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FINAL REPORT TO
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
(THEORETICAL CHEMISTRY INSTITUTE PORTION)

1 July 1962 - 30 September 1974

October 1974

MISC. NO. 109

FINAL REPORT TO NATIONAL AERONAUTICS AND SPACE ADMINISTRATION (NASA)

FOR: NASA RESEARCH GRANT NGL 50-002-001

PERIOD: 1 July 1962 - 30 September 1974

TITLE(S): "Multidisciplinary Research in Space Sciences and Engineering with Emphasis on Theoretical Chemistry" and "A broad program of research in theoretical chemistry, particularly in molecular quantum and statistical mechanics, directed toward determination of the physical and chemical properties of materials, relation of these macroscopic properties to properties of individual molecules, and determination of structure and properties of the individual molecules."

PRINCIPAL INVESTIGATOR(S): Joseph O. Hirschfelder
C. F. Curtiss

NAME & ADDRESS OF INSTITUTION: University of Wisconsin-Madison
Theoretical Chemistry Institute

FINAL REPORT TO NASA

It is with a feeling of considerable nostalgia and sorrow that I hereby submit our final report to NASA. Twelve years ago NASA set up our Theoretical Chemistry Institute and financed both our present quarters and our research. As long as NASA was able, they provided us with the wherewithal to pursue our scientific goals. We only wish that we had had greater intelligence and greater stamina so that we could have accomplished more.

We have very much enjoyed our associations with Edward Redding and his colleagues. I have especially fond memories of working with Jack Holloway, Don Holmes, Tom Smull, Jack Craig, Carl Palmer, Herb Quinn, Francis Smith, and many others. My only regret is that the University Grants Division shield us from having any contacts with the "practical" working end of NASA. I would have enjoyed very much the opportunity to lend a hand in tackling some of your technical problems. I believe that the University Grants Division would have been much more stable if it had been more closely associated with the working branches of the organization. However, you have treated us very well through the years. It has been a pleasure to be a member of your family.

My colleagues and I wish to thank you and wish you success in the years to come.

At the University of Wisconsin we have had the opportunity of setting up,with NASA support, a Theoretical Chemistry Institute with sufficient competence, vigor, and financial support to play a major role in the development of molecular quantum and statistical mechanics. Theoretical chemistry seeks to determine the physical and chemical properties of materials, to relate these macroscopic properties to the individual molecules, and to determine the structure and properties of the individual molecules. At the present time, all the required fundamental laws of nature are sufficiently well known. Thus, we can write down the mathematical relations which describe the physical and chemical properties. Then the problem becomes one of determining 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 gigantic high speed computing machines, theoretical chemistry is making very rapid and exciting 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 In relating the macroscopic properties to the individual molecules, we serve as the "middlemen" between the theoretical physicists and the practical engineers and experimental scientists. Under normal experimental conditions with normal substances, the usual engineering equations suffice. But the usual engineering equations do not suffice under extreme conditions, such as are encountered in (1) the highly ionized almost vacuum of the upper atmosphere; (2) the high temperature shock wave preceding a reentering nosecone; (3) the high pressure high temperature combustion gases in a rocket motor; (4) the partially ionized plasma of a nuclear reactor motor, or (5) metal fatigue. Under extreme conditions, where reliable experimental data are hard to obtain, theoretical predictions are useful. Under extreme conditions, the coupling becomes strong between the macroscopic and the molecular properties. The usual engineering equations apply to the linear Hooke's law regions, but it takes a deeper understanding to cope with materials near the fracture point. Thus, the more we can learn about the individual molecules, the better we can serve as "middlemen" to help the space scientists to cope with unusual environments.

The theory starts with the fundamental laws of physics: quantum mechanics, statistical mechanics, electromagnetic equations and relativity. With the use of quantum mechanics, one determines the properties of individual atoms and molecules in stationary states, cross sections for reactive and nonreactive molecular collisions, and the effects of electric and magnetic fields. With the use of statistical mechanics, the macroscopic properties and macroscopic equations of state and motion are expressed in terms of the molecular properties. And finally, these macroscopic equations are solved together with boundary conditions corresponding to particular experiments which may be important either from a practical or theoretical standpoint.

Thus, in the past twelve years with NASA support, the Theoretical Chemistry Institute has published 236 papers and 369 laboratory reports (which have received wide distribution on a wide range of topics covering each part of this chain of steps which lead from the fundamental physics to the experimental applications. Considerable emphasis has been given to the development of quantum mechanical perturbation theory for determining the properties of molecules. Considerable progress has been made in determining differential scattering cross sections in molecular collisions. This work has been extensively applied to the interpretation of experimental molecular beam scattering cross sections. However, research at the Institute has not been limited to one approach or one area The long range goal is to be able to obtain molecular properties and interactions with sufficient accuracy to obtain cross sections for energy transfer in chemical reactions and to carry out completely theoretical calculations of bulk properties, both for equilibrium and for transport

We hope that the research which we have performed will be applied to the development of new types of rocket propulsion and to better understanding the structure and properties of planetary atmospheres.

The University of Wisconsin Theoretical Chemistry Institute is an integral part of the Department of Chemistry and has excellent working arrangements with the Physics, Mathematics, Computer Sciences and various Engineering Departments All 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 one of the best.

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.

We want to take this opportunity to express our appreciation to NASA for providing the Theoretical Chemistry Institute with the opportunity for developing an excellent teaching and research program. In addition to financing our research, NASA has provided us with one and one-third floors of space in the Farrington Daniels Chemistry Building of the University of Wisconsin. During the past twelve years NASA has supported over fifty visiting faculty (long-term and short-term), and eleven professors who have been members of the Theoretical Chemistry Institute. We have had about seventy graduate students over the past twelve years who have received support from NASA, thirty-six of these students have received doctoral degrees. Through this help of NASA we were able to develop one of the best theoretical chemistry research groups in the world. We were able to train a large number of theoretical chemists and help a considerable number of physicists and engineers in the solution of their problems.

We have had very fine working relations with many departments at the University of Wisconsin such as Chemistry, Physics, Chemical Engineering, Mathematics Research Center, Mechanical Engineering, Astronomy, and Meteorology. Most of our professors and students are in the Chemistry Department so that we have been very much a part of the Chemistry Department, although in some respects, we have been fiscally separated. Saul Epstein and Ludwig Bruch are professors in the Physics Department, who together with their students, have worked very closely with the Theoretical Chemistry Institute. We have had many joint appointments of visiting professors with the Mathematics Research Center, and in 1965 the Mathematics Research Center and the Theoretical Chemistry Institute held a joint symposium on perturbation theory and its applications for quantum mechanics. We have had very close associations with the Chemical Engineering Department since we have many close interests in common, including kinetic theory of gases, aero and fluid dynamics including chemical reactions and heat transfers, etc. Our interactions with the Mechanical Engineering Department have concerned the theory of flames and detonations. Many of the problems of astronomy and meteorology involve theoretical chemistry. Thus, the Theoretical Chemistry Institute has been truly interdisciplinary.

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7

SUPPORTING AGENCY NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:

THE SPONTANEOUS IONIZATION OF A HYDROGEN ATOM IN AN ELECTRIC FIELD

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Joseph O. Hirschfelder, Director, Theoretical Chemistry Institute and Professor of Chemistry
Arturo Hardisson, Visiting Associate Professor, Theoretical Chemistry Institute
Albert Christoph, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION: University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue, Madison 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. (Please indicate the number of students supported by this project.)

This research has been going on for a long time. Currently we are considering the effects of relativistic interactions which arise in the Dirac Hamiltonian together with possible radiative processes. The relativistic corrections destroy the separability of the system in parabolic coordinates. At the present time we can calculate the energies and lifetimes corresponding to the elctrostatic Hamiltonian. We have completed the formal aspects of the relativistic corrections and will soon start the actual computing machine calculations.

The first phase of this work was published by Joseph O. Hirschfelder and Larry Curtiss in the Journal of Chemical Physics 55, 1395 (1971). In June 1971, George Hart prepared a preliminary report (WIS-TCI-445G) entitled "Square Well Model Calculations of Rate Ionization of Metastable Atomic States", which provides a simple idealization of the hydrogen atom spontaneous ionization and shows in a simple way exactly how the Wigner-Weisskopf model works and what are its limitations. This research would be of considerable interest with respect to the spectroscopy of of Stellar atmospheres. This research is still continuing.

Signature of
Principal Investigator Joseph O. Hirschfelder
University of Wisconsin
Professional School Theoretical Chemistry Institute

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SUPPORTING AGENCY:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:

QUANTUM MECHANICAL STREAMLINES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Joseph O. Hirschfelder, Director, Theoretical Chemistry Institute and Professor of Chemistry
William E. Palke, Professor of Chemistry, University of California, Santa Barbara
Albert C. Christoph, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:

University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue, Madison 53706

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Exact numerical calculations are made for the scattering of quantum mechanical particles from a square two dimensional potential barrier. This treatment is an exact analog of both Frustrated Total Reflection of perpendicularly polarized light and the longitudinal Goos-Hänchen shift. Quantum mechanical streamlines (which are analogous to either classical mechanical trajectories or optical rays) are plotted. These streamlines are smooth, continuous, and have continuous first derivatives even through the classically forbidden region. The streamlines form quantized vortices surrounding each of the nodal points (which result from interference between the incident and reflected waves). Similar vortices occur in reactive collisions of $H+H_2$ (McCullough and Wyatt; Kuppermann, Adams, and Truhlar) and undoubtedly play an important role in molecular collision dynamics. The theory for these vortices is given in a companion paper. A comparison is given between our numerical calculations and the stationary phase approximation (SPA). Although our incident wave packet has a half-width of more than one deBroglie wavelength in contrast to the SPA replaces the diffuse beams by rays with delta function profiles, the agreement was surprisingly good for both the Goos-Hänchen shifts and for the reflection coefficients. However, we found that the Goos-Hänchen shift for the transmitted beam is significantly smaller than for the reflected beam, although in the stationary phase approximation these two shifts are equal. Furthermore, we found that the scattering from the potential barrier has very little effect on the shape of the wave packets. The power series expansion of the incident Debye-Picht wave packet, Ψ_I, has an extremely small radius of convergence whereas the power series for $\Psi_I^* \Psi_I$ has a radius of convergence of more than two deBroglie wavelengths.

(continued on next page)

SIGNATURE OF PRINCIPAL INVESTIGATOR

PROFESSIONAL SCHOOL (medical, graduate, etc.)

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Students	Students	Completion Date:
Other	Publications	
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SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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TITLE OF PROJECT:

QUANTUM MECHANICAL STREAMLINES (Continued)

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

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The imaginary velocity, v_i , is introduced into the Madelung-Landau-London hydrodynamical formulation of quantum mechanics. The corresponding imaginary streamlines will be considered in a forthcoming paper. The time-independent Schrodinger equation for real wave functions is reduced to solving the non-linear first order partial differential equation:

$$\hbar \nabla \cdot v_i = 2(E-V)+v_i^2 .$$

Here v_i is irrotational. This equation may lead to interesting new methods of solving the Schrodinger equation. It does lead to a generalization of the Prager-Hirschfelder perturbation scheme which invokes an electrostatic analogy.

The philosophical implications of the hydrodynamical formulation of quantum mechanics are discussed. Penetration of a one dimensional square potential barrier is used to demonstrate exactly how tunneling occurs by particles "riding over the barrier" ala Bohm. Cases are cited where quantum and classical mechanical motions are identical. This research has now been accepted for publication and will appear in the December 15, 1974 issue of the Journal of Chemical Physics. See also our Theoretical Chemistry Institute Report No. 514.

SIGNATURE OF PRINCIPAL INVESTIGATOR Joseph O. Hirschfelder

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
Theoretical Chemistry Institute

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SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
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TITLE OF PROJECT:

QUANTIZED VORTICES AROUND WAVEFUNCTIONS NODES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Joseph O. Hirschfelder, Director Theoretical Chemistry Institute, Professor of Chemistry

Charles J. Goebel, Professor of Physics, University of Wisconsin

Ludwig W. Bruch, Associate Professor of Physics, University of Wisconsin

NAME AND ADDRESS OF INSTITUTION.

University of Wisconsin, Theoretical Chemistry Institute. 1101 University Avenue, Madison, 53706

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Quantized vortices can occur around nodal points in wavefunctions. This fact, discovered by Dirac (1931), but little noted since, is rederived here and examples are discussed. The derivation depends only on the wavefunction being single valued, continuous, and having continuous first derivatives. Since the derivation does not depend upon the dynamical equations, the quantized vortices are expected to occur for many types of waves (i.e. electromagnetic, acoustic, etc.). Such vortices have appeared in the calculations (McCullough and Wyatt, Kuppermann) of the $H + H_2$ molecular collisions and play a role in the chemical kinetics. In a companion paper, it is shown that quantized vortices occur when optical waves are internally reflected from the face of a prism or particle beams are reflected from potential energy barriers. This research has been accepted for publication and will appear in the December 15, 1974 issue of the Journal of Chemical Physics. See also Theoretical Chemistry Institute report number 515R.

