

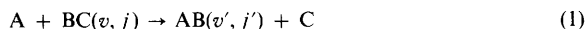
4 Quantum Calculations on Reactive Collisions

By D. E. MANOLOPOULOS and D. C. CLARY

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW

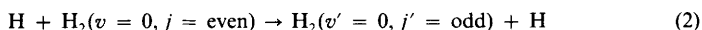
1 Introduction

The detailed study of the dynamics of simple chemical reactions in the gas phase is a major area of modern physical chemistry. Experimental progress in this field has now developed to such an extent that it is possible to study the state-to-state dynamics of atom-diatom reactions such as



where (v, j) labels a ro-vibrational state of the reactant molecule BC and (v', j') is a ro-vibrational state of the product molecule AB . This experimental work has stimulated much recent theoretical research into developing exact quantum mechanical methods and performing calculations on the dynamics of reactions in three dimensions (3D). Not only does this theory provide results for comparing with the experimental data on state-to-state dynamics, but it also provides a first principles approach for predicting rate coefficients over a wide range of temperatures. Developments in theoretical reaction dynamics should therefore be of interest to a variety of chemists.

Two books, published in 1985 and 1986, describe the state of the theory of chemical reaction dynamics up to that time.^{1,2} Accurate quantum mechanical calculations had then only been performed on the simplest 3D chemical reaction



although classical trajectory calculations were already possible on a wide range of reactions, including those involving polyatomic molecules. Since 1986 there has been remarkable progress in the quantum mechanical description of 3D chemical reactions. Indeed several important 'benchmark' calculations, on reactions considerably more difficult than (2), have already been performed. The aim of this chapter in *Annual Reports* is to review this recent progress in theoretical reaction dynamics.

The most detailed quantity that can be measured in a reaction dynamics experiment is the *differential cross section*³

¹ 'Theory of Chemical Reaction Dynamics' ed. M. Baer, CRC Press, Boca Raton, 1985.

² 'The Theory of Chemical Reaction Dynamics' ed. D. C. Clary, Reidel, Dordrecht, 1986.

³ R. D. Levine and R. B. Bernstein, 'Molecular Reaction Dynamics and Chemical Reactivity', Oxford University Press, Oxford, 1987.

$$\frac{d\sigma_{v,j \rightarrow v',j'}(\theta, E)}{d\Omega} \quad (3)$$

which gives a measure of the probability of producing the product state (v', j') from the reactant state (v, j) with a solid scattering angle $\Omega = (\theta, \phi)$ and fixed collision energy E . Crossed molecular beam experiments enable these differential cross sections to be fully resolved with respect to θ . However, averaging over the scattering angle gives the *integral cross section*³

$$\sigma_{v,j \rightarrow v',j'}(E) = 2\pi \int_0^\pi \frac{d\sigma_{v,j \rightarrow v',j'}(\theta, E)}{d\Omega} \sin \theta \, d\theta, \quad (4)$$

which can in principle be measured in less sophisticated bulk experiments. Thermal rate constants to specified product states are obtained by Boltzmann averaging these integral cross sections over the initial ro-vibrational state (v, j) and collision energy E . These rate constants can then be summed over all possible product states, (v', j') , to give the total reactive thermal rate coefficient $k(T)$. This thermal rate coefficient, in turn, can be measured quite directly in a bulb.

The theoretical methods reviewed in this chapter produce all of these quantities, ranging from state and energy selected differential cross sections to temperature dependent rate coefficients, in essentially a single set of calculations. Thus the theory of chemical reaction dynamics provides a crucial link between the results obtained in detailed state selective molecular beam experiments and thermally averaged bulb measurements. This unifying feature of the theory is in fact well illustrated by the diversity of the calculations described below.

While exact quantum mechanical methods are now well established for solving inelastic scattering (energy transfer) problems,⁴ it is really only very recently that practical and general quantum mechanical methods for the 3D reactive scattering problem have begun to emerge. The reason for this comparatively slow progress is that the coordinates which most conveniently describe the reactants of a chemical reaction are not particularly convenient for describing the products, and *vice versa*. Therefore, in order to obtain a complete description of the reactive scattering event, one has either simultaneously to retain *all* convenient sets of coordinates, both for the reactants and the products, or else to define a new set of (inevitably more complicated) coordinates which somehow encompass all possibilities at once. While each of these approaches has its pros and cons it is clear that new technical difficulties, over and above those encountered in the simpler inelastic case, will inevitably arise. In short it was not until the recent advent of large memory supercomputers that these new technical difficulties could routinely be overcome.

One might well wonder, since classical trajectory calculations on quite complicated reactions have been performed for some time,⁵ why the coordinate problem described above really is so obtrusive in the quantum mechanical case. The reason for this is simply that quantum mechanical calculations must, by virtue of the Uncertainty Principle, describe *all* regions of the available coordinate space at once. Classical

⁴ See, for example, D. Secrest in 'Atom-Molecule Collision Theory: A Guide for the Experimentalist', ed. R. B. Bernstein, Plenum, New York, 1979, chap. 8.

⁵ See, for example, D. G. Truhlar and J. T. Muckerman in 'Atom-Molecule Collision Theory: A Guide for the Experimentalist', ed. by R. B. Bernstein, Plenum, New York, 1979, chap. 16.

trajectory calculations effectively access only a *single point* in this space at a time, which by comparison is a great deal easier to arrange. In fact the coordinate problem encumbers classical calculations so little that just about *any* well defined (e.g. Cartesian) coordinate system will do.

In view of the tremendous progress made in quantum reactive scattering theory during the past three years, we have split the remainder of this chapter into several distinct parts. The first three of these parts deal with different approaches to the coordinate problem described above. Thus Section 2 summarizes the recent progress using natural collision coordinates,^{6,7} Section 3 discusses various hyperspherical coordinate schemes,⁸⁻¹⁴ and Section 4 describes variational approaches based on the simultaneous use of Jacobi coordinates in each of the chemical arrangements involved.^{15,16} The emphasis throughout these sections is placed on calculations with the different methods that have actually been performed to date.

Almost all of the methods described in Sections 2 to 4 use time-independent scattering theory, and our review of the 'exact' calculations performed using these methods is confined to 3D atom-diatom reactions. Unfortunately this still leaves several 'loose ends', including recent advances in the time-dependent wavepacket method,¹⁷⁻¹⁹ an optical potential formulation which effectively confines the reactive scattering calculation to a single arrangement,²⁰⁻²² and approximate quantum studies of more complicated (*i.e.* four atom) reactions.^{23,24} However, these topics, which are at the frontier of the field as we move into the 1990's, will surely be reviewed more fully in time. Here we shall simply end, in Section 5, by summarizing several important problems which remain to be solved.

2 Natural Collision Coordinates

The earliest exact 3D quantum reactive scattering calculations were those of Kuppermann and Schatz,²⁵ who reported converged integral and differential cross sections for the $\text{H} + \text{p-H}_2 \rightarrow \text{o-H}_2 + \text{H}$ reaction, at a range of collision energies above the

⁶ R. A. Marcus, *J. Chem. Phys.*, 1966, **45**, 4493.

⁷ M. S. Child, 'Molecular Collision Theory', Academic Press, London, 1974, chap. 10.

⁸ L. M. Delves, *Nucl. Phys.*, 1959, **9**, 391; 1960, **20**, 275.

⁹ F. T. Smith, *J. Math. Phys.*, 1962, **3**, 735; R. C. Whitten and F. T. Smith, *J. Math. Phys.*, 1968, **9**, 1103; R. C. Whitten, *J. Math. Phys.*, 1969, **10**, 1631.

¹⁰ A. Kuppermann, *Chem. Phys. Lett.*, 1975, **32**, 374.

¹¹ C. A. Mead, *Chem. Phys.*, 1980, **49**, 23; *J. Chem. Phys.*, 1980, **72**, 3839.

¹² B. R. Johnson, *J. Chem. Phys.*, 1980, **73**, 5051; 1983, **79**, 1906, 1916.

¹³ R. T. Pack, *Chem. Phys. Lett.*, 1984, **108**, 333.

¹⁴ G. C. Schatz, *Chem. Phys. Lett.*, 1988, **150**, 92.

¹⁵ W. H. Miller, *J. Chem. Phys.*, 1969, **50**, 407.

¹⁶ M. Baer and D. J. Kouri, *Phys. Rev. A*, 1971, **4**, 1924; *J. Chem. Phys.*, 1972, **56**, 4840; *J. Math. Phys.*, 1973, **14**, 1637.

¹⁷ R. Kosloff and D. Kosloff, *J. Chem. Phys.*, 1983, **79**, 1823; R. Kosloff, *J. Phys. Chem.*, 1988, **92**, 2087.

¹⁸ D. J. Kouri and R. C. Mowrey, *J. Chem. Phys.*, 1987, **86**, 2087; Y. Sun, R. C. Mowrey, and D. J. Kouri, *J. Chem. Phys.*, 1987, **87**, 339; Y. Sun, R. S. Judson and D. J. Kouri, *J. Chem. Phys.*, 1989, **90**, 241.

¹⁹ J. Z. H. Zhang, *Chem. Phys. Lett.*, 1989, **160**, 417; *J. Chem. Phys.*, 1990, **92**, 324.

²⁰ D. Neuhauser and M. Baer, *J. Chem. Phys.*, 1989, **90**, 4351; 1989, **91**, 4651.

²¹ D. Neuhauser and M. Baer, *J. Phys. Chem.*, 1989, **93**, 2872; 1990, **94**, 185.

²² D. Neuhauser, M. Baer, R. S. Judson, and D. J. Kouri, *J. Chem. Phys.*, 1989, **90**, 5882.

²³ A. N. Brooks and D. C. Clary, *J. Chem. Phys.*, 1990, **92**, 4178.

²⁴ Q. Sun and J. M. Bowman, *Int. J. Quantum Chem. Symp.*, 1989, **23**, 115; *J. Chem. Phys.*, 1990, **92**, 1021.

²⁵ A. Kuppermann and G. C. Schatz, *J. Chem. Phys.*, 1975, **62**, 2502; 1976, **65**, 4642, 4668.

