UNIVERSITY OF WISCONSIN

THEORETICAL CHEMISTRY INSTITUTE

TYPE OF REPORT:	SEMI-ANNUAL PROGRESS REPORT to National Aeronautics and Space Administration (Theoretical Chemistry Institute Portion)
NUMBER OF REPORT:	Eleven (11)
PERIOD REPORT COVERS:	1 July 1967 through 31 December 1967
GRANT NUMBER:	NsG-275-62
DATE:	31 December 1967
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NASA SEMI-ANNUAL PROGRESS REPORT

I. INTRODUCTION

A. Theoretical Chemistry

Theoretical chemistry seeks to explain quantitatively the physical and chemical properties of materials, to relate these macroscopic properties of the individual molecules, and to predict the structure and properties of the individual molecules. At the present time, most of the required fundamental laws of nature appear to be sufficiently well known, at least for low-energy phenomena. Thus, we can write down the mathematical relations which determine the physical and chemical properties. The problem then becomes one of finding the solutions to the mathematical equations. Because of, (1) the development of new methods of solution to nonlinear mathematical problems, (2) a greater insight into the basic workings of molecular quantum mechanics and the kinetic theory of gases, and (3) the availability of high-speed computing machines, theoretical chemistry is undergoing very rapid progress.

Theoretical chemistry is a natural focal point for interdisciplinary research since its problem areas overlap with physics, mathematics, astronomy, meteorology, chemical engineering, mechanical engineering, etc.

Thus, theoretical chemists serve as the middlemen between the theoretical physicists and the practical engineers and experimental scientists.

Figure 1 shows the feedback between the practical, socialogical, medical, and military needs with experiments and with theoretical developments. There are two kinds of theory: the playing of hunches and the systematic development of the mathematical theory. Organic chemistry has largely developed through the playing of hunches. This approach is carried out by the great scientific leaders or PROPHETS. After all, the Russian theoretical physicist, Frenkel, said: "Science advances by ILLOGICAL jumps".

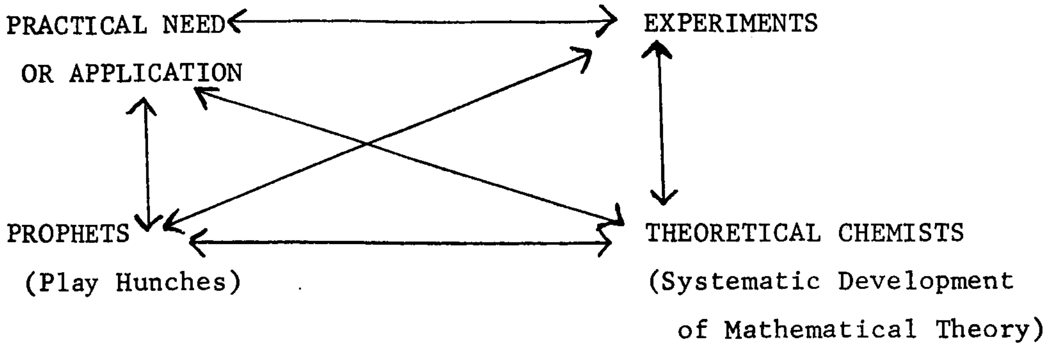

Figure 1.

The systematic development of the mathematical theory starts with the fundamental laws of physics and leads to the prediction of experimental results in the following manner:

I. The Fundamentals of Physics
   - Fundamental Laws
   - Fundamental Particles
   - Fundamental Constants

↓ QUANTUM MECHANICS

II. Microscopic of Molecular Phenomena
   - Microscopic Equations
   - Molecular Parameters
   - Molecular Properties

↓ STATISTICAL MECHANICS

III. Macroscopic Properties of Materials
   - Macroscopic Equations
   - Phenomenalogical Coefficients
   - Properties of Bulk Material

↓ SATISFACTION OF BOUNDARY CONDITIONS

IV. Predictions of Experimental Results
   - Laboratory Experiments
   - Mathematical Experiments

In somewhat more detail we have:

Table I. Fundamentals of Physics

THE BASIC EQUATIONS

Dirac equation generalized by Foldy-Wouthuysen transformation, etc. to form many-particle quantum field theory.

Feynman Path Integrals.

Many-particle generalization of the Breit-Pauli spin-relativistic modification of the Schrödinger equation.

Maxwell Equations of Electrodynamics.

Statistical Mechanics.

THE ELEMENTARY PARTICLES OR FIELD VARIABLES

Electrons, photons, nucleons, etc.

Scalar Potential, Vector Potential, Spin Annihilation-Creation Operators.

THE FUNDAMENTAL CONSTANTS

h, c, e, m, N

Table II. Microscopic or Molecular Phenomena

THE MICROSCOPIC EQUATIONS

The Boltzmann Equation generalized to include internal degrees of freedom of molecules and high density.

Equations for determining the differential scattering cross-sections.

Electromagnetic Local Field Equations for determining the interaction of radiation and matter.

THE MOLECULAR PARAMETERS

Quantum numbers, oscillator strengths, molecular distribution function, collision cross-sections; dipole, quadrupole, and multipole electric and magnetic moments.

THE MOLECULAR PROPERTIES

Energy levels, structure, and spectra of individual molecules.

Intermolecular Forces.

Transition probabilities and perturbations resulting from electromagnetic fields and collisions.

The kinds of interesting macroscopic phenomena are summarized:

Table III. The Macroscopic Phenomena

THE MACROSCOPIC EQUATIONS

Thermodynamic Relations

Equation of State: $P(V,T)$

Calorific Equation: $H(P,T)$ and $S(P,T)$

Thermodynamics of Irreversible Processes

Equations of Flux:

Equations of Continuity

Equation of Motion

Equation of Energy Balance

Equations of Diffusion

Equations of Chemical Kinetics

Maxwell Equations for Electromagnetic Phenomena in Dense Media

THE PHENOMENOLOGICAL COEFFICIENTS

Virial Coefficients: $B, C, \ldots$

Transport Coefficients: $\eta, \lambda, D, \ldots$

Reaction Rate Constants: k

Electric and Magnetic Susceptibility: ϵ, μ

Specific Heats and Energies of Formation

THE PROPERTIES OF BULK MATERIAL

P, V, T, E, H, S, . . .

Compressibility, Heat Capacity, . . .

Sound Propagation

Electrical Conductivity

Flame Propagation and Detonations

Finally, in order to predict the results of laboratory or mathematical equations, it is necessary to solve the macroscopic equations together with the boundary conditions or constraints imposed by the particular experiment. It is this stage of the problem where the theoretical chemists have the greatest interaction with the aeronautical, mechanical, and chemical engineers who are seeking the solution of practical problems. The theoretical chemists seek to provide the macroscopic equation. It then becomes the job of the engineers to go the rest of the way. Frequently engineers use the boundary layer approximation technique (which has been made mathematically respectiable by George Carrier). Here one neglects certain terms in the equations near the surface and neglects other terms in the body of the fluid. The two types of solutions are then matched at the boundary layer. Under extreme conditions of temperature, pressure, or electromagnetic fields, the boundary layer approximation is no longer valid -- one must not only consider all of the terms in the macroscopic equations, but one must also consider the close-coupling between the macroscopic and the microscopic equations. Thus, under extreme conditions it is desirable for the engineers and the theoreticians to work together. Such teamwork was responsible for the success of the atomic bomb. It is also essential for the solution of many of the space research problems confronting NASA.

Let us consider the various types of research which theoretical chemists are currently conducting:

(1) Quantum Chemistry

We are seeking ways and means of calculating the energetic stability of arbitrary molecular configurations. These potential energy surfaces and collision cross sections are used as input information in the statistical mechanical calculations. Most of chemistry requires a relatively low order of precision. However, nuclear magnetic resonance, electron spin resonance, laser optics, etc. require a fantastic degree of accuracy. Thus, it is not sufficient for quantum chemists to solve the Schrödinger equation. They must also treat relativistic corrections which lead to fine structure and hyperfine structure, and of course, they must make corrections for the inadequacy of the Born-Oppenheimer approximation.

(2) Statistical Mechanics and Transport Phenomena

The basic problem is the relation of macroscopic constants, which describe the rate of approach of the system to equilibrium, to the properties of the individual molecules and the potential energy of interaction between the molecules. Current research seeks to remove the various limitations of the well-developed kinetic theory of low density gases made up of spherical molecules. Thus, the theoretical chemists are determining the effects of rotational degrees of freedom of nonspherical molecules; are extending the theory to moderately dense gases; and are finding the quantum effects at moderately low temperatures. The calculation of virial coefficients and transport properties for polyatomic molecules will require the evaluation of a large number of many-dimensional integrals and hence will require a tremendous amount of computing effort.

(3) Molecular Beams and Scattering Theory

Recent developments in the techniques of molecular beam scattering have made it possible to study in detail the intermolecular collision process, thus providing a deeper insight into the underlying mechanism of chemical reactions. Much of the current theoretical work is directed toward an understanding of inelastic scattering of small molecules. Both time-independent (S-matrix) and time-dependent perturbation methods (e.g., the sudden approximation) are being investigated. The objective is to develop methods for predicting the cross sections (and rates) for inelastic and reactive molecular collisions. The reaction rate constant as a function of temperature is related to the collision cross section (corresponding to reactions) as a function of relative kinetic energy by a Laplace transform. Thus, the detailed calculations of molecular beam scatterings will lead to a very clear understanding of reaction kinetics. This type of research requires the solution of a large number of coupled partial differential equations and the use of fantastically large computing machines.

(4) Applications of Quantum and Statistical Mechanics to Biological Problems

A long range program has been undertaken to develop inter- and intramolecular forces in systems of biological importance. From a knowledge of these forces, the structure and physical properties of biological systems can be determined by statistical mechanical methods.

B. The University of Wisconsin Theoretical Chemistry Institute (see Appendix A) is an integral part of the Department of Chemistry and has excellent working arrangements with the Physics, Mathematics, Computer Sciences and various Engineering Departments. Most of the permanent staff members hold joint appointments with these departments. In addition to their research, these staff members carry normal teaching loads and take their teaching responsibilities very seriously. In addition to graduate courses, they also teach undergraduate courses in elementary physical chemistry (laboratory as well as lecture), thermodynamics and reaction kinetics. We believe that our teaching program in theoretical chemistry is the best in the world.

As a result of the NASA grant, the University of Wisconsin has been able to expand its theoretical chemistry faculty. We have noticed that the sharp improvement in the caliber of new graduate students and the quality of applicants of postdoctoral appointments at the Theoretical Chemistry Institute is continuing. In addition, a number of eminent professors are choosing to come to Wisconsin both for summer leaves and for sabbatical years in order to take advantage of the opportunities available at the Theoretical Chemistry Institute.

At the present time, we have 4 full professors of chemistry, 1 full professor of physics, 1 assistant professor of chemistry, 1 lecturer in chemistry, and 1 visiting assistant professor of mathematics and theoretical chemistry. During this period, we have had 9 post-doctoral associates. We have had 26 graduate students, including 11 research assistants (NASA supported), 4 research assistants (NSF supported), 3 teaching assistants (U.W. supported)*, 2 research/teaching assistants (NASA and U.W. supported), 2 NSF fellows, and 1 NASA fellow. These do not include the experimental students working under Professors Bernstein, Cornwell, and Harriman. We have had a supervisor of our Theoretical Chemistry Institute computing center and 5 computer programmers.

