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THEORETICAL CHEMISTRY INST 20 JUN 81 N00014-81-G-0073
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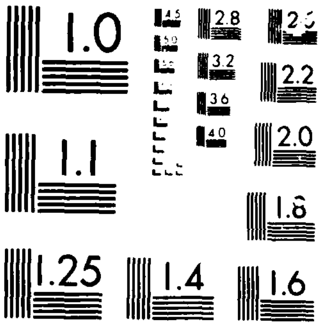
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International Symposium

New Directions for the Molecular Theory of Gases and Liquids

June 18 - 20, 1981

PROGRAM

[illegible] at the 1981

THURSDAY, JUNE 18, 1981

p.m.

4:00-6:00	Registration, Short Course Dorms	
7:00-8:00	Registration, Wisconsin Center	
8:00-8:45	Beer Party Reception and Poster Session I	Alumni Lounge, Wisconsin Center
9:15-10:00	Beer Party Reception and Poster Session II	

FRIDAY, JUNE 19, 1981

a.m.

SYMPOSIUM SESSION I, Wisconsin Center Auditorium

Chairman:	Professor Phillip Certain, University of Wisconsin
8:30	Dean Robert Bock, Graduate School, University of Wisconsin: Welcoming Remarks
8:35	J. O. Hirschfelder, Theoretical Chemistry Institute "New Directions for the Molecular Theory of Gases and Liquids"
9:30	T. F. George, University of Rochester "The Use of Intense Laser Radiation to Probe and Alter Gas-Phase Chemical Dynamics"
10:30	Coffee Break
11:00	R. B. Bernstein, Columbia University "Multiphoton Ionization and Fragmentation of Polyatomic Molecules"
12:00	A. H. Zewail, California Institute of Technology "Large Molecules in Coherent Laser Fields: Selective Bond Dynamics and Dephasing"

FRIDAY, JUNE 19, 1981

p.m.

SYMPOSIUM SESSION II, Wisconsin Center Auditorium

Chairman:	Professor Donald Truhlar, University of Minnesota
2:15	G. Herzberg, Herzberg Institute "Triatomic Hydrogen and Similar Free Radicals"
3:15	J. P. Toennies, Max-Planck-Institut, Göttingen "Rotational and Vibrational Transitions in Molecular Collisions"
4:15	Coffee Break
4:30	R. T. Pack, Los Alamos Laboratory "Anisotropy of Interactions of Octahedral Molecules with Atoms"
7:15	Cocktails (cash bar), Alumni Lounge, Wisconsin Center
8:00	Symposium Banquet, Wisconsin Center Dining Hall Chancellor Irving Shain presiding Remarks by Professors Henry Eyring, R. Byron Bird, and others

SATURDAY, JUNE 20, 1981

a.m.

SYMPOSIUM SESSION III, Wisconsin Center Auditorium

Chairman:	Professor William Meath, University of Western Ontario
8:30	R. N. Zare, Stanford University "The Role of Polarization in Reaction Dynamics"
9:30	W. Klemperer, Harvard University "The Structure of van der Waals Molecules"
10:30	Coffee Break
11:00	R. J. LeRoy, University of Waterloo "Theory, Potential Surfaces and Vibrational Predissociation of van der Waals Molecules"

p.m.

SYMPOSIUM SESSION IV, Wisconsin Center Auditorium

Chairman:	Professor John Dahler, University of Minnesota
2:00	B. J. Alder, Lawrence Livermore Laboratory "Stochastic Solution of the Schrödinger Equation"
3:00	A. D. Buckingham, Cambridge University "Light Scattering in Electric Fields"
4:00	Conclusion.

POSTER SESSION PARTICIPANTS

(ABSTRACTS WILL FOLLOW IN ORDER OF LISTING)

POSTER SESSION I

F. Weinhold

Daniel M. Chipman

Bernard Kirtman

John H. Detrich and Arnold C. Wahl

Worth E. Vaughan (presented by Gary Wesenberg)

