State-to-state chemistry: An *ab initio* approach

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Abstract. It has become possible in recent years to compute state-to-state reaction cross-sections and rate constants from first principles for a few elementary chemical reactions and for a few energy transfer processes. We illustrate the state-of-the art using examples of results obtained from our own laboratory.

Keywords. State-to-state reaction; reactive scattering; inelastic scattering; atom-diatom collisions.

1. Introduction

There was a time in the last century when it was thought, "Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry . . . If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible— it would occasion a rapid and widespread degeneration of that science" (Comte 1830). In contrast, in the early part of this century it was realized, "Insofar as we can accept quantum mechanics as exact, every problem of chemistry can be answered from direct calculation by a sufficiently skilful mathematician" (Eyring 1938). But accurate solutions to even simple chemical problems had to wait until the advent of modern electronic computers. To highlight the difficulties in solving problems of interest in the area of gas phase chemical kinetics, we must mention that although London (1929) published an approximate solution to the problem of potential-energy surface (PES) for the most elementary exchange reaction

$$H + H_2 \rightarrow H_2 + H, \tag{R1}$$

as early as 1929, it was only in 1973 that a PES of chemical accuracy (± 0.5 kcal mol^{-1}) for the collinear configuration was published (Liu 1973). It took another five years for the potential-energy (PE) values of comparable accuracy to be reported for noncollinear geometries (Siegbahn and Liu 1978). Various stages in the development of such an accurate PES for H_3 have been reviewed by Truhlar and Wyatt (1977).

Studies of the dynamics of elementary reactions did not wait until the availability of accurate *ab initio* surfaces. For example, Karplus *et al* (1965) computed the overall rate constant for the reaction (R1) on a 'reliable' surface (Porter and Karplus 1964) using the quasiclassical trajectory (QCT) method (Porter and Raff 1976; Truhlar and Muckerman 1979) almost twenty years ago. Results from converged three-dimensional (3D) quantum mechanical (QM) calculations (Kuppermann and Schatz 1975, 1976; Elkowitz and Wyatt 1975) on the same PES for the reaction (R1) were published nearly ten years ago and they have confirmed the earlier QCT results. Only preliminary results of an exact 3D QM calculation (Walker *et al* 1978) on the Siegbahn-Liu-Truhlar-Horowitz (SLTH) (Truhlar and Horowitz 1978, 1979) surface are available and they are similar to the

results on the Porter-Karplus surface. Rate constants computed by the QCT method on the SLTH surface for the ground vibrational state ($v = 0$) of H_2 have been reported recently (Mayne and Toennies 1981) and are in accord with the available experimental results summarized by Truhlar and Wyatt (1976). However, the enhancement of the rate constant caused by the vibrational excitation of H_2 from $v = 0$ to $v = 1$ as predicted by the QCT method is at variance with the enhancement reported from experimental studies (Kneba *et al* 1979; Glass and Chaturvedi 1982). Although approximate QM calculations (Sun *et al* 1980; Walker and Hayes 1983) suggest that part of the discrepancy is due to quantal effects, it is possible that the experimental results are also in error. Exact QM calculations on the SLTH surface for the $v = 1$ state of H_2 are needed to clarify the situation.

It is unfortunate that results of elaborate calculations of PES and dynamics for H_3 are to be compared with the experimental results at the level of rate constants which are averaged quantities (Polanyi and Schreiber 1974). It would be worthwhile to compare theoretical predictions with the experimental results at a much more detailed, state-to-state cross-section level. Such results are becoming available for reaction (R1) only recently (Rettner *et al* 1983). For certain other reactions, however, we have been closer to state-to-state chemistry for sometime now. That is, researchers have been able to select the vibrotational state of the reactants and/or follow the dynamics into specific vibrotational states of the products (Brooks and Hayes 1977; Zare and Bernstein 1980). In some cases, information on the effect of the relative orientation of reactants on the reaction probability (Beuhler *et al* 1966; Brooks 1976; Estler and Zare 1978), product angular distribution (Karny *et al* 1978) and product alignment (Prisant *et al* 1981) is also becoming available. Theory has kept pace with the experiment in the sense that although accurate *ab initio* PESs have not been available and exact QM calculations have not been possible for most of the reactions, considerable insight into the details of the state-to-state reaction dynamics has been gained using anything from simplistic model surfaces to fairly elaborate and 'reliable' *ab initio* surfaces, *via* QCT as well as approximate QM calculations. A knowledge of the state-of-the art of experimental and theoretical methodology and the present level of understanding of state-to-state reaction dynamics can be obtained from a variety of reviews and monographs in the area (for example, Polanyi 1972; Kuntz 1976; Brooks and Hayes 1977; Truhlar 1981; Bernstein 1982). Therefore, instead of attempting a comprehensive review of the field, which is well nigh impossible, we have chosen to illustrate the state-of-the art of the *ab initio* approach to a study of state-to-state chemistry citing some examples from our own laboratory.

