REACTIVE MOLECULAR COLLISIONS

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INTRODUCTION

The reactive molecular collision is the fundamental microscopic event that underlies the chemical reaction. The ability to describe this process from a knowledge of forces operating at the molecular level has long been the goal of the theoretical dynamicist.

The field of reactive molecular collisions, and fields related to it, have been reviewed frequently within the last five years. For the newcomer, two excellent textbooks on molecular collision dynamics provide a broad background of the subject: the introductory text, Molecular Reaction Dynamics, by Levine & Bernstein (1) and the more comprehensive text by Child (2), Molecular Collision Theory. In addition, there are several volumes whose chapters consist of excellent reviews of specific topics relevant to reactive collisions. The most recent of these, and the most comprehensive to date, is Bernstein’s handbook for the experimentalist, Atom-Molecule Collision Theory [Reference (3), abbreviated AMCT]. Every topic we consider in this review is represented by one or more chapters in Bernstein’s book. In addition to Bernstein’s volume, equally excellent review material (although now somewhat older) is contained in two volumes edited by Miller, Dynamics of Molecular Collisions, Part A [Reference (4), abbreviated DMCA], and Part B [Reference (5), abbreviated DMCB].

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Our review necessarily does not cover several topics that are inseparable from reactive molecular collision theory. These include the vast body of sophisticated and detailed experimental data, upon which the theory must be built. Experiments are discussed in many reviews, including Bernstein's AMCT chapter (6). The most recent experimental review is given by Levy (7), and includes a truly exhaustive compilation of data for every atom-diatom system studied in recent times.

We also cannot do justice to describing the efforts of the quantum chemist to generate the potential energy surfaces upon which all dynamical theories critically depend. In his AMCT review, Schaefer (8) describes considerable progress with ab initio methods. The dynamicist's need to evaluate points on potential surfaces often and cheaply prompts our interest in semiempirical methods, such as the method of diatomics-in-molecules (DIM). A detailed description of the DIM method presented by Kuntz (9) in an AMCT review, and the earlier DMCB review by Kuntz (10) describes how reaction dynamics is affected by specific properties of potential energy surfaces.

Information theoretic concepts now permeate almost every aspect of molecular collision dynamics, including reaction. This is an extremely vigorous field, and reviews appear on a yearly basis. The most recent is again an AMCT review, a chapter by Levine & Kinsey (11). Levine (12) has also given a review in the 1978 volume of the Annual Review of Physical Chemistry series. We consider other features of reaction dynamics here.

After describing what we do not cover in this review, we now turn our attention to the topics we do plan to discuss. There are three major sections in this review: the first describes the classical dynamical approach to reactions; the second concentrates on quantum dynamics; the third section considers some special topics.

Most dynamical treatments of reactive collisions use classical mechanics—assembling the global dynamics by calculating ensembles of trajectories evolving on the appropriate potential surface(s). We would do the calculations quantum mechanically, except that at present the only practical quantum technology for reaction dynamics that retains the full mathematical dimensionality of the problem is applicable only to the simplest systems. By assuming that nuclear motion can be treated classically, we opt instead for a practical (but at least well-defined) dynamical approximation. The classical approach is documented in many reviews: The most recent are the AMCT reviews by Pattengill (13) for inelastic rotational scattering and by Truhlar & Muckerman (14) for reactive scattering. The earlier DMCB review by Porter & Raff (15) presents an excellent discussion of classical methodology applied to
atom-diatom systems. This review describes in detail how to select initial conditions for trajectories; the Truhlar & Muckerman review gives a more detailed discussion for analyzing final conditions.

Although classical mechanics is itself well defined, its applications to molecular reactions and the interpretation of its results evolve with experience. Here we briefly consider the theory as it is most often applied (to atom-diatom systems), and we then discuss the problems we expect to encounter as these methods are extended to more complicated systems.

Exact quantum scattering calculations are limited by basis-set considerations to calculations in one physical dimension. There is only a handful of converged three-dimensional calculations. Several reviews of quantum collision methods are contained in Bernstein’s AMCT handbook. The review by Secrest (16) compares several numerical methods commonly used to solve the coupled equations characteristic of quantum collision theories. Light (17) presents a formal introduction to the reactive problem, and Wyatt (18) presents a detailed comparison of methods that have been applied in actual calculations. Wyatt (19) also presents a separate discussion of various approximate quantum approaches to reactive scattering. More recently, Connor (20) has reviewed reactive molecular collision calculations up to early 1979. This review contains extensive literature references. Earlier reviews of quantum reactive scattering include the 1976 review by Truhlar & Wyatt (21), concentrating on the H + H₂ reaction, and the 1975 review by Micha (22), covering quantum reactive scattering.

Exact, fully three-dimensional quantum reactive calculations are still sufficiently difficult that very little new work has been reported in the last year. Here we concentrate on approximation methods, because development of reliable approximate techniques is essential if we are to treat reactions quantum mechanically.

The final section briefly describes progress in several allied fields. There is considerable activity in statistical theories of reaction, including transition state theories and phase space theories. Truhlar (23) has recently reviewed transition state theories, and Pechukas’ DMCB review (24) presents a general and very readable discussion of statistical reaction theories. At higher collision energies, collision-induced dissociation (CID) becomes a significant alternative channel for reaction. A review of the classical treatment of CID processes is given in AMCT by Kuntz (25), and the quantum treatment is presented there by Diestler (26). Finally, dynamicists have become increasingly interested in whether or not intense electromagnetic fields can affect reaction dynamics. We conclude this review by discussing recent developments in this area.
CLASSICAL TRAJECTORY CALCULATIONS

Far more calculations of dynamical processes employ a classical trajectory approach than any other. Classical trajectory methods have been applied extensively to molecular systems ever since modern electronic computers have been available. The ease with which most problems can be adapted to the modern minicomputer environment ensures the viability of the method for the indefinite future. Almost any review article describing theoretical treatments of molecular dynamics emphasizes the contribution of classical mechanics. The classical approach itself has been reviewed often; in 1974 Porter (27) reviewed the application of classical methods from their inception up to the early 1970s. In the introduction, we mentioned several of the most recent reviews of classical methods (13–15). Classical calculations were also reviewed by Connor (20).

The trajectory approach to dynamics earns its popularity because it is the only method currently available that is general enough to treat the wide range of problems facing the dynamicist. Trajectory calculations of atom-diatom reactions now appear routinely; the treatment today is basically that originally described by Karplus et al (28) in 1965.

In the last year alone, many trajectory calculations have appeared. Because of its basic importance to the dynamics community, calculations for the H+H$_2$ exchange reaction continue to receive frequent attention. Osherov et al (29) provide a sketchy account of calculations for reaction from the initial v = 1 excited state of H$_2$. Mayne & Toennies (30) and Mayne (31) also report calculations for the H+H$_2$ reaction, using the most recent and accurate HHH potential surface of Truhlar & Horowitz (32). This surface is an analytic fit to the ab initio calculations of Liu (33) and Siegbahn & Liu (34).