Arthur E. Stillman and Jack H. Freed

Daniel D. Konowalow and Marcy E. Rosenkrantz

A. Isihara

Katharine L. C. Hunt and Barbara A. Zilles

Mark Ellenberger, Steven Richtsmeier, David Tweeten, and David Dixon

P. Malinowski, A. C. Tanner, K. F. Lee, and B. Linder

L. W. Bruch, J. M. Phillips

L. A. Curtiss, D. J. Frurip, and M. Blander

M. W. Bowers and K. T. Tang

R. S. Wilson and Jon Maple

POSTER SESSION II

R. A. Copeland, T. J. Foster, D. J. Pearson, and F. F. Crim

P. Habitz, K. T. Tang, J. P. Toennies, and Y. Y. Yung

M. D. Pattengill

Donald G. Truhlar, Todd C. Thompson, Bruce C. Garrett, and Robert B. Walker

R. F. Snider

C. R. Szmanda, K. B. McAfee, Jr., and R. S. Hozack

P. W. Langhoff

W. R. Gentry, C. F. Giese, and R. D. Johnson

Paul M. Hunt

Mark Hoffbauer, Kopin Liu, W. R. Gentry, and C. F. Giese

D. E. Fitz, D. J. Kouri, W.-K. Liu, F. R. McCourt, D. Evans, and D. K. Hoffman

J. Eccles and D. Secrest

Thomas K. Holley, Sunggi Chung, Chun C. Lin, and Edward T. P. Lee

John S. Dahler, Ralph E. Turner, and Svend E. Nielsen

Nora Sabelli and Arnold C. Wahl

Walter England

MASS POLARIZATION AND BREIT-PAULI CORRECTIONS FOR THE POLARIZABILITY OF ^{4}He

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We have evaluated the leading relativistic and nuclear motion corrections for the static dipole polarizability α_0 of the ^{4}He ground state, using accurate Hylleraas-type variational wave functions. The net correction is calculated to be 1.031×10^{-5} a.u., even though the contributions of some of the individual terms are more than 20 times this size. With this correction the theoretical polarizability, including all known effects but the Lamb shift, stands now at

$$\alpha_0^{\mathrm{theor}}(^4\mathrm{He}\ 1^1S) = 1.383199 \text{ a.u.}$$

compared with the experimental value measured recently by Gugan and Michel,

$$\alpha_0^{\mathrm{exp}}(^4\mathrm{He}\ 1^1S) = 1.383223 \pm 0.000067 \text{ a.u.}$$

The *a priori* theoretical value may be instrumental in establishing an absolute temperature scale in the 4-21 K region, and in refining the value of the gas constant R.

Perturbation Approach to a Molecular Orbital Theory of Intermolecular Forces

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University of Notre Dame
Notre Dame, IN 46556

Self-consistent-field molecular orbital calculations within finite basis sets have provided a most important theoretical tool for quantitative understanding of reaction mechanisms, molecular properties, various types of spectroscopy, and numerous other experimental results. In many such cases, it would be useful to describe a system in terms of the intermolecular forces between subunits which themselves are already well characterized. To this end, we present a perturbation analysis of how the molecular orbitals of two subunits interact to form molecular orbitals of the composite system. The theoretical difficulties associated with overlap of the subunit orbitals are taken into account. In addition to the total energy, which can be used to characterize reaction mechanisms, particular attention is also given to the individual orbital energies in order to provide a framework for understanding photoelectron spectra.

Molecular Electronic Structure by Combination of Fragments

Bernard Kirtman
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ABSTRACT

A method of combining fragments to obtain the electronic structure of a large molecule is presented. Our technique is based on an SCF treatment of the first-order density matrix, $\underset{\sim}{R}$. It is applicable within the Hartree-Fock, strongly orthogonal valence-bond and density functional models. Primary corrections to $\underset{\sim}{R}$, which occur in the vicinity of the bond(s) between the fragments, are calculated exactly; secondary delocalization effects are determined approximately. The approximations result in a substantial saving of computer time and storage requirements. Initial trial calculations using INDO and the unrestricted Hartree-Fock model show small errors for conformational energy differences and the total density matrix. The computation time increases quadratically with the size of the molecule rather than as the third power which is the case for a conventional INDO calculation. Most of the limitations inherent to the PCILO method are absent from our treatment.

A PRACTICAL GUIDE TO APPLICATIONS OF THE MCSCF AND MCSCF/CI METHODS

by

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Over the past decade it has become clear that the MCSCF method, both alone and when coupled with subsequent configuration interaction (MCSCF/CI), forms a powerful tool in Quantum Chemistry for the attainment of chemical accuracy for atomic and molecular systems. Recent advances[1] in MCSCF technology promise to enhance even further the efficacy of the MCSCF technique particularly in regard to its convergence behavior and applicability to excited states of the same symetry.