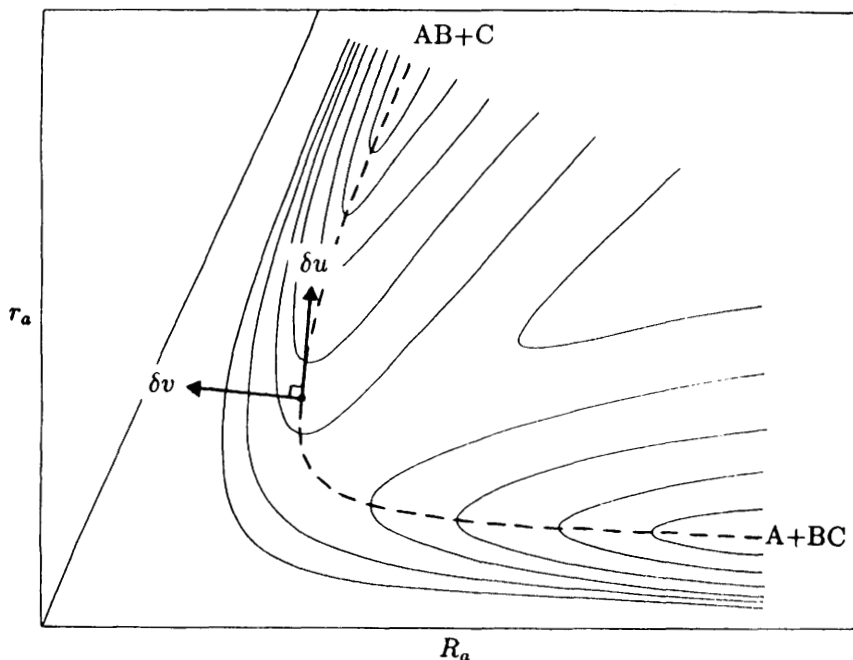


Figure 1 Increments of the translational (u) and vibrational (v) natural collision coordinates for collinear $A + BC \rightarrow AB + C$ reactive scattering. The axes labelled R_a and r_a denote mass-scaled Jacobi coordinates of the reactant arrangement $a(A + BC)$. These coordinates are defined in terms of the usual (unscaled) atom–diatom and diatomic displacements, R'_a and r'_a , as

$$R_a = \lambda_a R'_a, \quad r_a = \lambda_a^{-1} r'_a$$

where

$$\lambda_a = \left[\frac{m_A(m_B + m_C)}{\mu(m_A + m_B + m_C)} \right]^{1/2}$$

and μ is the three-atom reduced mass in equation 8. The faint solid lines in the plot are contours of the collinear interaction potential $V(R_a, r_a)$. This interaction potential has vibrational valleys in the reactant and product arrangement channels, and a saddle point somewhere along the dashed minimum energy path between the two.

reaction threshold, on the Porter–Karpus (PK2) potential energy surface.²⁶ Similar integral cross section calculations, but this time with a few minor dynamical approximations, were published simultaneously by Elkowitz and Wyatt.²⁷ A few years later these calculations were also repeated, on the improved Liu–Siegbahn–Truhlar–Horowitz (LSTH) potential energy surface,²⁸ by Walker, Stechel, and Light.²⁹ All

²⁶ R. N. Porter and M. Karplus, *J. Chem. Phys.*, 1964, **40**, 1105.

²⁷ A. B. Elkowitz and R. E. Wyatt, *J. Chem. Phys.*, 1975, **62**, 2504; 1975, **63**, 702.

²⁸ P. Siegbahn and B. Liu, *J. Chem. Phys.*, 1978, **68**, 2457; D. G. Truhlar and C. J. Horowitz, *J. Chem. Phys.*, 1978, **68**, 2466; 1979, **71**, 1514E.

²⁹ R. B. Walker, E. B. Stechel, and J. C. Light, *J. Chem. Phys.*, 1978, **69**, 2922.

three of these early $\text{H} + \text{H}_2$ calculations used extensions of the 'natural collision coordinates' introduced by Marcus,⁶ which we shall now very briefly describe.

For the simple case of a collinear atom-diatom reaction the natural collision coordinates swing smoothly from the reactants, $\text{A} + \text{BC}$, to the products, $\text{AB} + \text{C}$, as shown in Figure 1. Here δu is an increment of the 'translational' coordinate u , which asymptotically describes a mass-scaled separation between the atom, A or C, and the diatom, BC or AB. It is along this coordinate, from minus infinity to plus infinity, that the reaction actually proceeds. Similarly δv is an increment of the 'vibrational' coordinate v , which asymptotically describes a mass-scaled separation of the two atoms in the diatomic, BC or AB. The vibrational transitions that occur during the course of the reaction are easily rationalized in terms of coupling between the nuclear motions along u and v , one convenient model of which is based simply on the curvature of the reaction path.⁷

This easy physical interpretation of natural collision coordinates, combined with the fact that the translational motion along the reaction path can be solved using essentially standard inelastic scattering techniques,^{30,31} led to the success of the early $\text{H} + \text{p-H}_2 \rightarrow \text{o-H}_2 + \text{H}$ calculations and appeared to bode well for future applications of the approach.³² Unfortunately, attempts to generalize methods based on these coordinates beyond the simplest 3D reaction soon ran into technical difficulties which seemed impossible to overcome. These difficulties are not immediately apparent in the simple collinear model of Figure 1, but the following two observations should at least give the general idea:

(a) For an $\text{A} + \text{BC}$ atom-diatom reaction in 3D, at each value of the conserved total angular momentum quantum number J , the vibrational coordinate v in Figure 1 becomes a 2D (ro-vibrational) surface in the 3D internal coordinate space which specifies the size and shape of the three-atom triangle. This surface typically has quite complicated metric properties,³³ which in turn lead to lengthy algebra in the development of any new numerical approach.

(b) In general a third ($\text{B} + \text{CA}$) arrangement must also be considered in 3D, and this makes the idea of a translational 'reaction coordinate' somewhat more difficult to grasp. In practice one can avoid the problem by introducing 'matching surfaces' between the three arrangements, but this is a great deal easier to do for the symmetric $\text{H} + \text{H}_2$ reaction than it is for anything else.

Only very recently, after much concentrated effort by Light and coworkers in Chicago, have these tremendous technical difficulties finally been overcome. Two papers published by Webster and Light at the beginning of 1989, in which they describe a complete and general 3D atom-diatom reactive scattering methodology³⁴ and apply it to the calculation of $J = 0$ reaction probabilities for the seven deuterium substituted isotopomers of $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$,³⁵ represent the culmination of a project that has lasted more than a decade.²⁹⁻³³ Although these calculations were quite

³⁰ J. C. Light and R. B. Walker, *J. Chem. Phys.*, 1976, **65**, 472; E. B. Stechel, R. B. Walker, and J. C. Light, *J. Chem. Phys.*, 1978, **69**, 3518.

³¹ J. C. Light, R. B. Walker, E. B. Stechel, and T. G. Schmalz, *Comp. Phys. Comm.*, 1979, **17**, 89; J. V. Lill, T. G. Schmalz, and J. C. Light, *J. Chem. Phys.*, 1983, **78**, 4456.

³² R. B. Walker and J. C. Light, *Ann. Rev. Phys. Chem.*, 1980, **31**, 401.

³³ E. B. Stechel, F. Webster, and J. C. Light, *J. Chem. Phys.*, 1988, **88**, 1824.

³⁴ F. Webster and J. C. Light, *J. Chem. Phys.*, 1989, **90**, 265.

³⁵ F. Webster and J. C. Light, *J. Chem. Phys.*, 1989, **90**, 300.

successful, the difficulties associated with natural collision coordinates have still tended to direct recent research towards more convenient coordinate schemes.

3 Hyperspherical Coordinates

Perhaps the most annoying feature of natural collision coordinates is the need to define matching surfaces between the arrangements whenever more than one reaction channel is energetically allowed. In order to overcome this difficulty, while at the same time retaining many of the advantages that natural collision coordinates do have to offer, several groups have turned their attention to 'hyperspherical' coordinate systems in recent years.¹⁰⁻¹⁴

Once again taking the simple collinear atom-diatom reaction as an example, increments of the (in this case essentially unique) hyperspherical coordinates, ρ and θ_a , are illustrated in Figure 2. These collinear Delves⁸ coordinates are defined in terms of the mass-scaled Jacobi vectors of the reactant arrangement $a(A + BC)$ as

$$\rho = (R_a^2 + r_a^2)^{1/2} \quad (5)$$

and

$$\theta_a = \tan^{-1}(r_a/R_a) \quad (6)$$

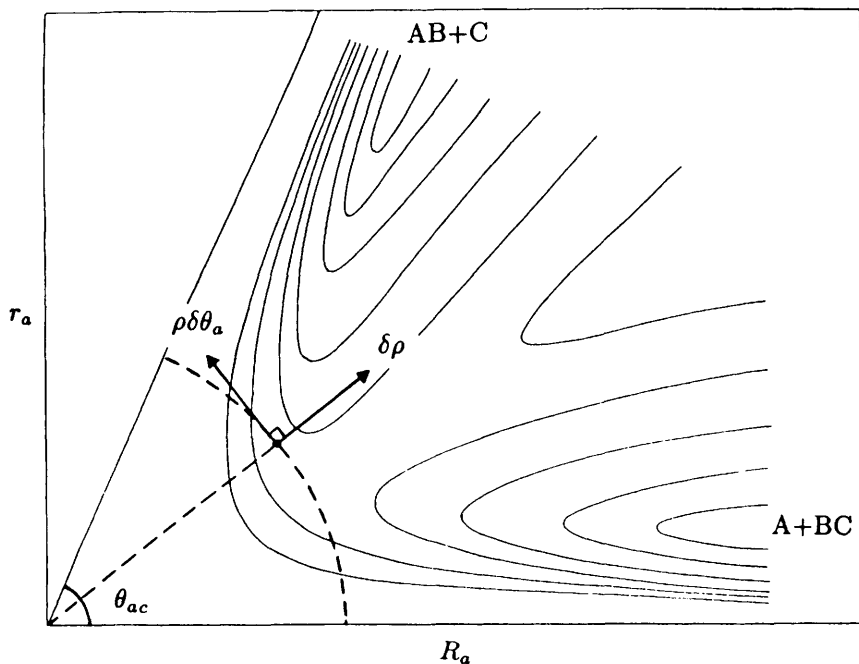


Figure 2 Increments of the radial (ρ) and angular (θ_a) hyperspherical coordinates for collinear $A + BC \rightarrow AB + C$ reactive scattering. The axis labels and potential contour lines are the same as in Figure 1, and the skewing angle θ_{ac} between the reactant and product asymptotes is defined in equation 7.

where R_a is a mass-scaled distance between A and the centre-of-mass of BC and r_a is a mass-scaled distance between B and C. The hyperradius ρ in equation (5) is universal, in the sense that it can equally well be defined in terms of the mass-scaled Jacobi vectors of the product arrangement $c(\text{AB} + \text{C})$. However, the Delves hyperangle, θ_a , is a function of the arrangement for which it is defined. In fact the reactant hyperangle θ_a and the product hyperangle θ_c are related here by $\theta_a + \theta_c = \theta_{ac}$, where

$$\theta_{ac} = \tan^{-1}(m_B/\mu), \quad (7)$$

with

$$\mu = \left(\frac{m_A m_B m_C}{m_A + m_B + m_C} \right)^{1/2}, \quad (8)$$

is the skewing angle shown on the plot in Figure 2. Fortunately, several quite general features of the hyperspherical coordinate approach are quite easy to describe in terms of this simple collinear model.

To begin with, one invariably solves the Schrödinger equation in hyperspherical coordinates in two distinct steps. The bound θ_a motion is solved first, at the centres of a number of different 'sectors' in the hyperradial coordinate ρ . This gives a set of 'surface' eigenfunctions and eigenvalues within each sector, which are then substituted back into the Schrödinger equation to leave a system of coupled second order linear differential equations in ρ . These 'close-coupled' equations have *exactly* the same form as those encountered in inelastic scattering, and so can be solved using well known, and highly efficient, numerical techniques.⁴

Unfortunately, however, the surface eigenfunctions and eigenvalues are themselves often quite difficult to obtain. The fundamental reason for this, which should be clear from Figure 2, is that the reactant and product arrangement channels are confined to smaller and smaller regions of the available hyperangular (θ_a) space as ρ increases. This unavoidable feature of hyperspherical coordinates, which is exacerbated in 3D, makes it difficult to devise numerical methods for solving the surface eigenproblem that work equally well for all required values of ρ . However, some progress has been made in this direction in recent years, as we shall describe in more detail below.