2. Reactive scattering on an accurate surface

McLaughlin and Thompson (1979) published, a PES including nearly 90% of the correlation energy and therefore within $\pm 1.2\,\text{kcal mol}^{-1}$ of the "true" (non-relativistic) surface for the reaction

$$He + H_2^+ \rightarrow HeH^+ + H. \tag{R2}$$

This system is of fundamental interest as (i) it is endothermic, (ii) it belongs to the family of ion-molecule reactions and (iii) accurate state-selected reaction cross-sections are available for a variety of vibrational states of H_2^+ over a wide range of relative

translational energies (E_{trans}). Therefore it offers an ideal ground for testing our present day theoretical (computational) predictive ability at the state-to-state dynamics level.

We have fitted the *ab initio* surface for the reaction (R2) successfully (standard deviation of 0·04 eV) using an analytic function of Sorbie and Murrell (1975). How difficult it is to fit an *ab initio* surface in three independent variables is well known to the practitioners in the field. Details of the problems involved and how to circumvent them are described elsewhere (Sathyamurthy 1984). We only state here that by plotting a series of PE contours for different arrangements of the triatomic system and by a preliminary comparison of QCT results on the analytic surface with those on a splinefitted surface for the collinear geometry, we have ensured that we have an accurate fit of the surface (Tomi Joseph 1983).

As a first stage of our elaborate study on the system, we have computed the integral cross-section (σ_R) for the reaction (R2) for $v = 0$–5 over $E_{\text{trans}} = 1$–4 eV using the 3D QCT method and found a nearly quantitative agreement with the classic photo-ionization experimental results of Chupka and coworkers (Chupka and Russell 1968; Chupka *et al* 1969; Chupka 1972). We have found excellent agreement between theory and experiment in describing the complementary collision-induced-dissociation

$$\text{He} + \text{H}_2^+ \rightarrow \text{He} + \text{H}^+ + \text{H} \tag{R3}$$

reaction also. We find that our 3D QCT studies using the accurate analytic fit of the *ab initio* surface are able to predict the product energy and angular distributions also at a high E_{trans} of 3·58 eV as could be verified by a comparison of our results with the molecular beam results of Paćak *et al* (1977). Such a quantitative agreement between results from detailed *ab initio* computations and those from high resolution experiments vindicates our faith in the present level of sophistication in experiment and theory.

In order to make sure that the agreement between experiment and theory for the reaction (R2) is not fortuitous, we have initiated a quantal study of the reaction. As a first step, we have computed the collinear reaction probabilities in the range $1 \leqslant E_{\text{trans}} \leqslant 1$·4 eV using the R-matrix approach of Light and Walker (1976). We have found several oscillations in our results and we have attributed them to reactive resonances, by analysing Argand diagrams of the S-matrix elements. An interesting question is, which (if any) of these resonances would survive in the results of a 3D QM investigation of the reaction. Our studies to answer this question have just begun.

3. Reactive scattering on a 'reasonable' surface

Most of the time we are not in the same enviable position as we were in studying the reaction (R2); accurate *ab initio* surfaces for most reactions are not available and would not be available for years to come. However, for a few reactions, 'reasonable' *ab initio* surfaces are available. An example is the reaction

$$\text{Li} + \text{FH} \rightarrow \text{LiF} + \text{H}. \tag{R4}$$

This is a nearly thermoneutral reaction; but it has such a large PE barrier that in a classical mechanical study the system would behave like a substantially endothermic reaction. This would serve as a prototype alkali-hydrogen halide exchange reaction. Therefore any insight we can gain on the dynamics of this reaction would enable us to

understand the dynamics of the whole family of alkali-hydrogen halide exchange reactions.

