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THEORETICAL RESEARCH--ELECTRONIC, IONIC, AND ATOMIC IMPACT PHENOMENA

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Introduction

This report summarizes the accomplishments of a long-lasting program on the theory of atomic and molecular collisions that has been supported by NASA under Contract No. NASr-49(07) from 1961 to 1970 and was supported in 1960-61 by an earlier NASA contract, NASw-80. The principal intent of this program has been to develop the understanding of the collisions of atoms and simple molecules, in close association with a major program of experimental investigations. The experimental investigations in our laboratory have been carried out under a number of sponsorships, but the overall program has had strong continuity and has developed extremely important and novel measurements of a number of classes of collision problems. The present contract, supplemented by support for theoretical work from other agencies, has supported a very fruitful and stable interaction between the parallel theoretical and experimental programs, making possible a developing understanding of important classes of collision problems in depth in a way that could not have been achieved by either theoretical or experimental investigations alone.

One of the important aims of this work is to develop, for some wide classes of collision problems, sufficient knowledge to generate simple and rapid methods for estimating cross sections and reaction rates needed for practical applications. We have recently developed such methods applicable to several classes of reactions important in atmospheric and ionospheric problems and elsewhere: ion-ion neutralization, charge transfer at large distances, and optical or metastable excitation connected with charge transfer.

Broadly considered, the work done in this theoretical program has had two major centers of gravity, one in the more general and formal aspects of collision theory and the other in specific applications of collision theory to specific scattering processes observed in the laboratory, with a heavy emphasis on the analysis and interpretation of experimental results in the light of theoretical principles. In the first three or four years of this program, the emphasis was distinctly on the more general aspects of scattering theory, with applications from time to time to specific processes that could be compared with experiments. Since about 1964 the emphasis has increasingly been on problems closely connected with experiments, especially experiments being conducted in our own laboratory. However, the more formal and general aspect of scattering theory has continued to play an essential part in the program. One of the particular strengths of this program

has been our capability of moving from a very detailed and narrowly focused examination of a specific, experimentally motivated problem to a broader and more detached point of view encompassing more general principles and broad classes of reacting systems. Our strength in the basic and formal collision theory has provided a foundation and a perspective that have been invaluable in making possible a sound understanding and a deep and searching analysis of the experimental problems on which we have focused attention.

In this report we shall outline our accomplishments in atomic and molecular collision theory over the last ten years or more, reviewing the overall pattern and the high points without going into technical details or reproducing the mathematical and theoretical arguments. All those details are set forth in publications that are listed later in this report and also in the thirty-one quarterly reports that have previously been issued. Our primary focus is on the accomplishments directly attributable to this contract, but we shall also mention, and list separately in the list of publications, related accomplishments under other sponsorship that have also contributed to the overall development of our understanding in this broad field of collision theory. These related works have often developed aspects of our knowledge that have then been of use in this NASA project, and conversely some of the work we have pursued under other sponsorship has naturally drawn on and carried further ideas that were first developed under this particular contract. Naturally, continuing developments at present and in the future will also be continually drawing on insights, concepts, and techniques that have been developed in the course of this very productive program. NASA, which has supported this work, deserves great credit for creating the foundation on which these new developments are taking place.

General Scattering Theory

The work in our laboratory on fundamental aspects of collision theory initially arose out of an interest in some specific experimental observations made in England and elsewhere on a class of reactions exemplified by $O_3 + H \rightarrow O_2 + OH$. The reactions in question were all exothermic, and the surprising observation had been made that a very large fraction of the reaction energy appeared in the form of vibration in the newly formed bond (i.e., in the molecule OH in this example), and no detectable excitation appeared in the other fragment (O_2). Our contribution to this problem was based on a consideration of the kinematics of this reacting system and led us to suggest a possible explanation, according to which the fraction of the available energy appearing in vibration would depend primarily on the mass ratios of the atoms

involved.[1] An examination of the then-available experimental evidence appeared to show reasonable agreement with the predicted ratios. Subsequent work in many laboratories has shown that the problem is considerably more complicated, and other factors probably exceed in importance the kinematic mass ratios we were concerned with.