SIGNATURE OF PRINCIPAL INVESTIGATOR Joseph O. Hirschfelder

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin Theoretical Chemistry Institute

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SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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TITLE OF PROJECT:

ROTATIONAL EXCITATION IN COLLISIONS OF DIATOMIC MOLECULES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

C. F. Curtiss, Associate Direccor, Theoretical Chemistry Institute,
and Professor of Chemistry

NAME AND ADDRESS OF INSTITUTION:

University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue,
Madison 53706

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The study of the theory of rotational excitation in collisions of diatomic molecules has continued. The equations for the quantities $Q^{(\pm)}(\bar{\ell}S_aS_b)$ which are related to the generalized phase shifts have been transformed from a matrix form involving discreet indices to a form involving continuous parameters. The resulting form is more convenient computationally and more closely related to the classical limit results. It is anticipated that these more recent results will lead to computational methods of computing cross sections. The studies will be carried further.

SIGNATURE OF PRINCIPAL INVESTIGATOR

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
Theoretical Chemistry Institute

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AGENCY NO.

SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
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TITLE OF PROJECT:
SYMMETRY OF PERTURBED HARTREE-FOCK AND X-α WAVEFUNCTIONS

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Saul T. Epstein, Professor, Theoretical Chemistry Institute

John O. Eaves, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue,
Madison, Wisconsin 53706

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Recently it has been suggested in the literature that the first order orbitals describing the perturbation of Hartree-Fock or X-α closed-shell atoms by a multipole electric field do not have the expected symmetry properties. We have shown that these fears are groundless. More precisely we have shown that the assumption of the expected symmetry is a self-consistent one. Since the perturbation equations are inhomogeneous linear equations we expect that this is the only solution. This work has been accepted for publication in the Journal of Chemical Physics.

SIGNATURE OF PRINCIPAL INVESTIGATOR

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
Theoretical Chemistry Institute

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AGENCY NO.

SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
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TITLE OF PROJECT:

DENSITY MATRICES AND SPIN PROPERTIES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

John E. Harriman, Associate Professor, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:

University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue, Madison, 53706

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The origin of spin-dependent terms in the Hamiltonian has been re-investigated in an attempt to remove certain ambiguities and to develop a more complete and unified treatment of the effects of interest to electron spin resonance than has previously been available. Publication is anticipated as part of a book now being written.

Other work on projects previously reported by NASA but not now so supported continued. The calculations by Jim Tortorelli of the spin distribution in LiH^+ are progressing. Symmetry and other properties of reduced density matrices are still of significant interest, but little has been done in this area in the last six months.

SIGNATURE OF PRINCIPAL INVESTIGATOR John E Harriman

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
~~Theoretical Chemistry Institute~~

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AGENCY NO.

SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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TITLE OF PROJECT:
1/Z EXPANSION FOR ATOMS

Give names, departments, and official titles of **PRINCIPAL INVESTIGATORS** and **ALL OTHER PROFESSIONAL PERSONNEL** engaged on the project.

Phillip R. Certain, Assistant, Professor, Theoretical Chemistry
Roger D. Ray, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue
Madison 53706

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The 1/Z expansion for atomic binding energies is of the form

$$E = Z^2(E_0 + E_1/Z + E_2/Z^2 + \dots) \ .$$

We are considering the three-electron isolectronic series and will compute the coefficients E_2, E_3, E_4, E_5 for the ground and low-lying excited states. We will also consider the radius of convergence of the series, and the Z^{-1} expansion of atomic properties other than the energy.

SIGNATURE OF PRINCIPAL INVESTIGATOR Phillip R Certain

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
Theoretical Chemistry Institute

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SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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TITLE OF PROJECT:

DIPOLE MENTS OF EXCITED STATE MOLECULES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Phillip R. Certain, Assistant Professor, Theoretical Chemistry Institute
Jeanne Fromm, Research Assistant, Theoretical Chemistry Institute
William Halchin, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:

University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue,
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We are calculating self-consistent-field dipole moments of molecules in singlet and triplet excited states with the aim of developing rules of thumb which allow predictions of the results on the basis of the ground state properties of the molecule.

SIGNATURE OF PRINCIPAL INVESTIGATOR Philip R Certain

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
Theoretical Chemistry Institute

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AGENCY NO.

SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
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TITLE OF PROJECT:

THE INTERACTION OF ATOMS WITH SOLID SURFACES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

Phillip R. Certain, Assistant Professor, Theoretical Chemistry Institute

Roger D. Ray, Research Assistant, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue, Madison 53706

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The interaction potential between an atom and a solid is usually approximated by pairwise-additive, inverse power potentials of the form

$$V^{(s)} = C^{(s)} \sum_{i} R_i^{-s} = C^{(s)} S(\tfrac{1}{2}s) ,$$

where $C^{(s)}$ is a strength parameter and R_i is the distance between the incident atom and the i-th atom of the lattice. The present work analytically transforms S into a rapidly convergent series by making use of the Poisson sum formula. The application of the technique to the gas/solid interaction problem is being considered, particularly with reference to the He/LiF system.

SIGNATURE OF PRINCIPAL INVESTIGATOR Phillip R. Certain

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin Theoretical Chemistry Institute

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AGENCY NO.

SUPPORTING AGENCY: **NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:

RHO-DOUBLING CONSTANTS

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

John H. Detrich, Project Associate, Theoretical Chemistry Institute

Phillip R. Certain, Assistant Professor, Theoretical Chemistry Institute

NAME AND ADDRESS OF INSTITUTION:
University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue,
Madison 53706

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We are considering methods for computing the constants associated with rho-doubling in diatomic $^2\Sigma$ molecules; this effect is related to spin-orbit coupling. A number of calculations on the contributions to these constants that predominate at fairly large internuclear separations for alkali-rare gas Van der Waals molecules have been carried out. In addition, much of the theoretical work preliminary to practical computations at equilibrium internuclear separations has been done. Our results are expected to be of considerable practical interest, in view of recent experimental studies of spin-rotational coupling. This research is still continuing.

SIGNATURE OF PRINCIPAL INVESTIGATOR

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
Theoretical Chemistry Institute

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SIE NO. 18

AGENCY NO.

SUPPORTING AGENCY: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Office of University Affairs
Sustaining University Program

TITLE OF PROJECT:

QUANTUM-MECHANICAL TREATMENT OF THREE BODIES

Give names, departments, and official titles of PRINCIPAL INVESTIGATORS and ALL OTHER PROFESSIONAL PERSONNEL engaged on the project.

John H. Detrich, Project Associate, Theoretical Chemistry Institute
Joseph O. Hirschfelder, Director, Theoretical Chemistry Institute, Professor of Chemistry
C. F. Curtiss, Assoc. Director, Theoretical Chemistry Institute, Professor of Chemistry

NAME AND ADDRESS OF INSTITUTION:

University of Wisconsin, Theoretical Chemistry Institute, 1101 University Avenue
Madison, Wisconsin 53706

SUMMARY OF PROPOSED WORK – (200 words or less.) – In the Science Information Exchange summaries of work in progress are exchanged with government and private agencies supporting research, and are forwarded to investigators who request such information. Your summary is to be used for these purposes. **(Please indicate the number of students supported by this project.)**

We are reinvestigating the quantum-mechanical description of the motion of three particles. We are studying several choices of both the rotational coordinates and the internal coordinates. As an aid to understanding the behavior of the treatment in more general cases, we are considering special choices for the interparticle potentials for which exact solutions exist. One of our objectives is a treatment of trimers which may be in highly excited vibrational-rotational states. A treatment suited to such problems may also be of interest when considering three-body scattering processes.

This research is still continuing.

SIGNATURE OF PRINCIPAL INVESTIGATOR

PROFESSIONAL SCHOOL (medical, graduate, etc.) University of Wisconsin
Theoretical Chemistry Institute

ANNUAL FUNDING *	NUMBER OF	PERIOD OF AUTHORIZATION
Faculty	Faculty	Date Initiated:
Students		
Other	Students	Completion Date:
Total	Publications	
*include overhead		

SUMMARY OF RESEARCH AT THE THEORETICAL CHEMISTRY INSTITUTE

THEORETICAL CHEMISTRY INSTITUTE PUBLICATIONS (REPRINTS)
SUPPORTED BY NASA DURING THE PERIOD
1 JULY 1962 THROUGH 30 SEPTEMBER 1974

Physical Review 129, No. 3, 1391-1396 (1963)
VIRIAL THEOREM AND ITS GENERALIZATIONS IN SCATTERING THEORY
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COMMENT ON THE USE OF UNITED-ATOM EXPANSIONS
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KINETIC THEORY OF NONSPHERICAL MOLECULES. V.
by C. F. Curtiss and J. S. Dahler

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by C. F. Curtiss and Robert S. Powers, Jr.

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HYPERVIRIAL THEOREM FOR COLLISIONS BETWEEN ELECTRONS AND ATOMS
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by C. F. Curtiss

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by R. A. Sack

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by Stephen Prager and Joseph O. Hirschfelder

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TWO-CENTER EXPANSIONS FOR THE POWERS OF THE DISTANCE BETWEEN TWO POINTS
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by R. A. Sack

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AN EQUATION OF STATE GASES AT HIGH TEMPERATURES AND DENSITIES
by J. S. Rowlinson

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RECENT DEVELOPMENTS IN PERTURBATION THEORY
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A STATISTICAL DERIVATION OF THE HYDRODYNAMIC EQUATIONS OF CHANGE FOR A SYSTEM OF IONIZED MOLECULES. I. GENERAL EQUATION OF CHANGE AND THE MAXWELL EQUATIONS
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MOLECULAR COLLISIONS. IX. RESTRICTED DISTORTED-WAVE APPROXIMATION FOR ROTATIONAL EXCITATION AND SCATTERING OF DIATOMIC MOLECULES
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MOLECULAR COLLISIONS. VIII
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APPRAISAL OF THE FOPIM FAST-CONVERGING PERTURBATION METHOD
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by Robert L. Matcha, William D Lyon, and Joseph O. Hirschfelder

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SUDDEN APPROXIMATION APPLIED TO ROTATIONAL EXCITATION OF MOLECULES BY ATOMS. II. SCATTERING OF POLAR DIATOMICS
by R. B. Bernstein and K. H. Kramer

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QUANTUM-MECHANICAL BOLTZMANN EQUATION
by David K. Hoffman, John J. Mueller, and C. F. Curtiss

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DIRECT CALCULATION OF CONTRIBUTIONS TO THE SECOND-ORDER ENERGY OF HELIUM
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DETERMINATION AND ASSESSMENT OF MORSE POTENTIAL FUNCTIONS FOR SOME NONPOLAR GASES
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RELATIONSHIP BETWEEN PITZER'S ACENTRIC FACTOR AND THE MORSE INTERMOLECULAR POTENTIAL FUNCTION
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A PERTURBATION THEORY OF ISOELECTRONIC MOLECULES: APPLICATION TO CO BASED ON N_2
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DOUBLE-PERTURBATION TREATMENT OF THE GROUND STATE OF THE HYDROGEN MOLECULE
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NUMERICAL EVALUATION OF BARRIER PENETRATION AND RESONANCE EFFECTS ON PHASE SHIFTS
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APPROXIMATE PERTURBATION TREATMENT OF H_2^+
by William D. Lyon, William A. Sanders, and Joseph O. Hirschfelder

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VARIATIONAL METHODS AND DEGENERATE PERTURBATION THEORY
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LONG-RANGE INTERATOMIC FORCES FROM PREDISSOCIATION DATA AND RESONANCES IN ATOMIC SCATTERING
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by A. M. Arthurs

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SPIN-SPIN INTERACTION FOR VERY LARGE ATOMIC SEPARATIONS
by Edwin A. Power, William J. Meath, and Joseph O. Hirschfelder

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A NOTE ON OPERATOR CALCULUS IN QUANTUM MECHANICS
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POTENTIAL-WELL CHARACTERISTICS FROM THE ENERGY DEPENDENCE OF THE GLORY EXTREMA IN TOTAL ELASTIC SCATTERING CROSS SECTIONS
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ELECTROSTATIC HELLMANN-FEYNMAN THEOREM APPLIED TO THE LONG-RANGE INTERACTION OF TWO HYDROGEN ATOMS
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POST-THRESHOLD ENERGY DEPENDENCE OF THE CROSS SECTION FOR ENDOERGIC PROCESSES: VIBRATIONAL EXCITATION AND REACTIVE SCATTERING
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by J. O. Hirschfelder and D. M. Chipman

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ENTROPY AND CHEMICAL CHANGE. I. CHARACTERIZATION OF PRODUCT (AND REACTANT) ENERGY DISTRIBUTIONS IN REACTIVE MOLECULAR COLLISIONS: INFORMATION AND ENTROPY DEFICIENCY
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CLASSICAL TRAJECTORY STUDY OF THE K + CH_3I REACTION
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MOLECULAR COLLISIONS. XXI. SEMICLASSICAL APPROXIMATION TO ATOM-SYMMETRIC TOP ROTATIONAL EXCITATION
by Dennis Russell and C. F. Curtiss

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SUMMARY OF RESEARCH AT THE THEORETICAL CHEMISTRY INSTITUTE

THEORETICAL CHEMISTRY INSTITUTE PUBLICATIONS (REPORTS)
SUPPORTED BY NASA DURING THE PERIOD
1 JULY 1962 THROUGH 30 SEPTEMBER 1974

QUANTUM MECHANICAL SOLUTIONS OBTAINED BY TRUNCATED REACTION OPERATORS
by William J. Meath, S. Osvaldo Goscinski, Kenneth M. Sando, and
Joseph O. Hirschfelder
WIS-TCI-5 (21 November 1962)

ABSTRACT

The use of truncated basis sets, comprised of eigenfunctions of the unperturbed Hamiltonian H_0, is discussed as a practical method for obtaining (i) an approximate solution for the reaction operator equation, $E_q = E_q^{(0)} + \langle \phi_q | t | \phi_q \rangle$; (ii) an approximate wave function for the perturbed system. The solution employs an iterative method which yields the matrix elements of the reaction operator. Connections between this approximate solution of the reaction operator equation and the linear variational, the Brillouin-Wigner and the Feenberg methods are derived.