Trajectory calculations are frequently used to compare theoretical dynamics with experimental results, at least at the rate constant level. Several calculations in this category have been reported in the last year. In a continuing study of the He+H$_2^+$ reaction, Zuhrt et al (35) consider the effectiveness of reactant translational, vibrational, and rotational energy in promoting reaction. Gittins & Hirst (36) report calculations for a single surface model of the N$^+$+H$_2$ reaction, in which the surface has an extremely deep well for C$_{2v}$ geometries. Schinke & Lester (37) report calculations for the O(3P)+H$_2$ reaction, using their own ab initio potential surface. Luntz et al (38) report a study of the O($^1$D)+H$_2$ reaction, in which both trajectory results and experimental product rotational state distributions differ significantly from phase space theory predictions. Herbst et al (39) studied the ion-molecule reaction O$^- +$ D$_2$
at relatively high energies, using the multisurface "trajectory-surface-leaking" model of Preston & Cohen (40). Jaffe (41) reports theoretical rate constants for the atmospherically important ClO + O reaction, and Persky (42) reports rate constants, isotope effects, and energy disposal features for the Cl + HD reaction.

Trajectory calculations are also used to investigate the relationship between scattering dynamics and potential surface effects or statistical theories. Polanyi & Schreiber (43) use trajectory results to test information theoretic predictions of branching ratios for the F + HD reaction. Polanyi & Sathyamurthy (44, 45) use trajectories to study the relationship between features of the potential surface and dynamics for model systems. Duff & Brumer (46) use trajectories as a tool for investigating statistical behavior in two reactions involving long-lived complexes, the K + NaCl and H + ICl reactions.

In the future we will undoubtedly see an increasing number of calculations involving more than three nuclei. Recent examples are the four-center reactions of HBr + Cl₂ and HBr + BrCl, studied by Brown et al (47). In this calculation, both reactants and products are diatomic molecules, but calculations are more difficult to interpret when triatomics and higher polyatomics are considered. We discuss some of these additional difficulties later, but a flavor for the problems involved can be detected in the unimolecular decomposition reaction studies of Hase et al (48) for C₂H₅ and of Grant & Bunker (49) for ethane.

**Classical vs Quantum Studies**

Apart from the practical problems that must be faced when implementing a classical trajectory calculation, there is always the conceptual question: How reliable is classical mechanics for treating nuclear motion in molecular systems? Truhlar & Muckerman (14) present a discussion of this point in their review. At the most detailed dynamical level, a failure of classical mechanics can usually be attributed to circumstances in which the important dynamics is associated with motion characterized by a large deBroglie wavelength. For this reason, classical mechanics does poorly at predicting reaction thresholds and misses resonance features altogether. On the other hand, when the dynamics of interest involves less detail (more averaging), classical mechanics tends to do a better job.

Of course, the best way to see how well a classical calculation works is to solve the problem both classically and quantum mechanically. Classical vs quantum studies are very popular in the literature. Because exact quantum reactive calculations are primarily restricted to collinear
geometries, virtually all collinear classical calculations are performed nowadays purely to provide a data base for classical vs quantum comparisons. Recent examples of this type of work may be found in papers by Truhlar and co-workers (50–53) for the collinear I + H₂, H + Cl₂, H + H₂, F + H₂, and Cl + H₂ systems, and in the papers of Connor and co-workers (54–56) for the collinear X + F₂ (X = Me, H, D, T) system. Hutchinson & Wyatt (57) have also studied the collinear F + H₂ reaction to investigate both classical vs quantum and classical vs statistical behavior. In connection with statistical behavior in this system, see also the related paper by Duff & Brumer (58).

Practical Considerations

Having decided to use classical trajectories to study a particular dynamical system, we must still face several practical considerations. For the basic single surface A + BC reaction, the methodology (13–15) is known, and the problems discussed below are generally not serious. But for polyatomic systems, many of these problems must be reconsidered [see References (48, 49) and references cited therein].

We consider classical trajectory calculations in three stages.

1. We must decide how to specify initial conditions for each trajectory.
2. The system is allowed to evolve according to the classical equations of motion.
3. We decide when each trajectory is over and the final coordinates and moments are analyzed to see what has happened.

Each stage of the calculation presents its own unique problems. We now consider some of these problems, as they occur for A + BC reactive systems.

INITIAL CONDITIONS  The conventional wisdom in molecular scattering calculations (whether reactive or not) is to prepare the molecular species so that its rotational and vibrational action variables correspond to integral quantum numbers (times ℏ) for the associated quantum system. Calculations done this way are termed quasiclassical trajectory calculations; this is the method almost universally used in molecular scattering systems. It is not difficult to prepare initial conditions this way for diatomic molecules; however, in treating triatomic and higher polyatomic species, this part of the problem becomes increasingly difficult because nonseparability of the internal molecular degrees of freedom becomes important. At higher energies it may no longer be possible to find good classical action variables for such systems.

A second problem with initial conditions is statistics. After quantizing the classical action variables, the uncertainty principle requires all
values of the conjugate angle variables to be equally likely. The common practice is to select these variables randomly in a multidimensional Monte Carlo integration procedure. The Monte Carlo approach is normally preferred to nonrandom initial condition selection methods (15) because (a) the associated statistical error is easily evaluated and (b) the accuracy of the Monte Carlo method can be systematically improved by running more trajectories, thus accumulating all the results. (If insufficient accuracy has been obtained in the nonrandom selection method and a greater number of trajectories has to be integrated, then the trajectories already computed are discarded.)

Statistical problems arise when the desired dynamical event occurs with a low probability. In such cases, many trajectories are required before enough of interest are found (for example, reactive trajectories at low collision energies). Several strategies can then be employed to improve the initial condition sampling problem. These strategies include importance sampling procedures, stratified sampling procedures, and the nonrandom initial condition selection method. These methods are discussed in detail in recent reviews (13–15); discussion and use of the importance sampling method may be found in several papers (43, 60–61). Furthermore, Suzukawa & Wolfsberg (62) recently presented evidence for the improved convergence properties of the nonrandom initial condition selection method.

INTEGRATING TRAJECTORIES Once an initial condition algorithm has been selected, integrating the equations of motion is usually straightforward. In terms of computer time, however, it is by far the most time-consuming part of the study. Many numerical methods for integrating the usual differential equations are discussed in earlier reviews (14, 15).

Collisions typically begin and end at separations large enough so that the interaction between unbound particles is negligible. Unfortunately, the interesting dynamics (reaction and energy transfer) occurs during the relatively short time that the particles are close together. Therefore, a significant part of the trajectory effort is expended in the nearly noninteracting region. Billing & Poulsen (63) propose an asymptotic perturbation theory to reduce the expense of bringing the collision partners close together. Their approach uses action angle variables and is therefore more difficult to apply to polyatomic molecules.

A problem associated with trajectory integration arises whenever the interesting dynamics occurs slowly on a time scale defined by the fastest molecular motions followed. In such cases, a very large number of trajectory integration steps become necessary. A standard procedure to verify the accuracy of (selected) individual trajectories is to run them
backwards from their final conditions to see how well the initial conditions are reproduced. Duff & Brumer (46, 58, 64-66) point out that many classical systems exhibit instabilities (exponential divergence between trajectories initially close together in phase space) that preclude reliable integration for extremely long times—times so long that trajectories cannot be back-integrated successfully. Related to this problem are questions of ergodic and stochastic behavior in molecular systems (64, 65, 67-72), which are beyond the scope of this review. These questions are now entering the reactive collision literature (46, 57, 58) and more work in this area is sure to follow in the 1980s.