In order to make past experience with the MCSCF technique more accessible to the new technologists we present[2] this practical guide which discusses 1) the selection of basis sets and basis set anxiety 2) the choice of initial orbitals, 3) choice of configurations included in the MCSCF process and, 4) typical first generation convergence behavior. Also presented is a directory of MCSCF and MCSCF/CI calculations reported in the literature. This chronological directory includes a brief summary of calculative decisions indicating 1) the number of configurations included in the MCSCF process, 2) the criteria used in selecting these configurations, 3) the number of subsequent CI configurations and 4) an indication of whether potential curves or sufraces, excited state energy levels, and properties were computed. Appropriate references are given in the Directory. Several goals are suggested for developing the MCSCF method in this new decade. Comments on, criticisms of, and additions to this guide are welcomed.

1. See proceedings of NRCC-MCSCF workshop held at Texas A&M University July 14-16, College Station, Texas.
2. A preliminary version of this MCSCF practical guide to applications was presented at the NRCC workshop (July 1980) and will appear in the proceedings (NRCC-MCSCF workshop, Texas A&M University, College Station, Texas July 1980).

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LATTICE OLIGOMER DYNAMICS

Worth E. Vaughan
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The dynamics of short polymer chains with excluded volume on the cubic lattice is derived from a site model formalism. Attention is focused on the symmetry adapted coordinates needed for construction of the vector end-to-end length correlation function. The results are compared to the Monte Carlo calculations of Kranbuehl and Verdier.

Stochastic Modeling of Generalized Brownian Diffusion

by

Arthur E. Stillman* and Jack H. Freed

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Cornell University
Ithaca, New York 14853

A method is presented which permits stochastic modeling of the non-Markovian many-body features of diffusing molecules. The set of dynamical variables is augmented with stochastic bath variables which are assumed to be Markovian. The augmented set then represents a multidimensional Markov process which obeys a stochastic Liouville equation which is, in general, incomplete because it ignores the back reaction of the molecule on the bath variables. The back reaction effects are incorporated into the model by adding terms to the stochastic Liouville equation which are obtained by the constraints required for detailed balance. The resulting augmented Fokker-Planck equation (AFPE) properly describes relaxation to thermal equilibrium and for the appropriate limiting conditions, reduces to the classical Fokker-Planck equation. Augmented Langevin equations may be readily obtained from the AFPE which by the constraint of detailed balance automatically obey the fluctuation-dissipation theorem. Several examples are presented which have been motivated by recent molecular dynamics studies by means of ESR spectroscopy. These include fluctuating torque models related to that used by Huang, Mason, Hwang, and Freed (HMHF) and the slowly relaxing local structure (SRLS) model of Polnaszek and Freed.

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Long-Range Interactions of Na $3s^2S$ with Na $3s^2S$ or Na $3p^2p$

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Abstract

The potential energy curves for the eight lowest-lying electronic states of Na_2 which correspond to the interaction of Na $3s^2S$ with Na $3s^2S$ or Na $3p^2P$ are calculated ab initio for internuclear separations in the range $15 \leq R \leq 30$ bohr. The binding energies are analyzed to obtain estimates of the exchange enrgies, first-order electrostatic energies and second-order dispersion energies.

Correlations in Molecular and Electron Fluids*

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The roles played by short and long-range potentials in dense gases and fluids are discussed. The electron correlations in a degenerate two-dimensional electron gas are expected to change their character at a relatively small r_s of order 2, where r_s is the usual density parameter defined as the radius of the area per electron measured in terms of the Bohr radius.

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*This work was supported by the ONR.

Van der Waals contributions to the polarizabilities of inert-gas atom pairs: long-range results and overlap corrections

by

Katharine L. C. Hunt and Barbara A. Zilles

The Department of Chemistry
Michigan State University
East Lansing, MI 48824

Both classical multipolar interactions and van der Waals interactions affect the polarizability of a pair of atoms separated by a large distance R. For two atoms A and B in S states, the increase in intrinsic polarizability of A produced by van der Waals interactions with atom B varies as R^{-6} to lowest order and depends upon the hyperpolarizability $\gamma^{A}_{\alpha\beta\gamma\delta}(\omega,\omega',\omega'')$ of A and the mean-square fluctuating dipole of B. If the AB pair is separated along the z-axis, the correlation contributions to the static pair polarizabilities $\alpha_{zz}(\omega=0)$ and $\alpha_{xx}(\omega=0)$ are

$$\tilde{A}^{(6)}_{zz}R^{-6} = (1+\mathcal{P}_{AB})\frac{\hbar R^{-6}}{4\pi}\int_{-\infty}^{\infty}[2\gamma^{A}_{zzxx}(0,iu,-iu)+4\gamma^{A}_{zzzz}(0,iu,-iu)]\alpha^{B}(iu)du$$