AN EXPANSION OF $J_\nu(\nu x)$ IN POWERS OF $(1/\nu)$
by C. F. Curtiss
WIS-TCI-7 (17 December 1962)

ABSTRACT

Series expansion in powers of $(1/\nu)$ of the Bessel function, $J_\nu(\nu x)$, $J_\nu(\nu x)^2$, and the integral of the product of the square with an arbitrary function are developed. Each term in the expansion of $J_\nu(\nu x)$ is a sum of a finite number of derivatives of the delta function, $\delta(x-1)$. Each term in the expansion of the square of the Bessel function is a sum of a finite number of derivatives of $g(x^2 - 1)$, where $g(x)$ is the discontinuous function defined by $g(x) = x^{-1/2}$ for $x \geq 0$ and $g(x) = 0$ for $x < 0$. Each term in the expansion of the integral is a finite number of integrals involving derivatives of the arbitrary function.

A STUDY OF ONE AND TWO ELECTRON CENTRAL FORCE PROBLEMS USING THE HYPERVIRIAL THEOREM

by Sidney L. Gordon
WIS-TCI-8 (10 January 1963)

ABSTRACT

The hypervirial theorem is used to develop expectation value relationships for one and two electron central force problems.

Ground state helium trial functions are scaled to identically satisfy a particular family of these relationships. It is shown that this procedure results in improved expectation values for positive powers of the radial coordinate.

TRUNCATED REACTION OPERATORS AND THE HELIUM PROBLEM

by William J. Meath, Kenneth M. Sando, S. Osvaldo Goscinski, and
Joseph O. Hirschfelder
WIS-TCI-10 (25 February 1963)

ABSTRACT

The truncated reaction operator is used to obtain approximate solutions to the helium problem. Basis sets comprised of configurational interaction wave functions which have been constructed from products of uniformly scaled hydrogenic 1s and 2s functions are used. Approximate energies, wave functions and reaction operator matrix elements for the

$(1s)^2$, $(1s)(2s)$ and $(2s)^2$ ^1S states are tabulated. The convergence of the method is discussed for specific examples with the aid of the Feenberg perturbation series.

RESONANCE METHOD IN SCATTERING THEORY

by Egil A. Hylleraas
WIS-TCI-14 (May 1963)

ABSTRACT

This article was originally meant to precede a second article, where now definitions and notations used here also are described in more detail. This part will here be cut down to a minimum.

The aim of the investigation is to replace the ordinary treatment of the scattering problem by an indirect one. This can be done by providing the scattering potential with an adjustable numerical factor which is used as an eigenvalue parameter of a discrete eigenvalue problem.

The term "resonance method" simply alludes to the structure of the formulae.

ON THE INVERSION OF EIGENVALUE PROBLEMS

by Egil A. Hylleraas
WIS-TCI-15 (May 1963)

DETERMINATION OF A PERTURBING POTENTIAL FROM ITS SCATTERING PHASE SHIFT AND BOUND STATES ENERGY LEVELS

by Egil A. Hylleraas
WIS-TCI-16 (May 1963)

HYPERVIRIAL FUNCTIONS AND THE POSITIVE POWERS OF THE RADIAL COORDINATE OPERATOR IN He AND H^-

by Sidney L. Gordon
WIS-TCI-18 (10 June 1963)

PERTURBATION THEORY FOR ILLUSTRATION PURPOSES

by Egil A. Hylleraas
WIS-TCI-23 (9 July 1963)

ABSTRACT

The general Laguerre equations provide the simplest examples for testing perturbation theories.

THE EXACT EXPANSION OF THE ELECTRONIC ENERGY OF ONE-ELECTRON DIATOMIC MOLECULES IN POWERS OF THE INTERNUCLEAR SEPARATION

by W. Byers Brown and Erich Steiner
WIS-TCI-33 (23 September 1963)

ABSTRACT

The exact expansion of the electronic energy of the ground state of one-electron diatomic molecules through the fourth order in powers of the internuclear separation is derived by using the methods introduced by Hylleraas (1931). It is thereby shown that the straightforward perturbation treatment of the electronic energy of molecules based on the united atom as given by Bingel (1959) leads to incorrect results for the third order coefficient. The exact fourth order coefficient is checked by using the Hellmann-Feynman theorem to relate the expansion to the well-known formula for the electrostatic potential due to a hydrogen-like atom.

AN APPROXIMATE VARIATIONAL CALCULATION OF PROPERTIES OF THE 1s AND 2p STATES OF H_2^+

by Sungwoon Kim, Tai Yup Chang, and J. O. Hirschfelder
WIS-TCI-40 (24 March 1964)

ABSTRACT

Calculations have been made for the energy of the hydrogen molecule ion at 54 internuclear separations ranging from 0 to 20 a_0 using the Guillemin and Zener approximate wave function[1]

$$\psi_s = N_s[e^{-\alpha r_A - \beta r_B} + e^{-\alpha r_B - \beta r_A}]$$

for the 1sσ ground state, and its anti-symmetric form

$$\psi_p = N_p[e^{-\alpha r_A - \beta r_B} - e^{-\alpha r_B - \beta r_A}]$$

for the 2pσ first excited state. The variational parameters, α and β were varied to give the minimum energy. For the 1sσ state, the Guillemin and Zener energy agrees with the exact energy to within 0.0005 (e^2/a_0) for the full range of internuclear separations. For the 2pσ state, at zero internuclear separation, the Guillemin and Zener energy (without nuclear repulsion energy) approaches -0.4 (e^2/a_0) instead of the correct value of -0.5 (e^2/a_0). Thus, at small internuclear separations, the Guillemin and Zener energy for the 2pσ state is not very accurate, but for internuclear separations larger than 4 a_0, it is accurate to within 0.0001 (e^2/a_0).

Following a suggestion of Guillemin and Zener, the energy was calculated varying only one parameter and fixing the value of the other by requiring that $H\psi$ remains finite at the nuclei. Using this method, the results for the $1s\sigma$ state agree with the exact energy to within 0.001 (e^2/a_0) for the full range of internuclear separations and to within 0.001 (e^2/a_0) for the first excited state at internuclear separations larger than 4 a_0 . For the $2p\sigma$ state this method gives less accurate results at smaller internuclear separations and fails to be applicable when the separation is less than 1 a_0 .

THE DENSITY EXPANSIONS OF THE TRANSPORT COEFFICIENTS

by David K. Hoffman
WIS-TCI-48 (15 May 1964)

ABSTRACT

The theory of transport phenomena in a gas is considered from a statistical mechanical viewpoint. The theory is based on the Liouville equation for the time evolution of an ensemble of systems and the B.B.G.K.Y. equations which are integrals of the Liouville equation. The B.B.G.K.Y. hierarchy is truncated by a factorization principle which is a generalization of the molecular chaos assumption. For purely repulsive potentials, the set of equations obtained by truncating at $F^{(3)}$ is shown to give rise to three body interaction term obtained by Hollinger and Curtiss and by a different argument by Bogolubov.

The two coupled equations obtained by truncating the B.B.G.K.Y. hierarchy at $F^{(3)}$ are considered in detail. An approximation to these equations leads to a Boltzmann equation which is a soft potential generalization of the Enskog dense gas equation for rigid spheres. This Boltzmann equation includes both collisional transfer and three-body collision effects. The equation is solved and expressions for the transport coefficients based on this solution are obtained.

Numerical calculations of the three-body collision corrections to the transport coefficients are made for a Lennard-Jones gas. These calculations, along with the collisional corrections obtained in a previous paper by Curtiss, McElroy and Hoffman, give in approximation, the contribution of the non-bound states to the full first density corrections. The calculations are compared with experimental values.

SOME NOTES ON GAUGE INVARIANCE
by Saul T. Epstein
WIS-TCI-52 (9 June 1964)

PERTURBATION THEORY OF ONE-ELECTRON DIATOMIC MOLECULES. I. HOMONUCLEAR
by Robert L. Matcha, William D. Lyon, and Joseph O. Hirschfelder
WIS-TCI-57 (14 July 1964)

ABSTRACT

The application of perturbation theory to separable systems is discussed. First order wave functions of H_2^+ are calculated using various zeroth order approximations. The energy through third order is calculated and compared with energies determined by Bates, Ledsham, and Stewart. Agreement is exact for the best zeroth order approximation.

PERTURBED OPERATORS IN HILBERT SPACE
by Theodore W. Palmer
WIS-TCI-62 (25 September 1964)

ABSTRACT

This report review the theory of perturbed operators in an abstract Hilbert space and some important applications of the theory to quantum chemistry. It is intended to serve as an introduction to the original papers of Rellich, Sz-Nagy, Kato and others. The theory developed by these authors, which is apparently little known among quantum chemists, rigorously justifies the use of Rayleigh-Schrödinger perturbabation theory in many important quantum chemistry problems.

AN INTEGRAL EQUATION APPROACH TO THE PLASMA SELF-CONSISTENT FIELD PROBLEM
by Peter M. Livingston
WIS-TCI-64 (3 September 1964)

ABSTRACT

The self-consistent field problem of a "collisionless," fully ionized, single component plasma is treated by means of a Green's function technique. The latter describes the streaming motion of non-interacting electrons in a time dependent, homogeneous, applied electric field. A formal perturbation series solution to the Liouville equation, obtained by iteration, is then considered in the limit of large number and volume. For a problem time scale of the order of the inverse plasma frequency, only the terms in the perturbation series describing the collective interaction survive the limiting process, and therefore a time-reversible, hierarchy of integral equations is recovered for the various orders of distribution functions. The non-linear integral Vlassov equation follows

from the first member of this hierarchy and a factorization assumption on the initial distribution function.

An approximate solution to the Vlassov equation is developed in terms of the solutions to the linearized form of this equation. In these calculations, the Green's function has been simplified by averaging it over a period of the external field.

Finally, after defining the inverse dielectric function by the relationship between the "dressed" and "free" electron number densities, a correction term of order e^2 to the usual linear theory result is found. It is expected that this correction will be found useful in subsequent studies of non-linear electrical behavior in plasmas.

MORSE POTENTIAL FUNCTIONS FOR NONPOLAR GASES
by Daniel D. Konowalow and Sergio Carra'
WIS-TCI-74 (7 December 1964)

ABSTRACT

"Most likely" Morse potential functions for Ne, Ar, Kr, Xe, N_2, and CH_4 are determined from experimental second virial coefficient [B(T)] and viscosity [$\eta(T)$] data. By employing variants of the usual statistical fitting procedures, the elucidation of different features of the potentials is emphasized. Our "most likely" potentials give a better description of the experimental B(T) and $\eta(T)$ and repulsive scattering potentials than do those based largely on crystal properties. The Morse potential is apparently less suitable than the Kihara potential for reproducing the experimental B(T) and $\eta(T)$ at least for Ar ; neither model is able to reproduce both properties within the limits of experimental error. A comparison is made with other selected model potentials.

SELF-CONSISTENT FIELD SCHEMES FOR THE TWO-ELECTRON ATOMIC IONS IN THE GROUND STATE

by George V. Nazaroff
WIS-TCI-77 (8 February 1965)

ABSTRACT

The formalism for the generalized N-configuration self-consistent (SCF) schemes is developed for the two-electron atomic ions in the ground state. The equations for the SCF orbitals are expanded in powers of the inverse nuclear charge according to the well-known perturbation scheme based on considering the electronic interaction potential as a perturbation. Several first-order SCF equations are solved numerically.

The formalism for the exact wave function is cast into SCF form by writing it in terms of the natural orbitals. Each natural orbital is considered as a function of an infinite number of parameters which are generalizations of the natural occupation amplitudes. The formalism for any N-configuration SCF scheme is obtained from the natural orbital formalism by setting all but the first N parameters equal to zero. The k-th N-configuration SCF orbital is thus the k-th natural orbital with all but the first N natural occupation amplitudes set equal to zero. The N-configuration SCF wave function is a generalization of the ordinary Restricted Hartree-Fock wave function and is the best possible N-configuration wave function.

The perturbation expansion of the N-configuration SCF schemes is effected by first developing the exact problem in terms of the inverse nuclear charge, transforming the exact problem into natural orbital form and then setting the appropriate parameters equal to zero. The natural occupation amplitudes are divided into the intrinsic and the correlation amplitudes. The intrinsic amplitudes can never be zero, while the correlation amplitudes go to zero as the inverse nuclear charge goes to zero. The natural orbitals are divided into intrinsic and correlation orbitals by their association with the occupation amplitudes. The first-order equations define only the zero-order correlation orbitals.

The first-order part of the Extended Hartree-Fock (EHF) scheme, defined as that SCF scheme which contains one correlation orbital of each angular symmetry type, is discussed in detail. The double-excitation parts of several second-order EHF energies are obtained numerically and compare very favorably with the exact values. These second-order energies are the lowest possible energies obtainable from an orbital product approximation to the double-excitation part of the exact first-order wave function.

A NEW ALGORITHM FOR QUADRATURE
by Gunter G. Weber
WIS-TCI-79 (26 March 1965)

ABSTRACT

A new algorithm for interpolation, inverse interpolation, and integration of functions given by a table is proposed and numerical examples are given.