Although the specific suggestion we made then has not been generally accepted, another aspect of the experimental observations is incontrovertible. That is the fact that the energy in the reaction was divided in a highly asymmetric way, very far indeed from any statistical distribution of the kind that would have been expected had the reaction taken place by way of a long-lived collision complex. On the contrary, the only plausible mechanism for producing so selective an excitation process is a very short-lived collision involving nothing more than initial impact and immediate fragmentation and dissociation in the new configuration. This general deduction certainly remains valid for this whole class of reactions. It led in turn to raising the question of how one might estimate the duration or lifetime of such a collision, in order to compare this lifetime with typical vibration times for a collision complex. In connection with such reactive or inelastic collisions, it appeared that no satisfactory general theory of collision lifetimes had ever been developed, although special formulations were available that were applicable to certain situations such as unimolecular decompositions. In considering this problem, we were led to formulate the general idea of the collision lifetime, which for inelastic processes in general becomes the lifetime matrix.[2] We were able to develop the theory of this matrix in considerable generality, relating it to the scattering matrix as a function of energy. This concept was apparently totally new, except for the special case of simple elastic scattering.

The lifetime matrix and its connection with the scattering matrix turned out to be a particularly useful new concept and led to a whole series of investigations. Among other things, a consideration of chemically reactive processes led immediately to the question of how one should formulate the scattering matrix and the collision lifetime for processes where two bodies are present before the collision, but three free particles are present afterwards. To describe this situation in a simple, general, and symmetric way, we were led to the concept of generalized angular momentum in three-body or many-body processes.[3] This also has turned out to be a very fruitful idea which has had important uses in the theory of the scattering matrix[4] and in the theory of three-body chemical reaction rates,[6] in connection with which we have written several papers. These have included an extensive review of the theory of three-body reactions in chemical kinetics.[30,31] This view of three-body processes has also enabled us to develop explicit

constructions for three-body and many-body collision lifetimes,[7] and for other aspects of three-body interactions.[5,9,25] All of these concepts were then applied to developing a simple and very satisfactory general treatment of the thermodynamics of gases, including density-dependent effects, in which the collision lifetimes play a leading role.[8,26] The result of these several pieces of work was to clarify the connection between collision properties as studied in single collisions in the laboratory and the bulk properties of gases, both static thermodynamics and time-dependent kinetic processes. We believe that these developments have made it much easier to apply our knowledge about collisions to the prediction of various types of behavior in bulk gaseous systems.

A theme running through a great deal of this work on collision theory has been our repeated use of the interplay between quantal and classical viewpoints. We have over and over managed to draw from a classical picture an intuitive and visualizable model of some of the essential physical principles, which we have then been able to exploit by reformulating the same picture in quantal terms. In this way an initial classical picture has enabled us to find our way to a more rigorous quantal formulation of our results. Conversely, we have exploited the other side of this relationship, in that classical expressions are often, under appropriate conditions, very good approximations to the correct quantal solution to a problem. In making use of this parallel we have tried to keep persistently in mind that the true physics of our atomic and molecular physics problems is really governed by quantal and not classical mechanics and that the limitations of classical models must always be attended to. By playing on the relationship between the two views in a creative way, we have in many cases succeeded in making use of classical calculational devices to express true quantal effects. This is the true domain of a semiclassical approach, and we have exploited its possibilities with great success.

Initially our approach to the semiclassical method was based on the formal developments previously described, and particularly on our familiarity with the use and importance of the scattering matrix in atomic collision problems. Motivated by the importance of the parallelism between classical and quantal versions of the collision lifetime, we investigated the role of the same parallelism in the theory of the scattering matrix, where the controlling fact is that quantal phase shifts (multiplied by $\hbar$) are directly related to classical action integrals, and often very well approximated by them.[10] Furthermore, the complex quantal scattering amplitude is often very well approximated by the semiclassical expression

$$f(E,\theta) \cong \Sigma_j \sigma_j^{\frac{1}{2}}(E,\theta) \exp[i\hbar^{-1} A_j(E,\theta) + i\alpha_j] ,$$

where σ_j is the classical differential cross section, A_j is the classical action integral for scattering over one of the classical trajectories (labelled by j) leading to scattering at the angle θ, and α_j is a small constant phase angle. Drawing on the fundamental work of Ford and Wheeler,[39] we developed these relationships further[28] and have applied them extensively in the specific calculations and analyses of experiments to be described later.