$$\tilde{A}^{(6)}_{xx}R^{-6} = (1+\mathcal{P}_{AB})\frac{\hbar R^{-6}}{4\pi}\int_{-\infty}^{\infty}[\gamma^{A}_{xxxx}(0,iu,-iu)+5\gamma^{A}_{xxzz}(0,iu,-iu)]\alpha^{B}(iu)du$$

where $\mathcal{P}_{AB}$ permutes the indices A and B. The van der Waals contributions plus the classical dipole-induced-dipole terms give

$$\alpha^{AB}_{zz} = \alpha_A+\alpha_B + 4\alpha_A\alpha_B R^{-3} + [4(1+\mathcal{P}_{AB})\alpha_A{}^2\alpha_B + \tilde{A}^{(6)}_{zz}]R^{-6} + \ldots$$

$$\alpha^{AB}_{xx} = \alpha_A+\alpha_B - 2\alpha_A\alpha_B R^{-3} + [(1+\mathcal{P}_{AB})\alpha_A{}^2\alpha_B + \tilde{A}^{(6)}_{xx}]R^{-6} + \ldots$$

in terms of the static polarizabilities of the isolated atoms, α_A and α_B.

At short range where overlap cannot be neglected, the classical electrostatic and van der Waals terms deviate from the asymptotic forms (above), and exchange and orbital distortion effects contribute significantly. To lowest order, the van der Waals term is corrected for overlap by representing the perturbation V due to the AB interaction in terms of spatial Fourier transforms $Q(\underset{\sim}{k})$ of the charge distributions

$$V = \frac{1}{2\pi^2}\int\frac{d^3\underset{\sim}{k}}{k^2}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}Q_A(-\underset{\sim}{k})Q_B(\underset{\sim}{k});$$

evaluating the change in polarizability of the AB pair due to the perturbation V then gives the van der Waals contribution in the overlap region as an integral over frequencies and wavevectors $\underset{\sim}{k}$ and $\underset{\sim}{k}'$ of a sum of terms, each involving the product of spherical Bessel functions with the wavevector- and frequency-dependent polarizability of one atom and the hyperpolarizability of the other. This method has previously been used to find overlap corrections to long-range expressions for dispersion energies and heterodiatom dipoles.

Intermolecular Potentials for Organic Molecules from Elastic Scattering Measurements

Mark Ellenberger, Steven Richtsmeier, David Tweeten and David Dixon
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Minneapolis, Minnesota 55455

Elastic scattering experiments using crossed molecular beams yield information about the microscopic intermolecular potential. A wide range of atom-atom and atom-molecule potentials have previously been obtained using this technique. We are studying experimentally the intermolecular potentials for a range of organic systems in order to determine hydrophobic interactions. These studies also yield information about the ratio of the elastic to inelastic total cross sections. Studies have been performed for a range of molecules, He, Ne, Ar, O_2, CO, C_2H_4, CH_4, C_3H_6 and CO_2, scattered from trans-2-butene. Our best data to date is for the D_2+trans-2-butene system where the rainbow angle can easily be observed. Parameters for a spherically averaged potential have been determined from semi-classical (JWKB) elastic scattering calculations. Data on other systems will also be presented.

Van der Waals Forces, Charge-Density Susceptibilities and Scattering Functions. Application to the He-He Potential.

P. Malinowski[†], A. C. Tanner, K. F. Lee and B. Linder, Department of Chemistry, The Florida State University, Tallahassee, Florida 32306

The formulation for the dispersion interaction in terms of charge-density susceptibilities (1) is extended to include polarization terms. The close connection between the momentum space ($\underset{\sim}{k}$-space) susceptibility and the dynamic form factor for scattering is pointed out and various approximations and asymptotic forms are mentioned. Using closure and uncorrelated wave-functions, we determine the second order dispersion and polarization energies of two interacting He atoms (without recourse to multipole expansion), as well as first order coulomb and exchange energies. The second order energies, so obtained, are expressible in terms of static form factors for X-ray scattering, a mean excitation energy and atomic charge-densities. The integrals may be solved analytically or numerically by the use of tabulated form factors. A consequence of the momentum representation is the drastic reduction in the number of dimensions of integration from twelve in $\underset{\sim}{r}$-space to six in general and one or two for spherical form factors. The He-He potential energy curve is compared with other theoretical and experimental curves and the results are discussed.

[†] Permanent address: Institute of Physics, Nicholas Copernicus University, 87-100 Torun, Poland.

[1] B. Linder, K. F. Lee, P. Malinowski, and A. C. Tanner, Chem. Phys. 52, 353 (1980).