GENERALIZED KEESOM POTENTIAL
by Bruno Linder
WIS-TCI-89 (26 April 1965)

ABSTRACT

A field theoretic approach is used to derive general expressions for the adiabatic interaction between two rotating dipolar systems, whose temperatures may differ. The results, which are expressed in terms of the dipole moments, moments of inertia and temperatures of the two systems are valid, in second order approximation, over the whole range of temperatures including the region where quantum effects are important. The classical limit reduces to the Keesom potential for equal temperatures When the temperatures are different the classical potential can take on positive (repulsive) values as well as negative (attractive) values, depending on the temperature difference and ratio of temperature to moment of inertia of the two systems; for large temperature differences the potential is always repulsive. The general equations are analyzed and the quantum-statistical implications underlying the theory are discussed.

SOME REMARKS ON THE STERNHEIMER POTENTIAL
by Saul T. Epstein and John H. Karl
WIS-TCI-90 (27 April 1965)

ABSTRACT

The definition of the Sternheimer potential is generalized to include wave functions which involve the spin.

AN INTRODUCTION TO QUANTUM ELECTRODYNAMICS
by Saul T. Epstein
WIS-TCI-93 (5 May 1965)

PREFACE

These lectures were given as part of a seminar course in Theoretical Chemistry in April, 1965. They were designed to make quantum electrodynamics appear as much like the familiar presentations of the non-relativistic quantum mechanics of particles, as possible. For this reason the techniques are very much "pre-war"--there are no propagators, no Feynman diagrams and no temporal or longitudinal photons. Also there are almost no positrons.

I wish to thank my colleagues, especially Prof. J. O. Hirschfelder and Prof. W. Byers Brown, for their enthusiastic and helpful comments on these lectures.

A STATISTICAL DERIVATION OF THE HYDRODYNAMIC EQUATIONS OF CHANGE FOR A SYSTEM OF IONIZED MOLECULES
by Raymond Beshinske
WIS-TCI-110 (5 August 1965)

ABSTRACT

Non-relativistic, classical statistical mechanics is used to describe a dense fluid of molecules composed of nuclei and electrons with a purely coulomb interaction potential. A general equation of change is derived for the time rate of change of any macroscopic (ensemble averaged) dynamical variable. From this general equation, Maxwell's equations in a medium and the hydrodynamical equations of change are derived and expressed in terms of molecular properties, e.g. polarization and magnetization densities. These equations are discussed in the limiting case of low density and compared with previous results.

THE QUANTUM CORRECTIONS TO THE TRANSPORT COLLISION INTEGRALS
by Herbert T. Wood
WIS-TCI-111 (10 August 1965)

ABSTRACT

The second quantum correction to the phase shift in a collision between particles with spherically symmetric potentials is obtained, using the method of Curtiss and Powers. In this expression the potential is not restricted to monotonic functions. The results apply to a potential with an attractive minimum. The classical limit and the first quantum correction, both developed earlier for monotonic potentials, are also rederived so that they may be used with potentials possessing a minimum. These expressions are then used to develop series expressions for $Q^{(1)}$ and $Q^{(2)}$, the so-called cross sections for diffusion and viscosity, respectively. These expressions for $Q^{(1)}$ and $Q^{(2)}$ are used to obtain the classical limit and the quantum corrections to the transport collision integrals.

In the case of $Q^{(2)}$ the effect of statistics on collisions between like molecules is also considered. It is found that $Q^{(2)}$ is not modified by statistics, at least through terms of order h^4.

THE THEORY OF ATOMIC COLLISIONS
by Donald Kouri
WIS-TCI-112 (30 July 1965)

ABSTRACT

The separation of the rotational degrees of freedom from the N particle Schrödinger equation is discused and applied to the system H^+-H. A symmetric definition of the Euler angles is employed thus facilitating the inclusion of the effects of the Pauli principle due to the identity of the protons. The solutions of the coupled partial differential equations which are obtained are expanded in terms of Born-Oppenheimer H_2^+ electronic wave functions and the resulting coupled equations investigated. A selection rule restricting the coupling to states of a single symmetry is derived and the asymptotic behavior of the coupled differential equations considered. Next a truncation scheme for treating the coupled equations is presented.

Use is then made of the formal scattering theory to obtain the asymptotic form of the desired wave function. This result is used to specify the arbitrary constants in the general solution of the Schrödinger equation. The resulting solution describes asymptotically an incoming plane wave and outgoing scattered spherical waves. The condition that this general solution vanish at the origin suffices to determine the scattering amplitudes, which in turn are shown to be related to the cross sections in a simple fashion.

Finally the practical aspect of obtaining the numerical solutions of the coupled equations is treated. The problem of determining the phase shifts for elastic scattering is discussed. A new numerical method for evaluating phase shifts based on the fact that the phase and amplitude of the wave function are slowly varying functions is developed. A new relation for the absolute phase shift is obtained and shown to be useful in generalizing the W.K.B. method for obtaining phase shifts to any number of turning points. Then an analogous numerical scheme for coupled equations is developed based on the same concept of slowly varying phase and amplitude of the solutions of the coupled equation.

THE 1/Z PERTURBATION THEORY OF THE HOOKE'S LAW MODEL FOR THE TWO-ELECTRON ATOM

by Ronald J. White and W. Byers Brown

WIS-TCI-116 (29 August 1965)

ABSTRACT

The aim of this paper is to contribute to the study of the first-order perturbation equation for the two-electron atom, which has not yet been solved. The corresponding equation for the ground state of a model atom is solved analytically. In the model the Coulomb attraction of the nucleus is replaced by a Hooke's law attraction (harmonic oscillator potential) while the interaction of the electrons remains coulombic. The first-order equation for the Hartree-Fock approximation is also solved analytically. The perturbation energies for the exact and Hartree-Fock treatments are obtained through third order.

THE CUSP CONDITIONS FOR MOLECULAR WAVE FUNCTIONS

by Russell T. Pack and Joseph O. Hirschfelder

WIS-TCI-123 (5 November 1965)

ABSTRACT

The cusp conditions are derived which describe the behavior of the wave function at the singularities of the Coulomb potential corresponding to the coalescence of two or more particles. In this derivation, the wave functions is not spherically averaged; the fixed-nuclei approximation is not required; and the wave function may have nodes at the singular points. In addition to the general treatment, the cusp conditions for diatomic molecules are discussed in three different coordinate systems.

THE SUDDEN APPROXIMATION APPLIED TO MOLECULAR PROBLEMS. I. NON-REACTIVE COLLISIONS

by J. L. J. Rosenfeld
WIS-TCI-128 (27 September 1965)

ABSTRACT

The sudden approximation for transition probabilities is derived using an evolution operator formalism The assumptions required are explicitly stated and their validity and applicability are discussed in relation to energy transfer during collisions between molecules and atoms It is shown that sufficient conditions ensuring the validity of the sudden approximation are (1) that a classical description be adequate to describe the relative motion of the molecules or atoms, and (2) that the energy levels of the states mainly involved in the process be such that the product of their energy difference and the collision time be small compared to $\hbar$.

THE APPLICATION OF PERTURBATION THEORY TOWARD THE DETERMINATION OF MOLECULAR ENERGIES AND PROPERTIES

by Robert L. Matcha
WIS-TCI-129 (15 October 1965)

ABSTRACT

The ground state energy of the hydrogen molecule is accurately determined with the aid of Rayleigh-Schroedinger perturbation theory, treating the electronic interaction as a perturbation to the remaining Hamiltonian. Techniques are developed for evaluating integrals containing zeroth order H_2^+ wave functions. A generalized Hylleraas variational method is used to determine wave functions beyond zeroth order

The perturbation energy through fifth order at the equilibrium separation is found to be comparable in accuracy to the most accurate variational calculations.

A PERTURBATION THEORY OF ISOELECTRIC MOLECULES: CONVERGENCE OF SERIES FOR ONE-DIMENSIONAL DELTA POTENTIAL MODEL

by Pearl S. C. Wang and W. Byers Brown
WIS-TCI-130 (17 November 1965)

ABSTRACT

The perturbation theory of heteronuclear molecules based on isoelectronic homonuclear molecules developed by Chang and Byers Brown is applied to the delta potential model. The radii of convergence of the series expansions for the energy and dipole moment are obtained. The errors in the perturbation treatment due to neglect of higher order terms are calculated. The results tend to support the application of this theory to the $CO-N_2$ problem.

THE QUANTUM MECHANICAL KINETIC THEORY OF LOADED SPHERES

by John J. Mueller
WIS-TCI-131 (25 October 1965)

ABSTRACT

The transport coefficients of a gas of loaded spheres, that is, spheres in which the center of mass does not coincide with the geometrical center are considered. The amount by which the center of mass is displaced from the center of the sphere is denoted by δ and the diameter of the sphere is σ . The scattering amplitude and cross section are found as power series in δ/σ ; the coefficients of the zero, first, and second power of δ/σ are obtained. Using these results, the quantum mechanical expressions for the relaxation time, coefficient of shear viscosity, and coefficient of thermal conductivity are also obtained explicitly to second order in δ/σ. These quantities are then evaluated, numerically, in the limit that Planck's constant approaches zero. The results are found to agree with results obtained by purely classical methods.

PATH-INTEGRALS IN DYNAMICS
by A. M. Arthurs
WIS-TCI-132 (1 November 1965)

ABSTRACT

The Lagrangian formulation of quantum dynamics in terms of path-integrals due to Feynman describes systems for which the Hamiltonian is classical in form and quantization is carried out in terms of commutators rather than anticommutators. The difficulty with the Feynman method is the actual evaluation of the path-integral itself. We give an explicit evaluation for classical wave motion in one-dimension. This requires an extension of the Feynman method which was introduced by Tobocman and studied in detail by Davies.

We also discuss the work of Corson on the question of a unified formulation of dynamics.

A PROBLEM ON SUMMATION OVER HISTORIES IN QUANTUM MECHANICS

by A. M. Arthurs
WIS-TCI-144 (17 January 1966)

ABSTRACT

The transition amplitude corresponding to a Dirac particle is evaluated as a sum over histories by a method based on unitary equivalence properties and the canonical formalism of quantum mechanics.

ELECTRONIC CHARGE DENSITY IN HELIUM IN THE FIRST ORDER SHIELDING APPROXIMATION

by Jean H. Epstein and Saul T. Epstein
WIS-TCI-145 (4 January 1966)

ABSTRACT

We have calculated the electronic charge density for the ground state of helium using the first order shielding approximation. The results are disappointing.

TIME-DEPENDENT HYPERVIRIAL THEOREMS AND THE LIKE FOR VARIATIONAL WAVE FUNCTIONS

by Saul T. Epstein
WIS-TCI-146 (10 January 1966)

ABSTRACT

Conditions are given under which optimal variational wave functions will satisfy time-dependent hypervirial theorems, Hellmann-Feynman theorems, etc.

AN ASSOCIATED SOLVENT THEORY OF POLYMER SOLUTIONS

by W. Byers Brown and William D. Taylor

WIS-TCI-160 (16 February 1966)

ABSTRACT

This paper describes an association theory of the thermodynamic properties of mixtures of a non-polar polymer with a polar solvent, based on the Flory-Huggins equation. The solvent molecules are assumed to associate to linear complexes which form an athermal Flory-Huggins mixture, while the polymer and the solvent complexes form a Flory-Huggins mixture with a single interchange energy parameter.

The experimental dilution properties of mixtures of polypropylene with diethylketone and with di-isopropyl ketone, obtained from vapour pressure measurements, are shown to be satisfactorily described by the theory. The volumes of mixing exhibit the cubic type of dependence on composition possible theoretically, but the value of the Flory-Huggins parameter required is inconsistent with the other dilution properties.

THE DISTORTION APPROXIMATION IN SCATTERING THEORY

by A. M. Arthurs

WIS-TCI-161 (1 March 1966)

ABSTRACT

The distortion approximation for heavy particle collisions is developed from a molecular model.

TWO LECTURES ON SECOND QUANTIZATION
by Saul T. Epstein
WIS-TCI-163 (17 March 1966)

ABSTRACT

These lectures were given as part of a seminar course in Theoretical Chemistry in February, 1966. In them we present an intuitive derivation of the formalism of Second Quantization, and some applications. I wish to thank Prof. Byers Brown for his comments, and for his encouragement.

MOMENTUM OPERATORS IN QUANTUM MECHANICS
by A. M. Arthurs
WIS-TCI-164 (28 April 1966)

ABSTRACT

A representation for momentum operators corresponding to real observables is obtained by using functional integration in phase space.

ON SECOND ORDER PERTURBATION ENERGIES AND HYPERVIRIAL RELATIONS
by A. M. Arthurs and P. D. Robinson
WIS-TCI-172 (17 May 1966)

ABSTRACT

A hypervirial criterion for the second order energy correction $E_n^{(2)}$ to vanish is examined in the context of standard perturbation theory. For ground state wave functions, the criterion leads to the trivial situation in which both the unperturbed and perturbed Hamiltonians have the same set of eigenfunctions.

The first order correction to a non-zero $E_n^{(2)}$ under a second perturbation is shown to vanish if another hypervirial criterion is satisfied.