Two final comments on the hyperspherical coordinate approach are in order before we move on. The first is that the solution of the surface eigenproblem is completely independent of the scattering energy, E . Once this eigenproblem has been solved all that remains is to call a standard close-coupled equation solver at each energy required.⁴ Since this is comparatively straightforward, calculations can be performed on a tight energy grid, which greatly facilitates the analysis of narrow scattering resonances due to short-lived meta-stable states.³⁶ The second is that the hyperspherical coordinates may well be the *only* practical approach to certain physical regimes. In particular heavy-light-heavy reactions, which have a small skewing angle θ_{ac} , and collision induced dissociation, which occurs between the two arrangement channel regions in Figure 2, are both much more difficult to study using any other approach.

While the collinear Delves hyperspherical coordinates in Figure 2 are essentially

³⁶ See, for example, A. Kuppermann in 'Potential Energy Surfaces and Dynamics Calculations', ed. D. G. Truhlar, Plenum Press, New York, 1981, p. 375.

unique, several different possibilities arise when one moves to 3D. A highly detailed account of these possibilities is given in the introductory sections of the paper by Pack and Parker,³⁷ of which we shall confine ourselves only to a brief summary here.

In short, the various 3D hyperspherical coordinate methods can be classified into two distinct groups. The methods in the first group, which we shall simply lump together under the heading of 'Delves coordinate' (DC) methods, are characterized by the use of 3D Delves hyperspherical coordinates in the close interaction region, irrespective of whether or not they are used doubled in one arrangement,¹⁰ or, as originally defined,⁸ in all three.¹⁴ The methods in the second group, which we shall refer to as 'principle axis' (PA) methods, are characterized by the use of a single hyperspherical coordinate system that treats all three arrangements in an equivalent way.^{9,11-13} It is probably fair to say that PA methods have been applied more extensively than DC methods during the past couple of years, so we shall deal with them first.

The adiabatically adjusting principle axis hyperspherical (APH) coordinate method of Pack and Parker is probably the best known, and certainly the best documented, of the recent PA techniques.³⁷⁻⁴² The APH coordinates were first introduced by Pack, in 1984, as a route to an optimum centrifugal sudden (CS) approximation for reactions.¹³ These coordinates are similar to the earlier PA hyperspherical coordinates of Smith and Whitten,⁹ and of Johnson,¹² but differ in that they do not require the use of half-integer angular momenta,^{9,12} and are better suited to the prolate symmetric top (e.g. collinear and asymptotic atom plus diatom) configurations that are most often energetically preferred.³⁷

The earliest applications of the APH coordinate method were to the calculation of $J = 0$ and $J = 1$ reaction probabilities for the $\text{H} + \text{H}_2$ and $\text{D} + \text{H}_2$ reactions.³⁷⁻³⁹ While these calculations demonstrated the feasibility of the method they used a general finite element program to solve the surface eigenvalue problem,³⁷ and were found to be comparatively expensive to perform. Fortunately, a careful comparison of other approaches to the eigenvalue problem, including variational basis set expansion and the discrete variable representation (DVR) developed by Light and coworkers,⁴³⁻⁴⁶ soon suggested that this bottleneck might more easily be overcome. Indeed the article by Parker *et al.*,⁴⁰ in which these approaches are compared, already contains $J = 0$ eigenvalue correlation diagrams for $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ and $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$, and plots of both ground (\tilde{X}) and excited (\tilde{A}) electronic state surface functions for $\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$.

The most recent work on the APH coordinate method is that of Bačić, Kress, Parker, and Pack.^{41,42} These authors use a symmetry adapted DVR,⁴⁴ combined with

³⁷ R. T. Pack and G. A. Parker, *J. Chem. Phys.*, 1987, **87**, 3888.

³⁸ G. A. Parker, R. T. Pack, B. J. Archer, and R. B. Walker, *Chem. Phys. Lett.*, 1987, **137**, 564.

³⁹ R. T. Pack and G. A. Parker, *J. Chem. Phys.*, 1989, **90**, 3511.

⁴⁰ G. A. Parker, R. T. Pack, A. Laganà, B. J. Archer, J. D. Kress, and Z. Bačić in 'Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules', ed. A. Laganà, Kluwer, Dordrecht, 1989, p. 105.

⁴¹ J. D. Kress, Z. Bačić, G. A. Parker, and R. T. Pack, *Chem. Phys. Lett.*, 1989, **157**, 484.

⁴² Z. Bačić, J. D. Kress, G. A. Parker, and R. T. Pack, *J. Chem. Phys.*, 1990, **92**, 2344.

⁴³ J. C. Light, I. P. Hamilton, and J. V. Lill, *J. Chem. Phys.*, 1985, **82**, 1400.

⁴⁴ R. M. Whitnell and J. C. Light, *J. Chem. Phys.*, 1988, **89**, 3674.

⁴⁵ Z. Bačić, R. M. Whitnell, D. Brown, and J. C. Light, *Comp. Phys. Comm.*, 1988, **51**, 35.

⁴⁶ J. C. Light, R. M. Whitnell, T. J. Park, and S. E. Choi in 'Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules', ed. A. Laganà, Kluwer, Dordrecht, 1989, p. 187.

the sequential diagonalization and truncation procedure of Light and coworkers,^{45,46} to solve the surface eigenvalue problem for the T5A potential energy surface representation of $F + H_2$.⁴⁷ The resulting surface eigenvalues and eigenfunctions are then used to calculate converged $F + H_2(v = 0, j = 0) \rightarrow HF(v', j') + H$ reaction probabilities, for total angular momentum $J = 0$, at a large number of scattering energies in the range $E_{\text{tot}} = 1.65$ to 2.40 eV (measured relative to the bottom of the asymptotic product well).⁴¹ The computed reaction probabilities show considerable structure as a function of the scattering energy E_{tot} , and a highly detailed analysis of this structure is given by Bačić and coworkers in terms of quantum mechanical resonance effects.⁴² The ultimate goal of such a detailed resonance analysis, which involves Argand diagrams, time delays, and adiabatic hyperradial potential curves, is to pave the way to a more thorough understanding of product angular distributions like those observed in the $F + H_2$ molecular beam experiments of Lee's group.⁴⁸

These calculations of Bačić and coworkers on the $F + H_2$ reaction provide an impressive demonstration of the APH coordinate and DVR surface eigenproblem approach. Moreover, Park and Light have recently published a paper in which they use virtually identical numerical techniques to obtain the thermal rate constant for $H + H_2$.⁴⁹ Of course the formulation adopted in this paper is somewhat complementary to that of Pack *et al.*, as we shall now describe.

The work of Park and Light is based on a direct relationship between the thermal rate constant, $k(T)$, and a time-dependent reactive flux-flux autocorrelation function, $C_f(t)$.⁴⁹ This relationship, which is derived independently by Yamamoto,⁵⁰ and by Miller and coworkers,⁵¹ avoids the intermediate calculation of detailed state-to-state scattering information as a function of the collision energy. However, the dynamical problem must still be solved, and for this Park and Light once again use APH coordinates,^{13,37} a symmetry adapted direct product DVR basis,⁴⁴ and the sequential diagonalization and truncation technique mentioned above.^{45,46} In this case the hyper-radial ρ motion is also solved within the framework of the direct product DVR.⁴⁹

Park and Light performed their thermal rate constant calculations for the $H + H_2$ reaction on the highly accurate LSTH potential energy surface.²⁸ These calculations involved several minor dynamical approximations, including the complete neglect of Coriolis coupling,⁴⁹ but were otherwise designed to be essentially 'exact'. In particular, they were very well converged with respect to the total angular momentum quantum number J . Happily, then, the calculated rate constant was found to be in reasonable agreement with available experimental measurements in the temperature range $T = 299$ – 549 K.⁴⁹

This time-dependent application of Park and Light completes our discussion of the APH coordinate approach. We shall now move on to discuss an alternative, and equally successful, use of principle axis hyperspherical coordinates by Launay and Le Dorneuf.⁵²

⁴⁷ R. Steckler, D. G. Truhlar, B. C. Garrett, N. C. Blais, and R. B. Walker, *J. Chem. Phys.*, 1985, **81**, 5700; F. B. Brown, R. Steckler, D. W. Schwenke, D. G. Truhlar, and B. C. Garrett, *ibid.*, 1985, **82**, 188; R. Steckler, D. G. Truhlar, and B. C. Garrett, *ibid.*, 1985, **82**, 5499.

⁴⁸ D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, *J. Chem. Phys.*, 1985, **82**, 3045.

⁴⁹ T. J. Park and J. C. Light, *J. Chem. Phys.*, 1989, **91**, 974.

⁵⁰ T. Yamamoto, *J. Chem. Phys.*, 1960, **33**, 281.

⁵¹ W. H. Miller, S. D. Schwartz, and J. W. Tromp, *J. Chem. Phys.*, 1983, **79**, 4889.

⁵² J. M. Launay and M. Le Dorneuf, *Chem. Phys. Lett.*, 1989, **163**, 178.

Launay and Le Dorneuf use essentially, although not exactly, the same PA hyperspherical coordinates as Pack and Parker. In particular, they choose the quantization axis for the internal motion as the axis of least inertia, so that the rotational couplings about this axis are minimized in a variational way.^{37,52} This leads to rapid convergence of reaction probabilities with respect to the total angular momentum projection quantum number, Ω , and so allows one to use far smaller basis sets for large J values than are required when all possible projections are retained.