A Dense Two-Dimensional Gas Phase

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and

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Experiments have shown that a relatively dense 2D gas may coexist with the 2D solid. Gas with density up to 15% of the 2D solid density has been observed[1,2] for Ar, Kr, and Xe adsorbed on Ag(111). Isosteric heat data for the 2D gas support an identification of this gas as intrinsic 2D gas rather than an extrinsic gas adsorbed at "strong sites" of the surface. The dense gas has posed a severe challenge to statistical mechanical theories since in 3D the gas density at the triple point is only 0.2% of the solid density, and in 2D computer simulations for a classical Lennard-Jones potential model show[3] the gas density at the 2D triple point is slightly less than 3% of the solid density. We have evaluated the equation of state of the 2D gas and solid phases for a realistic model of the adatom interactions of Xe/Ag(111), using a Monte Carlo simulation, and find that the gas density at the sublimation curve at 90 K is 14% of the solid density. The gas is highly nonideal, with large compressibility and large specific heat. The high gas density at a temperature below the triple point suggests that there is only a limited temperature range where coexistence of the gas and a 2D liquid is possible, i.e., there is only a small difference between the triple point and critical temperatures.

1. J. Unguris, L.W. Bruch, E. Moog, and M.B. Webb, Surface Sci. 87 (1979) 415.
2. J. Unguris, Ph.D. thesis (University of Wisconsin-Madison, 1980, unpublished).
3. J.M. Phillips, L.W. Bruch, and R.D. Murphy (to be published).

INVESTIGATIONS OF ASSOCIATION REACTIONS IN POLAR GASES USING THE PRESSURE AND TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITY*

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In the 1950's Hirschfelder considered the thermal conductivity of gases undergoing chemical reactions having reaction rates which are fast in either the forward or reverse directions (i.e. small activation energy) and deduced a theory for changes in thermal conductivity due to those chemical reactions in terms of heats of reactions, gas compositions, and binary diffusion coefficients. We have recently undertaken a systematic study of association reactions in polar gases by analyzing the pressure and temperature dependence of their thermal conductivities using expressions derived by Butler and Brokaw based on Hirschfelder's work. Among the gases considered were water, methanol, ethanol, isopropanol, t-butanol, acetic acid, trifluoroacetic acid, methanol-water, acetic acid-water, and trifluoroethanol-water. In this paper we summarize the results of these studies showing (1) how well the behavior of the thermal conductivity of polar gases is described by the theoretical model provided by Hirschfelder's work and (2) how this model is very useful in providing an understanding of the interactions between polar molecules.

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*Work performed under the auspices of the Material Science Office of the Division of Basic Energy Science of the Department of Energy.

Quantum Effects of Vibrational Excitation in an Idealized Three-Body Reactive Collision

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The $H + H_2$ reactive collision with the H_2 in the vibrational excited state is simulated by considering an idealized potential energy surface which is a two dimensional duct with a 60 degree bent [H.M. Hulburt and J.O. Hirschfelder, J. Chem. Phys. 11, 276 (1943)]. The activation energy is simulated by a step function barrier in the corner region. The exact transition probabilities and reaction rates are obtained from both quantum and classical mechanics. These results are compared with the corresponding ones with the target molecule in the vibrational ground state. They show (1) vibrational enhancement is much larger in quantum mechanics than in classical mechanics; (2) quantum mechanical tunneling is more pronounced in the case that the target molecule is in the excited state; (3) the quantum theory predicts that the vibrational adiabatic reaction channel ($v_\alpha = 1$ to $v_\beta = 1$) is strongly preferred to the nonadiabatic channel outside the tunneling region. These results suggest that the discrepancies between experiments with excited target molecules and classical trajectory calculations are due to quantum effects. Indeed the results of this model study are in qualitative agreement with recent approximate three dimensional quantum calculations.

VIBRATIONAL RELAXATION AND DEPHASING LIQUIDS: MOLECULAR DYNAMICS APPROACH

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ABSTRACT

We present a study of vibrational relaxation and dephasing using molecular dynamics. The model used consisted of 125 diatomic molecules which interact via an atom-atom Lennard-Jones potential. The vibrational relaxation and dephasing times τ_R and τ_D were calculated and compared at several densities and temperatures and it was found that vibrational relaxation contributes to vibrational dephasing at high temperatures, but not always at low temperatures. In addition the influence on τ_R and τ_D of vibrational frequency and of anharmonicities in the binding potential were also observed. Finally the validity of various approximations which are commonly used in theories of vibrational relaxation and dephasing were studied. We found that vibrational-rotational coupling effects should not be neglected in high temperature, low frequency molecular liquids and that vibrational phase correlations between neighboring molecules can not be ignored.