NON-RESONANT RELATIVISTIC INTERMOLECULAR FORCES
by William J. Meath
WIS-TCI-174 (10 June 1966)

ABSTRACT

The interaction of two like atoms in degenerate quantum states of the same energy and the interaction of two unlike atoms in arbitrary states is considered in the Breit-Pauli approximation. For these non-resonant interactions the calculation of the relativistic long range interaction energy, through $O(\alpha^2)$, is discussed with specific allowance for degeneracy in the interacting atoms. Possible interactions where relativistic effects may be important are discussed. As a specific example the interaction of two spin degenerate atoms $(L=0, S\neq 0)$ is calculated through $O(\alpha^2/R^6)$ (where R is the interatomic separation). The non-relativistic energy is given by the usual London dispersion energy which varies as $1/R^6$ while relativistic effects introduce an interaction energy which varies as α^2/R^3.

A PARTIAL WAVE EXPANSION IN SPHEROIDAL COORDINATES FOR DIATOMIC MOLECULES
by R. B. Hake and W. Byers Brown
WIS-TCI-177 (25 July 1966)

AN APPLICATION OF HIRSCHFELDER-SILBEY PERTURBATION THEORY TO THE H_2^+ ION
by Rodger B. Hake, Robert J. Silbey, and Joseph O. Hirschfelder
WIS-TCI-180 (18 August 1966)

ABSTRACT

The Hirschfelder-Silbey perturbation theory has been applied to the H_2^+ molecular ion. The first order perturbation equation has been solved

by means of a variational method and the resulting gerade and ungerade energies are given through third order.

The ungerade energy is in very good agreement with the exact energy, but the corresponding gerade energy is relatively poor. These results are currently under investigation.

THE EFFECT ON THE LIFETIME OF AN ATOM UNDERGOING A DIPOLE TRANSITION DUE TO THE PRESENCE OF A RESONATING ATOM

by Edwin A. Power
WIS-TCI-186 (31 August 1966)

ABSTRACT

The modification of the transition rate from the Einstein A coefficient for an atomic dipole transition due to the presence of a similar atom is obtained without the use of damping theory.

A PSEUDO-SECOND-ORDER EXTRAPOLATION METHOD FOR VECTOR ITERATIONS

by R. A. Sack
WIS-TCI-187 (12 September 1966)

ABSTRACT

A formula is derived which allows an extrapolation for vector iterations from any three successive vectors; its geometrical interpretation corresponds to finding the center of a plane equi-angular spiral. The method has already been successfully applied for SCF calculations. The new approach is compared to older methods, and the conditions under which it yields a close approximation to the true solutions are examined.

CORRECTIONS TO THE BORN-OPPENHEIMER APPROXIMATION

by Russell T. Pack
WIS-TCI-197 (15 November 1966)

ABSTRACT

Although the Born-Oppenheimer separation is usually an excellent approximation, it need not be for either very large or very small nuclear separations. And even near the equilibrium separation highly accurate calculations such as those of Kolos and Wolniewicz make the evaluation of corrections essential. In addition, due to rotational degeneracies, the usual single product of an electronic an a nuclear wave function is not always a proper zeroth-order solution of the Schrödinger equation.

In this study the center of mass and rotational motions of an arbitrary diatomic system are exactly separated off. The removal is simplified by the use of the rotation operator itself rather than the representations of the rotation group. The Breit-Pauli Hamiltonian (which allows magnetic and relativistic corrections to be included) is carried through the transformations.

Coupled equations for internal motion are obtained which form a basic starting point for any exact treatment of diatomic molecules. Use of angular momentum raising and lowering operators allows the coupled equations to be expressed in a simpler form than they have been previously.

The equations are treated here by perturbation methods which start from the adiabatic and Born-Oppenheimer approximations. Selection rules and formulas for the corrections to long range interatomic potentials are given, and significant corrections to the centrifugal potential are found. Finally, the interaction of two hydrogen atoms is treated as an example.

AN EXPLORATION INTO THE USE OF UNLINKED PAIR CORRELATIONS IN VARIATIONAL WAVE FUNCTIONS

by John H. Karl
WIS-TCI-198 (21 October 1966)

ABSTRACT

A general technique for including interelectronic coordinates in variational wave functions is developed. Details for handling the electron spin and the antisymmetrization of the trial function are included, and most important, a practical scheme for performing the resulting integration over r_{ij} coordinates is presented.

As an example of this method, a calculation on the ground state of Be is given which is an improvement over the r_{ij} treatment of Szasz. Using this method, it seems practical to obtain r_{ij} wave functions at least through neon.

INTERNAL EXCITATION IN MOLECULAR COLLISIONS

by Raphael D. Levine
WIS-TCI-203 (9 December 1966)

ABSTRACT

An analysis of molecular collisions which centers attention on internal excitation during collisions is reviewed.

In the zeroth order description no energy transfer between kinetic energy of relative motion and internal energy is allowed. The evolution of the system is then analyzed as a sequence of corrections to this description. The theory thus centers attention on the migration of energy from kinetic energy of relative motion to internal excitation and back. The collision event can involve participation of states (which are

stable to zero order) where the kinetic energy has been transferred into internal energy, so that the resulting motion is a bounded relative motion of internally excited collision partners. These states have only a temporary existence, as eventually energy flows back into the relative motion.

THE HELLMAN-FEYNMAN ELECTROSTATIC THEOREM AND LONG RANGE INTERACTION OF ATOMS

by Arthur A. Frost

WIS-TCI-204 (14 December 1966)

ABSTRACT

The long-range interaction energy for the ground states of the H_2^+ and H_2 molecules, proportional to $1/R^4$ and $1/R^6$ respectively, is discussed in terms of the electrostatic theorem. As expected the calculated interaction is very sensitive to the electron density distribution about each nucleus. Satisfactory R dependence of the interaction is found only with densities calculated from floating orbitals.

SEMI-EMPIRICAL POTENTIAL ENERGY CURVES FROM SIMPLE APPROXIMATE WAVE FUNCTIONS

by Morton A. Eliason and Joseph O. Hirschfelder

WIS-TCI-206 (12 December 1966)

ABSTRACT

Semi-empirical potential curves for the interaction of two hydrogen atoms in the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states have been calculated by assuming a simple approximate wave function, computing the expectation value of the

Hamiltonian for the system, and then considering the units of energy, e^2/a_0 , length, a_0 , and the screening parameter to be adjustable parameters, to be chosen to give as good a fit of the true curve as possible. The trial functions used were made up from 1s hydrogenic or Gaussian atomic orbitals; some allowance for polarization was included in a number of the computations. The resulting curves fail to give as faithful a representation of the true curves as had been desired. Further improvement would require the addition of undesirable complexity in the trial functions and therefore in the computations for this and for more complex systems.

ROTATIONAL EXCITATION AND SMALL-ANGLE MOLECULAR SCATTERING AND THE SUDDEN APPROXIMATION

by K. H. Kramer
WIS-TCI-212 (4 January 1967)

ABSTRACT

The quantum small-angle scattering formula for the differential cross section is extended to the calculation of inelastic differential cross sections for the system atom-diatomic polar molecule in a well defined rotational state (j,m) . Under the assumption of the sudden approximation being valid, the elastic and the inelastic differential cross section for a pure j-transition reveal the same functional behavior. For small angles, m-transitions become increasingly improbable.

TWO LECTURES ON THE VARIATIONAL PRINCIPLE IN QUANTUM MECHANICS
by Saul T. Epstein
WIS-TCI-216 (26 January 1967)

ABSTRACT

These lectures were given as part of a series of seminars on "Selected Topics in Theoretical Chemistry" in the second semester of 1966-67. They are concerned with various general theorems, like the virial theorem, or the Hellmann-Feynman theorem, rather than with numerical questions. The first lecture deals with bound states, the second with scattering states.

AN APPLICATION OF HIRSCHFELDER-SILBEY PERTURBATION THEORY TO THE H_2^+ ION: A CRITICISM OF AND CORRECTION TO WIS-TCI-180
by Paul A. Westhaus
WIS-TCI-227 (8 March 1967)

THE STRUCTURE OF CORRELATION AMPLITUDES IN MANY-FERMION SYSTEMS
by Paul A. Westhaus
WIS-TCI-234 (12 April 1967)

ABSTRACT

The structure of the corralation functions appearing in Sinanoglu's many-electron theory is analyzed. It is shown how these functions lead naturally to the definitions of correlation amplitudes satisfying a set of coupled integro-differential equations. Approximate solutions to a subset of these questions--the two-particle equations--correspond with solutions of the "exact pair" equations proposed by Sinanoglu. The relationship of these correlation amplitudes with those employed by Clark and Westhaus in cluster expansion techniques is also explored, and the equivalence of Sinanoglu's "exact pair" theory with their truncated factor-cluster formalism is demonstrated.

COMPOUND STATE RESONANCES IN MOLECULAR COLLISIONS: THE INTEGRAL ELASTIC CROSS SECTION FOR D_2-Xe SCATTERING

by David A. Micha
WIS-TCI-235 (3 May 1967)

ABSTRACT

Compound state resonances in molecular collisions are predicted, and numerical results are presented for the D_2-Xe system.

INTERNAL COORDINATES FOR THE H^+-H PROBLEM

by David G. Vaala and C. F. Curtiss
WIS-TCI-237 (25 May 1967)

ABSTRACT

Three translational and three rotational degrees of freedom are separated from the Schroedinger equation for H^+-H . The separation of the rotational degrees of freedom is carried out using two different definitions of the "body-fixed" axes. The resulting exact equations involve only the coordinates of the internal motion of the three particles, and the symmetric under the interchange of the two protons. Three different sets of internal coordinates are considered for each of two specifications of the standard configuration, or body-fixed axes.

THE STRONG QUANTUM LIMIT OF THE RELAXATION TIME AND SHEAR VISCOSITY OF A GAS OF LOADED SPHERE MOLECULES

by Jerry D. Drennan and C. F. Curtiss
WIS-TCI-238 (9 June 1967)

ABSTRACT

Quantum mechanical expressions for the relaxation time and shear viscosity have been derived by Mueller for a gas consisting of loaded sphere molecules. These expressions are expanded in power series in $1/\lambda^2$ where $\lambda = h/\sigma\sqrt{2\mu KT}$, i.e. in the strong quantum region. The coefficients of the first four terms for the reciprocal of the relaxation time are evaluated numerically.

HIGHER ORDER PERTURBATION ENERGIES FOR THE 2-ELECTRON HOOKE'S LAW MODEL ATOM

by John M. Benson and W. Byers Brown
WIS-TCI-242 (14 July 1967)

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}.

FIRST AND SECOND ORDER DENSITY MATRICES OF A SPIN-PROJECTED SINGLE DETERMINANT

by John E. Harriman
WIS-TCI-250 (21 August 1967)

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
WIS-TCI-251 (17 August 1967)

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 ANALYTIC SOLUTION OF THE SCHRÖDINGER EQUATION FOR THE TWO-ELECTRON ATOM

by Ronald Joseph White
WIS TCI-254 (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 solvable 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
WIS-TCI-255 (28 June 1967)

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.

COMMENTS ON THE STATISTICAL APPROXIMATION IN MOLECULAR COLLISIONS

by R. D. Levine
WIS-TCI-257 (20 September 1967)

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
WIS-TCI-258 (2 October 1967)

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 II - PART I. THE PARTITIONING TECHNIQUE

by R. D. Levine
WIS-TCI-259 (2 October 1967)

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 partioning technique in collision theory.

LECTURES ON COLLISION THEORY III - PART III. COLLISION PROCESSES IN ENSEMBLES

by R. D. Levine
WIS-TCI-260 (27 November 1967)

REDUCTION OF THE TWO-ELECTRON BREIT EQUATION

by Penny Estabrooks
WIS-TCI-264 (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.

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
WIS-TCI-268 (10 November 1967)

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
WIS-TCI-271 (29 December 1967)

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.

A JUSTIFICATION OF THE HYLLERAAS SOLUTION OF THE INVERSE SCATTERING PROBLEM

by T. J. P. O'Brien
WIS-TCI-274 (18 December 1967)

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.

ON THE DISSOCIATION ENERGY OF GROUND STATE $(X\ {}^1\Sigma_g^+)$

by Robert J. LeRoy and Richard B. Bernstein
WIS-TCI-284 (7 February 1968)

ABSTRACT

Combining Herzberg's[1] accurate *experimental* vibrational terms differences for H_2 with binding energies *computed* for the highest levels from Kolos and Wolniewicz's[2] (K.W.) potential (taking cognizance of the relativistic and nuclear motion correction terms), we obtain the result $D_0 = 36114.0\ (\pm 0.2)\ \text{cm}^{-1}$. This agrees with the previously preferred value of the experimental dissociation energy, namely $36113.6\ (\pm 0.3)\ \text{cm}^{-1}$ The present method of utilization of computed binding energies yields the true D_0 despite any small systematic inaccuracy in the *ab initio* potential, such as that responsible for the apparent 3-4 cm^{-1} error in the "best" theoretical dissociation energy.[3]

TWO NOTES ON PERTURBATION THEORY. I. INTERCHANGE THEOREMS AND THE VARIATION PRINCIPLE. II. PV IN A DIFFERENT NOTATION

by Saul T. Epstein
WIS-TCI-286 (19 February 1968)

WHY SIMPLE THEORETICAL MODELS WORK

by Joseph O. Hirschfelder
WIS-TCI-291 (29 March 1968)

ABSTRACT

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 Many simple theories 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.