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* 2 NSF Fellow/Teaching Assistants (NSF and U. W. supported), 1 Eastman Kodak Fellow/Teaching Assistant (Eastman Kodak and U. W. supported).

At this time before reviewing the progress of the latest semi-annual period, we want to express our appreciation to the National Aeronautics and Space Administration (NASA) for providing the Theoretical Chemistry Institute with the opportunity for developing an excellent teaching and research program. The University of Wisconsin has also liberally contributed to the program of the Institute by paying the salaries for most of the permanent staff members, awarding teaching assistantships and graduate fellowships to many of our graduate students, and providing very excellent computing facilities.

We are very grateful to NASA for financing new facilities for the Theoretical Chemistry Institute. In place of the old frame building at 1111 West Johnson and a small amount of space in the first unit of the chemistry building, we will occupy all of the eighth floor and a part of the ninth floor of the new chemistry building. It is anticipated that our group will move into these new quarters around the first of January, 1968. This will provide us with ample space for all of our activities. We are especially pleased to have a very large specially constructed computing area with raised floor, separate power source, and separate air conditioning. We are grateful to NASA for having provided us with funds to purchase computing equipment to be installed in this area. We will definitely have a teletype connection with the University of Wisconsin Computing Center Burroughs B5500. However, we have not yet placed orders for other computing equipment, since we are anxious that whatever we purchase be compatible with the giant Burroughs B8500 series computer which the University is purchasing. At the present time we do not know exactly what peripheral equipment the University Computing Center will obtain. The longer we can wait to place our orders the better computing facilities we can obtain with our limited funds.

In June of 1967 Professor Richard Bernstein obtained a one year grant of $150,000 for his research (experimental and theoretical) on molecular beams. This is the largest grant to a single project which the Chemistry Branch of the National Science Foundation has ever made. This grant helps relieve the financial strain on our Theoretical Chemistry Institute budget. The cost of our high speed computing is becoming increasingly larger as our research becomes more successful and as we progress from pure mathematical physics towards practical applications. Fortunately the cost of a unit of computing on the forthcoming Burroughs B8500 series will be on the order of one-fifth of the price which we are now paying.

RESEARCH INTERESTS OF THE THEORETICAL CHEMISTRY INSTITUTE STAFF

There is a wide range of research at the Theoretical Chemistry Institute. Saul T. Epstein and J. O. Hirschfelder are currently working on molecular and intermolecular quantum mechanics problems. C. F. Curtiss is concerned with the theory of statistical mechanics and transport properties. Richard B. Bernstein, C. F. Curtiss and William A. Lester, Jr. are interested in molecular beams and scattering theory. Dr. Lester is also working on molecular quantum mechanics. John E. Harriman is working on electron-spin resonance and quantum mechanical density matrices. C. Daniel Cornwell is working on microwave pressure broadening and other types of problems in molecular spectroscopy. The following is a summary of the detailed research interests of each of the staff members.

PERMANENT STAFF

Richard B. Bernstein

The research of R. B. Bernstein and associates remains centered in the area of molecular beam scattering. It may be conveniently divided into two categories: one, the primarily experimental aspects, supported until August by the U.S. A.E.C. and since then by the N.S.F., and two, the primarily theoretical aspects, receiving N.A.S.A. support. The following paragraphs describe work in progress in the latter category.

In the field of elastic molecular scattering, Mr. T. J. P. O'Brien is continuing his investigation of the validity and applicability of the elegant and general Hylleraas inversion scheme to deduce the interatomic potential from scattering data. Dr. R. E. Olson is carrying out a practical inversion program (developed earlier by himself and Prof. Mueller of Purdue) with the intent of ascertaining the Li-Hg ground state potential curve from the quantum interference observations previously reported by our experimental group. His principal efforts, however, have been in the development of a theory of quenching of glory extrema in atom-molecule collisions (described elsewhere in this report). Mr. T. G. Waech and Mr. M. E. Gersh have been computing quasibound states ("orbiting resonances") and elastic scattering cross sections for the H+H system, while Mr. R. J. LeRoy has been investigating the sensitivity of the bound state calculations to small changes in the interatomic (H_2) potential. Mr. R. E. Roberts is making use of the results of the resonance studies in connection with his ab initio computation of the recombination rate of atomic hydrogen (being done in collaboration with Prof. Curtiss). Mr. J. T. Muckerman is studying the compound state (rotational sub-excitation) resonances (particularly the "supporting potentials" and eigenvalues thereof) in collaboration with Dr. R. D. Levine (who is concerned primarily with the general theory) and Dr. B. R. Johnson (who is carrying out the exact numerical solution of the closed-channel problem using his newly developed (with Prof. Secrest of Illinois) method of amplitude density functions). Dr. W. A. Lester, Jr. is continuing his work on the (open-channel) aspects of the rotational excitation problem (as described elsewhere in this report). Mr. R. W. Fenstermaker is finishing up the research on the sudden approximation for rotational excitation and scattering, and Dr. A. Dickinson is working on extending the statistical (dominant coupling) approximation for rotational energy transfer employing the recent angular momentum recoupling scheme of Prof. Curtiss. The writer is also carrying out the final phases of the research on collision-induced absorption in collaboration with Dr. D. A. McQuarrie (of the North American Rockwell Science Center, formerly a visiting scientist at the Institute) and some work on phenomenological analysis of reactive scattering data (experiments of C. Riley and K. T. Gillen of our group) in collaboration with Dr. R. D. Levine.

C. F. Curtiss

We have continued our study of the theory of transport phenomena in gases. In particular we have continued the study of the effects of internal degrees of freedom of molecules, particularly rotational degrees of freedom, and also the effects of density on the transport coefficients.

For sometime, with the aim of obtaining expressions for the transport coefficients of a gas of non-spherical molecules, we have considered the quantum mechanical theory of molecular scattering processes. This has led to a series of papers on the theory of molecular collisions. The sixth paper of this series will soon appear in the Journal of Chemical Physics. In this paper we use diagrammatic techniques in handling the angular momentum coupling coefficients. Using these techniques, it is possible to systematize the development considerably. An interesting, and perhaps important, by-product of the use of these diagrammatic techniques has been a complete reformulation of the scattering integral equation. The implication of this reformulation and its possible use in the numerical aspects of scattering theory are being investigated by others in the institute.

Louis Biolsi and I have considered a generalization of the treatment of the scattering problem, to include the effects of nuclear spin and statistics. This study is now complete and a manuscript has been prepared. A number of interesting results of this treatment are evident, but we have not yet completely analyzed the resulting expressions.

The long-term aim of our study of scattering theory has been the development of expressions for the transport coefficients of a gas of non-spherical molecules. With this aim in mind, we have been attempting to obtain, analytically, the classical limit of the expressions for the cross sections. Some success has been obtained in this direction, but this study is still incomplete and actively underway.

We have also continued our study of density effects on the transport coefficients. Sometime ago, David Hoffman and I developed a classical theory of the effects of collisional transfer and of three-body collisions. David Bennett is now generalizing these results to the case of a mixture of gases. This generalization will provide information about the density variation of the coefficient of diffusion. The only previous information on this question are the results of the rigid sphere treatment of Enskog. These results have formed the basis of a number of engineering correlations of experimental data. The results of the present treatment may well be of value in providing a more adequate basis for such correlations. This study will form Bennett's Ph.D. thesis.

Some time ago, Imam-Rahajoe and I developed a quantum mechanical treatment of the collisional transfer effects. This study was his Ph.D. thesis, and a paper based on this will soon appear in the Journal of Chemical Physics. A surprising result of this study is the appearance in the expressions for the energy flux of a term proportional to the density gradient. This term is strictly a quantum effect and we are still attempting to understand its origin and interpretation. An investigation of this point has uncovered several mathematical questions which need considerable further study. We plan to extend this quantum treatment to include the effects of three-body collisions in a manner parallel to that used by Hoffman in the classical development.

Saul T. Epstein

Recent and Current Research (mainly in collaboration with Mr. R. E. Johnson)

Recently we have been concerned with theories of intermolecular forces including exchange. We have compared various theories by applying them to a simple model, and we have searched (with some success) for connections between the various theories which have been proposed.

Currently, in support of and in collaboration with Professor C. D. Cornwell, we are investigating the effects of nuclear motion on hyperfine structure.

Long Range Plans

We will continue to explore and search for approximate and exact quantum mechanical results applicable to atomic and molecular systems.

John E. Harriman

We continue to be interested principally in magnetic interactions and in wave functions for odd-electron systems, especially the calculation of spin densities.

The work in collaboration with Mr. Ken Sando on spin-extended self-consistent-field calculations, which has been discussed in previous reports, has gone well. The general technique has been developed and applied to pi-electron systems in the Pariser-Parr-Pople approximation. Spin densities have been calculated for a number of hydrocarbon molecules. This work will be reported in a paper that is nearly completed. We are now developing a program to do similar calculations in atoms, where the comparison of experimental and theoretical results is more direct. We are less interested in these systems, but hope to get a check on the accuracy of the method. Work is continuing with Mr. Lloyd Holm on spin polarization effects and the methods by which pi-electron spin densities are related to experimentally observable quantities. Mr. Jack Simons is beginning to investigate the possibilities of treating orbital angular momentum (for atoms) or point group symmetry (for molecules) by the combined projection operator density matrix method that has been developed for the spin-extended calculations.

The general theory of reduced density matrices and the N-representability problem continue to be of interest. We are concentrating principally on density matrices arising from functions of configuration-interaction type, and a paper on this with Miss Beth Ruskai has been submitted for publication. In August I went to a density matrix conference at Queen's University, Kingston, Ontario, where work of this type was discussed.

Dr. Ilana Tamir and I have developed a density matrix perturbation scheme for the direct calculation of the changes produced in an N-representable density matrix by a perturbation. We have applied it to spin-extended density matrices and considered a small change in internuclear distance as a perturbation. A paper is in preparation.

Our interest in the origin of magnetic interactions has led us to consider relativistic effects and the reduction of relativistic equations to a form suitable for a perturbation treatment starting with ordinary Schrödinger wave functions. Miss Penny Estabrooks has carried out the reduction of the Breit equation to non-relativistic form by the partitioning technique, but the results are not entirely satisfactory and we expect to continue along other lines starting from field theory rather than a relativistic many-particle equation.

Joseph O. Hirschfelder

During the past six months I have been working on six problems:

I. I edited a treatise entitled Intermolecular Forces (Advances in Chemical Physics, Volume 12)which will be published by John Wiley and Sons before January 1968. William J. Meath (Assistant Professor, Department of Chemistry, University of Western Ontario) and I wrote a survey chapter. A summary of the present status of the theory of intermolecular forces is given in Appendix B of this progress report (this summary will be published in the February 1968 issue of the Journal of Chemical Education). I am primarily interested in unusual types of intermolecular forces: (1) potential energy curves with humps or wiggles, (2) velocity dependent forces, (3) the "natural energy width" of potential energy curves as a function of separation (which result from deviations of the Born-Oppenheimer separation approximation), and (4) fine structural and hyperfine structural effects on intermolecular forces.