Vibrational and Rotational Energy Transfer in HF($v \geq 2$)

R. A. Copeland, T. J. Foster,
D. J. Pearson and F. F. Crim

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The combination of direct excitation of overtone vibrations with time-resolved spectroscopic detection measures both rotational and vibrational energy transfer rates in highly vibrationally excited hydrogen fluoride. The total vibrational relaxation probability for HF($v = 3,4,$or 5) shows a characteristic decrease with increasing temperature which indicates the dominance of long range forces in the energy transfer dynamics. The data correlate well with recent models based on the formation of transient complexes in such systems. A laser double resonance measurement probes the rotational energy transfer dynamics in HF($v = 2$). Rotational relaxation is highly efficient with a cross-section which substantially exceeds the gas kinetic value. The temporal evolution of the double resonance signal reflects the multiple relaxation paths available within the rotational manifold.

Theoretical Study of Inelastic Collisions of the He - H_2 System

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and
Department of Physics, Pacific Lutheran University
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The spherical symmetric Vo and anisotropic radial components V_2 and V_4 in the usual Lygendie expansion for the rigid rotor He - N_2 potential are obtained with the method of Tang and Toennies [J. Chem. Phys. 66, 1496 (1978)]. Potential curves are presented and compared with a recent experimental potential derived by Keil, Slanskas and Kuppermann [J. Chem. Phys. 70, 541 (1970)]. There are considerable differences between them. These potentials are used in close coupling calculations. The differential cross sections of 0 → 2 and 1 → 3 rotational excitations at 27.3 meV obtained from the present theoretical potential are in good agreement with the ones directly measured by Faubel, Kohl and Toennies [J. Chem. Phys. 73, 2506 (1980)]. At 64 meV, the experimental differential total cross sections, from which the experimental potential curves are derived, are also reproduced by the present potential model.

Model Studies of Polyatomic Direct Photofragmentation

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ABSTRACT

The classical trajectory method has been used to investigate polyatomic direct photofragmentation. To facilitate comparison with corresponding quantum mechanical calculations, attention has been restricted to model collinear triatomic systems, viz., ICN, N_2O and pseudotriatomic CH_3I. Results obtained provide a commentary on the usefulness of the classical approach to photofragmentation dynamics.

Abstract for a poster paper for the International
Symposium on New Directions for the Molecular
Theory of Gases and Liquids, University of
Wisconsin, Madison, June 18-20, 1981

Resonances in Reactive Molecular Scattering

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I will summarize some recent results on resonances in reactive scattering. Particularly interesting examples are the subthreshold shape resonances and the higher-energy Feshbach resonances in collinear H + FH and D + FD as studied on the model potential energy surface of Muckerman and Schatz. We have calculated the energies of these resonances four ways:

1. accurate quantal scattering calculations
2. quantal scattering calculations in the vibrationally adiabatic approximation
3. semiclassical vibrationally adiabatic calculations
4. vibrational self-consistent-field calculations

The calculations by method 4 are the first time that reactive resonances have been calculated by bound-state techniques using the stabilization method.

Kinetic Cross Sections in the Infinite Order Sudden Approximation

R. F. Snider

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The translational-internal coupling scheme allows a factorization of energy dependent and kinetic cross sections into internal and translational parts. WKB-IOS phase shifts for the N_2-Ar system are used to calculate the translational factors. A T-matrix version of the theory based on calculating only downward collisions is used as an attempt to lessen the effect of ignoring energy inelastic effects in the phase shift computation. All kinetic cross sections associated with the viscosity Senftleben-Beenakker effect are estimated in this manner.

Charge-Exchange Processes as Observed in Crossed Molecular Beam Experiments

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K. B. McAfee, Jr.
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Murray Hill, New Jersey 07974

The study of intermediate energy charge-transfer collisions by means of crossed beam techniques can yield a wealth of information concerning energy interconversion, quantum interference effects and spin fine structures. By accurately measuring the slow product ion differential scattering flux, it is possible to resolve and interpret the various state-to-state processes which are associated with the charge-exchange event. For example, the study of the N_2^+, N_2 collision system reveals the efficient exothermic conversion of up to nine vibrational quanta into translational energy, while endothermic processes are observed to occur up to $\Delta v = 3$. Other charge-exchange reactions will be discussed, including the symmetric Ar^+ on Ar system as well as the non-symmetric reactions of the ^3P, ^1D, ^1S and ^5S states of N^- with N_2, CO, CO_2 and Ar.