In the course of this work we also developed an expansion procedure[10] for calculating the relevant classical and semiclassical quantities that justified and extended a procedure that had for some time been used by Everhart in the analysis of experiments. In our demonstration that the reduced scattering angle $\tau = E\theta$ (where E is the energy and θ the angle of scattering) can be expanded as a power series in E^{-1} with coefficients depending only on the impact parameter, we were rediscovering a result of Leibfried.[40] However, in observing the existence of a companion reduced function, the reduced differential cross section, $\rho = \theta \sin\theta \, \sigma(\theta,E)$, where σ is the differential cross section, we were breaking new ground. A better proof of these impact expansions followed in a second paper,[15] together with a demonstration of how they could be used to analyze experimental data and to enable potentials to be deduced in a simple way from an extended measurement of cross sections, by using a simple inversion procedure. These procedures have turned out to be extremely valuable in the analysis of experiments and in specific calculations.

Atom-Atom and Ion-Atom Collisions

Since its inception, our theoretical work on atom-atom and ion-atom collisions has been very closely connected with the interpretation and prediction of experimental measurements, particularly those being conducted in our own laboratories. The experimental work has to a very large extent concentrated on the study of elastic and inelastic differential scattering cross sections, in which good resolution in both energy and angle is achieved. As a result, the experiments are able to resolve fine details of structure that grosser methods of observation would not have done. Identification and interpretation of the observed structure has been a major challenge that has had a very stimulating effect on our theoretical activities. Conversely, our growing theoretical understanding and predictions have greatly stimulated the experimental program and helped guide it to a recognition

and careful investigation of a number of phenomena that had never been previously observed. Our experimental program has also included a variety of important measurements of total cross sections of such processes as charge transfer into specific radiating or metastable states, charge neutralization of positive ions with negative ions, excitation transfer, and Penning ionization, most of which have also led to very productive interactions with this theoretical program.

We have surveyed the results of these types of work, emphasizing especially the connection between experiment and theory, in several readable brief reviews in the last three years.[18,27,28,29] The reader is urged to supplement the account we give here with a reading of some of those papers. For a simple but fairly comprehensive introduction, we especially recommend Reference 27.

The side of our work more closely connected with experimental measurements was initiated early in 1964 by our concern to help our experimental team to understand and analyze some scattering measurements in the interaction of the ion He^+ with the rare gases He, Ne, and Ar. In the first of these systems, $He^+ + He$, our experimental group had detected an extensive set of oscillations in differential scattering that had also been seen in early measurements at higher energies by Everhart's group at the University of Connecticut. At that time the general source of the oscillations was understood, but there were several mysteries. The simple theory available at that time had predicted a set of oscillations in the scattering cross section with the property that the value of the cross section at the minima should be identically zero. This result was distinctly contradicted by the experimental measurements, and the improved theory we developed showed that the observed non-zero minima were actually to be expected because the oscillations represented an interference between two waves of different magnitude.[11] (The same explanation was discovered independently at about the same time by Francis J. Smith at Belfast.)

In addition to this qualitative improvement in the theory, we were able, using potentials obtained from the literature, to calculate strictly ab initio the predicted scattering patterns for the system He_2^+. The results agreed quite satisfactorily with the experiments both in the locations of the maxima and minima and in the absolute magnitudes of the cross sections, thus both confirming the calculated potentials and providing a reassuring confirmation of the absolute cross sections measured in the laboratory.[11] Subsequent work by others has refined these results.

In doing these calculations on the scattering of He^+ by He, we were greatly aided by the semiclassical procedures to which we had been led through our study of the more formal aspects of the scattering theory.[10] In our calculations we were able to make very effective use of the semiclassical method for calculating scattering amplitudes, including both magnitude and phase, and our paper on this scattering problem provided, among other things, an important illustration of how classical calculations could be exploited to predict quantitatively interference patterns that are intrinsically quantal in nature. Beginning with this paper, semiclassical methods have played a central part in our analysis of experimental results and in our theoretical predictions of scattering phenomena. We have thus been able in very concrete problems to exploit techniques discovered through our development of the more formal and abstract theory.

