

[The advent of electronic computers has made possible the study of molecular collisions theoretically by solving classical/quantal equations of motion. At least for a few elementary reactions, now the computational chemists can calculate reaction attributes that are befitting of this era of state-to-state chemistry. The author provides a bird's eye view of the developments and futuristic trends in this area along with special references to the work that is (being) done in his own laboratory. The author received the Young Scientist Medal for the year 1980 for his contributions in the area of theoretical molecular reaction dynamics.—Ed.]

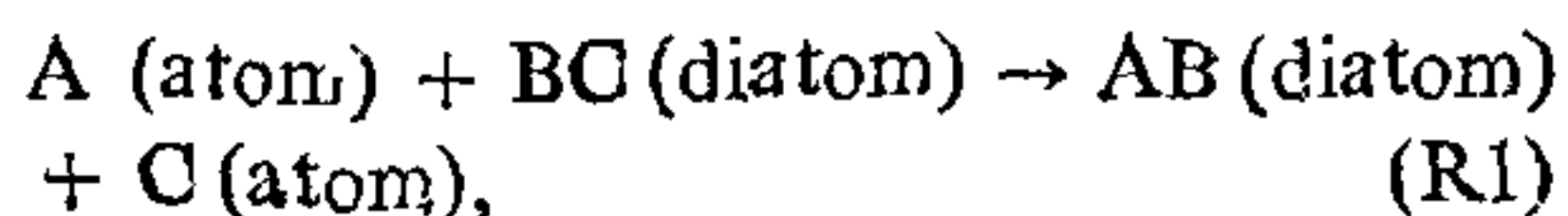
COMPUTER STUDIES OF MOLECULAR COLLISIONS AND CHEMICAL REACTIONS: A STATE-OF-THE-ART SURVEY*

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INTRODUCTION

ABOUT thirty years ago, even for the simplest bimolecular exchange reaction of the type



the measured rate constant k was related to the molecular parameters through a simple collision-theoretic expression,

$$k = p Z \exp(-E_a/RT),$$

where Z is the collision frequency. The Arrhenius activation energy $E_a = d(\ln k)/d(1/T)$ and the steric factor p is an adjustable parameter. Using transition state theory was a more sophisticated approach but the structural parameters of the transition state were not available from experiments, nor could they be computed *a priori*. Formalism for detailed studies of molecular collisions existed; but one could not turn the crank fast enough to get "numbers"

The situation changed in 1958, with the appearance of a paper by Wall, Hiller and Mazur¹. What was not possible until then became possible with the advent of modern electronic computers. Also, there was a dramatic change in the experimental study of chemical reactions at the molecular level. Following the development of detectors by Taylor and Datz², molecular beam studies became more common, infrared chemiluminescence was measured; lasers were used to excite the reagent molecules and to detect the product molecules by 'laser-induced fluorescence'. All these culminated in what is now called "state-to-state chemistry."³ Theory also has developed along the same lines.

WHAT IS INVOLVED AND WHAT HAS BEEN DONE?

Various stages in the computation of rate constant values starting from the first principles are outlined in Fig. 1. The quantitative relations among the various measurables can be found elsewhere⁴. Included in this figure are the links with experiments at various levels

*Discussion restricted to bimolecular collisions only.