SECOND MIDWEST THEORETICAL CHEMISTRY CONFERENCE, JUNE 13-14, 1968,
PROGRAM AND SUMMARIES
WIS-TCI-302

PERTURBATION THEORY OF SHORT RANGE ATOMIC INTERACTIONS
by James Dewey Power
WIS-TCI-311 (16 August 1968)

ABSTRACT

Comparatively little attention has been given to the problem of calculating the interaction energy of two atoms for small internuclear distances R . Since at $R = 0$, one has the united atom, a perturbation treatment based on the united atom as zeroth order should be accurate for R sufficiently small. In this paper, by performing a similarity transformation on the Hamiltonian, we obtain the perturbation parameter $\mu = Z_a Z_b / Z^2$ appearing linearly. The resulting "μ-series" for the electronic energy,

$$W = E_0 + \mu W^{I} + \mu^2 W^{II} + \mu^3 W^{III} + \dots ,$$

converges more rapidly for small R than any other known perturbation expansion obtained from this Hamiltonian. The similarity transformed Hamiltonian is slightly unusual in that it is no longer self-adjoint.

Because of the electronic energy is finite for all values of R, it is natural to expand it as a power series about $R = 0$,

$$W(R) = E_0 + R^2 W_2 + R^3 W_3 + R^4 W_4 + \ldots.$$

It turns out that the individual perturbation energies in the μ-series have the property $W^{\overline{\underline{m}}} = O(R^{2m})$; by expanding W^{I} and W^{II} in powers of R, we obtain general formulae for the coefficients W_2, W_3, and W_4. The coefficient W is of particular interest because it contains the leading effects of the distortion of the united atom

The accuracy of this perturbation theory is tested on one- and two-electron diatomic molecules, and it is shown to be very rapidly convergent for small R. For $RZ < 1$ Bohr, quite a good approximation can be obtained by using simply $W = E_0(\text{exact}) + \mu \tilde{W}^{I}$, where $\tilde{W}^{I}$ has been evaluated from an approximate zeroth-order wavefunction. The μ-series is then used to discuss the discrepancy between the experimental (atomic scattering) and theoretical (SCF-MO calculation) results for the short-range interaction of $He\text{-}Li^+$.

A VALIDATION OF THE METHOD OF AMPLITUDE DENSITY FUNCTIONS FOR COMPUTING THE REACTION MATRIX

by B. R. Johnson
WIS-TCI-312 (21 August 1968)

ITERATIVE SOLUTION OF PERTURBATION EQUATIONS

by D. K. Harriss, J. O. Hirschfelder, and Y. M. Chan
WIS-TCI-316 (10 September 1968)

ABSTRACT

Iterative procedures for the solution of perturbation equations are considered. Limitations of a procedure recently proposed by Harriss and Hirschfelder are discussed, and modifications are suggested. The relationships between the various procedures are shown. Illustrative applications are given.

THE RESOLUTION OF A PERTURBED WAVE FUNCTION INTO ITS SYMMETRY COMPONENTS

by Joseph O. Hirschfelder and Donald K. Harriss
WIS-TCI-317 (10 September 1968)

ABSTRACT

The various orders of the wave functions for a perturbed Hamiltonian can be resolved into components which transform in accordance with the irreducible representations of the unperturbed Hamiltonian. Each of these components satisfies a separate perturbation equation. It is hoped that this approach will be especially useful in considering the perturbation of degenerate states.

APPROXIMATE WAVE FUNCTIONS FOR THE HELIUM GROUND STATE INVOLVING $r_<$ AND $r_>$

by Y. M. Chan and J. O. Hirschfelder
WIS-TCI-319 (30 September 1968)

ABSTRACT

In using the coordinates $r_<$ and $r_>$ in an approximate wave function for the ground state of the helium atom, care must be used to insure that the in-out electron correlation or expectation value of $(r_> - r_<)^2$ is sufficiently large. An example is given where this electron correlation is much too small.

SOME PROBLEMS IN ATOMIC AND MOLECULAR THEORY
by Robert Edward Johnson
WIS-TCI-320 (1 October 1968)

ABSTRACT

Three separate problems are considered in the main body of this thesis. A comparison is made between approximate second-order properties calculated in the coupled Hartree-Fock approximation with those obtained from the unoccupied Hartree-Fock approximation with first-order corrections. Secondly, the accuracy of the dipole shielding constant calculated in the restricted Hartree-Fock approximation is considered. Further, the lead terms in the expansion of the shielding constant in inverse powers of the nuclear charge calculated in the coupled and various uncoupled methods are compared. Lastly, several recently proposed perturbation theories of intermolecular forces including exchange are considered. Some of the theories are shown to yield identical results. To compare and test the various methods they were applied to a simple model.

ASPECTS OF THE INVERSE PROBLEM OF SCATTERING THEORY
by Thomas Joseph Patrick O'Brien
WIS-TCI-321 (7 October 1968)

ABSTRACT

The Hylleraas procedure for determining the spherically symmetric potential energy function from a knowledge of the energy dependence of the phase shift is examined in detail and applied to several potential models, with and without bound states. A proof of the completeness of the biorthogonal set of functions used in this procedure is given and a

proof of its orthogonality is restated. Several new approximate inversion procedures are also derived.

PERTURBATION FOR NONRADIATIVE TRANSITIONS IN MOLECULES
by John H. Young
WIS-TCI-322 (10 October 1968)

MOLECULAR BEAM FOCUSING OF DIATOMICS IN SELECTED STATES: TWO NEW METHODS
by Theodore Gustav Waech
WIS-TCI-325X (16 October 1968)

ABSTRACT

Two methods have been developed for the focusing and state selection of diatomic molecules in thermal molecular beams. The first utilizes a pair of four-pole electric fields, with an interposed crossed beam of microwaves, to select beams of chosen vibrational-rotational states. No mechanical velocity selector is needed. The second (requiring a selector) involves a ten-pole electric field which allows weak focusing and selection of rotational states of negative (or positive) Stark energy, including the "rotationless" state $J,M = 0,0$.

Also, calculations are presented on the scattering of thermal beams of atomic hydrogen by hydrogen atoms.

ON THE SPHERICAL SYMMETRY OF THE EXCHANGE POTENTIAL PRODUCED BY A CLOSED SHELL
by Saul T. Epstein
WIS-TCI-327 (13 November 1968)

THE FIRST ORDER WAVE FUNCTION IN THE 1/Z EXPANSION
by Saul T. Epstein
WIS-TCI-328 (14 November 1968)

SOLUTION OF THE N-REPRESENTABILITY PROBLEM: SECOND ORDER DENSITY MATRICES OF FINITE RANK
by Mary Beth Ruskai
WIS-TCI-329 (27 November 1968)

ABSTRACT

The N-representability problem is approached by considering geminal product expansions of symmetric and antisymmetric functions. Necessary and sufficient conditions for N-representability of second order density matrices of finite rank are obtained. These conditions can be extended to give a solution to the N-representability problem for higher order density matrices The circumstances under which a density matrix can be derived from two or more different functions are considered.

CLASSICAL THEORY OF DENSITY CORRECTIONS TO THE GASEOUS TRANSPORT COEFFICIENTS OF MIXTURES
by David Ellwyn Bennett III
WIS-TCI-330 (20 December 1968)

ABSTRACT

A modified Boltzmann equation for mixtures is developed which includes the effects of collisional transfer and three-particle collisions. This equation is then solved by perturbation expansion techniques. General expressions for the fluxes are derived with the resulting transport coefficients expressed in terms of the perturbation coefficients. Finally, the various integrals encountered in the development are evaluated numerically

THE VARIATIONAL PRINCIPLE AND THE VARIATIONAL METHOD I
by Saul T. Epstein
WIS-TCI-336 (20 February 1969)

THE VARIATIONAL METHOD II -- PERTURBATION THEORY
by Saul T. Epstein
WIS-TCI-338 (10 March 1969)

THE VARIATIONAL METHOD III -- STEADY STATE TIME DEPENDENT PERTURBATION THEORY
by Saul T. Epstein
WIS-TCI-339 (18 March 1969)

NON-LOCALIZABLE π ORBITALS
by Janet Del Bene and John E. Harriman
WIS-TCI-340 (20 March 1969)

ABSTRACT

The procedure for localizing canonical molecular orbitals proposed by Edmiston and Ruedenberg, and modified by Trindle and Sinanoglu, has been applied to all-valence electron semi-empirical wave functions for the nitrogen heterocyclics pyridine, pyridazine (1,2-diazine), pyrimidine (1,3-diazine), and pyrazine (1,4-diazine). Some comparisons of the localized orbital description of the σ and π systems of these molecules are made. The failure of the procedure to converge to a unique set of localized π orbitals for 1,4-diazine is examined in detail, and rules for determining other cases of probable nonconvergence are given.

THE SPONTANEOUS IONIZATION OF A HYDROGEN ATOM IN AN ELECTRIC FIELD

by Larry A Curtiss
WIS-TCI-345 (3 June 1969)

ABSTRACT

The spontaneous ionization of a hydrogen atom in an electric field is considered Numerical methods are used to find the rates of spontaneous ionization and the resonance energies. The results agree with those of other papers which use WKB approximations in their calculations

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PERTURBATION THEORIES OF WEAK INTERMOLECULAR FORCES

by Phillip Robinson Certain
WIS-TCI-347 (16 July 1969)

ABSTRACT

This thesis is a contribution to the development of a workable exchange perturbation theory for intermolecular forces. It is divided into three parts The first part develops a perturbation formalism for degenerate and almost degenerate energy states The formalism is related to methods of Van Vleck, Kato, Bloch, Hirschfelder, Kirtman, and Löwdin and can have a greater range of validity than the Rayleigh-Schrödinger perturbation theory. The second part extends the formalism to exchange problems and leads to the Hirschfelder-Silbey perturbation theory A method of solving the first order equation is developed which reduces the many electron equation to one and two electron equations. The third part applies four different perturbation formalisms for exchange forces to three model problems: the hydrogen molecule at internuclear separations $R = 4,6,8\ a_0$; a harmonic oscillator model of the hydrogen molecule ion; and the delta-function model of the hydrogen molecule ion.

THE EXCHANGE FUNCTION W FOR H_2 AND H_2^+

by Phillip R. Certain and Joseph O. Hirschfelder

WIS-TCI-351 (12 August 1969)

ABSTRACT

In the new partitioning perturbation formalism for electron exchange problems, the exchange function W plays an important role. For H_2 and H_2^+ the W is determined variationally in terms of a 14 term Slater orbital basis set Tables are given for expressing W at 14 values of the internuclear separation ranging from $R = 1\ a_0$ to $20\ a_0$

COMPARISON OF PRIMAS AND RAYLEIGH-SCHRÖDINGER PERTURBATION THEORIES

by D. M. Chipman and J. O. Hirschfelder

WIS-TCI-353 (18 August 1969)

ABSTRACT

The Primas and Rayleigh-Schrödinger formulations of perturbation theory are compared in considerable detail. The Primas approach appears useful only in special cases where the operators involved form a Lie algebra with a small number of elements. For Hamiltonians with degenerate energy levels or for many-body systems, the Primas formalism does not appear practical.

ROTATIONAL COMPOUND STATE RESONANCES IN SUBTHRESHOLD ATOM-DIATOM COLLISIONS

by James Terry Muckerman

WIS-TCI-356 (28 August 1969)

ABSTRACT

Resonance behavior in subthreshold scattering of atoms by rigid diatomic molecules in demonstrated by exact (close-coupled) calculations

involving the solution of the Schrödinger equations with closed channels included in the basis set. These resonances arise from virtual (rotational) inelastic processes resulting in the formation of temporarily excited diatom-atom bound states, and are, in principle, observable as rapid disturbances in the energy dependence of the integral elastic scattering cross section.

Each "isolated" resonances is characterized by an energy and width by fitting the exactly calculated phase shifts to a Breit-Wigner resonance form. Decoupling approximations, which treat the interchannel coupling in a perturbative manner, are tested by comparison with the exact numerical results. The "adiabatic" decoupling approximation introduced by R. D. Levine is found to predict quite accurately the resonance energies (as well as the non-resonant phase shifts) for all partial waves. This decoupling procedure is extended to allow the prediction of resonance widths. The results are found to agree with the exact resonance widths for s-wave collisions (a two-state problem), but are much less accurate for higher partial waves (in general, a four-state problem). The approximation for the non-s-wave resonance widths is considerably improved by the use of a renormalization procedure.

The complete subthreshold rotational compound state resonance "spectra" for several physically realistic model systems (p-H_2-He, p-H_2-Xe, and o-D_2-Xe) are calculated using the extended adiabatic decoupling procedure. Results are discussed in terms of the possibility of observing such resonance behavior in future molecular beam scattering experiments.

A VERSATILE MOLECULAR BEAM APPARATUS UTILIZING ELECTRON BOMBARDMENT DETECTION: OBSERVATION OF THE RAINBOW EFFECT FOR ARGON-NITROGEN

by Robert William Bickes, Jr.
WIS-TCI-358X (15 September 1969)

THE VARIATIONAL METHOD IV - LOWER BOUNDS FOR THE ENERGY

by Saul T. Epstein
WIS-TCI-361 (21 October 1969)

DISSOCIATION ENERGY AND LONG-RANGE POTENTIAL OF DIATOMIC MOLECULES FROM VIBRATIONAL SPACINGS OF HIGHER LEVELS

by Robert J. LeRoy and Richard B. Bernstein
WIS-TCI-362 (13 November 1969)

ABSTRACT

An expression is derived which relates the distribution of vibrational levels near the dissociation limit D of a given diatomic species to the nature of the long-range interatomic potential in the region where the latter may be approximated by $D - C_n/R^n$ Fitting experimental energies directly to this relationship yields values of D,n , and C_n . This procedure requires a knowledge of the relative energies and relative vibrational numbering for at least four rotationless levels lying near the dissociation limit; however, it requires no information on the rotational constants, or on the number and energies of the deeply bound levels. D can be evaluated with a much smaller uncertainty than heretofore obtainable from Birge-Sponer extrapolations. The formula predicts the energies of all vibrational levels lying above the highest one measured, with uncertainties no larger than that of the binding energy of the highest level. The validity

of the method is tested with model potentials and its usefulness is demonstrated by application to the precise data of Douglas, Møller, and Stoicheff for the $B^3 \pi^{+}_{0u}$ state of Cl_2 .