Our calculations of the cross sections for differential scattering in the system He_2^+ led us to predict that, at comparatively large angles of scattering, the regular pattern of oscillations seen at smaller angles would be made more complicated by the superposition of additional oscillations of a higher frequency arising from a second type of interference peculiar to systems involving two identical nuclei; in our understanding of this effect we were greatly assisted by discussions with Dr. B. L. Moiseiwitsch of Belfast, who was working with us under this contract as a visiting scientist. Fortunately the experimental data available to us already showed this effect at large angles, although it had not been recognized. The theoretical prediction of this structure led Dr. D. C. Lorents to identify it in the measured data, and convinced us that the observed oscillations were not merely due to some accidental noise. Furthermore, the theory then provided sufficient incentive to warrant improved measurements with reduced noise and extending to larger angles. Further confirming measurements were then made eliminating the symmetry between the nuclei by studying the collision $^4He^+ + {}^3He$. The results dramatically illustrated the absence of the secondary oscillations[12] and provided the first direct illustration of this symmetry effect, which had implicitly been predicted thirty years earlier and which is the analogue in scattering of a well-known effect in the rotational spectra of symmetric diatomic molecules.

At a later date, following a suggestion of Dr. Aaron Temkin, we carried out a further measurement of the scattering of $^3He^+ + {}^3He$, in which the symmetry effect again occurs but is modified by the fact that the nuclei are fermions with spin 1/2; as a result, the secondary interference pattern has only half the amplitude that it has for ^4He, and the maxima and minima occur at different locations. The results confirmed these predictions, and the relations between all of these interference patterns contain a great deal of information, whose analysis has not yet been entirely completed. We expect still more understanding to develop in the future from a continued study of these very fruitful experiments and theoretical concepts.

In our initial attempt to understand the non-zero minima in the scattering patterns, we had considered what effect inelastic losses might have on the elastic scattering pattern. While it turned out that inelastic scattering was not required to explain the non-zero minima, our consideration of this effect suggested to us that inelastic processes connected with the crossings between two states in the potential energy diagram might show up as a localized disturbance in the scattering pattern for elastic scattering, and that the resulting effect could be used to determine the location of the crossing in question. Since our theoretical considerations had already suggested this possibility, we were prepared to recognize as possible examples of this effect certain disturbances in the otherwise regular experimental scattering patterns that might otherwise have gone unnoticed or been attributed to accidental fluctuations. Realizing that a perturbation due to a localized crossing would appear at essentially the same value of the reduced angle $\tau = E\theta$ at all energies and even for different isotopic combinations, we were able to identify these features in the experimental data even though they would otherwise have been masked by the noise. This creative interaction between theory and experiment enabled us to make the first identification of curve-crossing perturbations in the elastic scattering of He^+ by He, Ne, and Ar, and to measure the location of one of the crossings in the system $He^+ + He$.[13]

Once convinced of the reality of these perturbations and armed with information about the crossing location, our experimental team were able to search for and identify the inelastic scattering arising from this particular crossing, which excites the 2^3S state of He.[14] The observed inelastic scattering pattern showed clearly for the first time a type of oscillation predicted long before by Stueckelberg, due to the interference between two different inelastic trajectories; we were later able to identify the same type of oscillations in the elastic perturbation.

Following these calculations dealing with the system He_2^+, for which the basic potentials were already available in the literature, we turned our attention again to some aspects of formal collision theory and particularly to developing the impact expansion techniques mentioned above.[15] This work suggested the possibility of presenting experimental data on differential cross sections by using the reduced coordinates, ρ and τ, and compiling data taken at different energies in a single presentation. According to our theory, the results should fall on a single curve independent of energy, at least if the scattering arose from a single potential without major interference effects. To test this conclusion on data available in our laboratory, we made such ρ vs. τ plots of the experimentally measured scattering patterns in the systems $He^+ + Ne$ and $He^+ + Ar$ for which no calculated potentials were then available. This reduced presentation of the data turned out to

be particularly successful, giving us confidence in the absolute calibration of our data as well as in the theory we had developed.[16] Because of this initial success, we were led step by step into a much more thorough and profound analysis of the data than we had initially contemplated. The result was a major piece of work in which we were able for the first time to deduce potentials and information about curve crossings purely from analysis of experimental data. The resulting procedures form the basis of the techniques that we have called collision spectroscopy.