II. One of my graduate students (Phillip R. Certain) and I have been collaborating with two Polish professors (W. Kolos and L. Wolniewicz) who are visiting the University of Chicago. We have determined the exchange and coulomb energy of H_2 by various types of perturbation methods. Professors Kolos and Wolniewicz were able to make these calculations on the University of Chicago computing machine by making only small modifications of their existing program packages. Thus, they were able to use a large selected basis set of functions (together with the variational principles which Certain and I furnished them) to obtain, with high accuracy, the second order energy and the expectation value of the Hamiltonian corresponding to the wave function through the first order for the ground state and first excited state of H_2 at internuclear separations of 4,6 and 8 Bohr using three different techniques: Hirschfelder-Silbey, Musher-Amos or Murrell-Shaw, and Eisenschitz-London or Hirschfelder's modification (HAV) of the van der Avoird formalism. As I explained in two articles in Chemical Physics Letters (October and November 1967 issues) there is currently no unique way of determining the exchange energy of atoms at intermediate separations. The present calculations will provide us with a basis for improving our present procedures.

III. Together with two graduate students (Mac B. Milleur and Michael Twerdochlib) and one Junior year undergraduate (Larry A. Curtiss) we are considering the hyperfine splitting of the interaction energy between two hydrogen atoms, a hydrogen and a deuterium atom and two deuterium atoms. At separations greater than 5 Ångstroms the electron spins for most of the hyperfine molecular states become partially decoupled, and one can no longer refer to the molecule as being an electronic singlet or an electronic triplet. The concept of ortho and para hydrogen remains meaningful, however, if the definitions refer to the parity of the rotational states rather than to the spin of the nuclei (which is not a good quantum number at large separations). The practical importance of this hyperfine interaction is in connection with spin-exchange scattering. The hyperfine interaction produces line broadening in the hyperfine structure of atomic hydrogen and atomic deuterium. It causes an incoherence in the radiation emitted by H_2 , HD , or D_2 gas lasers. In addition, it affects the intensity of the microwave atomic hydrogen spectra observed in radio astronomy (especially the 21 cm line). Currently we are making an accurate calculation of the spin-exchange collision cross sections which previously have been estimated in a much more crude fashion.

IV. Together with a postdoctoral research associate (Donald K. Harriss) and two graduate students (Joseph D. Bowman and David M. Whisnant) I am trying to generalize the "local energy" scheme originally developed by Frost and Harriss. This is a long shot! If successful, it would provide an easy way to estimate the energy of a molecular system. The new approach which we are trying is concerned with using fewer points in configuration space and getting more information (in the form of constraints on the approximate wave function) at each of the points considered. We are also investigating the use of Conroy-type approximate wave functions which satisfy all of the cusp conditions and behave properly at large distances. The Conroy-type functions should give local energy which varies more slowly than the local energy calculated with the more conventional basis sets.

V. A postdoctoral research associate (Donald Harriss) and I are developing an iterative procedure for solving perturbation equations. This involves the solution of first-order partial differential equations by the method of characteristics. On the basis of a few simple examples we feel that this procedure shows considerable promise. We are also using group theory to resolve the perturbed wave functions into a set of functions of different symmetry types. This results in a considerable simplification of some types of perturbation problems.

VI. I am very much intrigued as to the reason why simple physical models work. The following is an abstract of a talk which I am going to present at the Langmuir Award Symposium in honor of Henry Eyring at the San Francisco meeting of the American Chemical Society in April, 1968.

WHY SIMPLE PHYSICAL MODELS WORK by Joseph O. Hirschfelder:

The accuracy and large range of validity of the simple models which Eyring and others have used to explain a wide range of physical and chemical properties is truly amazing. In any material system there is a wide range of relaxation times associated with intra-molecular, molecular-collisional, and macroscopic processes. Usually these relaxation times separate into distinct bands. I believe that the simple models result from suppressing those dynamical modes which are associated with relaxation times inappropriate for the phenomenon under consideration. This is the basis for von Neumann's mathematical approach to meteorology where the high frequency sound waves are absorbed by the introduction of a ficticious viscosity. The simplest example is the "pseudo-stationary" state approximation where deviations in the concentrations of the intermediate chemical species correspond to relaxation times small compared to the time of the over-all reaction. The derivation of the Navier-Stokes equations depends upon two facts: (1) in a molecular-collisional time the N-particle distribution function becomes a functional of the one-particle distribution function. (2) In an intra-molecular time the higher moments of the one particle distribution function become functionals of the first three moments (the Hilbert paradox). The Eyring theory of absolute reaction rates results from the characteristic time for motion along the reaction path being long compared to the relaxation times for the other vibrational and rotational modes.

W. A. Lester, Jr.

Research for the present report period has continued to focus on the time-independent S-matrix theory of rotational excitation of diatomic molecules by atom impact. The goal is to obtain a computationally feasible method for the reliable determination of integral cross sections.

The results of a study discussed in the last report concerned with the structure of the matrix of inelastic rotational transition probabilities, $|S|^2$, has been published in CHEMICAL PHYSICS LETTERS.

Recently, attention was directed at making a comparison of the present computational procedure involving the solution of coupled ordinary differential equations with the Amplitude Density Function method (ADF), an integral equation method developed by B. R. Johnson[+] and D. Secrest of the University of Illinois. The results of this investigation have appeared in CHEMICAL PHYSICS LETTERS.

A detailed description of the numerical method used in the differential equations approach is nearing completion and will be submitted to the JOURNAL OF CHEMICAL PHYSICS.

The investigations described above have been in collaboration with R. B. Bernstein.

Planning is now underway for the inclusion of closed channels in the computing program used in the studies mentioned above.

Also to be pursued are statistical approaches to the problem of describing the degree of randomness of the matrix elements of $|S|^2$ in the region of strong("dominant") coupling.

It is also planned to investigate the energy dependence of $|S|^2$ as a function of the coupling between states.

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[+] Present address: Theoretical Chemistry Institute, University of Wisconsin.

VISITING PROFESSORS

Raphael D. Levine

In the series of lecture notes on collision theory I have completed the third and last part dealing with applications. The part consists of eight chapters dealing with the partitioning technique, molecular collisions, variational principles, the theory of direct reactions, models in the theory of reactive collisions including the use of opacity functions, the statistical approximation, the theory of unimolecular processes and the general theory of relaxation in ensembles. I have also participated in the work on internal excitation resonances in molecular collisions described elsewhere.

POSTDOCTORAL STAFF

Louis Biolsi

Work on the effects of nuclear spin and collisions between indistinguishable molecules on the differential and degeneracy averaged scattering cross sections has been completed.[1] In the spherical limit the expressions are found to agree with previously known results.[2]

I am presently considering a "distorted wave" treatment of the wave function and cross sections for nearly spherical potentials. Use is being made of the diagrammatic techniques introduced by Professor Curtiss[3] and the results are expected to parallel those obtained previously.[4]

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1. WIS-TCI-273.

2. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, Inc., New York, 1954.

3. WIS-TCI-241.

4. C. F. Curtiss and A. Hardisson, J. Chem. Phys. 46, 2618 (1967).

A. S. Dickinson

I hope to consider some aspects of atom-atom and ion-atom elastic scattering and in particular the influence of quasi-bound states.

A somewhat formal approach to these states is being investigated through the use of complex angular momentum, as introduced by Regge. Earlier calculations with an ion-atom potential are being extended to explore both the threshold region and the region of large ℓ to test for the existence of a bound on a trajectory in real ℓ.

The accuracy of the Rydberg-Klein-Rees potential curve for Hydrogen Fluoride is being investigated and it is hoped to use this curve to predict the widths of levels undergoing predissociation by rotation.

Another manifestation of these quasi-bound states is in three body recombination and I intend to use a quantum treatment of this process under development by Mr. Roberts, Professor Bernstein and Professor Curtiss to evaluate the coefficient for He^+ in He and the triplet metastable helium atom in helium.

Using an alternative formulation of the distorted wave approximation, due to Curtiss and Hardisson, it is intended to reinvestigate the approximation scheme of Bernstein, Dalgarno, Massey and Percival for rotational excitation of diatomic molecules by atom impact.

Also it is hoped to consider whether any effects of rotational excitation should be detectable in the mobility of diatomic molecular ions in atomic gases.

Donald K. Harriss

Several problems are being actively pursued at the present time. Among the more promising seem to be:

1. The resolution of perturbed wavefunctions into symmetry components transforming as particular rows of the irreducible representations of the group of the zero-order Hamiltonian. This type of resolution, effected through the application of projection operators to the different orders of perturbation equations,

a) serves to separate the perturbation equations into ones of known symmetry therefore reducing the degree of complexity of an individual equation,

b) yields qualitative information such as; which orders of the perturbed energy are identically zero, the symmetry of the perturbed wavefunction when truncated after n-th order, and the number of components into which a particular order of the perturbed wavefunction can be separated.

2. An iterative procedure for the solution of the various orders of perturbation equations is being investigated. The method is based on the assumption that for a first approximation of a given order of the perturbed wavefunction certain terms in the perturbation equation can be neglected and need only be considered in higher approximations. Rapid convergence is found for systems such as coupled harmonic oscillators and the ground state hydrogen atom in a uniform electric field. Work is in progress on other systems.

Long range plans involve the above mentioned problems plus detailed investigation of the Local Energy procedures and the nature of solutions to the Prager-Hirschfelder lower bound to the second order energy.

B. R. Johnson

The work of B. R. Johnson has been mainly concerned with the numerical solution of multichannel scattering problems, in particular with the problem of the rotational excitation of a diatomic molecule upon collision with an atom. While at the University of Illinois, in collaboration with D. Secrest, he developed a new technique (A.D.F. method) for numerically solving this problem in the coupled channel approximation. A favorable comparison of this method has been made with W. A. Lester's procedure of solving the coupled differential equations. The results of this comparison have recently appeared in Chemical Physics Letters.

In collaboration with R. D. Levine, J. T. Muckerman and R. B. Bernstein, he is investigating the resonances in the $j=0$ channel due to the quasi-bound states in the closed $j=2$ channel. The parameters were chosen to approximate a Helium atom colliding with a Hydrogen molecule. The investigation has so far been limited to the case $J=0$ (J is total angular momentum, $\underline{J}=\underline{j}+\underline{\ell}$). Exact numerical calculations of phase shifts were carried out using the A.D.F. method. It was found that these phase shifts, except in the actual region of the resonance, and the resonance energies, could fairly well be approximated by simple calculations using best local potentials except in an anomalous region where potential curve crossing occurs. Results of these investigations will appear in the proceedings of the 1967 Belfast Conference on heavy particle collisions and in Chemical Physics Letters. Also a detailed article is being prepared for submission to the Journal of Chemical Physics.

It is planned to continue these resonance investigations for other interesting systems. Also to be pursued is the application to the A.D.F. method of a new procedure which Professor Curtiss has discovered for resumming degeneracy averaged cross sections. This should result in a considerable saving in computation time for certain problems.

Ronald E. Olson*

Present investigations with Professor R. B. Bernstein have been directed toward the development of a suitable theory to predict the quenching of glory extrema in atom-diatomic molecule scattering. The damping of the glory undulations in the velocity dependence of the total cross sections for atom-molecule scattering was first observed by Gislason and Kwei[1] and qualitatively explained by them in terms of inelastic and reactive processes concurrent with anisotropic elastic scattering. Subsequent experiments by Helbing and Rothe[2] confirmed the quenching phenomenon and extended the range of systems exhibiting such behavior. The present theory deals mainly with non-reactive atom-diatomic collisions, considering the coupled equations in the total angular momentum representation and taking full cognizance of the anisotropic distortion of the potential. The resulting equations yield a lower bound on the degree of quenching, but should be fairly generally applicable except for extremely reactive systems of the "stripping" type. The extent of the damping and its velocity dependence is expected to be increased for systems of larger reduced mass with deeper Van der Waals potential wells, larger size parameters and greater short-range anisotropy coefficients, and for diatomics of high moment of inertia.