FINAL CONDITIONS Although it is straightforward to analyze classical trajectory data and obtain estimates of averaged quantities such as rate constants and vibrational energies, there are no reliable methods for obtaining accurate quantum state-to-state cross sections from these data. Classical mechanics samples a continuous distribution of final action variables, whereas quantum mechanics produces only discrete distributions of action variables. To express the classical data in a quantum mechanical language, we must somehow “discretize” the classical distribution. The rare trajectory with quantized final conditions is of central importance to the semiclassical S-matrix theory of collisions (14, 73-75); unfortunately, as the phase space of the system increases, the task of finding these very special trajectories becomes insurmountably difficult.

Several methods are commonly used to quantize the final conditions obtained from trajectories. One is the histogram method, which takes the final quantum state as the state with quantum numbers closest to the actual nonintegral action variables obtained classically. A second approach finds the quantum final state distribution which reproduces (some of) the moments of the distribution obtained classically. Both methods have been reviewed in detail (13, 14). A third approach, called smooth sampling, assigns trajectories to more than one quantum bin in proportion to the difference between the actual final actions and the nearest integral actions (55, 76-79). How well these procedures actually work in practice is usually the central objective of the classical vs quantum comparison studies referred to earlier (50-57).

Calculations Involving Polyatomics

Calculations involving triatomic and higher polyatomic species are of increasing interest. In these larger molecules the distribution of energy among the molecular vibrational degrees of freedom may affect dynamical processes such as reaction and energy transfer. The problem of
quantizing final states (and also of preparing initial states) becomes much more difficult when molecules more complicated than diatomics are treated. Unfortunately, the quantity we most want to study in polyatomics is the energy distribution within the molecule.

In order to minimize the computational expense of trajectories, we want to use a coordinate system in which the equations of motion are efficiently formulated. It has been recognized for some time (27, 80) that the most efficient coordinate system is the space-fixed (SF) Cartesian reference frame. The task of preparing initial conditions and analyzing final conditions requires the canonical transformation between SF Cartesian coordinates and coordinates which directly express the degrees of freedom of the polyatomic in more separable terms. First, we want to separate the overall dynamics into translational, rotational, and vibrational components. Separating overall translational motion is easy. However, Coriolis interactions make it impossible to separate cleanly the rotational and vibrational motions of a polyatomic molecule. By viewing the motion of the polyatomic from a body-fixed (BF) reference frame satisfying the Eckart conditions (81–83), we minimize the Coriolis coupling between overall rotation (carried completely by the BF frame) and vibration. Before and after collision, the total energy of the polyatomic is constant in time, and so it is always possible to define the total energy transfer in a collision. However, the Coriolis interaction complicates apportioning this energy transfer between rotational and vibrational motions, because the rotational and vibrational energies of the polyatomic vary with time. By time averaging (83) the rotational and vibrational energies over several (of the lowest frequency) vibrational periods, we can define rotational and vibrational energy transfers.

At this point, we can now turn our attention to distributing the internal energy among the 3N–6 vibrational degrees of freedom. Thinking quantum mechanically about the states of a polyatomic, we are inclined to speak of internal excitations in terms of the system normal modes. However, the idea of normal modes to the practitioner of quantum mechanics differs significantly from the classical definition of normal modes. Classically, normal modes refer to the coordinate representation in which there are no off-diagonal quadratic terms in the multidimensional Taylor series expansion of the molecular force field about the equilibrium conformation of the molecule. The practitioner of quantum mechanics, in referring loosely to normal modes, really means those molecular degrees of freedom in which excitations are maintained indefinitely in the absence of perturbations (classical constants of motion). These degrees of freedom are classical normal modes only in the limit of infinitesimally small excitations. As soon as finite excitations are
allowed classically (even excitations so small that they correspond to quantum zero point energies), then normal modes are no longer classical constants of motion. Instead, the true constants of motion are expressed classically in terms of the "good" actions and action angle variables. Finding these variables is a subject of intense activity beyond the scope of this review. For recent work in this area, the reader should consult the papers of Schatz and co-workers (84–87), Marcus and co-workers (88–91), Miller and co-workers (92–94), Sorbie (95), Sorbie & Handy (96), Colwell & Handy (97), and Jaffe & Reinhardt (98). These workers have concentrated on triatomics; at present the methods appear practical enough that it should be possible to perform quasiclassical trajectory calculations for systems in which the most complicated polyatomic is a triatomic. How these methods will perform for higher polyatomics is presently unknown. Without a definition of good action variables, trajectory calculations will be limited in their ability to describe the role of energy distribution within a polyatomic molecule.

QUANTUM REACTIVE CALCULATIONS

Exact Methods

The development of practical methods capable of providing a dynamically accurate (quantum) description of molecular reactive scattering processes has been a field of considerable activity within the last 15 years. At first, accurate quantum calculations were restricted to A + BC reactions in the one-dimensional collinear (1D) world, whereas there are now several accurate, fully three-dimensional (3D) quantum calculations. Even in the last four years, progress in quantum reactive scattering has been reviewed often. Because of the central role the H + H₂ exchange reaction has played in this area, Truhlar & Wyatt reviewed both theoretical and experimental work on this reaction in 1976 (21). Further progress and some results for the 3D H + H₂ and F + H₂ reactions were again presented by Wyatt (99) in 1977. The 1979 review of reactive calculations by Connor (20) considers primarily the results of quantum collinear calculations, and Light's 1979 review (17) presents a formal introduction to the quantum reactive problem and discusses several formal considerations appropriate to the quantum reactive problem. By far the most comprehensive review of theoretical methods available to date is that of Wyatt (18), who presents a comparative discussion of similarities and differences in current 3D quantum scattering theories. After a brief introduction, we consider in this section both exact collinear and exact three-dimensional quantum approaches and point out newly proposed methods that may extend our capabilities in
the future. Only very limited work has been done on quantum systems more complicated than the single surface A + BC reaction, and so here we consider only this system.

Although other methods have been tried, the most productive current approach for accurate quantum calculations of chemical reactions consists of a coupled-channel solution of the Schrödinger equation, written in natural collision coordinates (NCC). In the coupled-channel formalism, all degrees of freedom except one are expanded in a target basis set of square integrable functions. The coupled-channel equations are then solved numerically for motion in the final degree of freedom, referred to variously as either the reaction, propagation, scattering, or translational coordinate. Algorithms for solving the coupled equations typically require computer times that go asymptotically as $N^3$, where $N$ is the number of channels in the wavefunction expansion. This $N^3$ dependence on basis-set size defines one primary goal of any close coupling theory of quantum reactive scattering—to devise a method that keeps the basis set as small as possible.

Of course, any quantum close-coupling study, reactive or not, requires a large basis expansion if particles with large masses, strong coupling and/or high energies are involved. Quantum dynamics is mostly concerned with light-mass low-energy systems anyway, because these presumably show the most pronounced quantum effects.

There are, however, problems peculiar to reactions that require special strategies for minimizing basis-set size requirements. One such strategy is the choice of natural collision coordinates. Because of the difference in asymptotic motions for reactants and products, we must use different coordinates for them. Natural coordinates transform (at least some of) these coordinates smoothly. Their use also minimizes the target basis-set size because they can be chosen to represent the "natural" motions of the three-body system (translation, rotation/bending, and vibration) everywhere along the scattering coordinate. The more "natural" the collision coordinates are, the more effectively we can choose a small internal basis to represent bound-like motion.