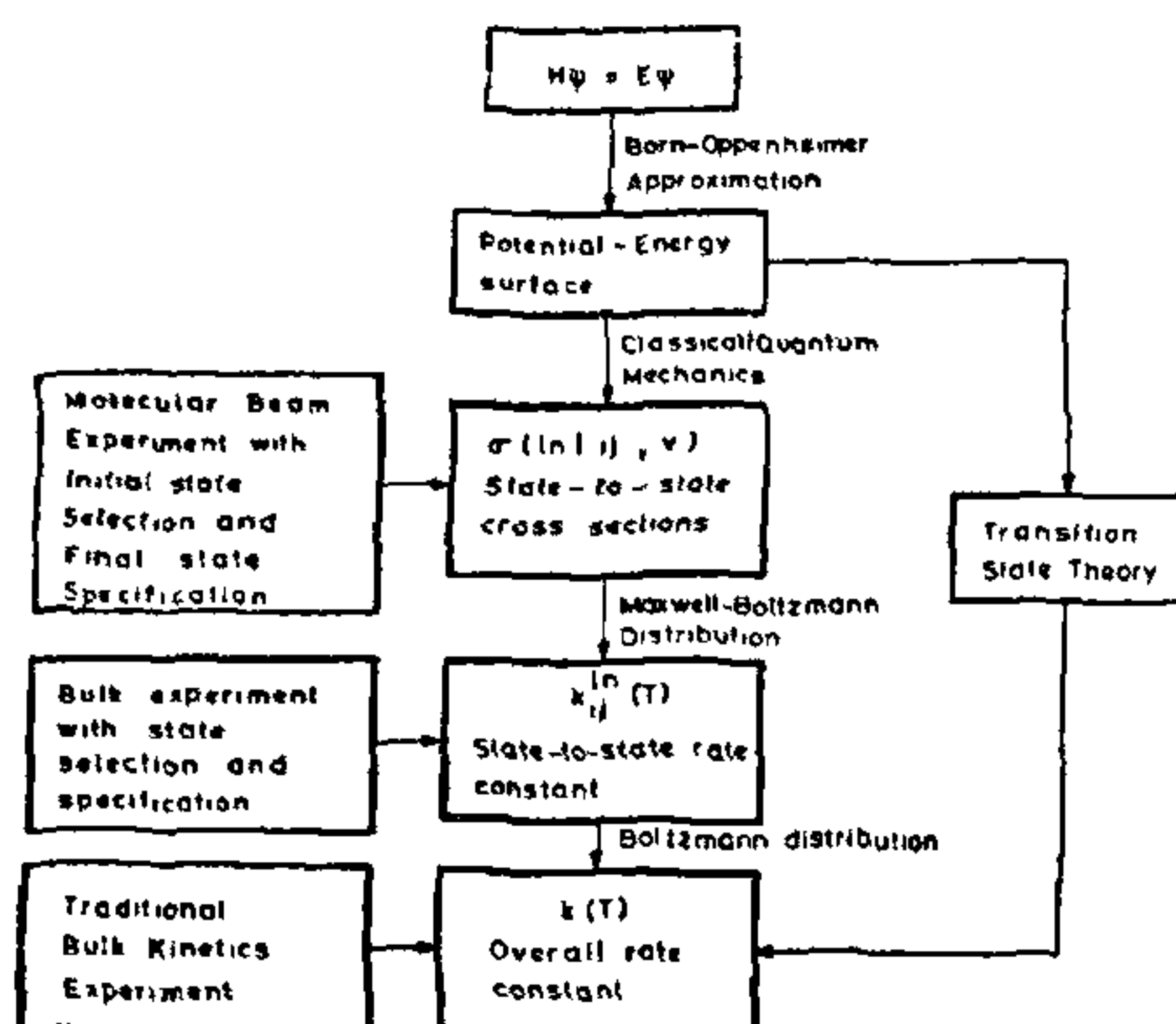


FIG. 1. Various stages in the computation of rate constant values starting from the Schrodinger equation for the system. Reagent and product internal states are labelled ij and ln respectively, v represents the relative velocity.

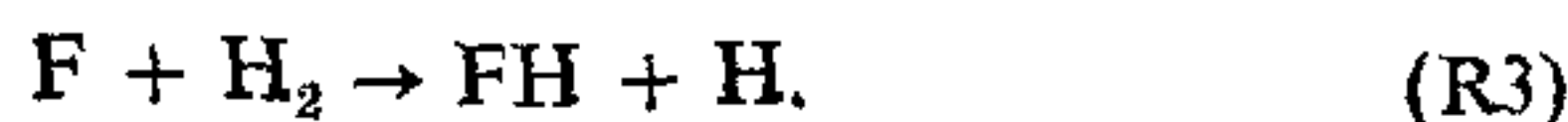
of sophistication. The adiabatic potential-energy surface (PES) for a chemical reaction is obtained by solving the time-independent Schrodinger equation within the Born-Oppenheimer approximation for different molecular conformations. The nuclear motion on the PES is followed by using either classical or quantum mechanics⁵. The former approach was initiated by Wall and coworkers¹. Soon results of extensive calculations for the reaction