In our first paper on collision spectroscopy, dealing with the systems $He^+ + Ne$ and $He^+ + Ar$, we were able to show that the reduced plot of ρ and τ was able to encompass not only the data from our laboratory in the energy range 10 to 600 eV, but also data from Everhart's laboratory over the region 25,000 to 100,000 eV, all in a single pattern.[16] From these results we were able to deduce very reasonable and plausible potentials covering a very large range of the internuclear separation and clearly showing effects of shell structure and shielded coulomb interactions at short distances and polarization interactions at large distances. In addition, perturbations were seen, one of which in each case could be clearly attributed to an isolated crossing, and its location on the potential diagram could be estimated because we had already determined the basic potential curve. Furthermore, a regular structure of oscillations were seen in the perturbations in question, and we were able to attribute this to an interference pattern due to the existence of two distinct trajectories in the region between the crossing point and the classical turning point, as predicted in 1932 by Stueckelberg. Like our earlier observation of the effect in inelastic scattering,[14] this was the first clear demonstration of the phenomenon in elastic scattering. Furthermore, our paper on impact expansions[15] provided us with a second tool needed to analyze them, a reduced phase relationship that predicted the scaling of the spacing between the oscillations as a function of energy. Finally, our analysis of the data also showed the effects of other crossings; these were apparently rather close together and had the effect of opening up a large number of competing channels and causing a major loss from the elastic scattering channel. Again, the region of internuclear distances in which these crossings occur could be identified.

This major study of the information that could be obtained from elastic scattering had allowed us to develop practical tools that could also be used to analyze inelastic scattering. For example, from the information we already had about the elastic perturbations, it was possible to predict the locations in which the corresponding inelastic processes would be seen. From this point on, our understanding of the

theory has had a great influence on the planning and conduct of our experimental investigations, as well as on the analysis of the data they produced. The first fruit of this work was a major investigation of one of the inelastic scattering transitions in the system $He^+ + Ne$, namely, the inelastic scattering producing Ne^* in its first excited state at 16.1 eV.[20] In this work we were able to measure interference oscillations of the Stueckelberg type corresponding to a pair of trajectories leading to the inelastic scattering. Again our analysis of the data was guided by theoretical principles previously developed here. In this case, from an analysis of the amplitude of the inelastic scattering as a function of energy together with our prior knowledge of the potential curves, we were able to estimate the magnitude of the coupling between the initial and final states in the neighborhood of the crossing point, the fundamental energy matrix element H_{12} of the Landau-Zener theory. Several papers on the theory of these interactions have resulted.[17,18,19] Recently we have carried out a more thorough theoretical analysis and prediction for the system $He^+ + Ne$ using both the Landau-Zener theory and the more accurate direct solution of the coupled equations, confirming our earlier results and improving our estimate of the matrix element.[22]

Our results in this field have also stimulated work in other laboratories. In particular, motivated by discussions with us, Fleischmann and Young at General Atomics studied charge transfer scattering in the system $He^+ + Ar$, and we participated in the detailed analysis of the data. Once again a thorough analysis of the experimental results enabled us to deduce much new information about curve crossings in this system, confirming and amplifying the information we had already deduced from the elastic scattering. A major paper on this work has recently appeared.[33] Still in the course of analysis are the data in our laboratory on inelastic scattering in the same system, $He^+ + Ar$. The combination of all these works, together with our ability to weave into the whole pattern such results as have been obtained in other laboratories, are giving us a unique understanding of the potential curves for repulsive and attractive states in various colliding systems. As the techniques become perfected and as our understanding of the types of phenomena to be seen increases, we are able to apply our knowledge with increasing confidence and speed to other systems.[34] For instance, we were able quite rapidly to analyze and understand some rather complicated oscillations seen in the elastic and inelastic scattering of Li^+ by Li.[35]

In the course of this work we have maintained our concern for developing the underlying general theory and also for developing improved connections between this branch of collision theory and the theorists working in a number of institutions on the electronic structure of diatomic systems. Originally the molecular electronic structure work was oriented mostly to bound-state potential curves, and the only experimental tests usually considered were those available from optical spectroscopy. The possibility of applying the same theoretical information to collision problems has only become recognized by the molecular theorists in the last two or three years, and we believe that a good deal of their interest has developed because of our own missionary work.

A particularly important piece of this missionary activity was a conference organized and held at SRI on the subject of Diatomic Collisions and Electronic Structure on May 4-6, 1967, which brought together in a very constructive interaction a number of experts working in the field of molecular electronic structure along with others working on collision problems from both the theoretical and experimental point of view.

As a contribution to clarifying the connection between electronic structure theory and collision problems, we have developed in a major paper the formal basis for the diabatic representation of collision problems,[21] thereby providing the formal and exact justification for procedures that have long been used in such connections as the Landau-Zener theory. In addition, the same paper provides explicit expressions for the various types of matrix elements needed for collision problems, matrix elements that should be computed in the course of adiabatic electronic structure calculations.