The second common strategy is prompted by the following consideration. For reactants, we want an internal basis that efficiently represents the molecular BC vibrational and rotational motions, whereas for products, the internal basis should be equally efficient in representing the (different) vibrations and rotations of the (AB or AC) product molecule(s). Consequently, it is common practice to deform the internal basis, either continuously or by segments, along the reaction coordinate. This procedure is unnecessary in nonreactive systems, where the deformation of the target induced by the projectile is much less severe.
Dynamical approximations for reactive scattering are interesting in so far as they effect a reduction in the number of coupled equations to be solved simultaneously. Approaches such as these, including reactive versions of the coupled states (CS) or infinite order sudden (IOS) approximations, are discussed later.

COLLINEAR CALCULATIONS The most drastic (and most effective) way to reduce the size of the reactive basis set is to restrict the nuclei to move along a common line. Today, collinear quantum calculations for the A + BC reaction are commonplace and quite inexpensive. So long as the mass combinations and energies of interest do not require too large a basis set, the quantum calculation is often cheaper than the corresponding quasiclassical trajectory calculation would be. For certain mass combinations (H–L–H, L–H–H, and H–H–H, where L=light, H=heavy), large basis expansions are necessary in an NCC close-coupling approach. The H–L–H mass combination is especially troublesome because it generates an extreme (mass dependent) skewing of the collinear configuration space. The NCC in such a skewed space do not represent effectively the natural motions of the triatomic in the strong interaction region; large basis expansions result from the coordinate defect. The L–H–H and H–H–H mass combinations are difficult because of the preponderance of heavy nuclei.

Collinear calculations, in spite of the severity of the dynamical approximation, are important for a variety of reasons. New coordinate systems and new theoretical approaches are most easily explored for collinear systems. For example, McNutt & Wyatt (100) discuss a generalized hyperbolic coordinate system, an extension of coordinates suggested by Witriol et al (101), which are not multivalued for ABC configurations typical of A+B+C. Coordinates such as these may be useful for coupled-channel treatments of collision-induced dissociation. A variety of alternative theoretical treatments of quantum reactive scattering have been introduced for collinear systems. Garrett & Miller (102) and Adams & Miller (103) have proposed an exchange kernel approach that avoids the use of natural collision coordinates at the expense of solving coupled integro-differential equations instead of ordinary coupled equations. Rabitz et al (104) and Askar et al (105) treat the collinear reactive problem using the finite-element method. This method is widely used in other fields (106), and also avoids using natural collision coordinates. Askar et al (107) also suggest that a combination of the finite-element method (in the strong interaction region) with the coupled-channel method (in the asymptotic region) may be computationally advantageous.
A variety of numerical methods have been proposed to solve reactive coupled-channel equations. We are naturally inclined to prefer the R-matrix propagation method (108–111). It is a fast and general numerical method, easy to program, stable to the inclusion of closed channels, and automatically produces unitary S-matrices with arbitrarily small basis expansions. There are, of course, several alternative methods, and the one actually used is mostly a matter of convenience. Those commonly used include Gordon’s (112) propagation method, the integral equation method proposed by Adams et al (113), and the state-path-sum method of Manz (114, 115) and Connor et al (116). The state-path-sum method and the R-matrix propagation method are similar in that they are both invariant imbedding solutions (16) to the Schrödinger equation; both methods obtain the global dynamics by assembling solutions of many boundary value problems, each localized in small regions (sectors) of configuration space. Recently, Basilevsky & Ryaboy (117) have also presented a sector-oriented method for the collinear reactive problem; to us, their approach seems very similar to our own. Because they do not factor the scattering wavefunction optimally (118), their coupled equations are complicated by first derivative operators. They then introduce several approximations, finally obtaining a tractable method. With comparable numerical effort, the R-matrix method gives accurate solutions.

We should also note that several new approaches for solving coupled-channel equations have been proposed. These have been proposed for nonreactive systems, and it would be interesting to investigate them within a reactive framework. Johnson (119) presented a renormalized Numerov algorithm that shares many of the computational advantages of the multichannel version of his log-derivative method (120, 121). Thomas (122) proposed an iterative method to solve coupled equations, which should be useful when extremely large basis expansions (on the order of 200 channels) are necessary. His method obtains each column of the S-matrix independently. Stechel et al (123) and Schmalz et al (124) proposed an R-matrix method using nonorthogonal coordinates and a nonorthogonal basis to study the charge exchange problem. This problem is interesting for quantum reactions because of its similarity to the H–L–H mass combination. Finally, Leasure & Bowman (125) have described a method based upon solving the Laplace transform of the Schrödinger equation.

Because collinear quantum calculations are feasible, much work in this area is devoted to comparing exact quantum dynamics to dynamics obtained by approximate methods. We have already mentioned the popularity of these calculations for estimating the reliability of qua-
siclassical trajectory calculations (50–57). In addition, exact collinear dynamics is useful in evaluating agreement with information theory methods, transition state theories, and phase space theories. Much of this work has been described in Connor’s review article (20) and is discussed later in this review.

THREE-DIMENSIONAL CALCULATIONS A fully converged coupled-channel calculation of the 3D A+BC reaction still represents the major challenge to the dynamicist. Theoretical approaches to the problem have been described by Wyatt and co-workers [see References (18, 99) and the references cited therein], Schatz & Kuppermann (127), and Light and co-workers (128, 129). These methods have in turn each produced converged calculations only for the low energy H+H2 reaction (130–134); it is gratifying that all calculations for this reaction are in substantial agreement with each other, especially at threshold energies.

Only a few accurate 3D studies have been reported since Wyatt’s reviews (18, 99). Using a reactive CS formalism, Redmon & Wyatt (135) have studied the F+H2 reaction, with emphasis on resonance behavior. The pronounced collinear resonance behavior is significantly broadened in the 3D reaction. Wyatt (136) observed 3D F+H2 resonance manifestations at collision energies consistent with recent experimental observations of Sparks et al (137) for the reactive differential cross section. Both the theoretical and experimental observations represent state-of-the-art achievements, and the similarities of these observations is remarkable.

In addition to these F+H2 results, Redmon (138) presented preliminary (unconverged) results for the extremely difficult H+O2 reaction. The H+H2 calculation of Walker et al (134) compared results of calculations on the Porter & Karplus (139) H3 potential surface with the Siegbahn & Liu (34) and Truhlar & Horowitz (32) surfaces. Low energy total reactive cross sections for this surface were also given. Clary & Nesbet (140, 141) have used these programs to investigate the evolution of entropy in the product internal state distribution along the reaction coordinate, with emphasis on applying information theory to 3D reactions.

There will not be, in the near future, many converged 3D quantum reactive calculations. Basis-set size limitations preclude the accurate study of reactions involving nuclei other than hydrogen and its isotopes. These few accurate 3D calculations will serve as reference points upon which to investigate approximations capable of providing dynamics of satisfactory accuracy at computationally feasible expense.
Approximate Quantum Theories of Reactive Scattering

Due to the formidable formal and computational problems associated with exact quantum treatments of reactive scattering, it is not surprising that there is considerable current research devoted to finding approximate quantum treatments that are relatively simple and accurate. Wyatt (19) has written an excellent review of the status of these efforts as of late 1978. Although we shall concentrate here on results of the past year, because of the importance of the area, we shall review some of the earlier work as well. Most of these efforts fall into three basic categories: (a) distorted wave Born approximations (DWBA) or adiabatic perturbation approximations, (b) overlap or Franck-Condon models, and (c) dimension-reducing approximations such as $J_z$-conserving (centrifugal sudden, coupled states, CS are aliases) or other sudden approximations that utilize exact quantum methods on decoupled Hamiltonians. In addition, we discuss a few other approaches that do not readily fit into the above categories.