Aspects of Molecular Photoionization

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Recent studies of molecular photoexcitation and ionization cross sections are reported. Detailed calculations of the complete dipole spectra in water and acetylene are presented, and comparisons made with measured values. Particular attention is focused on contributions to the calculated and measured spectra from virtual valence orbitals in these molecules. Calculated and measured outer-valence-shell cross sections in molecular nitrogen, oxygen, and fluorine are contrasted and compared, and the trends observed are clarified in an elementary fashion. Stieltjes orbitals constructed recently for molecular hydrogen and nitrogen are presented, and their use in clarifying the origins of strong spectral features illustrated. The effects of configuration mixing in molecular photoionization are exhibited by studies of inner-valence-shell cross sections in nitrogen, oxygen, and carbon monoxide. Finally, some indication is given of experimental and theoretical studies of molecular photoionization in progress in various compounds.

Pulsed Atomic Hydrogen Source

W.R. Gentry, C.F. Giese, R.D. Johnson

We have developed a pulsed atomic hydrogen source for use in crossed beam experiments. The hydrogen gas is partly dissociated by passing the pulse through a hot tungsten tube. The emerging gas has a speed of 8×10^5 cm/sec, a spread of 15% ($\Delta v/v$), an intensity of 5×10^{20} molecules/sr/s, and a pulse length of 90 μsec (FWHM). The ratio of atomic to total hydrogen is about .2.

The source consists of a pulsed valve with the nozzle replaced by a tungsten tube 1 inch long and .062 inches in diameter. The tube is heated by electron bombardment. A tungsten ribbon filament encircles the free end of the tube and is at a potential of 1000 V negative with respect to the tube. With the filament hot, a current flows between the tube and filament, heating the tube to 3100°C.

We are using this source to study the reaction of atomic hydrogen with chlorine, to give hydrogen chloride (in vibrationally excited states) and atomic chlorine.

New Applications of Classical Phase Space Pictures in Chemical Scattering

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The classical S-matrix for collinear scattering systems can be compactly represented with phase space pictures [1-3]. The continuing analytical usefulness of this approach is illustrated with two new applications. In the first, vibrational enhancement and inhibition in collinear collision-induced dissociation is elucidated and its model-dependence explained. In the second, the pictures provide an analogy between an atom-diatom scattering system with four semiclassical "root trajectories" and familiar diatomic Franck-Condon processes. Both examples demonstrate that the phase space pictures are a useful tool with which to compare and connect common theoretical models.

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PHOTODISSOCIATION DYNAMICS OF VAN DER WAALS CLUSTERS

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Recently, we have investigated the infrared photodissociation dynamics of van der Waals clusters of $(C_2H_4)_2$, $(C_2D_4)_2$, $(C_2H_4)\cdot(C_2D_4)$, $(OCS)_2$, $(OCS)_3$, Ar·OCS, $(CH_3OH)_2$, and $(CH_3OH)_3$ using a pulsed, line-tunable CO_2 TEA laser in combination with our pulsed molecular beam apparatus. A pulsed molecular beam source ($\sim$20 μsec fwhm) is operated with several atmospheres pressure of He or Ar seeded with a small amount (typically 0.1%-10%) of the desired monomer species. The source conditions are adjusted so as to maximize the concentration of the desired clusters while keeping the concentration of the interfering clusters low. The molecular beam pulse is collimated and crossed with the unfocused output of the CO_2 laser. Photodissociation is then detected as the laser induced change in the mass spectrum of the appropriate van der Waals cluster. Measurements of the attenuation as a function of laser pulse energy at fixed frequency suggest the dynamics are that of a single-photon absorption followed by rapid dissociation of the clusters into monomer fragments.

Attenuation of the molecular beam as a function of laser frequency at fixed laser energy yields the photodissociation spectra of the complexes. The peak absorption frequencies are close to those of the gas-phase monomers, with small shifts similar to those observed in liquids and solids of the same species. However, the observed linewidths are much wider than can be accounted for by either power broadening or rotational structure of the cluster. By using two lasers, one at a fixed frequency near the center of the absorption peak and the other scanning the absorption peak at fixed energy, it is possible to determine that the entire linewidth of the dissociation spectra must be due to homogeneous broadening. The broad bandshapes are characteristic of lifetime-broadened transitions, implying that the lifetime of the state excited in the cluster with respect to anharmonic intramolecular energy transfer and/or dephasing decays on a picosecond timescale.