The knowledge of inelastic collision processes and the principles governing the estimation of their cross sections, developed to such a large extent under the present project, are now being used more and more in our laboratories (and also elsewhere) in the interpretation and prediction of a number of collision processes. Notable areas where this knowledge is now being applied include charge transfer, electronic excitation in the course of collisions, inelastic energy transfer, charge transfer producing optically excited or metastable species, and neutralization by collisions of positive with negative ions. After almost forty years the full usefulness of the Landau-Zener formula in particular is becoming recognized, and its limitations are being taken care of by the development of more refined theoretical models. Enough experimental data and detailed calculations are now available for meaningful comparisons to be made and simple interpolations to be deduced,

allowing the needed numerical values for such quantities as matrix elements to be estimated from other information that we have about atoms and small molecules. We have been applying this kind of information to the understanding and prediction of a wide range of important processes including charge transfer,[32,36] ion-ion neutralization in the ionosphere and excitation processes in the upper atmosphere.[37] We have recently made an extensive correlation of information on matrix elements applicable to processes where an electron is transferred[24] and have generated from this a formula for obtaining these quantities from such simple and accessible atomic parameters as ionization potentials and electron affinities. The results have been applied with gratifying success already in a number of cases[38] and will be very valuable in the future.

Things Not Accomplished

In this section we wish to make brief mention of some tasks that we considered undertaking or even commenced but that were not carried through to the point of formal publication.

Electron Collisions

The initial work statement of this contract was a very broad one, authorizing work on electronic, atomic, and ionic collisions in support of the work being carried on experimentally in our laboratory. As things have actually developed, collisions with electrons have not been a major subject of our experimental work in this laboratory during most of the life of this contract. Electron collisions were more important in our program in the early years, particularly 1960 and 1961 when the preceding contract NASw-80 was in effect, and at that time a study of superelastic electron collisions with molecules and atoms was an important part of the work carried out under that contract.

In effect, our work on formal scattering theory is potentially applicable as much to electrons as to heavier particles, although we have not pushed such applications. However, as the subject of inelastic atomic collisions develops into the region of energies where ionization takes place, our studies of curve crossings are once again bringing us into the domain where processes involving the production of free electrons become important. For this reason we believe that the study of electron collisions or their inverse, namely, processes producing electrons, will become a larger part of our theoretical program in the future.

Collision Lifetimes and Three-Body Reactions

Early in our study of collision lifetimes it became clear that unstable transient pairs might, when they collide with a third partner, provide an important intermediate in recombination processes both for atom-atom recombination to neutral molecules and for electron-ion recombination or electron-molecule attachment. The formal treatment of the resulting reaction rates was fairly straightforward[4,6,31] and led to the hope that it would be possible to use the formalism actually to estimate a specific reaction rate such as that for the process $H + H + M \rightarrow H_2 + M$. To do this, one would need primarily the phase shifts for the collisions H + H as a function of energy, at close enough intervals so that the energy derivative of the phase shift, which is the collision lifetime, could be evaluated, particularly in the neighborhood of resonances. Unfortunately at that time (about 1963), the published phase-shift data for this collision were inadequate for the purpose. Since that time the necessary phase shifts have been generated, and used in just the way we had in mind, by Roberts, Bernstein, and Curtiss, at the University of Wisconsin.[41,42] The technique that we proposed has thus had a very successful application and will undoubtedly be used on other systems in the future.

Semiclassical and Quantal Theory of Scattering Amplitude

The paper "Classical and Quantal Scattering, I"[10] was intended as the first of a series, in which successive papers would be devoted in more detail to semiclassical and quantal formations and the relationships between them and the classical formula. Our initial work on these further developments became postponed, partly because the first draft of the work was clearly not ripe for publication, but more importantly because our work on the interpretation and prediction of experimental scattering measurements turned out so successfully and took a higher priority. However, many of the results of our initial studies of semiclassical expressions became applicable and were published in connection with the analysis of the experimental results.[11,16] Eventually the need for another formal work on this topic was filled by a very successful and gratifying set of papers by M. V. Berry,[43,44] so that further work here was unnecessary. This topic is now becoming more active again.[46]

Collision Lifetimes in the Theory of Transport Processes

We have used the theory of the lifetime matrix and the scattering matrix very successfully both in the statistical thermodynamics of gases and in chemical kinetics, including three-body reactions. The theory of transport properties also appears to be a promising one for

application of some of the same considerations. Although some work in this direction has been done by Kim and Ross,[45] we believe that the techniques we have developed could be applied with great success to generalizing and perhaps simplifying some of the results of transport theory. Such a piece of work has not been undertaken here, nor apparently elsewhere, in our own case because of the competition of other matters that seemed to have a higher priority. It is, however, an important piece of work that would seem to be worth carrying out in the future.