**DISTORTED WAVE BORN APPROXIMATION** Although the DWBA was developed for reactive scattering and used earlier, Choi & Tang (142) in 1974 showed that the integrals over the Euler angles in the matrix elements could be done analytically, thus greatly reducing the effort required to apply the approximation. We briefly review their formulation here before commenting on recent results. The DWBA is based on the exact equation for the differential cross section in terms of the T-matrix elements

$$
\frac{d\sigma_{\alpha\beta}}{d\Omega_{\kappa_\beta}} = \frac{\mu_\alpha\mu_\beta}{(2\pi\hbar)^2} \frac{k_\beta}{k_\alpha} |T_{\beta\alpha}|^2
$$

1.

where $\alpha$ and $\beta$ refer to channels (A + BC) and (C + AB), respectively, and the T-matrix element is defined as

$$
T_{\beta\alpha} = \langle \chi_{\beta}^{(-)} | V_\beta' | \psi_{\alpha}^{(+)} \rangle
$$

2.

where $\chi_{\beta}^{(-)}$ is the solution of the Schrödinger equation (with incoming boundary conditions) with the approximate Hamiltonian

$$
H_\beta = H - V_\beta'
$$

3.

and $\psi_{\alpha}^{(+)}$ is the solution (with outgoing boundary conditions) of the complete Hamiltonian, $H$. To be exact, $\psi_{\alpha}^{(+)}$ must contain all accessible internal states, although $\chi_{\beta}^{(-)}$ may, with a judicious choice of $V_\beta'$, contain only a single internal state. The DWBA consists, then, of replacing the
exact scattering wavefunction, $\psi_{\alpha}^{(+)}$, by a simpler approximate wavefunction satisfying the same boundary conditions. In practice $\psi_{\alpha}^{(+)}$ has been replaced by $\chi_{\alpha}^{(+)}$, a wavefunction corresponding to a single internal state only. Thus the DWBA contains the coupling potential only to first order, although both $\chi_{\alpha}^{(+)}$ and $\chi_{\beta}^{(-)}$ may correspond to waves with full potential scattering and adiabatically distorted internal states. With the Euler angle integrations performed analytically, Choi & Tang (142) reduced the numerical problem from an extremely lengthy five-dimensional integral to a much more manageable sum of three-dimensional integrals. The calculations are nevertheless nontrivial, because for each state-to-state cross section at a given scattering angle, (a) the adiabatic internal states must be determined at each value of the scattering coordinate, (b) the elastic scattering wavefunction must be determined for this state, and (c) the three-dimensional integrals must be done for all angular momentum components of the initial and final orbital angular momenta.

Remarkably, this approximation works very well for the $H + H_2$ (143) and $D + H_2$ (144) reactions at low energies. It has been applied to the $F + H_2$ reaction (145) using both unperturbed and adiabatically perturbed internal states, but with $H_2$ initially in the ground ($v=0, j=0$) state. They found that the adiabatically perturbed internal states produced much larger reactive cross sections, but that the product internal state distribution was largely unaffected. Although the internal energy distribution for the related $F + D_2$ reaction appears to be in good agreement with the experimental results (146), no quantitative measure of accuracy is available.

Clary & Connor (147) used the DWBA on the $H + F_2$ ($v=0, j=0$) reaction and compared it with both quasiclassical trajectory results and collinear close-coupling results. They also compared the full adiabatic internal states calculation to those keeping either the initial or final internal state unperturbed. They found quite good agreement in final state distribution between experiment (148)—the quasiclassical, the full adiabatic DWBA, and the “static product” DWBA—but poor agreement when the reactant internal state was not allowed to distort adiabatically in the DWBA calculation. The extent of agreement in this case is truly surprising because the $H + F_2$ reaction is highly exothermic and one would expect very significant vibrational coupling in the exit channel. Given the developments toward more general applicability of the DWBA method and the encouraging results to date, it is likely to be tested, developed, and used more widely in the next few years.

FRANCK-CONDON APPROACHES We consider here a number of different approaches, most of which utilize a Born approximation at some point.
They are bound together by the common expression of the T-matrix element in the form

\[ T_{\beta\alpha} = \langle \chi_{\beta}^{(-)} | \hat{T}_{\beta\alpha} | \chi_{\alpha}^{(+)} \rangle \]

where \( \chi_{\alpha}^{(+)} \) and \( \chi_{\beta}^{(-)} \) are (approximations to) scattering wavefunctions localized in reactant and product channels and the matrix element of the complicated operator, \( \hat{T}_{\beta\alpha} \), is usually further reduced to an overlap calculation \( \langle \chi_{\beta}^{(-)} | \chi_{\alpha}^{(+)} \rangle \) of the nuclear wavefunctions.

The formal approach was introduced by Halavee & Shapiro (149) and shortly followed by Schatz & Ross (150–152). Although this work was covered in Wyatt’s review (19), there has been intense activity since then. Concise reviews of the assumptions and development of the theory are given in two recent articles (153, 154), together with extensions and evaluations. The basic assumptions common to Franck-Condon (FC) theories are simple to state. The exact T-matrix element for electronically adiabatic scattering on a single electronic surface (Eq. 2) is considered (and is, in fact) a Born-Oppenheimer approximation to the solution of the full Schrödinger equation (including electronic coordinates) in the adiabatic approximation. Thus, as Halavee & Shapiro (149) pointed out, one can formally use a diabatic (or quasi-adiabatic) (155) electronic representation from which two nuclear surfaces result, corresponding to reactant and product nonreactive surfaces with a remaining electronic perturbation term [which would produce the adiabatic (lower) surface when diagonalized]. The T-matrix element then takes the form (Eq. 4). Franck-Condon type theories result when these two surfaces are used to define the reactant and product nuclear scattering and when the remaining perturbation is taken to first order only. If the electronic matrix element is slowly varying with nuclear coordinates, a pure FC overlap approximation results (153):

\[ T_{\beta\alpha} \approx M_{el} \langle \chi_{\beta}^{(-)} | \chi_{\alpha}^{(+)} \rangle \]

where \( M_{el} \) is formally the electronic matrix element between the quasi-adiabatic electronic states yielding the nonreactive surfaces for reactants and products.

Several approximations are made in deriving the Franck-Condon theory as represented by Eq. 5. They are (153): 1. neglect of all higher electronic states and transitions to them, 2. neglect of nuclear electronic coupling and nuclear kinetic energy coupling terms, and 3. the assumption that the electronic matrix element is slowly varying over the region where the wavefunctions \( \chi_{\alpha}^{(+)} \) and \( \chi_{\beta}^{(-)} \) overlap. In addition it appears (154) that 4. a weak coupling approximation between the two electronic surfaces is made (in 2 above), because the T-matrix element (Eq. 5) is only first order in the coupling potential.
From the Franck-Condon theory outlined above a number of Franck-Condon models result from further approximations (149–154, 156). In earlier versions, very crude approximations to evaluating the channel wavefunctions $\chi_{a}^{(+)}$ and $\chi_{b}^{(-)}$ were coupled with approximate evaluations of the multidimensional overlap integrals. Simple analytic approximations could then be obtained, particularly for the relative internal energy distributions of products. Two recent studies on collinear reactions report on the adequacy of these further approximations.