A collinear *ab initio* PES for the reaction (R4) was published by Balint-Kurti and Yardley (1977) (BKY) and it has been fitted by 2D spline interpolation (McLaughlin and Thompson 1973; Sathyamurthy and Raff 1975, 1976) for use in a dynamical study. The most striking feature of the PES is its *sudden* character. That is, the change in the PES in going from the reactants to products is sudden. Results of our earlier investigations (Polanyi and Sathyamurthy 1978) on model sudden and gradual surfaces suggested that we should find a substantial vibrational enhancement of the reaction probability for (R4). That is precisely what our collinear QCT studies showed (NoorBatcha and Sathyamurthy 1982b). In addition, we noticed a marked vibrational threshold equal to the barrier height for the reaction. That this result was due to the sudden nature of the PES was reiterated by our finding a translational but no vibrational threshold for the reaction on a model London-Eyring-Polanyi-Sato surface with a gradual character (NoorBatcha and Sathyamurthy 1983).

Around the time the above collinear study was being completed, Chen and Schaefer (1980) published an *ab initio* PES for the reaction (R4) in three dimensions. The PE values were fitted to an analytic function by Carter and Murrell (1980). Collinear QCT results on the Chen-Schaefer-Carter-Murrell (CSCM) surface confirmed our results on the BKY surface. Therefore we went on to investigate the dynamics of the reaction in three dimensions, using the QCT approach, on the CSCM surface. While we noticed a substantial vibrational enhancement, there was no evidence for a vibrational threshold to the reaction in three dimensions. This was attributed to the fact that the barrier height for the reaction decreased as the approach angle of Li to FH was decreased from 180° such that the reaction was dynamically allowed at the lowest energy values at which we investigated the dynamics. Also, the surface became less sudden as the LiFH angle was decreased from 180°. We must mention here that at $E_{trans} = 8.7$ kcal mol^{-1}, for $v = 0, J = 0$ of HF, the computed σ_R of 0.75 ± 0.24 Å^2 is in excellent agreement with the σ_R value of 0.94 Å^2 obtained by Becker *et al* (1980) from a molecular beam experiment..Our prediction of a predominant backward scattering of the product LiF molecule is also in agreement with the beam finding, thus lending credence to the quality of the PES and the validity of our QCT results. Therefore we thought that it would be worthwhile to investigate the effect of reagent rotation on the cross-section for the reaction and found some very interesting results (NoorBatcha and Sathyamurthy 1982a, 1983). For $v = 0$, at $E_{trans} = 8.7$ kcal mol^{-1}, σ_R increased slightly with increase in J from 0 through 9, but more than what we would expect from energy considerations based on the effect of increase in E_{trans} to 20.46 kcal mol^{-1} on σ_R and from the increase in the number of available product states from a phase space theory viewpoint (Pechukas *et al* 1966; Shukla and Sathyamurthy 1984). For $v = 2$, the effect of J on σ_R was much more dramatic. At $E_{trans} = 8.7$ kcal mol^{-1}, as J was increased from 0 to 5, σ_R decreased dramatically and then increased with increase in J to 7. This was followed by a decline and possibly a levelling off of σ_R with further increase in J to 9 and 15.