Upon the completion of the above work efforts will be directed to the inversion of existing Li-Hg experimental differential cross sections[3] to obtain the intermolecular potential. The potential so retrieved will then be compared with that arrived at by the analysis of the total cross section glory extrema.[4]

Anticipated also will be the development of a satisfactory theory of reactive scattering which allows for large changes in the orbital angular momentum on reaction. The specific cases to which this theory will be applied is K + HBr → KBr + H .

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* N.S.F. Postdoctoral Fellow.

1. E. A. Gislason and G. H. Kwei, J. Chem. Phys. 46, 2838 (1967).

2. E. W. Rothe and R. Helbing (private communication).

3. P. J. Groblicki and R. B. Bernstein, J. Chem. Phys. 42, 2295 (1965).

4. E. W. Rothe and L. H. Veneklasen, J. Chem. Phys. 46, 1209 (1967).

SUMMARY OF EXPENDITURES AND UNLIQUIDATED COMMITMENTS

Theoretical Chemistry Institute portion of NASA Grant NsG-275-62

July 1, 1967 - December 31, 1967

Salaries	$ 96,872.78
Computing Services	14,185.93
Travel	287.92
Publications	9,040.71
Services	1,267.32
Supplies	1,814.23
Communications	515.00
Honoraria for Consulting	837.83
Total Direct Costs	$ 124,821.72
Overhead*	24,964.34
Total Costs	$ 149,786.06

* 20% of Total Direct Costs

APPENDIX A

The University of Wisconsin Theoretical Chemistry Institute Brochure

The University of Wisconsin

Theoretical Chemistry Institute

Madison, Wisconsin

THEORETICAL CHEMISTRY

Theoretical chemistry seeks to explain quantitatively the physical and chemical properties of materials, to relate these macroscopic properties to the properties of the individual molecules, and to predict the structure and properties of the individual molecules. At the present time, *all* of the required fundamental laws of nature appear to be sufficiently well known, at least for low-energy phenomena. Thus, we can write down the mathematical relations which determine the physical and chemical properties. The problem then becomes one of finding the solutions of the mathematical equations. Because of the development of new methods of solution of nonlinear mathematical problems; because of a greater insight into the basic workings of molecular quantum mechanics and the kinetic theory of gases; and because of the availability of high-speed computing machines, theoretical chemistry is undergoing very rapid progress.

TABLE OF CONTENTS

1. ORGANIZATION

The Theoretical Chemistry Institute is an integral part of the Department of Chemistry of The University of Wisconsin, and has excellent working arrangements with the Physics, Mathematics, Computer Sciences, and various Engineering departments. At the present time, the principal financial support from outside the University is derived from a National Aeronautics and Space Administration grant. New theoretical laboratory facilities (partially funded by the National Aeronautics and Space Administration) are under construction and are expected to be occupied during the winter of 1967-68.

2. RESEARCH OPPORTUNITIES

At the Theoretical Chemistry Institute there are opportunities for research at various levels. These include graduate study leading to the Ph.D. degree and postdoctoral research. In addition, the Institute is an ideal place for advanced research personnel to spend a sabbatical year or a summer. Applications are invited from interested individuals. Suitable financial assistance can be arranged for a limited number of qualified applicants.

3. GRADUATE DEGREES

Theoretical chemistry is interdisciplinary. In the Institute, there are a variety of ways in which individuals can earn advanced degrees. Presently, most students take their degrees from among the areas of theoretical chemistry, physical chemistry, and physics. The degree in theoretical chemistry is administered jointly by the Physics and Chemistry departments. All degree candidates must become proficient in theoretical physics and mathematics as well as in chemistry. The detailed requirements are available upon request.

4. **COURSES OFFERED** (by members of the Theoretical Chemistry Institute staff)

In addition to a number of undergraduate courses, members of the Theoretical Chemistry Institute normally teach the following graduate courses:

Chemistry 661	Intermediate Chemical Thermodynamics	(Cornwell)
Chemistry 762	Chemical Kinetics	(Bernstein)
Chemistry 863	Molecular Spectroscopy	(Cornwell)
Chemistry 864	Statistical Mechanics	(Curtiss)
Chemistry 865	Transport Properties of Fluids	(Curtiss)
Chemistry 873	Elementary Quantum Chemistry	(Harriman)
Chemistry 874	Intermediate Quantum Chemistry	(Harriman)
Chemistry 875	Advanced Quantum Chemistry	(Hirschfelder and Harriman)
Chemistry 961	Selected Topics in Theoretical Chemistry	(Visiting Professors and staff)
Physics 531	Introduction to Quantum Mechanics	(Epstein)

These and other members of the Institute staff, as well as distinguished visitors, participate in seminars sponsored by the Institute.

5. RESEARCH PROGRAM

Members of the Institute are engaged in a broad program of research in theoretical chemistry. Current activities in the most active areas of research are outlined below:

Quantum Chemistry

J. O. Hirschfelder, S. T. Epstein, and their associates are mainly interested in finding and developing new techniques. Until recently, the Ritz variation method has been the basis for most calculations on molecules. Attention is now being directed to the application of perturbation theory to the fundamental problems of quantum chemistry. This approach appears promising in view of several important features of perturbation theory and their recent development: (a) Perturbation equations are inhomogeneous and easier to solve than the Schrödinger equation; in separable cases they can be integrated directly. (b) Variational principles exist from which good approximations can be obtained for perturbed wave functions of any order, and upper and lower bounds for perturbation energies may be found. (c) If the first order wave function is known, the energy can be calculated through the third order. For many chemical purposes this may be sufficient. (d) The Dalgarno "Interchange Theorem" can be used to simplify enormously the calculation of corrections to approximate expectation values of one-electron operators. The basic theory behind the perturbation approach is reviewed in the article, "Recent Developments in Perturbation Theory," in *Advances in Quantum Chemistry,* volume 1, Academic Press (1964).

The Theoretical Chemistry Institute maintains very close association with workers at the Argonne National Laboratory, the International Business Machines Research Laboratory at San Jose, California, and the University of Chicago, who are making *ab initio* computations of accurate wave functions for molecules using variational methods with large basis sets. Their goal is to obtain reliable energy surfaces and other properties for diatomic and simple polyatomic systems and to give an appealing interpretation of interatomic forces and chemical binding in terms of localized orbitals and atomic distortions. One of the aims of the Institute is the interpretation and use of these accurate wave functions.

The subject of intermolecular forces is of particular interest. These include long-range forces, resonance forces, relativistic effects, short-range repulsive forces, and the approach to the united atom limit. The application of perturbation theory to exchange forces is a challenging research problem. Background material is given in "Intermolecular Forces," Volume 12 of *Advances in Chemical Physics*, edited by J. O. Hirschfelder (John Wiley and Sons, New York, 1967).

Other topics being studied include natural spin orbitals, correlated wave functions, molecular force-constants and the Thomas-Fermi models. The long-term goal is to be able to calculate molecular properties and interactions with sufficient accuracy to obtain cross sections for energy transfer and chemical reactions, and thus to carry out entirely theoretical calculations of bulk equilibrium and transport properties.

Statistical Mechanics and Transport Phenomena

The theory of transport phenomena or the statistical mechanics of nonequilibrium gaseous systems is the subject of a continuing study by C. F. Curtiss. Background material on this field is given in *Molecular Theory of Gases and Liquids*, by J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, John Wiley and Sons, New York (reprinted with corrections and notes, 1964). The basic problem is the relation of macroscopic constants, which describe the rate of approach of the system to equilibrium, to the properties of the individual molecules, and the potential energy of interaction between the molecules. The study has been directed at removing the various limitations of the well-developed theory of low-density gases made up of spherical molecules. As examples, studies of the effects of rotational degrees of freedom of nonspherical molecules, research aimed at the extension of the theory to moderately dense gases, and investigations of the quantum effects at moderately low temperatures are under way.

Molecular Beam Scattering Theory

Recent developments in the techniques of molecular beam scattering have made it possible to study in detail the intermolecular collision process, thus providing a deeper insight into the underlying mechanism of chemical reactions. The research of R. B. Bernstein and associates consists of both theoretical and experimental studies in molecular scattering. Much of the current theoretical work is directed toward an understanding of inelastic scattering of small molecules. Both the exact time-independent (S-matrix) and the approximate time-dependent perturbation methods are being investigated. The objective of the research program is the development of practical methods for the prediction and correlation of cross sections (and rates) for inelastic and reactive molecular collisions. In addition, theoretical studies of quantum phenomena such as orbiting and compound resonances associated with low-energy elastic molecular scattering are in progress.

Magnetic Resonance

Studies of magnetic interactions, which are neglected in most of quantum chemistry, and of systems in which these interactions are important are becoming more common. The research of J. E. Harriman and associates includes both theoretical and experimental attacks on problems in this area. Present theoretical investigations involve the origin in relativistic quantum mechanics of magnetic interactions, and an attempt to gain a better understanding of electronic wave functions in open shell systems. Because it is experimentally most convenient to work with rather large, aromatic molecules, calculations are also done for such systems. These problems thus extend from the use of greater rigor than permitted by the ordinary nonrelativistic Schrödinger equation, on the one hand, to the use of necessarily rather crude approximations on the other.

The research of C. D. Cornwell involves both experimental and theoretical studies in nuclear quadrupole resonance, nuclear magnetic resonance, and microwave spectroscopy, with particular emphasis on measurement and interpretation of properties (*e.g.*, nuclear spin shielding, spin coupling, and quadrupole coupling constants) related to electronic structure and bonding in simple inorganic molecules. A further interest is in the study of nuclear spin relaxation observed in NMR spectra of gases.

Other Areas of Interest

It is expected that some of the techniques developed in studying small systems may be extended in the near future to molecules of biological importance.

6. COMPUTING FACILITIES

Members of the Theoretical Chemistry Institute have easy access to a broad spectrum of computational assistance. The Institute has a computing staff of five mathematician-programmers. The computing staff provides advice and programming assistance to members of the Institute. An extensive program library of specific use in theoretical chemistry is being developed and maintained by the Institute in cooperation with the University Computing Center. The major computing efforts utilize the University Center's CDC 3600, B-5500, and CDC-1604 computers. Plans are proceeding for a powerful and flexible satellite computing installation located in the Institute. It will be linked to the central University facilities and will ensure efficient access to the extremely powerful University computing complex currently under development which will feature a B-8500 computer.

7. **STAFF MEMBERS** (Listed below are the senior staff members of the Institute with a brief statement of their research interests and a partial list of their recent publications.)

Richard B. Bernstein, Professor of Chemistry; A.B. (Chemistry, Columbia), Ph.D. 1948 (Physical Chemistry, Columbia). Atomic and molecular beam scattering and intermolecular interactions; molecular collisions, elastic and inelastic; chemical kinetics.

"Determination of Intermolecular Forces via Low Energy Molecular Beam Scattering," with J. T. Muckerman, Chapter 8 of *Advances in Chemical Physics*, Vol. 12 (J. O. Hirschfelder, Ed., Wiley-Interscience, 1967).