Vila et al (153) constructed the quasiadiabatic channel potential surfaces from LEPS and anti-LEPS surfaces and a coupling function highly localized near the col. They then evaluated exactly the (two-dimensional) channel functions $\chi_{a}^{(+)}$ and $\chi_{b}^{(-)}$ on these surfaces by solving the close-coupling equations numerically and evaluated the overlap integral in Eq. 5 numerically. They compared, then, three sets of product vibrational distribution results—exact quantum close-coupling, “exact” Franck-Condon theory, and a simple Franck-Condon model (150–152). For the three reactions $[\text{H}_2(v=0)+\text{F}, \text{D}_2(v=0)+\text{F}, \text{H}+\text{Cl}_2(v=0)]$, they found very substantial agreement. The most probable vibrational state was almost always correct and the general shape of the distributions was correct. Although the “exact” FC results were somewhat better than the simple FC model results, even the latter are in good qualitative agreement. The results also appear relatively insensitive to the only free parameter in the model—the range of the coupling function.

Fung & Freed (154) generalized the Franck-Condon theory to polyatomic molecules (provided a single reaction coordinate is well defined). They reduced the multidimensional overlap integral to a “rapidly convergent series of one-dimensional bound-continuum integrals,” performed the adiabatic to quasi-adiabatic surfaces decomposition, and (again) applied the results to a model collinear system for which exact quantum calculations could be performed ($\text{D}+\text{IH}$). The channel wavefunctions were approximated using a forced oscillator model for the half-collisions, as well as various simpler (Airy function, delta function) approximations. They also found qualitatively good agreement between the exact quantum and their best FC model results for the relative product vibrational distribution. More interesting, perhaps, is that they reported values of the absolute reaction probabilities. [Vila et al (153) did not, even though the data were easily available from their work.] Fung & Freed (154) found that the absolute transition probabilities were extremely sensitive to the electronic coupling functions assumed, varying over several orders of magnitude ($\sim 10^6$), even though the relative distribution was rather insensitive. This sensitivity is presumably
attributable to assumption 4 or 2 in the original derivation in which weak coupling is assumed between the quasiadiabatic surfaces. Because these calculations were performed at low energies (for which tunneling is important), a high degree of sensitivity to the treatment of the col region is not surprising. These results, however, do indicate that the FC theory is currently not capable of reliably determining the magnitudes of reaction cross sections, irrespective of further model assumptions.

Other aspects of Franck-Condon models have also been scrutinized recently. Vila et al (156) investigated the angular distributions of reaction products in 2D and 3D models for several potential and kinematic coupling regimes. They used only simplified models, however, with angular wavefunctions given either by free rotor or (adiabatic) hindered rotor functions. Again the calculated angular distributions (hindered rotor basis) qualitatively agree with exact quantum and classical trajectory calculations where available, and again absolute magnitudes were not presented.

Very recently, Wong & Brumer (157) derived a Franck-Condon type theory from a Faddeev decomposition of the scattering wavefunction. A potential advantage of this approach is that three-channel $A + BC \rightarrow AB + C, AC + B$ reactions can easily be incorporated, whereas the quasiadiabatic decomposition of the potentials in the "standard" FC theory is quite arbitrary. Wong & Brumer reduce their equations to a simple form, the key to which is the solution of linear algebraic equations in momentum space. Comparison with exact quantum collinear results (158) for $H + Cl_2$ shows excellent agreement in the predicted relative vibrational products distribution, and again no absolute reaction probabilities were given.

The Franck-Condon approach to reactive scattering has been shown in the last few years to be qualitatively correct in predicting relative internal and angular distributions for simple reactive systems. Even in its simplest forms, it provides useful results. However, even in the most accurate forms, it appears to be completely unreliable in predicting absolute transition magnitudes and therefore absolute cross sections. This may be a defect basic to the theory in the sense that localizing the overlap of the quasiadiabatic scattering solutions requires large interaction potentials between the quasiadiabatic surfaces and thereby invalidates perturbation theory. Extension of the interaction region, while reducing the perturbations, will degrade the accuracy of the overlap approximation. Thus the approximations inherent in the FC theory may limit its accuracy. The optimal choice of surfaces has been considered by Mukamel & Ross (155) and a first order K-matrix approximation to include higher orders in the reactive perturbation was given. Its use by
Fung & Freed (154), however, did not appear to help the absolute accuracy. Until this can be remedied, the FC theory must be considered valuable as a guide to internal energy distributions only.

**REACTIVE DECOUPLING APPROXIMATIONS** Because very many close-coupled equations are required for the exact description of most atom-diatom systems, much attention has been given recently to approximations that reduce the dimensionality of the coupled equations and still permit the evaluation of state-to-state cross sections. Two of these approximations, the $J_z$-conserving approximation and the infinite order sudden approximation (IOS), have recently been applied to reactive scattering.

The only reviews to date that consider applications of $J_z$-conserving approximations to reactive collisions is again that of Wyatt (18, 19). The $J_z$-conserving work of Elkowitz & Wyatt (159) and Kuppermann et al (160) on H+H$_2$, and of Redmon & Wyatt (161) on F+H$_2$, is reviewed there.

The centrifugal sudden (CS) approximation was introduced by McGuire & Kouri (162) and Pack (163) for inelastic scattering (164). For inelastic scattering the CS approximations can be made directly by replacing the orbital angular momentum operator in a space-fixed coordinate system by an average eigenvalue, $\tilde{\ell}(\tilde{\ell}+1)\hbar^2$. Cross sections are then obtained by using “$\ell$-labeled” S-matrix elements and recoupling with appropriate sums over Clebsch-Gordan coefficients (165–168). Because body-fixed coordinates are used in reactive scattering, only the primary assumption of the CS approximation (the neglect of Coriolis-type coupling) was used by Wyatt et al and Kuppermann et al. They decouple the original complete set of coupled equations into independent sets, one for each value of the projection of the total angular momentum onto the body-fixed axis (165). Additional approximations may then be made to simplify the equations further (166–168).

Generalizing this approximation to reactive scattering is made difficult because the body-fixed axes of reactants and products must differ. Thus, the approximation, which imposes a conservation condition in the body-fixed frame, is not the same for reactions and products, and leads to continuity problems. Elkowitz & Wyatt (159) and Kuppermann et al (160) resolved this problem in different ways. The former, using a complete set of natural collision coordinates, define a “body-fixed” frame that rotates smoothly with the scattering coordinate from that for reactants to that for products. In this way, the CS approximation is imposed uniformly throughout the reaction, albeit at the cost of neglecting some complex effective potential terms.
Kuppermann et al (160) essentially switch coordinates on a surface, matching wavefunction and derivatives there. Continuity can only be preserved by coupling the set of solutions (for various values of $K$, the "$J_z$-conserved" quantity) for reactants with the set of solutions for the products. Both procedures appear to work, but greatly increase the complexity of the $J_z$-conserving approximation over that required for inelastic collisions. Nevertheless, this approximation greatly reduces the number of coupled equations to be solved, and permits the quantum calculation of reaction probabilities to be extended to heavier systems for which the number of open channels involved would prohibit exact close-coupling calculations at the present time [e.g. $F + H_2$; see Reference (161)].

The infinite order sudden (IOS) approximation, also reviewed by Kouri (164) for inelastic collisions, has recently been developed (169–171) for and applied (171–173) to reactive scattering. In the simplest terms (174), the IOS approximation for inelastic scattering consists of replacing the eigenvalues of the rotational angular momentum operator (in the CS equations) by a single effective energy; by utilizing closure of the rotational functions, we obtain a set of coupled equations for vibrational states containing the internal (A–BC) angle as a parameter. Thus the rotational manifold of states disappears completely from the coupled equations, being replaced by the necessity to solve this very much easier problem at a set of angles. The angle-dependent T-matrix elements are then projected onto the asymptotic rotor states to determine transition probabilities. This approximation does not conserve energy, even for inelastic collisions.