The method proposed by Launay and Le Dorneuf differs from that of Pack and Parker in the choice of the hyperangular surface Hamiltonian. Pack and Parker retain as many of the kinetic energy terms in this Hamiltonian as is possible, leaving fewer terms to be incorporated later in the solution of the coupled hyperradial equations.³⁷ Launay and Le Dorneuf retain fewer terms in the surface Hamiltonian, all of which are essentially independent of the total angular momentum J .⁵² (In fact they do retain a term which depends on the body-frame projection operator \hat{J}_z but, as discussed above, only a few eigenvalues Ω of this operator are ever likely to be required.) Unfortunately, this approach is only possible for atom-diatom reactions in which equilateral triangle configurations are energetically forbidden,³⁹ but it does mean that for these reactions, of which there are several, the surface eigenproblem can be solved once and for all independent of J . Launay and Le Dorneuf also describe a simple variational basis set expansion for the surface eigenvalue problem, and show how many of the required matrix elements can once again be evaluated independent of J .⁵²

As an example application of their method Launay and Le Dorneuf chose to calculate integral cross sections for the hydrogen exchange reaction, $\text{H} + \text{H}_2(v=0, j=0) \rightarrow \text{H}_2(v', \text{odd } j') + \text{H}$, in the energy range $E = 0.9\text{--}1.4\text{ eV}$. Theoretical interest in this reaction had been revitalized at the beginning of 1988, when Nieh and Valentini reported pronounced resonant structure in the experimentally observed cross-sections to $v' = 1$.⁵³ However, this structure was not seen in the subsequent variational calculations of Zhang and Miller,⁵⁴ and Manolopoulos and Wyatt,⁵⁵ so Launay and Le Dorneuf decided to study the reaction using their hyperspherical coordinate method as a check. They obtained good agreement with the variational results, at only a fraction of the cpu cost, which was certainly quite encouraging for this initial application of their technique.⁵²

Before we leave principle axis hyperspherical coordinate methods we should mention the work of Linderberg, Padkjaer, Öhrn, and Vessal, several of whom have been studying the approach for some time.^{56–59} Their method is based on finite elements, which they use both to solve the surface eigenvalue problem,^{56,57} and in a variational \mathcal{R} matrix propagation algorithm for the coupled hyperradial equations.⁵⁸ However, they also adopt the early PA hyperspherical coordinates of Mead,¹¹ which are probably less appropriate for reactions than the systems we have already described.³⁷ So far their method has only been applied to the $\text{H} + \text{H}_2$ reaction for total angular momentum $J = 0$.⁵⁹

⁵³ J.-C. Nieh and J. J. Valentini, *Phys. Rev. Lett.*, 1988, **60**, 519; *J. Chem. Phys.*, 1990, **92**, 1083.

⁵⁴ J. Z. H. Zhang and W. H. Miller, *Chem. Phys. Lett.*, 1988, **153**, 465.

⁵⁵ D. E. Manolopoulos and R. E. Wyatt, *Chem. Phys. Lett.*, 1989, **159**, 123.

⁵⁶ M. Mishra, J. Linderberg, and Y. Öhrn, *Chem. Phys. Lett.*, 1984, **111**, 439.

⁵⁷ J. Linderberg, *Int. J. Quantum Chem. Symp.*, 1986, **19**, 467.

⁵⁸ J. Linderberg and B. Vessal, *Int. J. Quantum Chem.*, 1987, **31**, 65.

⁵⁹ J. Linderberg, S. B. Padkjaer, Y. Öhrn, and B. Vessal, *J. Chem. Phys.*, 1989, **90**, 6254.

We shall now move on to describe the Delves coordinate (DC) methods of Kuppermann and co-workers,¹⁰ and of Schatz,¹⁴ both of which have been applied to novel reactive scattering problems in recent years. Since the symmetrized hyperspherical coordinate method of Kuppermann and co-workers is the earlier of the two methods we shall deal with this first.

Kuppermann introduced his symmetrized hyperspherical coordinates in 1975, round about the time when the original quantum reactive scattering calculations on the hydrogen exchange reaction were just beginning to appear.¹⁰ These coordinates are essentially the same as the 3D hyperspherical coordinates introduced by Delves,⁸ except that the angle θ_a in equation 6 is doubled to allow a more useful symmetric mapping of three-atom potential energy surfaces. Pack and Parker refer to Kuppermann's coordinates as 'doubled Delves' coordinates,³⁷ a label which we shall adopt again here, and give a rather lengthy discussion regarding their formal inapplicability to reactions with $J > 0$. However, doubled Delves coordinates have since been applied to the $\text{H} + \text{H}_2$ reaction for both parity blocks of $J = 1$, as we shall describe in more detail below, so it seems that any formal problems which they might have can in practice be overcome.

In 1986, more than a decade after they were first introduced, Kuppermann and Hipes reported the successful application of a method based on doubled Delves coordinates to the hydrogen exchange reaction for total angular momentum $J = 0$.⁶⁰ This modest calculation of $\text{H} + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}_2(v', j') + \text{H}$ reaction probabilities, which was the first 3D application of an exact quantum mechanical method without natural collision coordinates, ushered in the new (post 1985) era of quantum reactive scattering. A subsequent paper by Hipes and Kuppermann extends this work to higher energies,⁶¹ and gives detailed Eisenbud-Wigner time delay⁶² and Smith collision lifetime⁶³ analyses of the observed $J = 0$ resonance effects.

In their early calculations Hipes and Kuppermann used the finite element method to solve the surface eigenvalue problem at each required value of the hyperradius ρ .^{60,61} However, like Parker and co-workers,⁴⁰ they have since found that other techniques may make their calculations easier to do. Specifically, Cuccaro, Hipes, and Kuppermann have recently published two papers in which they describe a variational approach to the surface eigenvalue problem,⁶⁴ and apply it to the calculation of $J = 0$ and $J = 1$ reaction probabilities and collision lifetime matrices for the PK2 and LSTH potential energy surface representations of $\text{H} + \text{H}_2$.⁶⁵ In the first of these papers Cuccaro and co-workers note that their variational method is more than 20 times faster, and also a great deal more accurate, than the finite element method employed previously by their group.⁶⁴ In the second paper they use the variational approach to the surface eigenvalue problem to extend their earlier analysis of $\text{H} + \text{H}_2$ resonances to total angular momentum $J = 1$.⁶⁵ This second paper also has special relevance to the formal criticisms of Pack and Parker,³⁷ because it provides the first practical demonstration of the doubled Delves coordinate method for $J > 0$.

The last of the competing hyperspherical coordinate methods we shall consider was

⁶⁰ A. Kuppermann and P. G. Hipes, *J. Chem. Phys.*, 1986, **84**, 5962.

⁶¹ P. G. Hipes and A. Kuppermann, *Chem. Phys. Lett.*, 1987, **133**, 1.

⁶² L. Eisenbud, Ph.D. Thesis, Princeton, 1948; E. P. Wigner, *Phys. Rev.*, 1955, **98**, 145.

⁶³ F. T. Smith, *Phys. Rev.*, 1960, **118**, 349.

⁶⁴ S. A. Cuccaro, P. G. Hipes, and A. Kuppermann, *Chem. Phys. Lett.*, 1989, **154**, 155.

⁶⁵ S. A. Cuccaro, P. G. Hipes, and A. Kuppermann, *Chem. Phys. Lett.*, 1989, **157**, 440.

introduced in 1988 by Schatz.¹⁴ In order to avoid the problems caused by the non-equivalent treatment of the different arrangements, Schatz chooses to retain all three sets of 3D Delves coordinates at once. This can in principle lead to linear dependence problems if the coupled-channel basis functions, which in this case are only very roughly analogous to the surface eigenfunctions described above, are not chosen with some care. Schatz defines his basis functions in terms of the solutions to certain one-dimensional reference Schrödinger equations in each arrangement, which seems in practice to work quite well.^{66,67} The resulting methodology has much in common with the Fock coupling scheme proposed earlier by Schwenke and co-workers,⁶⁸ who used a mixed hyperspherical and Jacobi coordinate set. It also effectively bridges the gap between the earlier hyperspherical coordinate methods and the Jacobi coordinate variational methods described in Section 4.

We shall mention three different papers on Schatz's DC hyperspherical approach here.^{14,66,67} In the first of these papers Schatz introduces his method, and applies it to the calculation of $J = 0$ and $J = 1$ reaction probabilities for $\text{H} + \text{H}_2$, both with and without the centrifugal sudden (CS) approximation for $J = 1$.¹⁴ Also included in this paper are the first exact 3D quantum mechanical results for the prototypically heavy–light–heavy $\text{Cl} + \text{HCl}$ reaction. These results would have been difficult to obtain without hyperspherical coordinates because of linear dependence problems caused by the small skewing angle θ_{ac} in equation (7). In his second paper Schatz extends his original calculations to give a more detailed account of oscillating reactivity and resonances in $\text{Cl} + \text{HCl}$.⁶⁶ These effects are compared, contrasted, and analysed on two LEPS potential energy surfaces with significantly different parametric fits.

In his third paper Schatz simulates the photodetachment spectrum of ClHCl^- by calculating the Frank–Condon overlap between a $\text{Cl} + \text{HCl}$ scattering wave function and the ground ClHCl^- ro-vibrational state.⁶⁷ This obviously requires the explicit calculation of a reactive scattering wave function, which Schatz obtains using a non-trivial extension of his DC hyperspherical approach. The calculated ClHCl^- photodetachment spectrum shows a broad low energy peak due to direct scattering, and a narrow higher energy peak due to a resonance associated with the transition state region of the $\text{Cl} + \text{HCl}$ reaction.^{66,67} Moreover the positions and relative intensities of both peaks are found to be in good agreement with a spectrum measured recently by Neumark and coworkers.⁶⁹ Such a direct comparison with experiment is possible in this case because both the scattering and bound state wave functions have total angular momentum $J = 0$, and so are relatively easy to compute.

To complete this section we should note that several 3D hyperspherical coordinate schemes for reactions involving polyatomic molecules have also been proposed.^{70,71} Indeed quantum calculation on a (diatom + diatom) to (atom + triatom) reaction has already been carried out by Brooks and Clary.²³ This paper develops a collinear four-atom hyperspherical coordinate system and reports the first converged collinear reaction probabilities for $\text{H}_2 + \text{CN} \rightarrow \text{H} + \text{HCN}$.

⁶⁶ G. C. Schatz, *Chem. Phys. Lett.*, 1988, **151**, 409.

⁶⁷ G. C. Schatz, *J. Chem. Phys.*, 1989, **90**, 3582.

⁶⁸ D. W. Schwenke, D. G. Truhlar, and D. J. Kouri, *J. Chem. Phys.*, 1987, **86**, 2772.

⁶⁹ R. B. Metz, T. Kitsopoulos, A. Weaver, and D. M. Neumark, *J. Chem. Phys.*, 1988, **88**, 1463.

⁷⁰ Y. Öhrn and J. Linderberg, *Mol. Phys.*, 1983, **49**, 53.

⁷¹ X. Chapuisat, *Chem. Phys. Lett.*, 1987, **136**, 153.

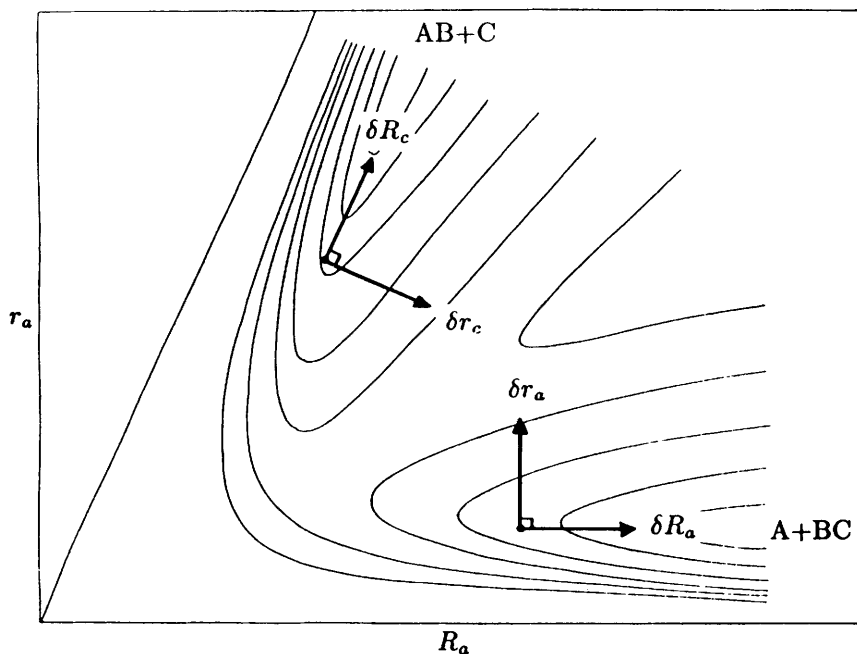


Figure 3 Increments of the reactant (R_a , r_a) and product (R_c , r_c) arrangement mass-scaled Jacobi coordinates for collinear reactive scattering. In their respective asymptotic limits R_a and R_c describe atom–diatom translational motions and r_a and r_c describe diatomic vibrations. In the close interaction exchange region, where R_a and r_a are both small, the motions in the two arrangements are coupled by the collinear interaction potential $V(R_a, r_a)$. The axis labels and potential contour lines are once again the same as in Figure 1.