"Potential Well Characteristics from the Energy Dependence of the Glory Extrema in Total Elastic Scattering Cross Sections," with T. J. O'Brien, *J. Chem. Phys. 46*, 1208 (1967); *Disc. Far. Soc. 40*, 35 (1965).

"Sudden Approximation Applied to Rotational Excitation of Molecules by Atoms. II. Scattering of Polar Diatomics," with K. H. Kramer, *J. Chem. Phys. 45*, 4473 (1966).

"Long-Range Interatomic Forces from Predissociation Data and Resonances in Atomic Scattering," *Phys. Rev. Letters 16*, 385 (1966).

"Quantum Effects in Elastic Molecular Scattering," Chapter 3 of *Advances in Chemical Physics*, Vol. 10 (J. Ross, Ed., Wiley-Interscience, 1965).

"Thermal Scattering of Atoms by Homonuclear Diatomic Molecules," with A. Dalgarno, H. S. W. Massey and I. C. Percival, Proc. Roy. Soc. (London) *A274*, 427 (1963).

C. D. Cornwell, Professor of Chemistry; B.A. (Chemistry, Cornell), Ph.D. 1951 (Chemical Physics, Harvard). Nuclear quadrupole resonance, nuclear magnetic resonance, and microwave spectroscopy; interpretation of properties related to electronic structure and bonding in simple inorganic molecules; relaxation effects in NMR and microwave spectra of gases.

"Interpretation of the Chemical Shift of $C\ell F$," *J. Chem. Phys. 44*, 874 (1966).

"NMR Spectra of $C\ell F_3$ and $C\ell F$: Gaseous Spectra and Gas-to-Liquid Shifts," with L. G. Alexakos, *J. Chem. Phys. 41*, 2098 (1964).

C. F. Curtiss, Associate Director of The University of Wisconsin Theoretical Chemistry Institute, and Professor of Chemistry; B.S., Ph.D. 1948 (Chemistry, Wisconsin). Theory of equation of state and transport phenomena in gases and liquids; theory of atomic and molecular collisions.

"Quantum-Mechanical Kinetic Theory of Loaded Spheres," with John J. Mueller, *J. Chem. Phys. 46*, 283 (1967).

"Low-Energy Atomic Collisions. I. The Schrödinger Equation for H^+-H," with Donald J. Kouri, *J. Chem. Phys. 44*, 2120 (1966).

"Quantum-Mechanical Boltzmann Equation," with David K. Hoffman and John J. Mueller, *J. Chem. Phys. 43*, 2878 (1965).

"Kinetic Theory of Dense Gases. V. Evaluation of the Second Transport Virial Coefficients," with David K. Hoffman, *Phys. of Fluids 8*, 890 (1965).

"Numerical Evaluation of Quantum Effects on Transport Cross Sections," with S. Imam-Rahajoe and R. B. Bernstein, *J. Chem. Phys. 42*, 530 (1965).

Saul T. Epstein, Professor of Physics; S.B., Ph.D., 1948 (Physics, Massachusetts Institute of Technology). Quantum mechanics.

"Some Remarks on the Use of the Variational Principle for the Second-Order Energy," with Jean H. Epstein, *J. Chem. Phys. 42*, 3630 (1965).

"Gauge Invariance of the Hartree-Fock Approximation," *J. Chem. Phys. 42*, 2897 (1965).

"Hartree-Fock Hamiltonians and Separable Nonlocal Potentials," *J. Chem. Phys. 41*, 1045 (1964).

"Hypervirial Theorems for Variational Wave Functions," with J. O. Hirschfelder, *Phys. Rev. 123*, 1495 (1961).

"On the Anisotropy of Inertia," *N. Cim. 16*, 587 (1960).

"Note on Perturbation Theory," *Am. J. Phys. 22*, 613 (1954).

"Note on the Relativistic Properties of Self-Energies," with A. Pais, *Rev. Mod. Phys. 21*, 445 (1949).

"Remarks on H. W. Lewis' paper 'On the Reactive Terms in Quantum Electrodynamics,'" *Phys. Rev. 73*, 177 (1948).

John E. Harriman, Assistant Professor of Chemistry; B.S. (Chemistry, Wisconsin), Ph.D. 1963 (Chemical Physics, Harvard). Theory of magnetic effects in molecular systems, molecular quantum mechanics.

"The Use of Spin Projection in SCF Spin Density Calculation" in *La Structure Hyperfine Magnetique des Atoms et des Molecules* (CNRS, Paris, 1967).

"Temperature Dependence of ESR Linewidths of Some Nitrobenzene Anion Radicals," with F. Millett, *J. Chem. Phys. 44,* 1945 (1966).

"Chemical Substitution Treated by Partitioning in the Hückel Approximation," *J. Chem. Phys. 42,* 2412 (1965).

"On the Reduction of the Dirac Equation to Two-Component Form," Technical Note 127, Uppsala Quantum Chemistry Group (June, 1964).

"Natural Expansion of the First Order Density Matrix for a Spin-Projected Single Determinant," *J. Chem. Phys. 40,* 2827 (1964).

"Intramolecular Electron Transfer in Bis(p-nitrophenyl) Anions and Its Effect on Electron Spin Resonance Hyperfine Structure," with A. H. Maki, *J. Chem. Phys. 39,* 778 (1963).

Joseph O. Hirschfelder, Director of The University of Wisconsin Theoretical Chemistry Institute and Homer Adkins Professor of Chemistry; B.S. (Chemistry, Yale), Ph.D. 1936 (Physics and Chemistry, Princeton). Member of the U.S. National Academy of Sciences and Norwegian Royal Society. Honorary Life Member of American Society of Mechanical Engineers. Recipient of American Chemical Society 1966 Peter Debye Award and the Sir Alfred Egerton Gold Medal of the Combustion Society. Molecular quantum mechanics; intermolecular forces; statistical mechanics; physical properties of gases and liquids; theory of reaction rates.

"Intermolecular Forces," *Advances in Chemical Physics,* Volume 12 (Editor and Chapter Author; John Wiley and Sons, New York, 1967).

"New Type of Molecular Perturbation Treatment," with Robert Silbey, *J. Chem. Phys. 45,* 2188 (1966).

"Applicability of Perturbation Theory to Molecular Problems," *Perturbation Theory and Its Application in Quantum Mechanics* (John Wiley and Sons, New York, 1966).

"Approximation of Expectation Values," with William A. Sanders, *J. Chem. Phys. 43,* 10, S204 (1965).

Molecular Theory of Gases and Liquids, with C. F. Curtiss and R. B. Bird (John Wiley and Sons, New York; reprinted with corrections and notes, 1964).

William A. Lester, Jr., Assistant Director of The University of Wisconsin Theoretical Chemistry Institute; B.S., M.S. (Chemistry, University of Chicago), Ph.D. 1964 (Chemistry, Catholic University of America). Molecular quantum mechanics, molecular collision processes.

"Structural Features of the S-Matrix for the Rotational Excitation of Homonuclear Diatomic Molecules by Atom Impact: Close-Coupled vs. Approximate Computations," with R. B. Bernstein, *Chem. Phys. Letters 1*, 000 (1967).

"Some Aspects of the Coulomb Hole of the Ground State of H_3^+," with Morris Krauss, *J. Chem. Phys. 44*, 207 (1966).

"Gaussian Correlation Functions: Two-Electron Systems," with Morris Krauss, *J. Chem. Phys. 41*, 1407 (1964).

APPENDIX B

Recent Developments in the Theory of Intermolecular Forces

by

Joseph O. Hirschfelder

A few years ago, the parametrized potential energy functions of Morse, Lennard-Jones, Buckingham, Stockmayer, and Kihara were satisfactory for representing the available experimental data. With the development of a variety of ingenious experimental techniques which provide detailed information regarding individual molecular collisions, it has become necessary to provide a more realistic basis for describing the energy of interaction.

A few years ago, we limited our discussions of intermolecular forces to the interactions of two noble gas atoms in their ground states. Now we are trying to understand the collisions between other kinds of atoms, in both excited and ground states. Corresponding to a particular type of collision, there are usually a considerable number of possible sets of electronic quantum numbers for the "diatomic molecule". For each of these electronic quantum states, we seek the potential energy curves which determine the forces on the atoms as a function of their separation R . It is clear that the problems of both interatomic and intermolecular forces are inseparably linked with molecular spectroscopy. It is also clear that the detailed fine structure and hyperfine structure which plays an important role in spectroscopy corresponds to whole families of closely spaced potential energy curves. Thus, the determination of intermolecular forces is inherently complex.

Very little detailed information is now available regarding the interaction of diatomic or polyatomic molecules with either atoms or molecules. Such interactions must be described in terms of many-dimensional potential energy surfaces which describe the energy as a function of the configurations of the separate molecules, the relative orientations of the molecules, and the separation between the molecules. These energy surfaces would serve as the input information required in the statistical mechanical calculation of not only a wide variety of macroscopic properties of materials but also the calculation of the rates of chemical reactions. Clearly, the theory and experiments must work together in order to unravel the complexities of intermolecular forces.

The long range forces between two polyatomic molecules can be explained in terms of the permanent and induced electric moments of the isolated molecules. The formulae for asymmetric molecules are exceedingly complicated for human comprehension but they may be programmed on computing machines.

Thanks to the availability of high speed computing machines and new types of variation and perturbation procedures, the theory of intermolecular forces is developing rapidly. The long range forces between atoms can be determined quite accurately with the use of perturbation theory and a number of new mathematical techniques. Instead of expressing the perturbed wave functions as a sum over all of the discrete energy states plus an integral over the continuum, the perturbed wave functions are determined explicitly by solving partial differential equations. Unfortunately, it is still difficult to calculate the forces between atoms at intermediate separations where the atomic wave functions overlap and exchange forces become important. Currently, a new type of perturbation procedure is being developed to cope with this problem.

It has been experimentally demonstrated that the force of attraction between the molecules in two separated sheets of mica in a vacuum agrees with the long range (relativistically retarded) Casimir and Polder forces. The same type of quantum electro-dynamical considerations are used to explain the "excitons" which produce the energy of interaction of aromatic molecules in a crystal. It is likely that these same techniques will prove useful in considering the forces between biologically active molecules.

Chang and others are working on the fine structural interactions between two atoms, neither of which are in S states. As a result of spin-orbit interactions, the atoms have quadrupoles; hence, the fine structural energy of interactions vary as the minus fifth power of their separation.

Recently, we have considered the hyperfine structural interaction of two hydrogen atoms. At separations larger than 5 Å the interaction between the spin of the nuclei and the spin of the electrons becomes stronger than the interactions between the electron spins. Thus, the electron spins become partially decoupled and one can no longer say that the H_2 molecule is in either an electronic singlet or an electronic triplet state. The concept of ortho and para hydrogen remains meaningful, however, if the definitions refer to the parity of the rotational states rather than to the spin of the nuclei (which is not a good quantum number at large separations).

Stephens has discovered a type of intermolecular energy varying as the minus sixth power of the separation, which only applies to optically active molecules and changes its sign when a molecule is replaced by its mirror image.