The difficulties of extending the IOS to reactive scattering are even greater than for the $J_z$-conserving approximation alone, because the approximation is more extreme in each chemical channel and, although the wavefunction matching on a channel-matching surface appears straightforward, the momentum (or derivative) matching appears more difficult to justify (169–171, 175). Barg & Drolshagen (170) confine their discussion to a two channel light-heavy-light atom (L–H–L) exchange reaction where they find that a one-to-one angle matching on the surface produces complete orbital-to-rotational angular momentum conversion (and vice versa) on the matching surface. Their preliminary results (176) on $D + HCl$ "show agreement with quasi-calculations...as good as a factor of one to three for the reactive integral rotational cross sections."

The work of Bowman & Lee (171, 172) appears to be more general, allowing for asymmetric three-channel reactions. They, however, assume that $l_\alpha=l_\beta$ and $j_\alpha=j_\beta$ on the matching surface (although the
opposite result of Barg & Drolshagen could be used as well), thus also finding a one-to-one angular matching procedure. In applications to $H + H_2$ they find (171) that their low energy cross sections overestimate the true cross sections by as much as a factor of ten, but better (although not quantitative) agreement is found at higher energies ($E = .55$ to $.7$ eV). As might be expected in a theory for which energy is not conserved and rotational transitions occur well into closed channels, the product rotational distributions are in poor qualitative agreement with exact results.

The matching equations derived by Khare et al (169) are more general than those above, but similar simplifications are suggested [cf Eqs. 81 and 91–102 of Reference (169)]. As in Bowman & Lee's work, Baer et al (173) find the IOS cross section is too large at threshold, but improves somewhat with increasing energy.

In summary, the search for an adequate IOS description of reactive collisions has been very active, and with good reason. The IOS approximation permits one to replace a very large intractable set of equations by numerous very small sets (involving vibrational states only) for describing quantum reactive scattering. The IOS approximations, however, are quite strong and it remains to be seen whether this approach will produce scattering results more accurate than classical trajectory results. The preliminary results to date offer some hope, but also indicate that rather extensive tests (and probably modifications) will be required before the IOS approach can be used with confidence. Other inelastic scattering decoupling approximations (e.g. $l$-dominant) have not yet been developed for reactive scattering.

**OTHER QUANTUM APPROXIMATIONS** Several recent models of reactive systems have been proposed in which a portion of the dynamics is done quantum mechanically, the remainder being treated classically, statistically, or by a crude quantum model. We shall discuss these briefly.

Fischer et al (177) proposed a "statistical dynamic" model of exchange reactions in which the vibrational-translational degrees of freedom are treated in the FC manner (see above), but with a statistical treatment of rotational degrees of freedom. By assuming the factorization of T-matrix elements into independent elements for the different degrees of freedom and utilizing the concept of an internal temperature for the "statistical" degrees of freedom, they obtain approximate analytic results for product energy distributions. Comparison of these distributions with experiment for $H(D) + F_2(Cl_2)$ and $Cl + H(D)I$ shows quite encouraging agreement (178). Correlations in the distributions for
the various degrees of freedom are suppressed and absolute cross sections presumably will not be obtained accurately.

A related approach by Baer (179) attempts to take distributions known from exact quantum calculations on reduced (1D or 2D) models and, using statistical arguments, generate full quantum distributions. Relatively good agreement with classical trajectory results on $\text{H} + \text{Br}_2$ was obtained from 1D quantum vibrational distributions using this method.

Basilevsky & Ryaboy, after deriving a collinear three atom reactive scattering method (117), make quasiclassical approximations on the collinear dynamics (180, 181) and finally obtain a very crude analytical solution, which, however, may give some qualitative insight into the causes of vibrational population inversions.

Finally, Wyatt & Walker (182) and Wyatt (183) used full quantum close-coupling methods over a portion of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ surfaces of the $\text{F} + \text{H}_2$ system to study quenching of the $^2P_{1/2}$ in the reactive system. Because the ground state reaction is very exothermic and cannot be handled exactly by current close-coupling methods, he included the effects of reaction by applying the detailed quantum transition state theory (DQTST) (184, 185) at a surface just beyond the col.

OTHER TOPICS

Transition State and Statistical Theories

Although the transition state theory (TST) of chemical reactions has been in textbooks for many years, it has been examined, reformulated, and tested extensively in the past few years. Pechukas (24) has given an excellent (and entertaining) review of statistical approximations (primarily TST) including work up to 1976. Chesnavich & Bowers (186) in 1979 review both TST and other statistical theories and their application to ion-molecule reactions. Garrett & Truhlar (23, 187) give very extensive references.

It has been known for many years that classical transition state theory, in either the canonical or microcanonical form, provides an upper bound on classical reaction rates. Pechukas & Pollak (188–190) have, in the past few years, defined the mathematical conditions required for this bound to be exact. Building on previous work (188, 189) they (190) recently showed that for a collinear atom-diatom system, microcanonical TST would be exact for all systems and energies for which a unique transition state exists. (In their definition, the transition
state is defined by a periodic vibration in the interaction region. More than one such periodic trajectory in the interaction region may define a collision complex.) Although extension of these rigorous classical results to 3D and the examination of real potentials to determine their applicability may be difficult, at least the mathematical framework for this examination has been constructed.

Garrett & Truhlar (187, 191) considered the relationship of variational microcanonical TST (which should yield the least upper bound to the rate constant at fixed $E$) with other more approximate (but more easily applied) formulations such as the minimum density of states criteria (192, 193) and Miller's unified statistical theory (194). Very recently, they applied their generalized theory (canonical variational TST) to a number of 3D reactions, showing it superior to conventional TST (195, 196). In comparing the results of all these theories with the exact classical canonical rate constants determined from classical trajectory calculations for nine collinear triatomic systems, Garrett & Truhlar (187, 191) show that the microcanonical variational and unified statistical theories are superior to conventional canonical and canonical variational theories, although the differences are not great. On the other hand, quantized versions of these approaches show that the generalized variational TST can give significant improvements over conventional TST (197).

Truhlar has also considered the effects of the classical nature of most TST calculations by comparing them with quantum calculations (23). The accuracy of quantum tunneling corrections was investigated by Garrett & Truhlar for the several collinear systems for which accurate quantum calculations are available (198). Most recently they applied the generalized TST theories with quantum corrections to the H + D$_2$ and D + H$_2$ reactions using the accurate a priori surface of Liu & Siegbahn (33, 34) and found excellent agreement for both rate constants and kinetic isotope effects (199) with the best available experimental data. From this last work it appears that TST, when carefully applied, should produce rate constants of quite useful accuracy (within a factor of 2) at least for reactions with a single activation energy barrier and with reasonable skewing angles. It should, however, be tested further on qualitatively different potential energy surfaces and at higher energies.

We shall not detail all the work using TST, but only mention the significant new work for ion-molecule reactions presented by Chesnavich & Bowers (186), and the construction of a TST for three-body ion-molecule recombination reactions considered by Herbst (200). Finally, Chesnavich et al (201) also used microcanonical variational TST
and classical trajectories to obtain an upper bound for capture cross sections in ion-dipole collisions (long a problem because of the long-range anisotropic potential). They find good agreement between the bound, trajectory, and experimental results.