THE DISSOCIATION OF DIATOMIC MOLECULES FROM THE VIEWPOINT OF THE INTEGRAL HELLMANN-FEYNMAN FORMULA: H_2, LiH, AND Li_2

by Michael T. Marron
WIS-TCI-364 (10 November 1969)

ABSTRACT

The integral Hellmann-Feynman formula is used to compute the dissociation energies of H_2, LiH, and Li_2 . The derivation of the transition densities and the method of taking the limit of the transition densities as one of the nuclei is removed to infinity, is discussed. The expression for the dissociation energy of LiH is examined in detail. While the results (except for H_2) are inaccurate, it is argued that the essential characteristics of the transition density are correctly determined and that the method provides a basis for the physical interpretation of the factors which contribute to the dissociation energy.

NOTE ON THE SIMPLE COLLISION THEORY OF REACTIVE HARD SPHERES

by Michael T. Marron
WIS-TCI-368 (21 November 1969)

DIRECT CALCULATION OF SECOND-ORDER DENSITY MATRIX I. THEORY OF THE GREEN'S FUNCTION TECHNIQUE

by Jack Simons
WIS-TCI-374 (16 December 1969)

ABSTRACT

We present a method for directly determining the second-order density matrix of a system of particles with pairwise additive interactions. The result is obtained as a contour integral involving the two-particle Green's function. The random phase approximation is made and the evaluation of the Green's function is reduced to a simple matrix problem. An outline of the computational method is presented, and possible applications are discussed.

A PROPOSAL CONCERNING TERMINOLOGY IN REDUCED DENSITY MATRIX THEORY

by Vedene H. Smith, Jr. and John E. Harriman
WIS-TCI-379 (23 February 1970)

CROSSED MOLECULAR BEAM STUDY OF THE REACTIVE SCATTERING OF $K + I_2$: PRODUCT KI RECOIL (VELOCITY-ANGLE) DISTRIBUTIONS AND ENERGY DEPENDENCE OF REACTION CROSS SECTION

by Keith Thomas Gillen
WIS-TCI-380X (26 February 1970)

TABLES FOR GAUSSIAN QUADRATURE OF $\int_0^\infty 2x^2 \exp(-x^2)\, f(x)\, dx$

by James L. Kinsey
WIS-TCI-386 (15 April 1970)

ABSTRACT

Weights and abscissae for N-point Gaussian quadrature of integrals of the form $\int_0^\infty 2x^2 \exp(-x^2)\, f(x)\, dx$ are given to 20 places for $N = 2$ through $N = 17$.

METHODS FOR THE DIRECT CALCULATION OF REDUCED DENSITY MATRICES
by John Peter Simons
WIS-TCI-390 (19 June 1970)

ABSTRACT

This thesis contains the results of four separate efforts to overcome some of the mathematical difficulties involved in formulating atomic and molecular quantum mechanics in terms of reduced density matrices. First the problem of constructing approximately N-representable density matrices which can be used in variational calculations is studied in detail. The effects of approximate N-representability on calculated properties are also analyzed

Secondly use is made of field theoretical Green's functions to directly determine the second-order density matrix of an N-fermion system This method is applied to the ground state of the helium atom as a test case. Thirdly a new technique for calculating, in a self-consistent fashion, the first- and second-order density matrices of atoms and molecules is put forth. This scheme makes use of a generalized random phase approximation to obtain equations for various spin components of the density matrices The results of applying this new method to helium, lithium, and beryllium are presented Finally, the first- and second-order density matrices of symmetry-projected single determinants are derived and analyzed.

INELASTIC MOLECULAR SCATTERING
by Roger William Fenstermaker
WIS-TCI-392X (3 August 1970)

DISPERSION DIPOLE BETWEEN S-STATE ATOMS

by David Melvin Whisnant
WIS-TCI-395 (13 August 1970)

ABSTRACT

When two unlike atoms collide a dipole moment may be induced due to different distortions of their charge clouds. This thesis is concerned with the long-range contribution to this interaction dipole. This contribution can be expanded in a series in R^{-n} in a manner analogous to the long-range interaction energy. We develop an approximation to the first term in this series, D_7. This coefficient is first expressed in a convenient form involving integrals of frequency-dependent properties of the isolated atoms and then an approximate method which involves fairly simple properties of the individual atoms is developed making use of this form. The approximation is tested with accurate variation-perturbation values of D_7 for a model system, for helium-hydrogen, and for helium-helium and is found to be accurate to within 10% or less for these three cases. It is finally used to calculate D_7 for interactions of the rare gas atoms.

QUANTUM THEORY OF DENSITY CORRECTIONS TO THE GASEOUS TRANSPORT COEFFICIENTS

by Dennis Alan Gibboney
WIS-TCI-398 (16 October 1970)

ABSTRACT

The first density corrections to the transport coefficients are investigated for the case of a quantum gas of spherical particles. The development is based upon a truncation of the quantum mechanical BBGKY equations. For this purpose, the pair distribution function is expressed in terms of singlet distribution functions through the definition of a quantity Y The BBGKY hierarchy is then truncated by the approximation that Y may be replaced by its equilibrium value. The first of the BBGKY equations is shown, on the basis of a pair distribution function obtained in this manner, to lead to a quantum mechanical Boltzmann equation which is generalized to include both collisional transfer and three-body contributions. This equation is solved by the method of Chapman and Enskog and expressions obtained for the transport coefficients

Numerical computations fc the two-body contributions to the first transport virial coefficients are presented for a quantum gas of rigid spheres. The three-body terms are shown to lead, in the classical limit, to the results of Hoffman.

GREEN'S FUNCTIONS FOR STURM-LIOUVILLE PROBLEMS
by Jack Simons
WIS-TCI-400 (17 August 1970)

ABSTRACT

It is shown how the Green's function for any inhomogeneous Sturm-Liouville (S-L) problem can be constructed once two independent solutions of the homogeneous problem are known. The general technique is illustrated by considering two specific S-L problems. When the parameter appearing in the S-L equation is equal to an eigenvalue of the homogeneous S-L problem an added difficulty arises. The method of constructing a generalized Green's function which deals with this difficult case is also treated by example.

THE RANDOM PHASE APPROXIMATION IN THE THEORY OF PRESSURE BROADENING AND SHIFT OF SPECTRAL LINES

by R. D. Levine
WIS-TCI-412 (1 December 1972)

ABSTRACT

The general impact theory of relaxation in the gas phase can be considerably simplified using the random phase approximation of collision theory. As an example, it is shown that, apart from the far microwave regime, interline collisional transfer will usually be very small at pressures where the binary collisions approximation is valid. Collisional transfer will be important in those experiment (e.g. nonresonant absorption) where there is no absorption in the absorption in the absence of collisions.

CLASSICAL MECHANICS OF MOLECULAR COLLISIONS

by Robert Arthur LaBudde
WIS-TCI-414 (14 March 1973)

ABSTRACT

The joint methods of classical mechanics and numerical analysis have been used to attack several molecular scattering problem,s including elastic total cross sections, rotational excitation, and bimolecular chemical reactions. Most of the qualitative effects observed in experiments of these types can be well-explained using either classical mechanics or the quasiclassical approximation. In the case of glories in the total elastic cross section (Chap. III), simple quasiclassical scattering from a model central potential was sufficient to reproduce the results of contemporary experiments. Studies of rotational excitation in the $Li^+ + H_2$ and $Ar + N_2$ systems by trajectory methods (Chap. V)

have provided direct interpretation of structure found in the angular and inelastic differential cross sections, supplying motivation for possible future experiments. Application of classical mechanics to the reactive scattering of $K + CH_3I \rightarrow KI + CH_3$ (Chap. V) has suggested an explanation for the experimentally observed maximum in the total reactive cross section with translational energy. The calculations have illustrated the inter-dependence of the distributions of inelasticity, reaction, and dissociation products, and elucidated the mechanisms of these processes.

DIATOMIC PREDISSOCIATION LINE WIDTHS
by M. S. Child
WIS-TCI-416 (30 March 1973)

THE SEMI-CLASSICAL PROPAGATOR AND WKB MECHANICS
by M. S. Child
WIS-TCI-419 (8 June 1973)

ABSTRACT

The relation between the WKB and semi-classical propagator approaches to molecular collision theory is examined in terms of the properties of a new WKB propagator. It is found that the conditions for a valid stationary phase approximation to this quantity may be more severe than hitherto supposed. A novel aspect of the relation between the nature of the classical trajectory and a semi-classical transformation between coordinate and momentum representations is also examined.

INTERATOMIC FORCES FROM SPECTRAL DATA, AND UTILIZATION OF POTENTIAL CURVES IN SPECTROSCOPY, SCATTERING AND KINETICS

by Robert James LeRoy
WIS-TCI-428 (15 January 1971)

ABSTRACT

Part I considers divers means of determining diatomic potential curves, placing particular emphasis on utilization of the spectroscopically-observed distribution of vibrational-rotational energy levels. The widely-used RKR procedure is applied to ground-state $(X\ {}^1\Sigma_g^+)I_2$. A new approach is introduced which allows the determination of the dissociation limit and long-range potential tail from the distribution of the upper-most vibrational levels. It also yields a simple expression for the vibrational spacings which leads to a "better than Birge-Sponer" plot for determining the dissociation limit. These procedures were applied successfully to $B({}^3\pi_{0u}^+)$-state $C\ell_2$, Br_2 and I_2 . Other methods for the determination of diatomic potentials are reviewed, including one utilizing 3-body atomic recombination rate constants.

The best known ab initio diatomic potential is that calculated by Kolos and Wolniewicz (KW) for ground-state molecular hydrogen. Nevertheless, a comparison of the calculated and observed vibrational energy levels indicated that a small correction is required by the KW potential; this is evaluated empirically.

Part II of the thesis considers a number of problems in which a knowledge of the appropriate potential curves allows a better understanding of certain physical phenomena. Application of the new method of Part I leads to a reassignment of some I_2 uv lines emitting into a shallow van der Waals excited state with a potential hump.

A study was made of spectroscopic and scattering-theory manifestations of the quasibound diatomic levels which lie above the dissociation limit, but are bound by a potential barrier. Results of illustrative computations are presented for ground-state molecular hydrogen, showing extensive barrier penetration. This implies that Bernstein's method of extracting long-range potentials from rotational predissociation data should not be applied to hydridic diatomics. The eigenvalues, and the expectation values of R, R^2, R^{-2} and kinetic energy are calculated for all bound and quasibound levels of ground-state H_2 , HD and D_2 , using the ab initio relativistic-adiabatic potential of Kolos and Wolniewicz.

A method for calculating exact tunnelling probabilities for one-dimensional potential barriers is presented and used to test Bell's approximate tunnelling factor formulae for truncated parabolic barriers.

Most of the results in this thesis have by now been published.

THE VARIATION METHOD - I
by Saul T. Epstein
WIS-TCI-431 (19 February 1971)

THE VARIATION METHOD - II
by Saul T. Epstein
WIS-TCI-437 (7 May 1971)

C-2

LASER INDUCED GAS BREAKDOWN: SPECTROSCOPIC AND CHEMICAL STUDIES

by Philippe de Montgolfier
WIS-TCI-442X (21 June 1971)

ABSTRACT

In this paper we report the results of several investigations on laser induced gas breakdown. These experiments included, time resolved spectroscopy, direct detection of H atoms, chemical reactions; each of them provided insight into the behavior of the medium at different times. Comparison of the intensity of the observed signals showed that the species formed were probably created during collisions with electrons. In addition, no primary multiphotonic absorption and no macroscopic chemical reaction were observed below the breakdown threshold.

THEORY OF REACTIVE SCATTERING. VI. VOLTERRA EQUATION FORMALISM FOR COUPLED CHANNEL AMPLITUDE DENSITIES AND MODIFIED WAVEFUNCTIONS

by Donald J. Kouri
WIS-TCI-447 (26 July 1971)

ABSTRACT

The homogeneous integral solution procedure of Sams and Kouri is applied to integral equations derived using the coupled channel operator formalism. It is shown how one may obtain Volterra integral equations of the second kind for solving the equations for a "modified channel wavefunction" (or the channel amplitude density). The modified channel wavefunction is found to behave like the scattered portion of the wavefunction.

NON-PARTIAL WAVE TREATMENT OF REACTIVE AND NONREACTIVE SCATTERING: COUPLED INTEGRAL EQUATION FORMALISM

by Edward F. Hayes and Donald J. Kouri
WIS-TCI-448 (28 July 1971)

ABSTRACT

Coupled integral equations are derived for the full scattering amplitudes for both reactive and nonreactive channels. The equations do not involve any partial wave expansion and are obtained using channel operators for reactive and nonreactive collisions. These coupled integral equations are similar in nature to equations derived for purely nonreactive collisions of structureless particles. Using numerical quadrature techniques, these equations may be reduced to simultaneous algebraic equations which may then be solved.

