REGULAR ARTICLE

Theoretical characterization of reaction dynamics in the gas phase and at interfaces

Hua Guo

Abstract Reaction dynamics is a central topic in physical chemistry, and tremendous progress has been made in theoretical characterization of gas phase and surface scattering processes. Here, an overview is given on several important frontiers represented by the following articles.

Keywords Reaction dynamics · Scattering · Potential energy surface

Dynamics of chemical reactions in the gas phase and at interfaces is of fundamental importance in physical chemistry. Since the advent of crossed molecular beam technique, it has become possible to experimentally measure almost all quantum state resolved attributes resulting from both reactive and non-reactive scattering (see, for example, Ref. [1]). These quantities, including translational, internal, and angular distributions of the products, provide a wealth of information concerning the interaction potential between the colliding partners. The ability to accurately measure scattering attributes with quantum state resolution challenges theoreticians to develop accurate and efficient methods for characterizing reaction dynamics. On the other hand, reliable theoretical predictions can in turn provide guidance to further experimental exploration. The intimate interplay between experiment and theory has led,

and will continue to lead, to deeper understanding of reaction dynamics in many molecular systems.

There are two major challenges in theoretical characterization of reaction dynamics. First, one has to establish an accurate global potential energy surface (PES) that covers the all necessary configuration space accessed by the scattering event. (In some systems where non-Born-Oppenheimer effects are important, one has to map out the non-adiabatic coupling as well). This is typically achieved by using a high-level electronic structure theory, followed by fitting the global PES. For atom–diatom reactions, for example, the ab initio points can be fit with the spline method. In larger systems, however, more sophisticated fitting methods are needed. The second challenge is the characterization of the reaction dynamics itself on the PES. As in other molecular processes, reaction dynamics is quantum mechanical in nature, and should be treated as such whenever possible. In many cases, nonetheless, classical mechanics with appropriate quantum modifications can also yield valuable and sometimes accurate information about reaction dynamics [2]. Here, we focus on the second challenge, namely theoretical characterization of reaction dynamics, assuming the relevant PES is known.

Since the first full-dimensional quantum scattering calculation on the $H + H_2$ reaction 35 years ago [3], tremendous progress has been made [4]. It is now routine to quantum mechanically compute nearly all observable attributes for atom–diatom reactive scattering events, even for those systems dominated by a long-lived reaction intermediate and those with no hydrogen atom [5]. While the time-independent scattering theory has made tremendous progress, it is the wave packet approach that has greatly extended our abilities to study complex reactions [6]. The basic idea is to propagate an initial state-specific wave packet from the reactant channel to the product

H. Guo (✉)
Department of Chemistry and Chemical Biology,
University of New Mexico, Albuquerque, NM 87131, USA
e-mail: hguo@unm.edu

channel, and to extract the necessary scattering information such as the S-matrix elements. Due to its time dependence, it is particularly suitable for direct reactions, which complete in a relatively short time. In addition, only one column of the S-matrix is calculated, which is less computationally demanding than that required for the entire S-matrix. Besides numerical efficiency, the wave packet approach is also physically intuitive. The crowning achievement of this approach is the recent work on the $H_2 + OH \rightarrow H + H_2O$ reaction, in which the exact quantum state-to-state differential cross sections were shown to be in excellent agreement with the latest crossed molecular beam experiment [7].

In this anniversary issue, Zhang and coworkers report a wave packet study on another tetra-atomic reactive system, namely the $OH + CO \rightarrow H + CO_2$ reaction. This is an important combustion reaction, representing the major production pathway for CO_2 in the flame. This exothermic reaction has a complex-forming mechanism, due to the existence of both *cis* and *trans* HOCO intermediates. Comparing with the direct $H_2 + OH$ reaction, its dynamics is much more challenging because of its involvement of three, instead of one, non-hydrogen atoms; as well as the deep HOCO potential wells. As a result, a huge number of basis functions and/or a large grid are needed to converge the scattering calculations. In addition, the reaction is essentially barrierless, necessitating a large number of partial waves to converge the cross sections. For these reasons, the work of Zhang and coworkers did not have the product state resolution. Nevertheless, this work represents the first full-dimensional quantum mechanical calculation of the total reaction cross section and rate constant for the $OH + CO$ reaction.