4 Jacobi Coordinates

It is clear from the above discussion that hyperspherical coordinate methods have already been applied to an interesting variety of atom–diatom reactions. In this section we shall move on to consider variational methods based on the simultaneous use of mass-scaled Jacobi coordinates in all three arrangements.⁷² These methods have also been applied quite successfully in the past couple of years, and their comparative simplicity may well be a decisive factor when more difficult (e.g. 3D four-atom) reactions are addressed.

Once more taking the simple collinear atom–diatom reaction as an example, increments of the reactant and product mass-scaled Jacobi coordinates, (R_a , r_a) and (R_c , r_c), are shown in Figure 3. As we have now discussed several times (see in particular the caption to Figure 1 and the discussion at the beginning of section 3), R_a is a mass-scaled distance between A and the centre-of-mass of BC and r_a is a mass-scaled distance between B and C. The mass-scaling factors are chosen so that the kinetic energy operator contains only the single three-body reduced mass, μ , in

⁷² For a general discussion of mass-scaled Jacobi coordinates see J. O. Hirschfelder, *Int. J. Quantum Chem. Symp.*, 1969, 3, 17.

equation (8). The product mass-scaled Jacobi coordinates, R_c and r_c , are defined in an analogous way.

It should be clear from Figure 3 that either set of mass-scaled Jacobi coordinates alone provides a complete description of the available collinear coordinate space. However, it should be equally clear that while R_a and r_a are better suited to describing translational and vibrational motions in the reactant channel, R_c and r_c are more appropriate for a corresponding description of the products. It therefore seems natural to retain both sets of coordinates at once, using each set for convenience as required. Moreover, formulations of quantum reactive scattering based on this idea are quite easy to construct. Indeed a comprehensive account of such a formulation, for the general case of a 3D atom–diatom reaction, was given by Miller more than twenty years ago.¹⁵ Several other formulations have also been proposed by Baer, Kouri, and coworkers over the intervening years,¹⁶ and have recently been reviewed and extended by Baer.⁷³

Because the translational and vibrational motions in the reactant channel are coupled non-locally to those in the product channel, it is usually most convenient to use basis functions to describe the motions in each arrangement. The non-local couplings between the reactant and product channels then appear as *exchange integrals* between basis functions in different chemical arrangements.¹⁵ These exchange integrals are simply a mathematical manifestation of the interactions which cause the reaction to proceed. They are augmented by direct interaction potential integrals between basis functions in the same chemical arrangement, which in turn are responsible for all the elastic and inelastic scattering effects.

Having chosen to adopt this description of reactions one must still find some way of extracting the desired scattering information. The best way to do this is to use a *variational principle* for the scattering matrix of interest, which is then obtained one order more accurately in the error than the scattering wave function itself.⁷⁴ The advantage of the approach stems in part from the fact that the scattering wave function is only very rarely explicitly required. In fact it is never required in purely reactive scattering problems, but only in more exotic applications to photofragmentation like the ClHCl^- calculations of Schatz.⁶⁷

The computational effort in variational reactive scattering has two main sources. First one must evaluate costly multi-dimensional exchange integrals between basis functions in different chemical arrangements, and then one must solve a large system of linear algebraic equations for the scattering matrix of interest. While it is probably fair to say that these computational problems have both been solved by ‘brute force’ in most applications to date, several ingenious approaches to their solution have also recently been proposed. We shall describe these approaches more fully below in the context of each specific variational technique.

The three variational principles in common use in scattering theory are due to Kohn,⁷⁵ Schwinger,⁷⁶ and Newton.⁷⁷ Two of these variational principles, those due to Kohn and Newton, have been successfully developed and applied to reactive scatter-

⁷³ M. Baer, *Phys. Rep.*, 1989, **178**, 99.

⁷⁴ See, for example, R. K. Nesbet, ‘Variational Methods in Electron–Atom Scattering Theory’ Plenum, New York, 1980, chap. 2.

⁷⁵ W. Kohn, *Phys. Rev.*, 1948, **74**, 1763.

⁷⁶ J. Schwinger, *Phys. Rev.*, 1947, **72**, 742.

⁷⁷ R. G. Newton, ‘Scattering Theory of Particles and Waves’ Springer, New York, 1982, p. 320.

ing problems in the past couple of years. We shall begin our discussion of these applications here with the 'S-matrix Kohn' method of Zhang, Chu, and Miller, and the related 'log derivative Kohn' method of Manolopoulos, D'Mello, and Wyatt. We shall then complete this section by summarizing the already extensive literature on the ' \mathcal{L}^2 -Amplitude Density Generalized Newton Variational Principle' (\mathcal{L}^2 -AD GNVP) method of Schwenke, Kouri, and Truhlar.

The Kohn variational principle is perhaps the simplest of the three scattering variational principles mentioned above.⁷⁵ In particular, it requires that one calculate matrix elements only over the total Hamiltonian H of the system, and not over the Green's function $G_0(E)$ of some reference Hamiltonian H_0 . While matrix elements of H between energy-independent basis functions are also energy-independent, all matrix elements of $G_0(E)$ have to be re-evaluated at each new scattering energy E . The Kohn variational principle is therefore somewhat easier to apply than the Schwinger and Newton variational principles, which involve the use of $G_0(E)$, when calculations are required on a tight energy grid. This is invariably the case, for example, in any detailed analysis of quantum mechanical resonance effects.³⁶

Unfortunately, traditional applications of the Kohn variational principle in electron-atom and electron-molecule scattering have been plagued by spurious singularities, or 'Kohn anomalies', of the kind observed originally by Schwartz.⁷⁸ A convenient solution to this problem did not really arrive until 1987, when Miller and Jansen op de Haar published a paper describing a new basis set method for quantum scattering problems.⁷⁹ Their method is based on a variational basis set expansion for matrix elements of the full scattering Green's function

$$G^+(E) \equiv \lim_{\epsilon \downarrow 0} (E + i\epsilon - H)^{-1} \quad (9)$$

and involves, in addition to the usual square integrable basis functions of bound state calculations, certain damped scattering functions which enforce the outgoing wave boundary conditions implied by the $+i\epsilon$.⁸⁰ This direct application of outgoing wave boundary conditions leads to a complex symmetric matrix representation of $(E - H)$, rather than the real symmetric matrix representation obtained when conventional standing wave boundary conditions are applied.^{74,75} The Kohn anomalies found by Schwartz are now known to be an artifact of these standing wave boundary conditions, and so are not expected to appear in Miller and Jansen op de Haar's approach.^{81,82} The significance of this development is rather nicely illustrated, in view of the opening sentence to this paragraph, by the subsequent application of complex boundary conditions in electron-atom and electron-molecule scattering calculations by McCurdy, Rescigno, and Schneider.⁸³

In their original paper Miller and Jansen op de Haar only applied their method to simple elastic and inelastic scattering tests.⁷⁹ The first practical demonstration of its efficacy came about six months later, when Zhang and Miller used the method to

⁷⁸ C. Schwartz, *Phys. Rev.*, 1961, **124**, 1468; *Ann. Phys.*, New York, 1961, **10**, 36.

⁷⁹ W. H. Miller and B. M. D. D. Jansen op de Haar, *J. Chem. Phys.*, 1987, **86**, 6213.

⁸⁰ See, for example, A. Messiah, 'Quantum Mechanics' Wiley, New York, 1962, chap. 19.

⁸¹ L. F. X. Gaucher and W. H. Miller, *Israel J. Chem.*, 1989, **29**, 349.

⁸² See, however, R. R. Lucchese, *Phys. Rev. A*, in press.

⁸³ C. W. McCurdy, T. N. Rescigno, and B. I. Schneider, *Phys. Rev. A*, 1987, **36**, 2061; C. W. McCurdy and T. N. Rescigno, *Phys. Rev. A*, 1989, **39**, 4487.

calculate $J = 0$ reaction probabilities, over quite a wide energy range, for the already heavily studied $\text{H} + \text{H}_2$ reaction.⁸⁴ Their results agreed well with the earlier calculations, and appeared to be quite easy to converge.

The next development came at the beginning of 1988, when Zhang, Chu, and Miller recast their approach in terms of a direct variational expression for the scattering matrix S .⁸⁵ This paper uses the Löwdin–Feshbach partitioning identity to separate out the real and complex parts of the problem, and exploits the complex conjugation symmetry between incoming and outgoing wave scattering functions to reduce the number of integrals and linear equations involved. Interestingly, the resulting methodology bears more relation to the original (K -matrix) version of the Kohn variational principle than does the earlier work of Miller and Jansen op de Haar. However, Miller has since shown quite explicitly that both versions of his methodology are at least formally, if not practically, the same.^{86,87}

The final streamlined version of the S -matrix Kohn method proposed by Zhang, Chu, and Miller has been applied quite successfully in the past couple of years. In particular, and after a preliminary calculation of $J = 0$ reaction probabilities for $\text{F} + \text{H}_2$,⁸⁸ Zhang and Miller have concentrated more or less exclusively on the calculation of high energy integral and differential cross sections for the $\text{H} + \text{H}_2$ and $\text{D} + \text{H}_2$ reactions.^{54,89,90} Their first major application came at the end of 1988, when they reported fully converged integral cross sections for $\text{H} + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}_2(v' = 1, j' = 1, 3) + \text{H}$ in the energy range $E_{\text{tot}} = 0.9$ to 1.4 eV .⁵⁴ This was the first calculation of integral cross sections for the hydrogen exchange reaction at sufficiently many energies above the $v' = 1$ threshold, and on a sufficiently accurate potential energy surface,²⁸ to allow for a detailed comparison with the resonant structure observed in the bulk experiments of Nieh and Valentini.⁵³ However, while Zhang and Miller's calculations did show resonant structure in the low partial waves, this structure was 'washed out' of their integral cross-sections by the angular momentum averaging in the partial wave sum.⁹¹

Since they had observed some resonant structure in their low total angular momentum calculations, semi-classical arguments led Zhang and Miller to suggest that Nieh and Valentini's experimental apparatus might preferentially be measuring differential cross sections in the backward direction, rather than the integral cross sections that were claimed.⁵⁴ In order to test this suggestion Manolopoulos and Wyatt,⁵⁵ and Zhang and Miller,⁸⁹ have since calculated these differential cross sections in the relevant energy range. While some resonant structure as a function of the scattering energy is indeed seen in these calculations, this structure is not nearly so pronounced as, nor even really compatible with, that which is experimentally observed.⁵³ This and other attempts to 'explain' the Nieh and Valentini experiment have recently been reviewed in some detail by Miller.⁹²

⁸⁴ J. Z. H. Zhang and W. H. Miller, *Chem. Phys. Lett.*, 1987, **140**, 329.