Applications

The developments we have reported here are applicable to a great variety of problems in chemical kinetics, thermodynamics, shock waves, atmospheric processes, gaseous lasers, and other diverse fields. A number of these applications are being made outside SRI, and about many of them we are uninformed; an application to atomic recombination rates by Bernstein, et al.[41,42] has already been cited.

In our own laboratory we have recently been applying the knowledge we have gained in this program to some very specific calculations of ion-ion recombination rates,[23] of charge transfer in symmetric and asymmetric systems,[32,36] and of inelastic electron transfer processes leaving one of the products in an electronically excited state, either radiating or metastable.[37,38] A number of these reactions have specific applications in the upper atmosphere and ionosphere of the earth,[37] and also of other planets. The techniques we have developed for making simple estimates of these cross sections and reaction rates are expected to be of considerable utility to other workers in these and related fields.

As we have surveyed this whole program and its salient results, two features of it stand out as especially important. First, the creative effect of a very close interchange between experiment and theory is evident, and, second, the value of a close interplay between the more abstract and fundamental view of collision problems and the more directly applied calculations and analyses. We believe that the alternation between and interaction of these varied points of view have had a very constructive effect on our ability to treat specific applied problems. A number of the practical and simple computing methods that we are now using very effectively would never have been discovered had it not been for the place that a more long-range viewpoint had in this program.

As a practical matter, the ultimate aim of work of this type is the development of an understanding of large classes of reactions, so that numerical values for specific processes that are needed for practical purposes (for example, in predicting reactions in the upper atmosphere or in shock waves, etc,) can be obtained rapidly and economically when needed. For rapidity and simplicity, one would like to develop procedures whereby one could produce the needed information by a simple and rapid calculation using already accessible auxiliary information (such as tabulated atomic or molecular properties, spectra, and ionization potentials). Somewhat less favorable but still very valuable would be the ability to generate the needed data by a standardized and inexpensive computer calculation, particularly if the calculation procedure could be applied readily and in a routine way to a large number and variety of systems. Thirdly, still feasible but somewhat more time consuming, would be methods of prediction whereby one could generate the information needed after a simple and routine measurement of certain atomic or maoecular properties, which might,indeed have to be measured specifically for the purpose in mind. For example, it has long been routinely possible to measure various features of the optical spectra of various atoms or molecules and from these spectra to predict reliably various properties that depend on them, including molecular force constants, specific heats and other thermodynamic properties, and the like. We believe that the measurement of a number of collision properties may soon become equally practicable and equally fruitful in generating standard types of information that could be used for predictive purposes in the same way as optical spectroscopic data are now routinely used.

Related Programs and Sources of Support

In addition to the major and continuing support provided to our over-all program of theoretical research by NASA, related theoretical studies supported by other agencies have also contributed to the productivity of our total effort over the past decade. SRI has provided considerable support through two principal channels, internal research funds allocated by the Institute and the endowed support of the Atholl McBean Fellowships, which have been held at different times by three participants in the work reviewed in this report. The National Science Foundation has supported theoretical work at various times under several research grants. The Atomic Energy Commission, Division of Research, has for several years supported a research program entitled "Fundamental Principles of Collision Spectroscopy in Diatomic Systems", under which we have carried out several pieces of research that have been included in the present survey. The Institute for Defense Analyses has supported

the writing of three papers in which we have reviewed aspects of the field of collision physics.

Numerous aspects of this work have been stimulated by various developments arising out of the experimental side of our studies in atomic and molecular collisions. These experimental studies have been supported by a number of agencies, including ARPA, ARO, DASA, AFCRL, AFWL, NSF, AEC, Division of Biology and Medicine, and ONR. In several cases theoretical work done in close conjunction with the experimental program has been supported as part of these experimental contracts or grants.

In the next section we list the publications arising from our over-all theoretical program in the field of collisions, and indicate the major sources of support for each.

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A. Papers on Collision Theory Preceding this Contract

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