The reaction field technique which Linder has developed treats intermolecular forces from a strictly phenomenological standpoint. For example, dispersion forces are related to frequency-dependent polarizabilities by averaging over the fluctuating instantaneous dipole-induced dipole interactions. In this approach both quantum mechanical and statistical mechanical fluctuations are simultaneously averaged. Reaction field techniques are especially suited to the determination of forces in liquids, thermally averaged energies of interactions, and susceptibilities of gases and liquids. The method which has been developed up to now, in common with other field theoretic approaches, is restricted to sufficiently weak interactions so that the response function is linear. This approximation neglects the effects of the molecular distortions on the response function. However, the many-body forces including the fourth and higher order non-additive terms can be included in the reaction field formulation.

For many practical problems it is necessary to understand the forces between molecules in a liquid. This is a very difficult problem since it involves the detailed packing of the molecules in a liquid as well as the many-body forces between neighboring molcules. For asymmetric and polar molecules there are additional complications, especially in the vicinity of the surfaces of the liquid. Sinanoglu has set up this problem in a truly elegant fashion and obtained numerical solutions for some non-polar liquids.

It is indeed a sad commentary that up to the present time, except for the interaction of two hydrogen atoms, the best potential energy curves are not obtained from *a priori* theoretical calculations. The Rydberg-Klein-Rees method of analyzing band spectra provides an excellent direct determination of the intermolecular potential. Good potential energy curves are also obtained by adjusting the parameters in an idealized potential function so as to fit a set of experimental observations. There are many different types of experimental data which can be used for this sort of semi-empiricism. Of these, molecular beam scattering provides the most direct and sensitive means for estimating the intermolecular forces.

APPENDIX C

University of Wisconsin Theoretical Chemistry Institute Short-Term Visitors

During the Period July 1, 1967 through December 31, 1967

NAME AND ADDRESS	PERIOD OF VISIT	LECTURES GIVEN
Prof. S. K. Zaremba Visiting Professor Mathematics Research Center University of Wisconsin	7/27/67	Quasi-Monte Carlo Methods of Integration
Prof. L. Wolniewicz Visiting Professor Laboratory of Molecular Structure and Spectra Department of Physics University of Chicago	9/21-22/67	Recent Theoretical Results for Excited States of H_2
Prof. W. Kolos Visiting Professor Laboratory of Molecular Structure and Spectra Department of Physics University of Chicago	9/21-22/67	Recent Theoretical Results for Excited States of H_2
Prof. Yngve Öhrn Quantum Theory Project University of Florida Gainesville, Florida	10/18-20/67	Field Theoretical Methods in Molecular Quantum Mechanics
Prof. Ernest Davidson Department of Chemistry University of Washington	10/24/67	Correlation Effects in Molecules
Dr. Vedene H. Smith, Jr. Quantum Chemistry Group University of Uppsala Uppsala, Sweden	10/31-11/1/67	Core Polarization and the Hyperfine Interaction in Li
Dr. Robert A. Harris Department of Chemistry University of California Berkeley, California	11/14/67	Sigma-Pi Coupling in Conjugated Molecules

APPENDIX D

University of Wisconsin Theoretical Chemistry Institute Staff During the Period July 1, 1967 through December 31, 1967

FACULTY

Name	Title
Joseph O. Hirschfelder	Professor of Chemistry; Director, Theoretical Chemistry Institute
C. F. Curtiss	Professor of Chemistry; Associate Director, Theoretical Chemistry Institute
Richard B. Bernstein	Professor of Chemistry
C. D. Cornwell	Professor of Chemistry
Saul T. Epstein	Professor of Physics
John E. Harriman	Assistant Professor of Chemistry
Raphael D. Levine	Visiting Assistant Professor of Mathematics and Theoretical Chemistry
William A. Lester, Jr.	Lecturer in Chemistry; Assistant Director, Theoretical Chemistry Institute

POSTDOCTORAL STAFF

Louis Biolsi Rensselaer Polytechnic Inst. Ph.D. 1966	Project Associate
Tai Yup Chang University of Wisconsin Ph.D. 1966	Project Associate
Alan S. Dickinson Queen's University of Belfast Ph.D. 1967	Project Associate
Donald K. Harriss Northwestern University Ph.D. 1963	Project Associate

POSTDOCTORAL STAFF (Continued)

Name	Title
B. Robert Johnson University of Illinois Ph.D. 1967	Project Associate
John H. Karl University of Wisconsin Ph.D. 1966	Project Associate
David A. Micha University of Uppsala Fil. Dr. 1965	Project Associate
Ronald E. Olson Purdue University Ph.D. 1967	NSF Postdoctoral Fellow
Ilana Tamir Technion-Israel Ph.D. 1966	Project Associate

COMPUTING STAFF

Carol M. Burkhalter	Project Specialist
Carol E. Constable	Project Supervisor
Nancy L. Dennin	Project Specialist (Part-time)
Wanda W. Giese	Project Specialist (Part-time)
Linda W. Hulbert	Project Specialist
Tony T. Warnock	Project Specialist (Part-time)

GRADUATE STUDENTS

Name	Title
John W. Baughn	NSF Fellow/Teaching Assistant
David E. Bennett	Research Assistant
Joseph D. Bowman	Research Assistant
Phillip R. Certain	NSF Fellow
Daniel M. Chipman	Eastman Kodak Fellow/Teaching Assistant
Penny G. Estabrooks	Research/Teaching Assistant
Roger W. Fenstermaker	Research Assistant
Dennis Gibboney	Research Assistant
Lloyd M. Holm	Research Assistant
Lawrence Hunter	Teaching Assistant
Robert E. Johnson	Research Assistant
Barbara A. Kennedy	Teaching Assistant
Robert J. LeRoy	Research Assistant
Mac B. Milleur	Research Assistant
James T. Muckerman	Research Assistant
Thomas J. O'Brien	Research Assistant
Larry J. Pitzner	Teaching Assistant
James D. Power	Research Assistant
Robert E. Roberts	NASA Fellow
M. Beth Ruskai	NSF Fellow
Kennth M. Sando	Research Assistant
John P. Simons	NSF Fellow/Teaching Assistant
Michael Twerdochlib	Research Assistant

GRADUATE STUDENTS (Continued)

Name	Title
Pearl S. C. Wang	Research Assistant
David M. Whisnant	Research/Teaching Assistant
Ronald J. White	Research Assistant

SECRETARIAL STAFF

Name	Title
Linda L. Becker	Stenographer 2
Gloria M. Lawton	Stenographer 3
Karen A. Rick	Project Specialist
Mary A. Wilson	Typist 3

APPENDIX E

Summary of Research at the Theoretical Chemistry Institute

During the period July 1, 1967 through December 31, 1967

SUDDEN APPROXIMATION APPLIED TO ROTATIONAL EXCITATION OF MOLECULES BY ATOMS. III. ANGULAR DISTRIBUTION AND ENERGY DEPENDENCE OF THE INELASTIC SCATTERING by Roger W. Fenstermaker and Richard B. Bernstein (supported by NASA)

Report No. WIS-TCI-240 dated 3 July 1967

Scheduled to be published in the 12/1/67 issue of J. Chem. Phys.

ABSTRACT

The present study is an extension of previous work on the application of the sudden approximation to the problem of rotational excitation of diatomic polar molecules by atomic impact. Semi-classical computations are presented of the angular distributions of various rotational transition cross sections and their energy dependence for a model system (intended to approximate TℓF-Ar). The results are not inconsistent with the experimental findings of Toennies. The dominant excitations are those allowed by first order time-dependent perturbation theory, but the strong coupling (due principally to the large long-range anisotropy in the potential) gives rise to extensive excitation to open channels remote from the incident one, i.e., transitions forbidden by low-order perturbation theory. The main prediction of the present work is the presence of a single major peak in each of the various differential polar inelastic cross sections; with increasing collision energy, these maxima trend to smaller angles and show an increase in peak intensity.

MOLECULAR COLLISIONS, VI: DIAGRAMMATIC METHODS by C. F. Curtiss (supported by NASA)

Report No. WIS-TCI-241* dated 10 July 1967

Accepted for publication in J. Chem. Phys.

ABSTRACT

The expressions, developed in previous papers of this series, for the coefficients in spherical harmonic expansions of the degeneracy averaged cross sections for collisions between diatomic molecules are reformulated. The reformulation is based on the introduction of a new basis set of functions in the expansion of the wave functions. In the new basis set, the three basic angular momenta of the problem (the angular momenta of each of the molecules and that associated with the relative motion) are treated symmetrically. The manipulation of the vector coupling coefficients is facilitated by the use of diagrammatic methods.

HIGHER ORDER PERTURBATION ENERGIES FOR THE 2-ELECTRON HOOKE'S LAW MODEL ATOM by John M. Benson and W. Byers Brown (supported by NASA and NSF Graduate Fellowship)

Report No. WIS-TCI-242 dated 14 July 1967

May be published in a revised form.

ABSTRACT

The Rayleigh-Schrödinger perturbation energies E_n for the ground ^1S state of the Hooke law model atom are calculated through tenth order. The E_n are expressed as singly infinite sums whose terms are obtained from recurrence relations. Very slow convergence limited the method to E_{10} and below.

The results are compared with those of Midtdal (1965) for helium-like atoms, and it appears that the convergence of the Hooke series is more rapid. However, no persistent patterns are observable in the Hooke E_n through E_{10}.

LONG-RANGE INTERATOMIC FORCES by Tai Yup Chang (supported by NASA)

Report No. WIS-TCI-243* dated 27 July 1967

Accepted for publication in Molecular Physics.

EXCHANGE EFFECTS IN THE DEGENERATE PERTURBATION THEORY OF INTERMOLECULAR POTENTIALS by David A. Micha (supported by NASA)

Report No. WIS-TCI-244 dated 31 July 1967

Submitted for publication in a revised form.

ABSTRACT

The contribution of electron exchange to intermolecular potentials is studied using the operator form of perturbation theory, when the non-interacting system of atoms or molecules is degenerate. A general, symmetry adapted degenerate perturbation theory is developed including the almost-degeneracy case. Perturbation expansions are given up to second order in the energy. Differential equations for the perturbed wavefunctions are obtained, as well as their associated variational principles.

PERTURBATION THEORY FOR EXCHANGE FORCES by Joseph O. Hirschfelder (supported by NASA)

Report No. WIS-TCI-246 dated 7 August 1967

Chem. Phys. Lett., 1, 325 and 363 (1967)

ABSTRACT

The mathematical problems associated with the development of a satisfactory perturbation theory for exchange forces are discussed. Different treatments give different results for the second order energy. A new formalism called HAV is proposed. Also, the derivation of the Hirschfelder-Silbey treatment is improved. Many of the ideas expressed are the result of a series of seminars at the University of Wisconsin in which Jansen, Epstein, Byers Brown, Certain, Buckingham, Harriman, Micha, Levine, and Eliason participated.

SELECTION AND FOCUSING OF POLAR DIATOMICS IN STATES OF POSITIVE INDUCED ELECTRIC DIPOLE MOMENT WITH A TEN-POLE FIELD by T. G. Waech, K. H. Kramer, and R. B. Bernstein (supported by NASA, AEC, and APL)

Report No. WIS-TCI-248X* dated 8 August 1967

Will be submitted for publication in an extended version.

ABSTRACT

Using a ten-pole electric field (with two-pole symmetry) it has been possible to select and focus the rotational states $J,M = 0,0;\ 1,\pm1$; and $2,\pm2$ for velocity-selected thermal molecular beams of CsF and RbCl. However, because of the non-ideality of this focusing field, the enhancement in intensity of the separated states (focusing effect) over the thermal population is only about a factor of two.