EXACT QUANTUM CROSS SECTIONS FOR A THREE-DIMENSIONAL ANGLE DEPENDENT MODEL FOR THREE-BODY REACTIONS

by Michael Baer and Donald J. Kouri
WIS-TCI-450 (30 July 1971)

ABSTRACT

Exact quantum mechanical reactive cross sections are reported for a three-dimensional angle dependent model surface. The surface simulates an atom-heteronuclear diatom system $A + BC \rightarrow AB + C$ where atom B is much heavier than A or C. The molecules BC and AB are taken to be rotating vibrators which can dissociate. Results for two angle dependent potentials are given.

MEASUREMENT OF THE ENERGY DEPENDENCE OF THE REACTION CROSS SECTION FOR $K + CH_3I \rightarrow KI + CH_3$ FROM 0.1 to 1 EV (C.M.) USING A NEW CROSSED MOLECULAR BEAM SCATTERING APPARATUS

by Michael Elliot Gersh
WIS-TCI-451X (11 August 1971)

COMPUTATIONAL INVESTIGATIONS OF LOW-DISCREPANCY POINT SETS

by Tony T. Warnock
WIS-TCI-453 (27 August 1971)

ABSTRACT

The quasi-Monte Carlo method of integration offers an attractive solution to the problem of evaluating integrals in a large number of dimensions; however, the associated error bounds are difficult to obtain theoretically. Since these bounds are associated with the L^2 discrepancy of the set of points used in the integration, this paper presents numerical calculations of the L^2 discrepancy for several types of quasi-Monte Carlo formulae.

OPTIMAL UTILIZATION OF TOTAL ELASTIC SCATTERING CROSS SECTION DATA FOR THE DETERMINATION OF INTERATOMIC POTENTIALS

by R. B. Bernstein and R. A. LaBudde
WIS-TCI-469 (18 February 1972)

ABSTRACT

With the advent of improved experimental data on absolute total cross sections $Q(v)$ for atom-atom collisions and their velocity dependence, on the glory undulations and the transition to high-velocity behavior, it is timely to reconsider the problem of inversion of such data to yield information on the interatomic potential. In the absence of additional data in the form of differential cross sections there is a limit to the amount of information available from Q(v) even when observations of good accuracy (e.g. ±0.25%) are in hand over an extended energy range (e.g. from "thermal" energies upward by a factor of $\gtrsim 10^3$ in relative kinetic energy). A number of commonly used procedures for data inversion are no longer adequate to deal optimally with the high quality experimental results now becoming available. The present paper attempts to develop improved methods for data utilization, which take full advantage of the accuracy of the experimental Q(v) measurements.

IMPULSIVE MODEL FOR REACTIVE COLLISIONS
by Michael T. Marron and R. B. Bernstein
WIS-TCI-470 (25 February 1972)

ABSTRACT

A simple classical mechanical model of the reactive scattering of a structureless atom A and a quasi-diatomic BC is developed which takes full advantage of energy, linear and angular momentum conservation relations but introduces a minimum of further assumptions. These are as follows: (1) the vibrational degree of freedom of the reactant (BC) and product (AB) molecules is suppressed, so the change in vibrational energy is simply a parameter; (2) straight-line trajectories are assumed outside of a reaction "shell" of radius R ; (3) within this zone, momentum transfer occurs impulsively (essentially instantaneously) following mass transfer; (4) the impulse $\underset{\sim}{I}$, which may be either positive or negative, is directed along the BC axis, which may, however, assume all orientations with respect to the incident relative velocity $\underset{\sim}{g}$. Assumption (3) is not as drastic as it appears since one may alternatively

consider the reaction to have occurred on a potential surface such that the net force integrated over the entire "interaction region" yields the particular value of the impulse $\underset{\sim}{I}$. Differential and integral reaction cross sections are scaled according to R^2 (evaluated via molecular size considerations), but the model is not a member of the "hard-sphere" class. Potential surface information enters the model in two ways: (1) by the choice of sign of the impulse, positive corresponding to net exit-channel repulsion ("late-downhill" Polanyi-type), negative to a net approach-channel energy release ("early-downhill"); (2) by the weighting function for impulse directions, $\underset{\sim}{I}$ vs $\underset{\sim}{g}$, i.e. the distribution function of (non-collinear) ABC configurations. The model yields differential and total cross sections and product rotational energy distributions for a given collision exoergicity Q , or for any known distribution over Q . Numerical results are presented for several prototype reactions whose dynamics have been well-studied in several molecular beam scattering laboratories. Many of the main experimental features are readily accounted for by the model without adjustment of parameters. However, it is difficult to reproduce the often-found "uncoupling" of the product angular and recoil energy distributions.

THE HOHENBERG-KOHN THEOREM I
by S. T. Epstein and C. M. Rosenthal
WIS-TCI-483 (20 July 1972)

GENERALIZED AIRY FUNCTIONS FOR USE IN ONE-DIMENSIONAL QUANTUM MECHANICAL PROBLEMS
by John O. Eaves
WIS-TCI-486 (18 August 1972)

ABSTRACT

The solution of the one-dimensional time-independent Schrödinger equation in which the energy minus the potential varies as the n-th power of the distance is obtained from proper linear combinations of Bessel functions of order $(n + 2)^{-1}$. The linear combinations, which we call "generalized Airy functions" $\mathcal{Ai}_\nu(x)$ and $\mathcal{Bi}_\nu(x)$, reduce to the usual Airy functions $Ai(x)$ and $Bi(x)$ when $n = 1$ and have the same type of simple asymptotic behavior. Expressions for the generalized Airy functions which can be evaluated by the method of generalized Gaussian quadrature are obtained.

THEOREMS SATISFIED BY VARIATIONAL WAVE FUNCTIONS IN SCATTERING THEORY
by Saul T. Epstein
WIS-TCI-487 (7 September 1972)

ANALYSIS OF MOLECULAR COLLISIONS: AN INFORMATION-THEORETIC APPROACH
by R. D. Levine
WIS-TCI-495 (13 July 1973)

ROTATIONAL AND VIBRATIONAL SPECTRA OF MOLECULAR IONS: FEASIBILITY OF LABORATORY AND ASTROPHYSICAL OBSERVATION
by R. C. Woods, P. R. Certain, and R. B. Bernstein
WIS-TCI-503 (14 January 1974)

ABSTRACT

The rotational spectra of a number of small molecular ions should be detectable in the microwave or millimeter wave regions in laboratory experiments using currently available techniques. The dipole moments and absorption coefficients of polar diatomics (e.g. CO^+ and NO^+) as well

as asymmetric isotopically-enriched species, like $(^{18}O^{16}O)^+$, $(^{20}Ne^{22}Ne)^+$ and $(^{18}OC^{16}O)^+$, are calculated to be sufficiently large to allow observation of their spectra. In addition to the detailed molecular structure information which such spectral data would provide, precise knowledge of the transition frequencies would render likely the detection of certain of these ions in interstellar sources or in planetary atmospheres. All of these ions also possess vibrational spectra which should be detectable in the infrared region in laboratory or astrophysical sources.

NOTE ON THE SYMMETRY OF PERTURBED HARTREE-FOCK X-α WAVEFUNCTIONS

by John O. Eaves and Saul T. Epstein
WIS-TCI-509 (29 March 1974)
(To be published in the J. Chem. Phys. 10/15/74 issue.)

ABSTRACT

It is shown that the first-order orbitals for X-α or Hartree-Fock atoms perturbed by multipole electric fields have the expected symmetry properties.

KINETICS OF HOMOGENEOUS NUCLEATION IN MANY-COMPONENT SYSTEMS

by Joseph O. Hirschfelder
WIS-TCI-510 (5 April 1974)
(To be published in the J. Chem. Phys. 9/15/74 issue.)

ABSTRACT

Reiss's classical treatment of the kinetics of homogeneous nucleation in a system containing two chemical components is extended to many-component systems. The formulation is analogous to the

pseudo-stationary state theory of chemical reaction rates with the free energy as a function of the composition of the embryo taking the place of the potential energy as a function of interatomic distances.

THE POLARIZABILITY OF DIATOMIC HELIUM
by Patrick John Fortune
WIS-TCI-511 (26 April 1974)

ABSTRACT

In this thesis, the calculation of the electric dipole polarizability tensor of the He_2 dimer is described, and the results are used in the computation of several dielectric and optical properties of helium gas, at both high (322°K) and low (4°K) temperatures. The properties considered are the second dielectric virial coefficient, the second Kerr virial coefficient, and the depolarization ratio of the integrated intensities for the Raman scattering experiments.

The thesis consists of five parts. In the first part, the polarizability and various properties are defined. In the second part, the calculation of the polarizability in the long-range region in terms of a quantum mechanical multipole expansion is described. The formulas which are obtained are applied to the H_2, He_2, and HeH diatomics, and the results are compared to those of model calculations. In the third part, the calculation of the He_2 polarizability in the overlap region via coupled Hartree-Fock perturbation theory is described, and a basis set selection procedure is delineated which allows the Hartree-Fock limit to be approached with sets of reasonable size. It is further shown that the long-range limit of the coupled Hartree-Fock polarizability

is identical to that of the point dipole model. The calculation of the quantum pair distribution for both the ^{3}He and ^{4}He isotopes at 4°K is discussed in the fourth part. The calculated values of the properties of helium gas are given in the fifth part. The order of the computed second dielectric virial coefficients for ^{3}He and ^{4}He at 4°K is found to be opposite to that of experiment. This experimental-computational discrepancy is discussed in detail; while there is an uncertainty in the computed results due to the neglect of electron correlation, it is concluded that the discrepancy is probably due to inaccuracies in the experiments.

QUANTUM MECHANICAL STREAMLINES. I. SQUARE POTENTIAL BARRIER

by Joseph O. Hirschfelder, Albert C. Christoph, and William E. Palke
WIS-TCI-514 (19 July 1974)
(To be published in the 12/15/74 issue of J. Chem. Phys.)

ABSTRACT

Exact numerical calculations are made for the scattering of quantum mechanical particles from a square two-dimensional potential barrier. This treatment is an exact analog of both Frustrated Total Reflection of perpendicularly polarized light and the longitudinal Goos-Hänchen shift. Quantum mechanical streamlines (which are analogous to either classical mechanical trajectories or optical rays) are plotted. These streamlines are smooth, continuous, and have continuous first derivatives even through the classically forbidden region. The streamlines form quantized vortices surrounding each of the nodal points (which result from interference between the incident and reflected waves). Similar vortices

occur in reactive collisions of $H + H_2$ (McCullough and Wyatt; Kuppermann, Adams, and Truhlar) and undoubtedly play an important role in molecular collision dynamics. The theory for these vortices is given in a companion paper A comparison is given between our numerical calculations and the stationary phase approximation (SPA) Although our incident wave packet has a half-width of more than one de Broglie wavelength in contrast to the SPA which replaces the diffuse beams by rays with delta function profiles, the agreement was surprisingly good for both the Goos-Hänchen shifts and for the reflection coefficients However, we found that the Goos-Hänchen shift for the transmitted beam is significantly smaller than for the reflected beam, although in the stationary phase approximation these two shifts are equal Furthermore, we found that the scattering from the potential barrier has very little effect on the shape of the wave packets The power series expansion of the incident Debye-Picht wave packet, Ψ_I , has an extremely small radius of convergence whereas the power series for $\Psi_I^* \Psi_I$ has a radius of convergence of more than two de Broglie wavelengths

The imaginary velocity, $\underset{\sim}{v}_i$, is introduced into the Madelung-Landau-London hydrodynamical formulation of quantum mechanics. The corresponding imaginary streamlines will be considered in a forthcoming paper. The time-independent Schrödinger equation for real wavefunctions is reduced to solving the nonlinear first order partial differential equation: $h \nabla \cdot \underset{\sim}{v}_i = 2(E-V) + v_i^2$. Here $\underset{\sim}{v}_i$ is irrotational This equation may lead to interesting new methods of solving the Schrödinger equation. It does lead to a generalization of the Prager-Hirschfelder perturbation scheme which invokes an electrostatic analogy

The philosophical implications of the hydrodynamical formulation of quantum mechanics are discussed. Penetration of a one-dimensional square potential barrier is used to demonstrate exactly how tunneling occurs by particles "riding over the barrier" àla Bohm. Cases are cited where quantum and classical mechanical motions are identical.

QUANTIZED VORTICES AROUND WAVEFUNCTION. II.

by Joseph O. Hirschfelder, Charles J. Goebel, and Ludwig W. Bruch
WIS-TCI-515R (24 September 1974)
(To be published in the 12/15/74 issue of J. Chem. Phys.)

ABSTRACT

Quantized vortices can occur around nodes of wavefunctions. This fact, discovered by Dirac (1931) but little noted since, is rederived here and examples are discussed. The derivation depends only on the wavefunction being single valued and continuous. Since the derivation does not depend upon the dynamical equations, the quantized vortices are expected to occur for many types of waves (i.e. electromagnetic, accustic, etc.). Such vortices have appeared in the calculations (McCullough and Wyatt, Kuppermann) of the $H + H_2$ molecular collisions and play a role in the chemical kinetics. In a companion paper, it is shown that quantized vortices occur when optical waves are internally reflected from the face of a prism or particle beams are reflected from potential energy barriers.

CRITICAL POINT PARAMETERS OF HELIUM
by L. W. Bruch, I. J. McGee, and R. O. Watts
WIS-TCI-518 (17 October 1974)
(Has been submitted for publication.)

ABSTRACT

Calculations of the critical point parameters of the helium isotopes using integral equation closures for the pair distribution function are reported for two pair potentials.