⁸⁵ J. Z. H. Zhang, S.-I. Chu, and W. H. Miller, *J. Chem. Phys.*, 1988, **88**, 6233; 1988, **89**, 4454.

⁸⁶ W. H. Miller, *Collect. Czech. Chem. Commun.*, 1988, **53**, 1873.

⁸⁷ W. H. Miller, *Comments At. Mol. Phys.*, 1988, **22**, 115.

⁸⁸ J. Z. H. Zhang and W. H. Miller, *J. Chem. Phys.*, 1988, **88**, 4549; 1989, **90**, 7610.

⁸⁹ J. Z. H. Zhang and W. H. Miller, *Chem. Phys. Lett.*, 1989, **159**, 130.

⁹⁰ J. Z. H. Zhang and W. H. Miller, *J. Chem. Phys.*, 1989, **91**, 1528.

⁹¹ G. C. Schatz, *Ann. Rev. Phys. Chem.*, 1988, **39**, 317.

⁹² W. H. Miller, *Ann. Rev. Phys. Chem.*, in press.

A more demanding demonstration of the S -matrix Kohn method came at the beginning of 1989, when Zhang and Miller reported converged integral and differential cross sections for the less symmetric $D + H_2 \rightarrow HD + H$ reaction.⁹⁰ These results were obtained at a number of total energies between 0.4 and 1.35 eV, on the LSTH potential energy surface,²⁸ and required partial waves right up to $J = 31$ to converge. State-to-state rate constants were also calculated by Boltzmann averaging over the relative translational energy, allowing comparisons to be made with a wider variety of experimental results. On the whole, while some specific disagreements akin to those observed previously for the $H + H_2$ reaction were noted, the agreement with experiment was found to be quite good.⁹⁰ In particular, the predicted thermal rate constant for reaction from the vibrationally excited ($v = 1$) state of H_2 was found to be quite 'low', in agreement with the latest experimental results.⁹³

Before leaving the S -matrix Kohn method we should perhaps mention several theoretical developments which may facilitate its application to still more 'difficult' problems in the future.⁹⁴⁻⁹⁸ These developments relate to the two major computational bottlenecks in variational scattering described above. First, with regard to the exchange integral problem, Peet and Miller have described a pointwise representation,⁹⁴ and more recently Yang, Peet, and Miller have described a collocation approach,⁹⁵ both of which reduce the complexity of the integrals involved. Second, with regard to the linear equation problem, Yang and Miller have proposed two different iteration schemes and applied them to inelastic and reactive scattering tests.^{96,97} Finally, and also largely with regard to the linear equation problem, Zhang and Miller have recently proposed a 'quasi-adiabatic' contraction of their internal (ro-vibrational) basis functions, and applied it with some success to the calculation of $J = 0$, $J = 5$, and $J = 10$ reaction probabilities for $H + H_2$.⁹⁸

We now come to the log derivative Kohn method,^{74,75} which was introduced to quantum reactive scattering in 1988 by Manolopoulos and Wyatt.⁹⁹ This method has much in common with the S -matrix Kohn method described above. However, in this case the log derivative matrix, and not the scattering matrix, is obtained directly from Kohn's variational form.⁷⁵ This turns out to have certain advantages. In particular, on the theoretical side, the unitarity of the resulting scattering matrix is guaranteed. On the practical side the log derivative boundary conditions allow one to split the calculation up into reactive and inelastic regions, and so to solve the inelastic scattering part of the problem using standard, and highly efficient, close-coupling techniques.⁴

The initial application of the log derivative Kohn method was once again to the calculation of $J = 0$ reaction probabilities for $H + H_2$.⁹⁹ In this paper Manolopoulos and Wyatt give a brief account of their method, and introduce a convenient basis set, based on Gauss-Lobatto quadrature, for the description of the radial motion. This basis set lends itself quite naturally to a discrete variable representation (DVR),⁴³ which is used by Manolopoulos and Wyatt to simplify certain of the integrals

⁹³ T. Dreier and J. Wolfrum, *Int. J. Chem. Kinet.*, 1986, **18**, 919.

⁹⁴ A. C. Peet and W. H. Miller, *Chem. Phys. Lett.*, 1988, **149**, 257.

⁹⁵ W. Yang, A. C. Peet, and W. H. Miller, *J. Chem. Phys.*, 1989, **91**, 7537.

⁹⁶ W. Yang and W. H. Miller, *J. Chem. Phys.*, 1989, **91**, 3504.

⁹⁷ W. Yang and W. H. Miller, *J. Comp. Phys.*, in press.

⁹⁸ J. Z. H. Zhang and W. H. Miller, *J. Phys. Chem.* in press.

⁹⁹ D. E. Manolopoulos and R. E. Wyatt, *Chem. Phys. Lett.*, 1988, **152**, 23.

involved.⁹⁹ The resulting $J = 0$ reaction probabilities are once again found to agree well with those obtained in earlier work.

The second application of the log derivative Kohn method was to the calculation of integral and differential cross sections for $\text{H} + \text{H}_2(v = 0, j = 0) \rightarrow \text{H}_2(v' = 1, j' = 1, 3) + \text{H}$ in the energy range $E_{\text{tot}} = 0.95$ to 1.35 eV .⁵⁵ Here the computed integral cross sections were found to be in good agreement with the earlier results of Zhang and Miller.⁵⁴ The computed differential cross sections were found to show some resonant structure in the neighbourhood of the backward direction, as Zhang and Miller had predicted they might, but, as noted above, this structure did not bear much relation to the experimental measurements of Nieh and Valentini.⁵³

The largest single source of error in their $\text{H} + \text{H}_2$ dynamical calculations was attributed by Manolopoulos and Wyatt to the LSTH potential energy surface used.²⁸ In order to estimate the extent of this error they have subsequently calculated converged integral cross sections for the same reaction on the more recent double many body expansion (DMBE) potential energy surface of Varandas and co-workers.¹⁰⁰ They find that the DMBE and LSTH cross sections are qualitatively similar, but that the DMBE results are some ten per cent larger because of the reduced classical barrier height.¹⁰¹ Of course this does not prove that the resonant structure observed by Nieh and Valentini is 'wrong', but it does at least reveal the extent to which errors in the best available H_3 potential energy surfaces are likely to affect the calculated dynamical results.

With these successful $\text{H} + \text{H}_2$ applications in hand Manolopoulos, D'Mello, and Wyatt went on to give a detailed theoretical description of the log derivative Kohn method in the context of a general bimolecular reaction.¹⁰² Here the Löwdin-Feshbach partitioning identity is used to eliminate the log derivative matrix from a basis set representation of Kohn's principle, leaving a unitary and symmetric variational expression for the scattering matrix S . This expression is expected to find its most fruitful application in the iterative solution of very large quantum scattering problems for which transitions from only a few initial states are required. Indeed one such model application, albeit not to a reactive scattering problem, has already been reported by Manolopoulos, Wyatt, and Clary.¹⁰³

The Lobatto shape functions introduced in the original paper by Manolopoulos and Wyatt are used in all of the applications of the log derivative Kohn method described above.⁹⁹ In their most recent methodological development Manolopoulos, and co-workers contract this primitive translational basis set to the energy-independent box eigenfunctions of a selected one-dimensional reference Hamiltonian H_0 .¹⁰⁴ A simple 'preprocessor' which automatically generates basis sets and quadrature rules for any atom-diatom reaction is also described in this paper, and example applications to the $J = 0$, $\text{F} + \text{H}_2$ reaction are chosen to illustrate the feasibility of the approach.¹⁰⁴ The results of these applications are found to be in good agreement with the earlier calculations of Yu and co-workers,¹⁰⁵ who used the \mathcal{L}^2 -AD GNVP method of Schwenke, Kouri, and Truhlar.

¹⁰⁰ A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais, *J. Chem. Phys.*, 1987, **86**, 6258.

¹⁰¹ D. E. Manolopoulos and R. E. Wyatt, *J. Chem. Phys.*, 1990, **92**, 810.

¹⁰² D. E. Manolopoulos, M. D'Mello, and R. E. Wyatt, *J. Chem. Phys.*, 1989, **91**, 6096.

¹⁰³ D. E. Manolopoulos, R. E. Wyatt, and D. C. Clary, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1641.

¹⁰⁴ D. E. Manolopoulos, M. D'Mello, and R. E. Wyatt, *J. Chem. Phys.*, in press.

¹⁰⁵ C. Yu, D. J. Kouri, M. Zhao, D. G. Truhlar, and D. W. Schwenke, *Chem. Phys. Lett.*, 1989, **157**, 491.

This new translational basis set contraction scheme for the log derivative Kohn method has since been applied to the calculation of $J = 0$ reaction probabilities for both the deuterium substituted isotopomers of $F + H_2$.^{106,107} In the $F + D_2$ application of D'Mello and co-workers rotational distributions are plotted for the DF ($v' = 3$) and ($v' = 4$) product vibrational levels, and the results are discussed in the light of previous experimental and theoretical work.¹⁰⁶ In the $F + HD$ application of Manolopoulos and co-workers the HF product vibrational probabilities are found to show quite dramatic resonant structure as a function of the collision energy, whereas those to DF are comparatively bland.¹⁰⁷ Eisenbud–Wigner time delay curves are plotted for the predominant HF ($v' = 2$) resonance, and the results are again discussed in the light of previous experimental and theoretical work.

These recent applications of D'Mello and co-workers complete our discussion of methods based on the Kohn variational principle. We shall now move on to summarize the \mathcal{L}^2 -AD GNVP method of Schwenke, Kouri, and Truhlar. This method, with a closely related non-variational method from the same collaboration, has already been applied to a more diverse variety of atom–diatom reactions than any other competing approach.