and its analogs followed from three different research groups led by Bunker, Karplus and Polanyi⁶. This method came to be called the quasiclassical trajectory (QCT) method in which the atoms are treated as classical particles but the internal energies (rotation and vibration) are selected corresponding to the quantum mechanically allowed values in an *ad hoc* manner. Marcus, Miller and their coworkers⁷ examined the Feynman's path integral approach to quantum mechanics and tried to extract quantal information from classical trajectories. The result was the semiclassical S-matrix theory. It was gratifying

formally but prohibitive computationally for three-dimensional collisions. Nevertheless it made clear what was and what was not to be expected from the QCT studies. Except at threshold energies and when tunnelling, symmetry and resonance effects were important, the QCT results were in accord with the quantal results. Time-dependent quantum mechanical studies⁸ also reiterated the general validity of the QCT approach.

By the early seventies, QCT method had become a practical tool. Even though it was used to study the dynamics on model and approximate PES only, enough was learnt⁹ from it about the correlation between features of PES and the dynamical outcome. The results had found expression in the form of computer generated movies¹⁰ also. The agreement between theory and experiment was excellent at a qualitative and even semiquantitative level, particularly for reactions like (R2) and



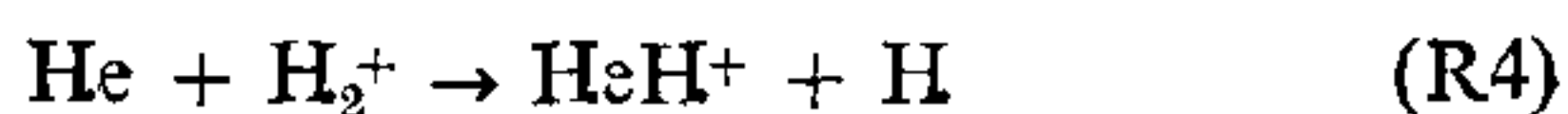
Simultaneously, researchers had extended the methodology to more complex systems as well. Bunker and Pattengill¹¹, and Raff¹² successfully completed a detailed QCT study of hot tritium + methane reaction and obtained results in agreement with experiment.

The late sixties and early seventies saw the time-independent quantum mechanical studies also of (R1) emerging but at the collinear level. Three-dimensional 'exact' (*i.e.*, converged) quantal scattering calculations were completed by Kuppermann¹³ and Wyatt¹⁴ and their coworkers in the year 1975 for the reaction (R2) on a realistic PES. Recently, similar results have been obtained for the reaction (R3) also. These results are the first milestones in the complete quantum mechanical study of chemical reactions and will serve as references against which new approximate and computationally faster theories could be tested. Already they have provided stimulus for the development of Franck-Condon-type theories¹⁵

which predict certain reaction attributes like product vibrational energy distribution using pocket calculators only.

The detailed dynamical studies led to a careful re-examination of the assumptions involved in the celebrated transition state theory (TST.) Miller¹⁶ and coworkers developed the quantum mechanical version of it. Recently, Truhlar¹⁷ and coworkers have developed the variational transition state theory which gives results better than the conventional TST for a large number of systems.

The quantum structural chemists had nearly perfected their tools by the early 1970s. The first PES of chemical accuracy (± 0.5 kcal. mol⁻¹) appeared¹⁸ in the year 1973 for reaction (R2) but was restricted to the collinear geometry. In the following years, the nonlinear collisions were also described for this reaction with comparable accuracy. Now nearly complete configuration-interaction surface is available for at least one more reaction¹⁹:



Slightly less accurate surfaces are available for a few other systems as well.

The classical and quantum mechanical scattering studies on adiabatic PES yield valuable insight into the factors governing the course of a chemical reaction, but are by no means restricted to that realm. They have been applied to vibrational and rotational energy transfer (RET) processes⁵ as well. Particularly for the latter, the computational methods have been developed very well. Exact quantal results are available for a selected few systems like H₂-He, H₂-Li⁺, on very accurate PES. The method has been extended to H₂-H₂, and HF-HF and a few other systems of astrophysical interest (e.g., H₂CO-He). Various approximate theories (effective potential, *J*_z-conserving, decoupled *I*-dominant and sudden approximations) have also been developed and they have reduced the computational time considerably, to the

extent that routine quantum mechanical studies of RET in A + BC collisions at suprathreshold energies have become possible. QCT studies also have led to results that are in accord with experiments. They have proved valuable in the formulation and testing of the various energy gap laws²⁰ for the RET processes.