The high numerical costs in computing reaction cross sections for tetra-atomic systems underscores the bottleneck faced by conventional quantum mechanical approaches to reaction dynamics. In such a basis/grid-based approach, the size of the problem scales exponentially with the dimensionality of the system, and it is difficult to foresee the same kind of high-level treatment for higher dimensional systems in the near future. Consequently, it is highly desirable to explore alternative approaches. One possible solution is the multi-configuration time-dependent Hartree (MCTDH) method [8], which scales more favorably with dimensionality. Another approach resorts to the so-called Bohmian mechanics (also called quantum hydrodynamics), which is essentially a reformulation of time-dependent quantum mechanics [9]. Here, the wave packet is approximated by an ensemble of trajectories on the regular PES augmented by the so-called quantum potential, which is responsible for all quantum effects. This approach is very appealing because of the linear scaling of classical mechanics, which can easily handle larger

systems. It also offers a basis for more approximate quantum methods. However, the Bohmian approach is also fraught with difficulties, primarily due to the non-locality of its quantum potential. In this anniversary issue, progress in this direction is reported by two experts. Garashchuk discusses a Bohmian inspired imaginary time propagation method that allows the approximate calculation of the zero-point energy of large quantum systems up to 11 particles (33 dimensions). This is made possible by a low-order polynomial approximation of the quantum potential and its derivatives in Cartesian coordinates. Kendrick, on the other hand, proposes a numerical algorithm for propagating wave packet in the Bohmian formulation based on an iterative finite difference method. This method was demonstrated successfully in several model problems, including collinear reactive scattering. These advances hold promise for applications to larger systems in the future.

The final contribution by Troya deals with gas-surface collisional dynamics, which highlights the general methodology for describing extended systems. Due to the larger number of degrees of freedom, it is impractical to treat the dynamics quantum mechanically. As a result, the quasi-classical trajectory (QCT) method has been used to describe the dynamics. The appropriateness of classical mechanics in treating reaction dynamics has been extensively discussed in the literature [2], and it is widely accepted that such a treatment is reasonable, provided that quantum effects, such as tunneling and zero-point energy, are properly accounted for. QCT methods are particularly suitable for highly averaged quantities such as cross sections and rate constants. An added bonus is that the trajectories offer an intuitive description of the collisional encounters. In this particular contribution, the scattering of OH molecular from a fluorinated alkane self-assembled monolayer surface was investigated. Although no reactive channel is considered, this study addresses several important issues common in many surface processes, including reactions. Particular attention is paid to mechanistic questions, namely whether the scattering is direct or via surface trapping. In addition to the good agreement with experiment, such atomistic simulations provide valuable insights into microscopic details of the molecular encounters.

It is obviously impossible to cover the vibrant research area of reaction dynamics with only four articles. Nevertheless, these contributions, ranging from a state-of-the-art exact quantum scattering study based on the conventional basis/grid approach, the latest advances in Bohmian mechanics, to quasi-classical trajectory investigation of gas-surface scattering, offers some snapshots of the latest advances in theoretical characterization of gas phase and gas-surface reaction dynamics. Looking into the future, we expect more method development in quantum reactive scattering to mitigate the dimensionality bottleneck, as well

as various semi-classical and quasi-classical treatments of collisional events with accurate inclusion of various quantum effects. An interesting future research area is concerned with the role played by dynamics in solution phase and enzymatic reactions, which is believed so far to be amenable to transition-state theory [10]. However, there is an increasing body of evidence that dynamics might play an important role in these processes [11].

References

1. Yang X (2007) Annu Rev Phys Chem 58:433
2. Aoiz FJ, Banares L, Herrero VJ (2006) J Phys Chem A 110:12546
3. Schatz GC, Kuppermann A (1976) J Chem Phys 65:4642
4. Althorpe SC, Clary DC (2003) Annu Rev Phys Chem 54:493
5. Sun Z, Liu L, Lin SY, Schinke R, Guo H, Zhang DH (2010) Proc Natl Acad Sci USA 107:555
6. Zhang JZH (1999) Theory and application of quantum molecular dynamics. World Scientific, Singapore
7. Xiao C, Xu X, Liu S, Wang T, Dong W, Yang T, Sun Z, Dai D, Xu X, Zhang DH, Yang X (2011) Science 333:440
8. Beck MH, Jackle A, Worth GA, Meyer H-D (2000) Phys Rep 324:1
9. Wyatt RE (2005) Quantum dynamics with trajectories: introduction to quantum hydrodynamics. Springer, New York
10. Truhlar DG, Garrett BC, Klippenstein SJ (1996) J Phys Chem 100:12771
11. Hammes-Schiffer S, Benkovic SJ (2006) Annu Rev Biochem 75:519