The history of the \mathcal{L}^2 -AD GNVP method can be traced back to the original integral equation formulations of Baer and Kouri.¹⁶ However, we shall begin our discussion of the method here with an early 1987 paper by Staszewska and Truhlar,¹⁰⁸ in which they compare 35 different square integrable (\mathcal{L}^2) methods for potential scattering. Before discussing this paper in detail we should first mention that the total Hamiltonian for scattering problems is conveniently, and therefore frequently, partitioned as

$$H = H_0 + V, \quad (10)$$

with the constraint that H_0 tend to H , and hence V to 0, in the limit as the two fragments in the system (e.g. an atom and a diatom) move far apart. With this partitioning established, Staszewska and Truhlar consider methods based both on expansions of the wave function, ψ , and of the amplitude density, $V\psi$. They conclude that the most efficient methods are variational methods for the amplitude density, and that the non-variational 'method of moments for the amplitude density' (MMAD) might also be useful since it leads to reasonable accuracy with a smaller programming effort.¹⁰⁸ The superiority of the amplitude density methods over the wave function methods, with regard to expansion in an \mathcal{L}^2 basis set, is attributed by Staszewska and Truhlar to the fact that $V\psi$ is itself square integrable, whereas ψ alone is not.¹⁰⁸

The relevance of this paper to the subsequent development of the \mathcal{L}^2 -AD GNVP method follows because the Schwinger variational principle is it not directly amenable to an expansion of the amplitude density, whereas the Newton variational principle most certainly is.¹⁰⁸ Moreover, Staszewska and Truhlar did not include the Kohn variational principle in their tests, largely because they wanted to avoid the spurious singularities associated with the real K -matrix version.⁷⁸ Several potential scattering comparisons between the S -matrix version of the Kohn principle and the T -matrix versions of the Schwinger and Newton principles have since been published by Ramachandran, Wei, and Wyatt.¹⁰⁹ The general conclusion of these comparisons is

¹⁰⁶ M. D'Mello, D. E. Manolopoulos, and R. E. Wyatt, *Chem. Phys. Lett.*, 1990, **168**, 113.

¹⁰⁷ D. E. Manolopoulos, M. D'Mello, R. E. Wyatt, and R. B. Walker, *Chem. Phys. Lett.*, 1990, in press.

¹⁰⁸ G. Staszewska and D. G. Truhlar, *J. Chem. Phys.*, 1987, **86**, 2793.

¹⁰⁹ B. Ramachandran, T.-G. Wei, and R. E. Wyatt, *J. Chem. Phys.*, 1988, **89**, 6785.

that the Schwinger and Newton methods do indeed converge more rapidly, but that the Kohn method is somewhat easier to apply.

Having chosen to opt for a square integrable expansion of the amplitude density, the Kouri and Truhlar groups began their three dimensional reactive scattering work with the comparatively simple, but non-variational, MMAD.¹⁰⁸ A comprehensive summary of the resulting atom–diatom scattering methodology, with amplitude density components arrangement coupled according to the Fock scheme of Schwenke, Truhlar, and Kouri,⁶⁸ did not take long to arrive.¹¹⁰ This paper by Zhang and co-workers contains a wealth of numerical details, including discussions of elastic distortion potentials, distributed Gaussian translational basis sets,¹¹¹ finite difference boundary value methods,¹¹² and rotational, vibrational, and translational quadrature schemes. Several other computational considerations, including particular storage management strategies, were also subsequently discussed elsewhere.^{113,114}

The MMAD was soon applied to a wide variety of new atom–diatom reactions. In particular, and after initial test applications to $\text{H} + \text{H}_2$,¹¹⁰ and $\text{D} + \text{H}_2$,¹¹⁵ it was used to obtain the first exact 3D quantum scattering results for the $\text{O} + \text{H}_2$ ^{116,117} and $\text{H} + \text{HBr}$ ¹¹⁸ reactions. Both of these $\text{O} + \text{H}_2(v = 0, 1) \leftrightarrow \text{OH}(v' = 0, 1) + \text{H}$ calculations were performed on a single electronic potential energy surface, correlating to $\text{O}(^3P) + \text{H}_2(^1\Sigma_g^+)$ and $\text{OH}(^2\Pi) + \text{H}(^2S)$, and were for total angular momentum $J = 0$. The original calculations of Haug and co-workers were compared with approximate quantum (coupled states distorted wave) results,¹¹⁶ while the subsequent calculations of Zhang and co-workers were compared with variational transition state theory for the threshold energies and a least action semiclassical method for tunnelling probabilities.¹¹⁷

The H_2Br calculations of Zhang *et al.* were the first on this system to include both the exchange ($\text{H} + \text{H}^*\text{Br} \rightarrow \text{HBr} + \text{H}^*$) and the abstraction ($\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$) channels.¹¹⁸ However, an earlier integral cross-section calculation had been reported by Clary, in which the abstraction channel was ignored and the Br assumed to have an infinite mass.¹¹⁹ Happily, Zhang and co-workers computed $J = 0$ reaction probabilities for the exchange channel were found to be in good agreement with the corresponding partial wave results from this earlier work. The exoergic abstraction channel was also found to lead to vibrationally hot H_2 , with the extent of the product vibrational population inversion depending both on the initial HBr rotational state and on the collision energy.¹¹⁸

¹¹⁰ J. Z. H. Zhang, D. J. Kouri, K. Haug, D. W. Schwenke, Y. Shima, and D. G. Truhlar, *J. Chem. Phys.*, 1988, **88**, 2492.

¹¹¹ I. P. Hamilton and J. C. Light, *J. Chem. Phys.*, 1986, **84**, 306.

¹¹² D. G. Truhlar and A. Kuppermann, *J. Am. Chem. Soc.*, 1971, **93**, 1840.

¹¹³ D. W. Schwenke, K. Haug, D. G. Truhlar, R. H. Schweitzer, J. Z. H. Zhang, Y. Sun, and D. J. Kouri, *Theor. Chim. Acta*, 1987, **72**, 237.

¹¹⁴ D. J. Kouri, Y. Sun, R. C. Mowrey, J. Z. H. Zhang, D. G. Truhlar, K. Haug, and D. W. Schwenke in 'Mathematical Frontiers in Computational Chemical Physics', ed. D. G. Truhlar, Springer, New York, 1988, p. 207.

¹¹⁵ K. Haug, D. W. Schwenke, Y. Shima, D. G. Truhlar, J. Z. H. Zhang, and D. J. Kouri, *J. Phys. Chem.*, 1986, **90**, 6757.

¹¹⁶ K. Haug, D. W. Schwenke, D. G. Truhlar, Y. Zhang, J. Z. H. Zhang, and D. J. Kouri, *J. Chem. Phys.*, 1987, **87**, 1892.

¹¹⁷ J. Z. H. Zhang, Y. Zhang, D. J. Kouri, B. C. Garrett, K. Haug, D. W. Schwenke, and D. G. Truhlar, *Faraday Discuss. Chem. Soc.*, 1987, **84**, 371.

¹¹⁸ Y. C. Zhang, J. Z. H. Zhang, D. J. Kouri, K. Haug, D. W. Schwenke, and D. G. Truhlar, *Phys. Rev. Lett.*, 1988, **60**, 2367.

¹¹⁹ D. C. Clary, *J. Chem. Phys.*, 1985, **83**, 1685.

Having thus demonstrated the feasibility of the MMAD, the Kouri and Truhlar groups moved on to the development of the \mathcal{L}^2 -AD GNVP. In their preliminary report on this variational method, which appeared in 1987, Schwenke and co-workers used a multichannel distortion potential to accelerate the convergence of their results.¹²⁰ They found, in accordance with the potential scattering tests of Staszewska and Truhlar, that the \mathcal{L}^2 -AD GNVP gave well converged low energy, $J = 0$, $\text{H} + \text{H}_2$ reaction probabilities with only 2 to 4 translational basis functions per channel. This was certainly a significant improvement over the non-variational MMAD.

Encouraged by its rapid convergence Schwenke *et al.* soon went on to describe the \mathcal{L}^2 -AD GNVP method in more detail.¹²¹ Here they introduced a rotationally inelastic distortion potential, and described a 'method of half-integrated Green's functions' to simplify the evaluation of matrix elements over the corresponding distorted wave Green's function $G_0(E)$. Detailed computational strategies for the \mathcal{L}^2 -AD GNVP, somewhat akin to those reported earlier for the MMAD, have also more recently been described.¹²² Because of the inevitable energy dependence of $G_0(E)$ these strategies are designed to be as efficient as possible for calculations at a single scattering energy E .

The most important early applications of the \mathcal{L}^2 -AD GNVP method were once again to the $\text{H} + \text{H}_2$ reaction.^{123–26} To begin with, and quite soon after the experimental results of Nieh and Valentini first appeared,⁵³ Mladenovic and co-workers considered the effect of orbital and rotational angular momentum averaging on branching ratios of dynamical resonances in $\text{H} + \text{p-H}_2 \rightarrow \text{o-H}_2 + \text{H}$.¹²³ This study involved the calculation of fully converged $J = 0$, $J = 1$, and $J = 2$ reaction probabilities, on the DMBE potential energy surface,¹⁰⁰ in the relative energy range $E_{\text{col}} = 0.60$ to 1.20 eV. Both ground and excited initial rotational states were considered, and the general conclusion of the study was that angular momentum averaging tends to 'wash out' much of the resonant structure seen in individual partial waves.⁹¹ This conclusion was of course verified in the subsequent LSTH integral cross section calculations of Zhang and Miller,⁵⁴ and in the DMBE integral cross section calculations of Manolopoulos and Wyatt.¹⁰¹

In the second application of the \mathcal{L}^2 -AD GNVP method to the $\text{H} + \text{H}_2$ reaction, Zhao and co-workers compared quantum mechanical and classical trajectory calculations, on the DMBE potential energy surface, at a relative translational energy of 1.1 eV.¹²⁴ Total angular momenta up to $J = 4$ were included in this comparison, and it was found that for most final states the classical and quantum mechanical results agreed to within a factor of two. Indeed the classical trajectory value for the important $v' = 1$ over $v' = 0$ product vibrational branching ratio was only found to be too high by a factor of 1.6. The classical trajectory calculations were then fully converged with respect to the total angular momentum quantum number J ,¹²⁴ and the resulting

¹²⁰ D. W. Schwenke, K. Haug, D. G. Truhlar, Y. Sun, J. Z. H. Zhang, and D. J. Kouri, *J. Phys. Chem.*, 1987, **91**, 6080.

¹²¹ D. W. Schwenke, K. Haug, D. G. Truhlar, Y. Sun, J. Z. H. Zhang, and D. J. Kouri, *J. Phys. Chem.*, 1988, **92**, 3202.

¹²² D. W. Schwenke, M. Mladenovic, M. Zhao, D. G. Truhlar, Y. Sun, and D. J. Kouri in 'Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules', ed. A. Laganà, Kluwer, Dordrecht, 1989, p. 131.

¹²³ M. Mladenovic, M. Zhao, D. G. Truhlar, D. W. Schwenke, Y. Sun, and D. J. Kouri, *Chem. Phys. Lett.*, 1988, **146**, 358.