NATURE OF INTERMOLECULAR FORCES by Joseph O. Hirschfelder and William J. Meath

Report No. WIS-TCI-249 dated 9 August 1967

Intermolecular Forces, Advances in Chemical Physics, Vol. 12, John Wiley and Sons, 1967

FIRST AND SECOND ORDER DENSITY MATRICES OF A SPIN-PROJECTED SINGLE DETERMINANT by John E. Harriman (supported by NASA)

Report No. WIS-TCI-250* dated 21 August 1967

Scheduled to be published in "Reduced Density Matrices with Applications to Physical and Chemical Systems - Survey Lectures and Contributed Papers of a conference held at Queen's University from August 28 through September 1, 1967" edited by A. J. Coleman and R. M. Erdahl.

Queen's Papers in Pure and Applied Mathematics - No. 11

ABSTRACT

This is an assembly of previous work, with some new results, prepared for presentation at the Density Matrix Conference, Queen's University, Kingston, Ontario, August 28 - September 1, 1967. Natural orbitals, natural spin orbitals and natural geminals are given explicitly. Reasonably simple matrices

of which the natural spin geminals are eigenfunctions are given. These expressions provide illustrations of some of the symmetry properties discussed by Bingel. Some numerical examples are also presented.

EXCITED STATES OF THE HYDROGEN MOLECULE A COMPILATION OF DATA by James D. Power (supported by NASA)

Report No. WIS-TCI-251* dated 17 August 1967

May be published in a revised form.

ABSTRACT

A table is given which collects some of the available experimental and theoretical data for the known states of hydrogen and indicates which excited states remain to be studied theoretically.

ON THE N-REPRESENTABILITY PROBLEM FOR AN ODD NUMBER OF FERMIONS by Mary Beth Ruskai and John E. Harriman (supported by NASA and NSF Predoctoral Fellowship)

Report No. WIS-TCI-252* dated 31 August 1967

Submitted for publication.

ABSTRACT

The N-representability problem for the first and second order density matrices is considered when N is an odd integer. Attention is restricted to those density matrices derivable from functions whose NSO's have certain paired properties. Neither pairing of spatial orbitals nor special spin properties are required in general, but are discussed as special cases.

New sufficient conditions for N-representability of the first order density matrix are given. The second order density matrix is studied in detail. Special cases in which the N-representability problem for the second order density matrix can be solved are considered.

INTERMEDIATE BRACKETING THEOREMS FOR LOWER BOUNDS by P. S. C. Wang (supported by NASA)

Report No. WIS-TCI-253* dated 31 August 1967

Submitted for publication.

ABSTRACT

A set of intermediate resolvents is formed from the truncated Hamiltonians of Bazley and Fox. On replacing the resolvent operator in Löwdin's bracketing theorem by these intermediate resolvents, one obtains lower bound expressions suitable for calculations involving molecules. This method is applied to the ground state of H_2^+ (exact energy $E_o = -1.10263$ a.u.). The results are -1.10529 a.u. for a one-term and -1.10438 a.u. for a two-term truncated Hamiltonian.

ON THE ANALYTIC SOLUTION OF THE SCHRÖDINGER EQUATION FOR THE TWO-ELECTRON ATOM by Ronald Joseph White (Ph.D. Thesis) (supported by NASA)

Report No. WIS-TCI-254 dated 21 August 1967

ABSTRACT

The Schrödinger equation for the ground state of the two-electron atom is examined in detail and a technique is introduced by means of which an analytic solution may be realized. The technique, which may be called a partial series expansion method, consists of assuming a series form for the wavefunction in powers of the inter-electron separation with coefficients which are functions of two variables and of determining the coefficients so that a satisfactory solution of the Schrödinger equation results. The coefficients are related by first-order differential recursion relations which may be integrated explicitly. The method is not complete because the initial coefficient, independent of the inter-electron separation, is undetermined. The extension of the method to the hydrogen molecule and the two-electron

atom in the presence of a uniform electric field is also considered. Two model atomic systems, the Hooke's law model and the delta-function model, for the two-electron atom are also discussed and it is shown that these systems, which are sölvable through first order in a perturbation series, yield information about the difficulties which arise in the helium atom.

LECTURES ON COLLISION THEORY. II. by R. D. Levine (supported by NASA)

Report No. WIS-TCI-255* dated 28 June 1967

Will be published as part of the book "Quantum Mechanics of Molecular Rate Processes" by Oxford University Press.

ABSTRACT

These lecture notes form an expanded version of a series of lectures given as part of the course "Selected Topics in Theoretical Chemistry" in the second semester of 1966-67. They are concerned with the formal aspects of non-relativistic collision theory and its application to molecular rate processes.

POLAR (VELOCITY-ANGLE) FLUX CONTOUR MAPS FOR KBr FROM THE CROSSED BEAM REACTIONS K+HBr, DBr: EVIDENCE FOR BOTH FORWARD AND BACKWARD (C.M.) SCATTERING by Clyde Riley, Keith T. Gillen and R. B. Bernstein (supported by AEC)

Report No. WIS-TCI-256X dated 24 July 1967

J. Chem. Phys. 47, 3672 (1967).

COMMENTS ON THE STATISTICAL APPROXIMATION IN MOLECULAR COLLISIONS by R. D. Levine (supported by NASA)

Report No. WIS-TCI-257* dated 20 September 1967

Submitted for publication.

ABSTRACT

A derivation of the statistical approximation which is not based on the physical model of a collision complex is reviewed.

These comments followed Prof. J. C. Light's paper at the Faraday Society meeting on the Molecular Dynamics of Chemical Reactions. Toronto, September, 1967.

LECTURES ON COLLISION THEORY III - Part II. APPROXIMATION METHODS by R. D. Levine (supported by NASA)

Report No. WIS-TCI-258 dated 2 October 1967

Will be published as part of the book "Quantum Mechanics of Molecular Rate Processes" by Oxford University Press.

ABSTRACT

These lecture notes form an expanded version of a series of lectures given in the first semester of 1967-68. They are concerned with models in collision theory and their application to molecular rate processes.

LECTURES ON COLLISION THEORY III - PART I. THE PARTITIONING TECHNIQUE by R. D. Levine (supported by NASA)

Report No. WIS-TCI-259 dated 2 October 1967

Will be published as part of the book "Quantum Mechanics of Molecular Rate Processes" by Oxford University.Press.

ABSTRACT

These lecture notes form an expanded version of a series of lectures given as part of the course "Selected Topics in Theoretical Chemistry" in the second semester of 1966-67. They are concerned with the use of the partitioning technique in collision theory.

LECTURES ON COLLISION THEORY III. - PART III. COLLISION PROCESSES IN ENSEMBLES by R. D. Levine (supported by NASA)

Report No. WIS-TCI-260 dated 27 November 1967

Will be published as part of the book "Quantum Mechanics of Molecular Rate Processes" by Oxford University Press.

ON THE DISTORTED WAVE-MAGNUS APPROXIMATION IN MOLECULAR COLLISIONS by R. D. Levine (supported by NASA)

Report No. WIS-TCI-261 dated 26 December 1967

Submitted for publication.

ABSTRACT

The distorted wave-Magnus approximation for inelastic transition rates is induced in an attempt to incorporate the distortion induced by the interaction in a computationally feasible scheme.

THE HYPERFINE SPLITTING OF THE INTERACTION ENERGY IN H+D AND IN D+D by Mac B. Milleur, Larry A. Curtiss, Michael Twerdochlib and Joseph O. Hirschfelder (supported by NASA)

Report No. WIS-TCI-262* dated 13 October 1967

Submitted for publication.

ABSTRACT

The hyperfine interaction of a ground state D atom with either a ground state H or a ground state D atom is treated. For H + D there are 24 hyperfine states with 12 potential energy curves, and for D + D there are 36 hyperfine states with 22 potential energy curves. At separations greater than 9 a_o to 10 a_o, the electronic spins (for most of these hyperfine states) become partially decoupled and one can no longer refer to the molecule as being an electronic singlet or an electronic triplet.

A VALIDATION OF THE METHOD OF AMPLITUDE DENSITY FUNCTIONS IN COMPUTING THE S-MATRIX FOR A SCATTERING PROBLEM by B. R. Johnson, D. Secrest, W. A. Lester, Jr. and R. B. Bernstein (supported by NASA and NSF)

Report No. WIS-TCI-263* dated 27 October 1967

Chem. Phys. Lett. 1, 396 (1967).

ABSTRACT

The method of Amplitude Density Functions compares favorably in speed and accuracy to a direct coupled-equations solution in the computation of the

S-matrix elements for rotational excitation of a diatomic molecule by atom impact.

REDUCTION OF THE TWO-ELECTRON BREIT EQUATION by Penny Estabrooks (supported by NASA)

Report No. WIS-TCI-264 dated 2 November 1967

ABSTRACT

By means of a partitioning method similar to that applicable to the one-electron problem, the sixteen-component two-electron Breit equation is reduced to a four-component equation, involving only the "large" (i.e., positive energy) components of the wave function. The equation obtained by this method is compared to the results of a F-W transformation on the two-electron Hamiltonian.

THE APPLICATION OF PERTURBATION THEORIES FOR EXCHANGE FORCES TO A SIMPLE MODEL by S. T. Epstein and R. E. Johnson (supported by NASA)

Report No. WIS-TCI-265 dated 3 November 1967

Will be submitted for publication in a revised form.

CONNECTIONS BETWEEN SEVERAL PERTURBATION THEORIES OF INTERMOLECULAR FORCES by R. E. Johnson and S. T. Epstein (supported by NASA)

Report No. WIS-TCI-266 dated 7 November 1967

Will be submitted for publication in a revised form.

UPPER AND LOWER BOUND ENERGY CALCULATIONS FOR ATOMS AND MOLECULES IN THE THOMAS-FERMI THEORY by Robert E. Roberts (supported by NASA)

Report No. WIS-TCI-267* dated 1 November 1967

Submitted for publication.

ABSTRACT

Using simple functions, upper and lower bounds for the Thomas-Fermi energies of atoms and homonuclear diatomic molecules at various internuclear

separations are calculated which differ by less than 0.2% in the atomic case and at most by 0.5% for molecules. The calculation verifies that for this model molecules are not stable for short and intermediate nuclear separations. The possibility of a long range attraction is also examined and again the conclusions are found to be in agreement with Teller's Theorem.

A THEORETICAL STUDY OF THE $^1\Sigma^+$, $^3\Sigma^+$, $^3\Pi$, $^1\Pi$ STATES OF NaLi AND THE $^2\Sigma^+$, STATE OF $NaLi^+$ by P. J. Bertoncini (Ph.D. Thesis) (supported by AEC)

Report No. WIS-TCI-268 dated 10 November 1967

Will be submitted for publication in a revised form.

KINETIC OF UNIMOLECULAR BREAKDOWN, VIII. THE LINDEMANN-HINSHELWOOD MECHANISM by R. D. Levine (supported by NASA)

Report No. WIS-TCI-269* dated 3 November 1967

Submitted for publication.

ABSTRACT

A quantum mechanical theory of thermal unimolecular breakdown based on the Lindemann-Hinshelwood mechanism is presented. The kinetic equation is derived on the basis of the averaged density operator of Karplus and Schwinger (Phys. Rev. 73, 1020 (1948)). The kinetic equation is solved under stationary experimental conditions, and the pressure dependence of the rate of formation of products is related to the detailed time evolution of activated molecules.