The volume of theoretical and experimental state-to-state data was increasing so much that it was becoming impossible to keep up with. A compaction of data was badly needed and was provided by the Information-Theoretic Surprisal Analysis of Levine and Bernstein and their coworkers²¹. This also enabled the separation of dynamic and kinematic factors. The effect of changing collision partners²² in RET processes, for example, could be analysed in this framework.

So far we have mentioned only about the collision processes that occur on a single PES. When more than one electronic state is involved, the logical extension of QCT is the surface-hopping trajectory method²³. It has yielded results that are comparable with the experimental results for the reaction D⁺ + H₂ → DH⁺ + H (R5). Recently Baer²⁴ and others have formulated the quantum mechanical nonadiabatic theory and have obtained "numbers".

Another development of the last few years is the theory of "laser-assisted chemistry"²⁵ which examines the change in the dynamics due to the presence of a photon during the collision. The experimental tests of this theory are already underway²⁶.

WHERE ARE WE HEADING?

Measurements of state-to-state differential and integral cross-sections, rate constant data and the effect of reagent vibration, rotation and translation thereupon, are becoming available for a larger number of reactive and nonreactive systems. The corresponding theoretical studies²⁷ are leading to a better understanding of the influence of the PES

on the course of the collision. At least a few more exact quantum mechanical scattering calculations and a large number of QCT and approximate quantal studies are expected in the near future. Computation of PES of chemical accuracy are bound to come for a larger number of systems. A nagging question is, "How accurate should these *ab initio* surfaces be?". It is fairly straightforward and affordable to compute PES at the Hartree-Fock limit. To include the electron correlation term to obtain the nonrelativistic limit of the energy value requires configuration-interaction type calculations. These are prohibitively expensive and time consuming. An assessment of the effect of the (partial) inclusion of the correlation energy in reaction dynamics studies is needed; and has just begun for a few systems²⁸. When very accurate surfaces are computed, they ought to be utilized without any loss of accuracy in the scattering studies. Unfortunately, a real bottle neck lies here. PES calculations yield tables of PE values for a limited number of geometries. They have to be carefully interpolated analytically or numerically to obtain the PE values and their partial derivatives with respect to molecular coordinates for their use in quantal/classical calculations. Sometimes, small errors in interpolation leads to dramatically different dynamical results and defeat the purpose of painstaking PE calculations. Recent attempts to fit *ab initio* surfaces accurately have yielded encouraging results²⁹.

Application of QCT studies to $A + BCD$ type systems has been slow mainly because the classical actions corresponding to the normal modes of polyatomic systems are not separable. Recent research has led to the construction of "good" quantum numbers for these systems and a small number of papers on the $A + BCD \rightarrow AB + CD$ dynamics have started appearing³⁰.

Even the QCT studies of $A + BC$ collisions are time consuming. Therefore one likes to find ways of getting maximum information with

minimum effort. If a few trajectories are computed, the results analysed and the "pattern recognized", any need to complete additional trajectories will be eliminated³¹. Results could still be predicted within acceptable limits. If the first and a few higher moments (i.e., averages) of amounts of energy transferred are computed from a small number of trajectories, use of these constraints would lead to "Information-Theoretic Predictions". Initial results in this direction are encouraging³².

Exact three-dimensional quantum calculations for a few more reactive $A + BC$ systems are needed if only to test the approximate theories; we have started on such a study of (R4). Development of approximate theories will continue. Incorporating certain approximations in the 'exact' framework has already yielded encouraging results³³.

The field of computational study of molecular collisions has matured enough to go beyond the theoretician's favourite reaction (R2). Research in this area has already borne fruits in the form of chemical lasers and isotope separation through vibrational excitation.

In India, very little research is done in this area. Until recently, good computational facility was limited to one or two institutions. In the last couple of years, a significant number of fairly sophisticated computers have become available across the country. It is hoped that many investigators will be inspired to take active interest in following the "molecular dance" and unravel the mysteries of chemical reactions.

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