These QCT results are qualitatively in agreement with the results obtained from molecular beam/laser experiments (Dispert *et al* 1979; Man and Estler 1981; Heismann and Loesch 1982; Hoffmeister *et al* 1983) and chemiluminescence depletion studies (Blackwell *et al* 1978) of other related reactions. From a detailed investigation of the effect of initial orientation on the reaction cross-section and from an analysis of individual trajectories, we (NoorBatcha and Sathyamurthy 1982c) attributed the initial

decline in $\sigma_R(J)$ to the disruption of the preferred orientation for the reaction by rotation and the subsequent increase in $\sigma_R(J)$ to the molecule coming back to the proper orientation with further increase in J. At very high J, the molecule is rotating so fast that the incoming atom sees only a 'blur' and the reaction cross-section levels off (Dispert *et al* 1979). This interpretation is particularly meaningful for the family of reactions belonging to the mass combination

$$H + HL \rightarrow HH + L$$
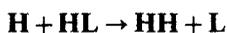
where **H** and **L** represent heavy and light atoms respectively. Such reactions are dominated by planar collisions as is evident from $|\vec{L}| \rightarrow |\vec{J'}|$ correlation (NoorBatcha and Sathyamurthy 1983), where L and J' refer to the orbital angular momentum of the reactants and the rotational angular momentum of the product molecule respectively. The effect of reagent rotation on reaction cross section is a very interesting subject. The amount of experimental and theoretical results available on the topic is limited and has been reviewed recently (Sathyamurthy 1983). Hence we will not dwell upon this topic any further.

4. Inelastic scattering in atom-diatom collisions

In recent years, considerable amount of data has accumulated on the vibrational inelastic scattering in atom-diatom collisions and the subject has been reviewed by others (for example, Toennies 1976; Schinke and Bowman 1983). We only mention here that the QM close-coupling calculations for the inelastic scattering are much more tractable than those for the reactive scattering. Still considerable insight into the dynamics of inelastic collisions is gained by a QCT study. For instance Choi and Tang (1975) had shown that the differential and integral cross-sections for rigid rotor

$$H_2(J_i = 0) + H \rightarrow H_2(J_f = 2) + H$$
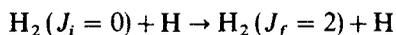
are sensitive to the features of the anisotropy of the potential. We (Margolies *et al* 1983) have been able to show that this can be attributed to the changing ellipticity of the PE contours for the rigid rotor H_2–H system.

While investigating the reactive scattering in Li + FH collisions we have also computed rotationally inelastic integral cross sections for $v = 2$, $J = 0$ and E_{trans} = 8·7 kcal mol^{-1} using the CSCM surface (NoorBatcha 1982). We are in the process of comparing these results with those on the rotational inelasticity in rigid rotor HF–Li collisions on the CSCM surface and on an *ab initio* surface of Lester (1970) with the aim of (i) further understanding the sensitivity of the dynamics to the features of the PES and (ii) evaluating the effect of vibration-rotation interaction on the rotational inelasticity. These results can also be compared with a wide range of rotational inelastic cross section data for the related HF–M (=He, Ne, Ar, Kr) systems (Barnes *et al* 1980, 1982; Viswanathan *et al* 1981; Thompson 1982, 1983).

5. Inelastic scattering in larger systems

In contrast to the QM calculations whose complexity increases disproportionately with an increase in the number of available final states and the size of the system, the QCT method can be applied with almost as much ease to a larger system as for a smaller

system. We were able to compute successfully state-to-state integral cross-sections for different initial rotational states at two different E_{trans} for CO_2–H_2 collisions (Sathyamurthy and Raff 1980). We could only compare our results with QCT results on other CO_2-M(=He, Ar) systems as there were no experimental results available at that time. It is likely that molecular beam results on CO_2-H_2 collisions will become available in the near future (Buck 1982).

6. Analysis of state-to-state data

With an increase in the volume of theoretical and experimental state-to-state cross-section and rate constant data becoming available for a large number of systems, under a variety of conditions, their analysis through compaction, digestion and interpretation was becoming a serious problem. There was also the interesting question of how much more 'information' was going to be available by performing 'one more experiment' on any system. Levine and Bernstein (1974) tried to provide an answer to these problems through their information theoretic analysis (Levine 1978; Levine and Kinsey 1979). That is, one compares the observed (computed) cross-sections (and rate constants) with a priori values of σ° and k° computed from a consideration of the number of available product states, at a given energy. If a plot of the surprisal $I = \ln(\sigma/\sigma^\circ)$ (or $\ln k/k^\circ$) as a function of the variable under consideration, say v' or J', yielded a straight line with a zero slope, there is no information gained by performing the experiment (dynamical calculation) as the results could have been predicted from statistical considerations. If, on the other hand, one obtained a linear surprisal plot with a non-zero slope, there was some dynamical information contained in the result, but it was contained in one parameter λ_1; one could have predicted the results using an energy constraint, for example. If the surprisal plot was non-linear, more than one parameter would be needed to fit the data and one has to discern additional constraints on the dynamics.