¹²⁴ M. Zhao, M. Mladenovic, D. G. Truhlar, D. W. Schwenke, Y. Sun, D. J. Kouri, and N. C. Blais, *J. Am. Chem. Soc.*, 1989, **111**, 852.

classical branching ratio was found to be 2.5 times larger than that observed experimentally by Nieh and Valentini.⁵³

Following this comparison between quantum mechanical and classical trajectory results, Mladenovic and co-workers moved on to a highly detailed quantum mechanical analysis of product state distributions at $E_{\text{tot}} = 1.0687$ eV.¹⁵ This calculation of $\text{H} + \text{H}_2$ integral cross sections, which again included both ground and excited initial rotational states, was the first application of the \mathcal{L}^2 -AD GNVP method to very high total J . Reasonable agreement was also found with Nieh and Valentini's experimental $v' = 1$ over $v' = 0$ product vibrational branching ratio at this one energy for which the calculations were performed.¹²⁵

In the most recent work of the Kouri and Truhlar groups on the $\text{H} + \text{H}_2$ reaction, Zhao *et al.* have reported a detailed 'spectroscopic' analysis of the transition state region of H_3 .¹²⁶ This analysis amounts to $J = 0$, $J = 1$, and $J = 4$ reactive scattering studies in which state-to-state time delays and Argand diagrams are plotted to elucidate the nature of the observed resonance effects.³⁶ In particular, reaction probabilities in the energy range $E_{\text{tot}} = 0.85$ to 1.15 eV are found to show energy dependences attributable to dynamical resonances with vibrational quantum numbers (10^0) and (11^0) .¹²⁶ Interestingly, earlier such resonance analyses for $J = 0$ are referenced by Nieh and Valentini to explain the structure seen in their experimental cross section curves.⁵³

With these successful $\text{H} + \text{H}_2$ applications in hand Zhao and co-workers moved on to the less symmetric, and therefore more difficult, $\text{D} + \text{H}_2$ reaction.^{127–129} In their first paper on this reaction they reported a state-to-state time delay analysis, in the energy range $E_{\text{tot}} = 0.93$ to 1.23 eV, which included total angular momenta up to $J = 14$.¹²⁷ For $J = 0$ they found that the lowest energy (0.95 eV) resonance showed enhanced vibrational excitation, in agreement with the experimental measurements of Phillips, Levene, and Valentini.¹³⁰ However, this trend was reversed in the calculations at higher J .¹²⁷

The next application of the \mathcal{L}^2 -AD GNVP method to the $\text{D} + \text{H}_2$ reaction was once again a comparison of quantum mechanical and quasiclassical trajectory calculations on the DMBE potential energy surface.¹²⁸ These calculations involved total angular momentum quantum numbers $J = 0, 1$, and 2, at four total energies in the range $E_{\text{tot}} = 0.98$ to 1.33 eV, and concentrated on rotationally excited ($j = 1$) H_2 . The general conclusion of the investigation was that, although the two methods agreed quite well for certain rotationally averaged product states, the partial cross sections calculated by the quasiclassical trajectory method were systematically larger than the accurate quantum mechanical results.¹²⁸

In their latest paper on the $\text{D} + \text{H}_2$ reaction Zhao and co-workers consider the effect of H_2 rotational excitation on state-to-state differential cross sections at five separate energies in the range $E_{\text{tot}} = 0.82$ to 1.35 eV.¹²⁹ These differential cross section calculations on the DMBE surface are compared with the earlier results of Zhang and

¹²⁵ M. Mladenovic, M. Zhao, D. G. Truhlar, D. W. Schwenke, Y. Sun, and D. J. Kouri, *J. Phys. Chem.*, 1988, **92**, 7035.

¹²⁶ M. Zhao, M. Mladenovic, D. G. Truhlar, D. W. Schwenke, O. Sharafeddin, Y. Sun, and D. J. Kouri, *J. Chem. Phys.*, 1989, **91**, 5302.

¹²⁷ M. Zhao, D. G. Truhlar, D. J. Kouri, Y. Sun, and D. W. Schwenke, *Chem. Phys. Lett.*, 1989, **156**, 281.

¹²⁸ N. C. Blais, M. Zhao, M. Mladenovic, D. G. Truhlar, D. W. Schwenke, Y. Sun, and D. J. Kouri, *J. Chem. Phys.*, 1989, **91**, 1038.

¹²⁹ M. Zhao, D. G. Truhlar, D. W. Schwenke, and D. J. Kouri, *J. Phys. Chem.*, in press.

Miller on the LSTH surface.⁹⁰ In some specific cases the effect of H_2 rotational excitation, which was not considered by Zhang and Miller, is found to be quite substantial. Indeed certain backward differential cross sections are found to increase by factors of up to 45 when one quantum of rotational excitation is added to the H_2 .¹²⁹ Moreover, the extensive tabulation of results given by Zhao *et al.* has already proved useful, for example, in a comparison with experimental $HD(v' = 1, j')$ product rotational distributions at $E_{\text{col}} = 1.05 \text{ eV}$.¹³¹

While all of this work on the $H + H_2$ and $D + H_2$ reactions was in progress, Yu and co-workers were also using the \mathcal{L}^2 -AD GNVP methodology to study the highly exoergic, and therefore still more demanding, $F + H_2$ reaction.^{105,132} Here the early work was on the well studied M5 potential energy surface of Muckerman,¹³³ for which Yu *et al.* reported the first fully converged $J = 0$ reaction probabilities for $F + H_2$.¹³² In this paper the authors also compare versions of their methodology with and without $A + B_2$ symmetrization. They find that, while both versions eventually give the same results, the unsymmetrized calculations are somewhat more difficult to converge.¹³²

Having established these benchmark results for the M5 surface, Yu and co-workers have since moved on to use the improved T5A surface of Steckler, Truhlar, and Garrett.^{47,105} Here they report converged $J = 0$ reaction probabilities and delay times for $F + H_2(v = 0, j = 0, 2, 4) \rightarrow HF(v') + H$, summed over j' , in the total energy range $E_{\text{tot}} = 0.30\text{--}0.46 \text{ eV}$. The computed reaction probabilities show no delay threshold for $v' = 3$ relative to $v' = 2$, and the computed state-to-state delay times show no resonant structure for initial orbital angular momentum $l = 0$. Both of these observations are in good agreement with experiment.⁴⁸ Moreover, the $v' = 3$ over $v' = 2$ product vibrational branching ratio, which is inverted relative to experiment for $l = 0$, is found to decrease quite rapidly as a function of l .¹⁰⁵

Several new methodological developments have also recently been proposed to facilitate future applications of the \mathcal{L}^2 -AD GNVP approach. These developments, which once again address the two major bottlenecks in variational reactive scattering described above, include the study of Duneczky, Wyatt, and co-workers on iterative methods for solving the resulting linear equations,¹³⁴ the direct application of complex boundary conditions by Sun *et al.*, which make the method amenable to iterative solution for transitions from a single initial state,¹³⁵ and a basis set contraction scheme introduced recently by Zhao *et al.* and tested in applications to $F + H_2$.¹³⁶ To give some idea of what these new methodological developments might bring we note that the direct application of complex boundary conditions, for example, has already proved useful in an extension of Yu and co-workers' $F + H_2$ study to total angular momenta $J = 1$ and 2.¹³⁷

¹³⁰ D. L. Phillips, H. B. Levene, and J. J. Valentini, *J. Chem. Phys.*, 1989, **90**, 1600.

¹³¹ D. A. V. Kliner, K.-D. Rinnen, and R. N. Zare, *Chem. Phys. Lett.*, 1990, **166**, 107.

¹³² C. Yu, Y. Sun, D. J. Kouri, P. Halvick, D. G. Truhlar, and D. W. Schwenke, *J. Chem. Phys.*, 1989, **90**, 7608.

¹³³ J. T. Muckerman, *Theor. Chem. Advan. Persp., Sect. A*, 1981, **6**, 1.

¹³⁴ C. Duneczky, R. E. Wyatt, D. Chatfield, K. Haug, D. W. Schwenke, D. G. Truhlar, Y. Sun, and D. J. Kouri, *Comp. Phys. Comm.*, 1989, **53**, 357.

¹³⁵ Y. Sun, C. Yu, D. J. Kouri, D. W. Schwenke, P. Halvick, M. Mladenovic, and D. G. Truhlar, *J. Chem. Phys.*, 1989, **91**, 1643.

¹³⁶ M. Zhao, D. G. Truhlar, D. W. Schwenke, C. Yu, and D. J. Kouri, *J. Phys. Chem.*, in press.

¹³⁷ C. Yu, D. J. Kouri, M. Zhao, D. G. Truhlar, and D. W. Schwenke, *Int. J. Quantum Chem. Symp.*, 1989, **23**, 45.

5 Conclusions

It should be clear from the preceding sections that there are now a variety of 'exact' ways to solve the Schrödinger equation for three dimensional atom-diatom reactions. Happily, the various methods are also giving excellent numerical agreement with one another, both at the $J = 0$ reaction probability and integral and differential cross section levels. This quantitative agreement, for a fairly diverse variety of elementary chemical reactions, represents a significant advance over the situation in theoretical reaction dynamics as recently as five years ago.^{1,2}

At present the two leading approaches to quantum reactive scattering are hyperspherical coordinate methods,³⁷⁻⁶⁷ and variational methods based on the simultaneous use of mass-scaled Jacobi coordinates in each of the chemical arrangements involved.⁷⁹⁻¹³⁷ These two approaches are somewhat complementary: both have already seen numerous important applications, and it is as yet unclear which will ultimately prove the 'best' to use. Hyperspherical coordinate methods provide a new physical picture of reactive scattering in terms of adiabatic hyperradial potential energy curves, which correlate asymptotically with the bound ro-vibrational energy levels of the reactant and product fragments and are useful for interpreting dynamical resonance effects. They also lead quite naturally to optimum angular momentum decoupling approximations of the 'coupled states' or 'centrifugal sudden' form. Jacobi coordinate variational methods do not at present provide such a useful physical picture of the dynamics, but are nevertheless somewhat more amenable to perturbation theory approximations of the 'distorted wave' type. Natural collision coordinate methods,²⁵⁻³⁵ which still give the most intuitive physical picture of all, appear to be computationally intractable for the more demanding reactions studied to date.

For a more detailed summary of the present situation we note that converged $J = 0$ reaction probabilities can now be obtained quite routinely for a wide variety of atom-diatom reactions. Moreover, differential and integral cross sections, which are really necessary for anything but a hand-waving comparison with experiment, can also be obtained, at quite high scattering energies, for all the deuterium substituted analogues of $\text{H} + \text{H}_2$. However, cross sections for highly exoergic reactions with heavier atoms are still quite difficult to obtain. Since a large number of experimentally interesting reactions fall into this latter category the need for further methodological developments is clear.

Several other important problems also await detailed theoretical formulations and efficient three dimensional numerical implementations. These include the study of electronically non-adiabatic reactions,¹³⁸ the description of subtle geometric effects caused by the conical intersection of ground and excited electronic potential energy surfaces,^{139,140} collision induced dissociation,¹⁴¹ and reactions involving polyatomic molecules.^{23,24} However, since potential energy surfaces and dynamics calculations appear at last to be converging on a realistic *ab initio* quantum theory of reactive scattering, the future prospect for each of these problems is good.

¹³⁸ See, for example, M. Baer in 'Theory of Chemical Reaction Dynamics', ed. M. Baer, CRC Press, Boca Raton, 1985, vol. II, chap. 4.

¹³⁹ G. Herzberg and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, 1963, **35**, 77; H. C. Longuet-Higgins, *Proc. Roy. Soc. A*, 1975, **344**, 147.

¹⁴⁰ C. A. Mead and D. G. Truhlar, *J. Chem. Phys.*, 1979, **70**, 2284; C. A. Mead, *J. Chem. Phys.*, 1980, **72**, 3839.

¹⁴¹ See, for example, D. J. Diestler in 'Atom-Molecule Collision Theory: A Guide for the Experimentalist', ed. R. B. Bernstein, Plenum, New York, 1979, chap. 20.