Additional information on the dissociation process is provided by our measurements of the speed and angle distribution of the monomer products. From these data it is found that the average product translational energy is small, leaving most of the energy available to the products in internal excitation. The angular distribution is isotropic in center of mass coordinates implying the actual dissociation lifetime is longer than one rotational period(about 10^{-11}-10^{-10} seconds) of the excited cluster.

The Utility of the CS and IOS Approximations for Calculating Generalized Phenomenological Cross Sections in Atom-Diatom Systems

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The calculation of shear viscosity and thermal conductivity coefficients in the presence of a magnetic field requires the accurate calculation of several types of generalized phenomenological cross sections in which velocity and angular momentum tensors are coupled with the orbital and rotational motion of the system. These cross sections are then averaged over energy in a fashion appropriate for the phenomenon of interest. The coupled states (CS) and infinite order sudden (IOS) approximations have been used to calculate several such cross sections for systems such as He-HCl, He-CO, He-H_2, HD-Ne, and Ne-H_2. Excellent results are obtained compared with close coupled methods for cross sections which are symmetric in tensor index especially in the CS approximation and these results are not very sensitive to the choice of orbital wave parameter. On the other hand, the cross sections which are asymmetric in tensor index are much more sensitive to interference effects and are unsatisfactory in many cases. Furthermore, cross sections of this type may vary drastically depending on the choice of orbital wave parameter.

The Coupled Arrangement Approach to Electron-Hydrogen Atom Scattering

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Equations for the coordinate space wavefunction in a coupled arrangement scheme have been obtained. These can be shown to be formally equivalent to the T operator method of Kouri, Craigie and Secrest[1,2] but with define practical advantages. These equations, then form the basis of a numerically tractable scattering formalism including rearrangement. They have been explicitly formulated for the $e^- + H$ s-wave scattering system, and have been numerically solved for energies below the first excitation threshold using an expansion basis including only hydrogenic s-state functions. Sufficient size basis sets were used to obtain converged results with respect to this subspace at most energies considered.

The ^1S resonance reported by other workers[3] has been found in these calculations, and the resonance energy is in good agreement with earlier results. At very low energies the phase shift is not monotonic with energy, in disagreement with variational calculations.[4,5]

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A CLASSICAL PATH THEORY OF LASER-INDUCED CHEMIIONIZATION

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ABSTRACT

Miller's classical path theory of field free chemiionization is extended to laser assisted and laser enhanced processes. The heavy particle dynamical motion is treated classically while quantum mechanics enters only through its implicit involvement in the atomic interaction potentials and in the rates of the electronic transitions that occur, viz., photoexcitation, photoionization and autoionization. A number of special cases are considered, each of which illustrates a different mechanism for laser induced collisional ionization. Integral and heavy particle differential cross sections are obtained for these mechanisms.

THE DEVELOPMENT AND USE OF COMPUTER GENERATED EDUCATIONAL AIDS IN QUANTUM CHEMISTRY

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Recently a renewed interest has been expressed in several computer generated films[1] and charts[2] developed in the 1960's and 1970's as aids for teaching Quantum Chemistry. In this poster session these materials will be on display. Information concerning several contour hunting techniques and plotting equipment used will be presented. Also available will be relevant reprints which discuss the wavefunctions used in producing the contour diagrams. Also the conceptual and to some extent artistic role that these qualitative symbols played in formulating a chemically accurate model of diatomic molecular formation will be outlined.

Finally, experienced gained by a number of chemistry teachers in using these aids in their courses will be discussed.

1. Atoms to Molecules, Arnold C. Wahl and Uldis Blukis, McGraw-Hill, Inc. (A series of eight 8mm computer-based cassette film loops.) 1969-1974.

2. Wall charts on Atomic and Molecular Structure, Arnold C. Wahl and Maria T. Fernandez-Wahl, McGraw-Hill, Inc. (A set of large charts on atomic electron densities, covalent molecule densities, ionic molecule densities and diatomic molecule formation.) 1970.

GENERALIZED HARTREE-FORK THEORY FOR THE DESCRIPTION OF BOND FORMATION AND DISSOCIATION

by

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A self-consistent formalism is applied to the BCS Ansatz in the manner of Bogolyubov, Nambu, and Valatin. Particle nonconservation is incorporated with Lipkin's Hamiltonian. The result is a self-consistent formalism which properly describes bond formation and dissociation, and which admits a Feynmann-Dyson diagrammatic expansion. The latter is achieved using the Nambu matrix Green function. A Rowe-type equations-of-motion method may also be developed.

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