Initially we (Gayatri and Sathyamurthy 1980) were able to analyse considerable amount of data on rotational inelastic cross-sections for CO_2-M and H_2-M systems using an exponential gap relationship (Polanyi and Woodall 1972). We were able to compact the data and study the dependence of the rotational inelasticity on factors like initial E_{trans} and rotational state of the rotor, intermolecular potential and the collision partner by focussing attention on one (exponential) parameter. Soon, it became clear that the state-to-state rotational inelastic cross-section values could not be adequately represented by an exponential gap relationship and that a power gap law was needed (Brunner et al 1978). Analysis of our results for CO_2-H_2 collisions revealed that two different 'powers' were needed for two different ranges of ΔJ values (NoorBatcha and Sathyamurthy 1981). Subsequently we have found this behaviour to be valid for OH-Ar and HF-Li system also (Raghavan et al 1984). Tentatively we have attributed the two different powers to two different (energy and angular momentum) constraints. A detailed study is in progress.

The fact that the angular momentum constraint plays an important role in deciding the dynamics has become clear from an analysis of product energy distribution for the reactive Li + FH collisions also. A traditional surprisal plot yields a straight line for $v = 0$, $J = 0$ at $E_{trans} = 8.7 \, \text{kcal mol}^{-1}$, but with increase in v and E_{trans}, the plot becomes distinctly nonlinear and this is in keeping with the $|\vec{L}| \rightarrow |\vec{J'}|$ correlation for

this system. A more detailed analysis of our results in terms of the angular momentum constraint is in progress.

7. What happens during a collision? or Spectroscopy of the transition state

In addition to computing reliable state-to-state cross-section values and compacting them in a meaningful way, it is of utmost importance to study and understand what happens during the collision. In this context, the QCT method has contributed a great deal in the last two decades. By a careful examination of individual trajectories, Polanyi and coworkers (Polanyi 1972; Polanyi and Schreiber 1974; Polanyi and Sathyamurthy 1978) have been able to relate the features of the potential-energy surface to the dynamical outcome for several systems. Recently Polanyi and coworkers have carried this one step further. By constructing a probability density function for the transition state in the configuration space and assuming a vertical electronic transition, they could compute the absorption spectrum of the transition state (Polanyi and Wolf 1981). Mayne *et al* (1983a, 1983b) have carried out the dynamics for the reaction (R1) on the chemically accurate SLTH surface and using a variety of model upper surfaces and a diatomics-in-molecules representation of the upper state that correlates with the $2p$ state of the H atom, they could predict the 'wings' to the Lyman-α absorption line. They could also show that most of the wings survive on vibrational and translational excitation of the reactants and on inclusion of nonlinear collisions.

The QM approach that is directly comparable to the QCT method, is the method of time-evolution of the wave-packet (McCullough and Wyatt 1969, 1971; Kellerhals *et al* 1976; Agrawal and Raff 1981). By suitably constructing the wavepacket representing the reactants and numerically solving the time-dependent Schrödinger equation using the SLTH surface we could construct the QM probability density function for $H_3^{\ddagger}$. By assuming a vertical transition to the upper electronic state (see above), we have obtained the wings to the Lyman-α absorption line for $H + H_2$ collisions (Agrawal *et al* 1984). A detailed study of the implications of our results to the possible experimental determination of the spectrum of the transition state for H_3 and other systems is in progress.

8. Conclusion

We have tried to illustrate in this article that we have finally arrived at an era in which state-to-state rate observables could be computed *ab initio* for at least a few elementary reactive as well as non-reactive systems. We are in a position to ask and answer many questions about the dynamics that could not be answered a decade ago. The time is ripe for us to reap the full benefit of elaborate dynamical calculations which cause nightmares to most practicing chemists.

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