A hyperspherical coordinate method [17], which treats the size of the reactive system as a collision coordinate, proved to be more general and has been applied to reactions such as $F + H_2 \rightarrow HF + H$ and $H + O_2 \rightarrow OH + O$ [18], and to four-atom reactions such as $OH + H_2 \rightarrow H_2O + H$ [19]. Variational methods, involving expansion of the wavefunction in asymptotic ro–vibrational states, were also successfully applied to several atom–diatom reactions [20]. In addition, powerful wavepacket techniques that solve the time-dependent Schrödinger equation were developed and applied to several three-atom and four-atom reactions [21]. Also, an absorbing-potential method was formulated that enabled the total reactive flux into particular arrangement channels to be calculated [22]. Furthermore, new quantum methods were developed to calculate rigorously the cumulative reaction probability (i.e. reaction probabilities summed over all reactant and product states) by considering only the region close to the transition-state geometry of a reaction [23].

Although these more recent methods are not based directly on the algorithm of Schatz and Kuppermann, the psychological impact of their paper was enormous as it showed for the first time that a chemical reaction in three dimensions could be treated to convergence using quantum reactive scattering theory. Several books, reviews, and collections of papers on this subject have subsequently been published [24–28], an international conference is held regularly on this topic[1], and quantum reactive scattering was a main component of a recent Faraday Discussion on chemical reaction theory [29]. Quantum reactive scattering is now the technique of choice for comparison with experiments on the detailed dynamics of chemical reactions. The method also enables rigorous rate constants to be calculated that have useful applications in areas such as combustion, atmospheric and astrophysical chemistry.

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[1] The Conference on the Quantum Theory of Chemical Reaction Dynamics has been held in Cambridge, UK (1990), Harvard, USA (1994), Nottingham, UK (1995), Telluride, USA (1997) and Perugia, Italy (1999)