There has been some further development of statistical theories in which a strong coupling collision complex is formed. In addition to the relevant work mentioned above (23, 196, 197), Brumer et al (46, 202) have investigated, via classical trajectory studies, the dependence of complex formation on geometrical and mass factors, as well as energy and potential energy characteristics. They characterize the subset of trajectories that form complexes by passage through a region of the potential surface in which substantial exponential divergence takes place. In comparing the product distributions of this subset with that obtained from the Wagner & Parks formulation (203) of statistical theories in terms of a strong coupling region, they find that the criterion of substantial exponential divergence indeed produces a statistical distribution in qualitative agreement with phase space theory. A more detailed analysis of the subset of trajectories showed clearly the statistical nature of the distributions independent of the specific assumptions of phase space theory.

Pollak & Levine (204) have recently shown how the definition of a strong coupling region and assumption of maximal entropy of the final distributions can lead to a variety of statistical theories depending on constraints imposed on the distributions. They show that Miller's unified theory, TST, and phase space theory can be related by constraints on flux across appropriate boundary surfaces. In application to collinear H + H₂, they find that addition of a second constraint [average number of (re)crossings of a surface] produces excellent agreement with the probability of reaction determined by trajectory calculations. However, trajectory calculations are required to determine the constraint, which is then used in the statistical theory.

Pollak & Pechukas (205) also re-derived Miller's unified statistical theory, applied it to collinear H + H₂, and derived a lower bound as well as an upper bound on the reaction probability. It proved to be remarkably accurate.

We have considered information theory approaches to reaction dynamics beyond the scope of this review. We take this position not because the work is not relevant—it is—but because it has been reviewed with some frequency and space limitations preclude its inclusion here. The interested reader should see reviews by Levine and co-workers (11, 12).
Collision-Induced Dissociation

Whenever the relative A+BC collision energy exceeds the BC bond energy, we open up the product reaction channel A+B+C. Such processes are called collision-induced dissociation (CID) and have been investigated using (extensions of) methods developed for rearrangement collisions. Both classical and quantum methods have been used to study CID; for detailed recent reviews, see the discussions of Kuntz (25) and Diestler (26).

Most recent work on CID uses the quasiclassical trajectory approach and focuses attention on the dependence of the dissociation rate (or cross section) on the initial internal molecular energy (206–211). Molecular rotational energy plays an important part in the dissociation dynamics (206, 208, 209, 211), suggesting that a purely vibrational ladder-climbing model oversimplifies the actual process. The ladder-climbing model allows only a single vibrational quantum transition per collision, with dissociation occurring only from the highest bound vibrational state. The actual process is better characterized by a combined vibration-rotation ladder climbing (206) in which the dissociation step occurs from molecules whose total energy is near the dissociation limit, but with a significant spread of internal energy between vibration and rotation (208, 209, 211). Blais & Truhlar (209) and Lehr & Birks (211) present excellent discussions of the importance of rotations to CID and should be consulted for references to earlier literature.

Semiclassical (212, 213) and quantum mechanical (214–218) calculations of CID have been reported for collinear ABC systems. Semiclassical and time independent quantum methods (212–216) require a discretization of the continuum molecular states; dissociation is then defined as a sum over transitions to the continuum. Time-dependent wave-packet approaches (217, 218) avoid this difficulty; the dissociation probability is determined by projecting out the bound state components of the wavefunction at large times. These calculations demonstrate that dissociation occurs from vibrational states well below the continuum and that the ladder-climbing model oversimplifies the dynamics even without rotations.

Considering the importance of rotations demonstrated by the 3D classical calculations discussed previously, it is doubtful that collinear calculations will be quantitatively reliable for CID. Extending quantum CID methods to higher dimensions (to include rotations) will cause a substantial increase in complexity. In the near future, detailed CID dynamics will be best treated by quasiclassical techniques. These calculations will be accurate to the extent that good potential energy surfaces
are available and to the extent that quantum effects (presumably near the threshold for dissociation) are minimal. Studying quantum effects in three dimensional CID will require substantial future developments in the methodology of the problem.

**Laser-Collision Reactive Processes**

Although lasers have been used for many years to modify the initial states of reactants, to analyze the products of reactions, and to cause (collisionless) photodissociation, it is only in the last five years or so that the effects of strong laser fields on collision dynamics have been studied. Because the field of multiphoton dissociation has been the subject of recent conference proceedings (219) and because lasers used for reactant preparation and product detection are primarily experimental tools for studying state-to-state chemical reactions, we shall comment here only on recent developments in laser-collision dynamics, particularly reaction dynamics. To date the preponderance of work in this area (meager though it is) has been theoretical and the only laser-collision-induced reactive processes observed have been laser-induced associative ionization (220) \((A + B + h\nu \rightarrow AB^+ + e^-)\) and, very recently, a laser-induced exchange reaction (221) \((K + HgBr_2 + h\nu \rightarrow KBr + HgBr^*)\).

The former process was studied formally (qualitatively) by Bellum & George (222), using the discretization techniques for the continuum previously developed for field free associative ionization (223) and the "electronic-field" representation of the scattering process in the laser field, also advocated by George et al (224). In this representation, the zero order-time independent states are taken to be those determined by the fixed nuclei electrons plus field Hamiltonian, and scattering (with or without non-Born-Oppenheimer coupling) occurs on these surfaces. This leads to coupled-time independent equations for the scattering. Using this representation George and co-workers have also investigated laser-induced unimolecular dissociation (225) and electronically inelastic scattering of F on H\(_2\) (226). Yuan & George (227) investigated the reactive scattering of F on H\(_2\) in the presence of a laser field using semiclassical methods.

Light & Altenberger-Siczek (228) also used this framework to consider the effects of near resonant laser radiation on atom-diatom exchange reactions in collinear, two electronic surface models. By assuming near resonant fields and electronically allowed transition couplings, they showed that significant alterations in transition probabilities to excited states could be obtained, although "true" laser catalysis would
be unlikely. The recent experiments of Hering et al (221) appear to confirm that such processes can occur at modest (<10^7 W/cm^2) laser powers, but the cross sections appear to be small (~10^{-17} cm^2).

An alternative approach to these processes has been taken by Copeland (229) and by Orel & Miller (230, 231). Copeland derives, but does not apply, semiclassical dynamical equations in a time-dependent representation not utilizing the "electronic-field" states. Orel & Miller treat everything classically, with the laser field modifying the classical dynamics of the motion of the nuclei on a single electronic energy surface due to a time dependent perturbation (the laser field). They show that the field will affect the dynamics even for infrared inactive species due to the lack of symmetry of the motion along the reaction coordinate and that the effective threshold for reaction will be lowered. In a qualitative analytic model, however, they also show that laser powers on the order of 10^{10} - 10^{12} W/cm^2 would be required to produce significant effects.

Overall, the research in this area has produced mixed results. Processes are reasonably well understood theoretically—the framework of both time-independent multiple surface approaches and time-dependent single surface approaches has been established. However, the paucity of experimental data confirms the general trend of theoretical prediction that to make laser-collision-induced processes occur with reasonable probability, very strong (\geq 10^9 W/cm^2) fields are required. In addition, the difficulty of obtaining experimental data suggests that the utility of these processes as probes of potential energy surfaces of reaction complexes is severely limited and that the prognosis for such processes as general synthetic tools is poor.

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