A ONE-DIMENSIONAL MODEL FOR EXCHANGE FORCES by Phillip Certain (supported by NASA and NSF Graduate Fellowship)

Report No. WIS-TCI-270 dated 1 December 1967

Submitted for publication.

ABSTRACT

Four different types of perturbation theories for the exchange forces between two atoms is applied to the lowest gerade and ungerade state of a simple one-dimensional model. It is shown that the second order energy in one of the expansions (the Eisenschitz-London, van der Avoird, or Hirschfelder HAV expansion) exhibits undesirable behavior in the limit corresponding to large internuclear distances.

THE HYPERFINE WAVE FUNCTIONS FOR H-H, H-D, AND D-D by Michael Twerdochlib, Mac B. Milleur, Larry A. Curtiss, and Joseph O. Hirschfelder (supported by NASA)

Report No. WIS-TCI-271 dated 29 December 1967

Will not be published.

ABSTRACT

In two previous reports the hyperfine splitting in H-H, H-D, and D-D has been considered. The hyperfine interaction gives 16, 24, and 36 hyperfine states for H-H, H-D, and D-D, respectively. This report includes three tables giving the hyperfine wave functions for various internuclear separations.

INTERNAL EXCITATION IN NON-REACTIVE MOLECULAR COLLISIONS: RESONANCES IN ELASTIC SCATTERING OF ATOMS BY DIATOMIC MOLECULES by R. D. Levine, B. R. Johnson, J. T. Muckerman, and R. B. Bernstein (supported by NASA and NSF)

Report No. WIS-TCI-272 dated 5 December 1967

Scheduled to be published in the 12/67 or 1/68 issue of Chem. Phys. Lett.

ABSTRACT

Resonances in slow molecular collisions are demonstrated by exact numerical solution of the close-coupled equations for rotational excitation, including closed channels. The breakdown of the adiabatic approximation is exhibited. Resonance energies can be essentially predicted by a "best local" approximation.

MOLECULAR COLLISIONS VII: NUCLEAR SPIN AND STATISTICS EFFECTS by Louis Biolsi and C. F. Curtiss (supported by NASA)

Report No. WIS-TCI-273 dated 6 December 1967

Submitted for publication.

ABSTRACT

The effect of nuclear spin on the expressions for the differential and degeneracy averaged scattering cross sections for collisions of two diatomic molecules, developed in previous papers in this series, is considered. These expressions are then reformulated in terms of another basis set of functions, making use of the diagrammatic techniques introduced earlier. Collisions between indistinguishable molecules are also considered. The resulting expressions reduce, in the limiting case of spherical molecules, to previously known results.

A JUSTIFICATION OF THE HYLLERAAS SOLUTION OF THE INVERSE SCATTERING PROBLEM by T. J. P. O'Brien (supported by NASA)

Report No. WIS-TCI-274 dated 18 December 1967

Submitted for publication.

ABSTRACT

The validity of Hylleraas' solution of the inverse scattering problem depends upon the establishment of the completeness of a certain bio-orthogonal system of functions. The proof of the completeness is accomplished by a method of contour integration.

EXCHANGE AND COULOMB ENERGY OF H_2^+ DETERMINED BY VARIOUS PERTURBATION METHODS by P. R. Certain, J. O. Hirschfelder, W. Kolos, and L. Wolniewicz (supported by NASA, NSF, and ARO)

Report No. WIS-TCI-275 dated 11 December 1967

Submitted for publication.

ABSTRACT

Three different types of perturbation theories for the exchange forces between two atoms is applied to the ground and first excited state of the hydrogen molecule at internuclear separations $R = 4,6,8$ Bohr. The energy through second order and the expectation value of the Hamiltonian using the wave function accurate through first order are calculated to compare the theories. The results for the Hirschfelder-Silbey procedure are very nearly equivalent to those for the Murrell-Shaw or Musher-Amos formulation and both are satisfactory. The Eisenschitz-London, van der Avoird, or Hirschfelder (HAV) results are good at small separations but at large separations they give a second order energy which appears to be about one-half the correct dispersion energy. At the separations considered, deviations from the virial theorem are unimportant.

ON THE ADIABATIC APPROXIMATION FOR NON-REACTIVE, SUB-EXCITATION, MOLECULAR COLLISIONS by R. D. Levine (supported by NASA)

Report No. WIS-TCI-276 dated 15 December 1967

Submitted for publication.

ABSTRACT

The decoupling approximation, which neglects the interaction between open and closed channels, is discussed and derived from the Lippmann-Schwinger variational principle. The adiabatic approximation is shown to be the "best local" decoupling approximation in that the adiabatic phase shift is the highest lower bound to the exact phase shift obtainable from a local potential.

COMPUTATIONAL INVESTIGATION OF INTERNAL EXCITATION IN NON-REACTIVE MOLECULAR COLLISIONS: RESONANCES IN ROTATIONAL EXCITATION by R. D. Levine, B. R. Johnson, J. T. Muckerman, and R. B. Bernstein (supported by NASA)

Report No. WIS-TCI-277 dated 15 December 1967

Submitted for publication.

ABSTRACT

Resonances in sub-excitation molecular collisions are demonstrated by exact numerical solution of the close-coupled integral equations for the rotational excitation including closed-channels, in the total angular momentum representation. These results serve as a reference for comparing various approximate theoretical predictions. In particular, the limitations of the adiabatic approximation are exhibited. The resonance energies can be essentially predicted by a "best local" potential approximation. The resonance line shapes are fitted by a simple Breit-Wigner form.

A COMPUTATIONAL PROCEDURE FOR THE CLOSE-COUPLED ROTATIONAL EXCITATION PROBLEM: $|\mathbb{F}^J|^2$ FOR THE SCATTERING OF DIATOMIC MOLECULES BY ATOMS by William A. Lester, Jr. and R. B. Bernstein (supported by NASA)

Report No. WIS-TCI-279 dated 22 December 1967

Submitted for publication.

ABSTRACT

A computational procedure is described for the integration of the coupled differential equations and determination of the $|\mathbb{F}^J|^2$ matrices required for the accurate evaluation of cross sections for rotational excitation of diatomic molecules. The Arthurs-Dalgarno theory of scattering of an atom by a rigid rotator is employed. The approach developed takes advantage of several of the computational schemes used in the field of electron-atom, scattering, particularly those of K. Smith. The principal virtue of the present computational method is its capability of generating "exact" results to serve as standards against which to compare various approximations such as the sudden, dominant-coupling, and distorted wave.

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* Copies of this report are not available. Reprints of most of these articles will be available at a later date.

Additional Publications During the Period July 1, 1967 - December 31, 1967

"Transport Phenomena in Gases" by C. F. Curtiss, Annual Review of Physical Chemistry, Annual Reviews, Inc., Vol. 18, 1967 (WIS-TCI-207)

"A Single Variable Variational Approximation for a Perturbed Schrödinger Equation" by W. Byers Brown and Phillip R. Certain, Proc. Nat. Acad. Sci. 57, 1206 (1967) (WIS-TCI-226)

"Compound State Resonance in Molecular Collisions: The Integral Elastic Cross Section for D_2-Xe Scattering" by David A. Micha, Chem. Phys. Lett. 1, 139 (1967) (WIS-TCI-235)

"The Hyperfine Splitting of the Interaction Energy of Two Hydrogen Atoms" by John E. Harriman, Michael Twerdochlib, Mac B. Milleur, and Joseph O. Hirschfelder, Proc. Nat. Acad. Sci. 57, 1558 (1967) (WIS-TCI-224)

"Atomic r_{ij} Integrals for Many-Electron Wave-functions" by John H. Karl, J. Chem. Phys. 46, 4219 (1967)

"Spin-Projected and Extended SCF Calculations" by Kenneth M. Sando and John E. Harriman, J. Chem. Phys. 47, 180 (1967) (WIS-TCI-195)

"The Perturbation Theory of the Extended Hartree-Fock Approximation for Two-Electron Atoms" by W. Byers Brown and G. V. Nazaroff, Int. J. Quant. Chem. 1, 463 (1967)

"Structural Features of the S-Matrix for the Rotational Excitation of Homonuclear Diatomic Molecules by Atom Impact: Close-Coupled vs. Approximate Computations" by William A. Lester, Jr. and Richard B. Bernstein, Chem. Phys. Lett. 1, 207 (1967) (WIS-TCI-239)

"Erratum: Structural Features of the S-Matrix for the Rotational Excitation of Homonuclear Diatomic Molecules by Atom Impact" by W. A. Lester, Jr. and R. B. Bernstein, Chem. Phys. Lett. 1, 347 (1967) (Erratum to WIS-TCI-239)

"The Energy of Interaction Between Two Hydrogen Atoms by the Gaussian Type Function" by Hojing Kim and Joseph O. Hirschfelder, J. Chem. Phys. 47, 1005 (1967) (WIS-TCI-222)

"Electrostatic Hellmann-Feynman Theorem Applied to the Long-Range Interaction of Two Hydrogen Atoms" by Joseph O. Hirschfelder and Morton A. Eliason, J. Chem. Phys. 47, 1164 (1967) (WIS-TCI-205)

"On a Theory of Absolute Reaction Rates" by C. A. Coulson and R. D. Levine, J. Chem. Phys. 47, 1235 (1967) (WIS-TCI-219)

"Evaluation of Long-Range Retarded Interaction Energies" by Robert E. Johnson, Saul T. Epstein, and William J. Meath, J. Chem. Phys. 47, 1271 (1967) (WIS-TCI-228)

"Integrated and Integral Hellmann-Feynman Formulas" by S. T. Epstein, A. D. Hurley, R. E. Wyatt, and R. G. Parr, J. Chem. Phys. 47, 1275 (1967)

"Intermediate-Range Intermolecular Forces in H_2^+" by Donald A. McQuarrie and Joseph O. Hirschfelder, J. Chem. Phys. 47, 1775 (1967) (WIS-TCI-217)

"Scaled Unsöld Approximation for Atoms and Molecules" by Robert E. Roberts, J. Chem. Phys. 47, 1873 (1967) (WIS-TCI-232)

"Perimetric Coordinates" by Pearl S. C. Wang, J. Chem. Phys. 47, 2229 (1967) (WIS-TCI-213)

"Improvement of Uncoupled Hartree-Fock Expectation Values for Physical Properties. II." by S. T. Epstein and R. E. Johnson, J. Chem. Phys. 47, 2275 (1967) (WIS-TCI-231)

"Compound-State Resonances in Atom-Diatomic Molecule Collisions" by David A. Micha, Phys. Rev. 162, 88 (1967) (WIS-TCI-223)

"Moderately Long-Range Interatomic Forces" by Tai Yup Chang, Rev. Mod. Phys. 39, 911 (1967) (WIS-TCI-201)

"Comment on van der Avoird's Wave Operator Formalism" by R. E. Johnson and P. R. Certain, Chem. Phys. Lett. 1, 413 (1967)

"Time-Correlation-Function Expressions for Linear and Nonlinear Transport Coefficients" by Frank C. Andrews, J. Chem. Phys. 47, 3161 (1967)

"Time Correlation Function Expressions for Nonlinear Chemical Rate Constants" by Frank C. Andrews, J. Chem. Phys. 47, 3170 (1967)