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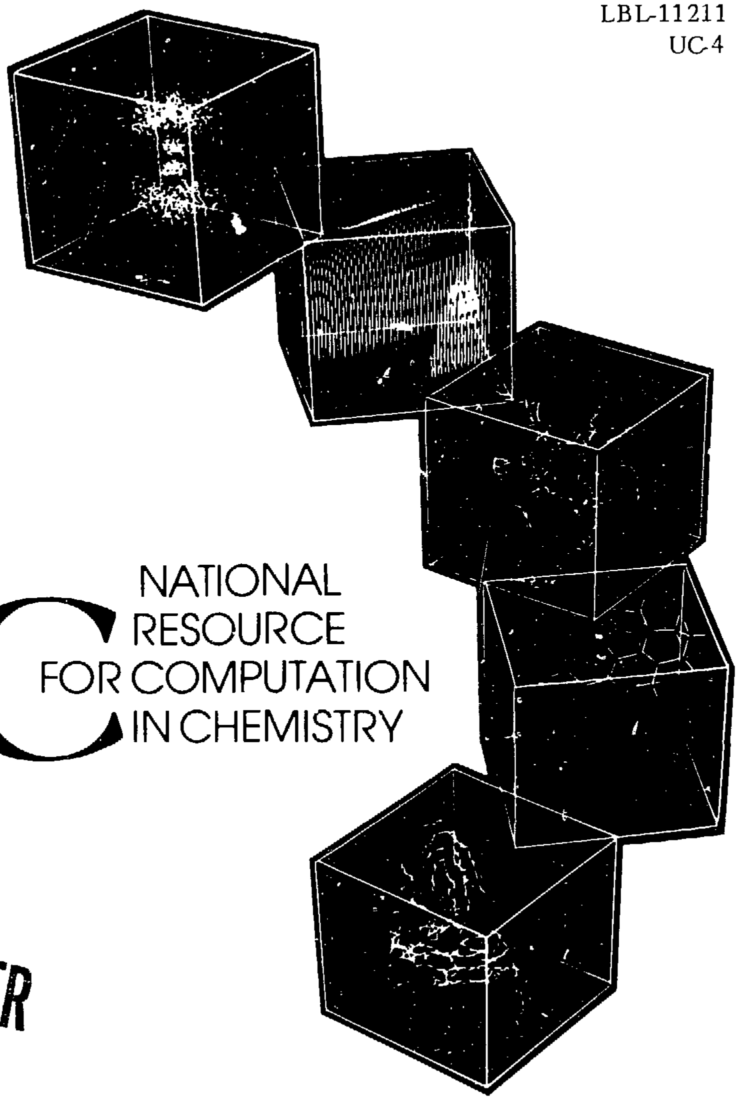

NRCC

NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY

MASTER

ANNUAL REPORT
1979

NOVEMBER 1980

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA

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LBL-11211

NRCC ANNUAL REPORT

1979

November 1980

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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FOREWORD

This annual report of the National Research for Computation in Chemistry (NRCC) Division describes the program of research workshops, software development, and scientific research of the Division in 1979. This year marked the first full calendar year of activity of the Division. Initial staffing in the core scientific areas was completed by the addition of a crystallographer.

The thrust of the effort in 1979 was directed towards establishing and extending the basic activities outlined in the NAS-NRC reports prepared by the committees chaired by K. Wiberg and by J. Bigeleisen. The year was one of vigorous activity directed towards demonstrating the utility of these programs in anticipation of a joint Department of Energy-National Science Foundation review to determine the future course of the NRCC scheduled for the Spring 1980. This report summarizes activities for the year in all areas.

William A. Lester, Jr.
Director, NRCC

INTRODUCTION

The NRCC was established to provide facilities and personnel dedicated to advancing chemistry and related sciences through widespread, intensive use of high-speed computational equipment. This mission is accomplished by making appropriate facilities available to a wide group of scientists, by providing and developing software to expedite and upgrade computer use, by encouraging and supporting research efforts to build new and more effective computational methods, and by carrying out an informational and educational program to bring the benefits created through the Resource to the widest possible scientific public.

At the National Academy of Sciences conceptual workshop on the NRCC in the summer of 1976, the participants agreed that the NRCC, in addition to providing major computing hardware, should provide the manpower needed to ensure that existing chemical computing software be made more efficient, accessible, and widely usable. Moreover, there was a commonly expressed desire to cooperate in the creation of needed software and to set up means to facilitate such cooperation across areas of chemistry and within them, as well as between chemists, numerical analysts, and computer scientists. Through workshops and other interactions among users, the NRCC should promote agreement, without stifling innovation, on unification, standardization, and on clarification of codes used in chemical computation, thereby making them more readily comprehensible and transferable. The NRCC should function catalytically to increase the productivity and long-term benefits of the present large investment in computational chemistry. Such a course of action is now in progress.

Many of the organizational and management requirements of the NRCC are similar to those that govern the use of high-energy accelerators and astronomical facilities. These include a Policy Board, a Program Review Committee, a User Association, and an administrative structure as part of the facility.

The responsibility for management resides with the Policy Board and an executive officer, the director, who is selected by the board. The Policy Board has the responsibility for determining the operating rules of the Program Committee, which is authorized to approve proposals for utilization of the NRCC and to recommend scientific priorities. The User Association consists of representatives from the group of outside users of the NRCC and from the resident scientific staff. It is patterned after similar groups associated with national laboratories and has an elected Executive Committee that implements the program of the association. It provides feedback to the NRCC on matching operations to user needs. The Association also provides a means for exchange of information between scientists both in and outside the NRCC.

TECHNICAL PROGRESS

Efforts for the year focused on the development of the research and educational functions of the NRCC through a vigorous workshop program and creation of the software library. A brief description of the progress arising from each of the workshops, the software library, staff research, and other activities follows.

Workshops Conducted in 1979

The workshops held in 1979 have focused on identifying and posing solutions to theoretical and computational problems in forefront areas where computation has or may have impact. Our experience shows that important considerations for a successful workshop of this type include a) identification of a timely topic, b) selection of a recognized leader in the subject area to help guide the development of the agenda and to identify active workers in the field to participate, c) detailed planning of the program in order to have focused discussion on the key items to be considered, and d) restriction of participants to those most likely to contribute, in order to maximize open discussion.

ALGORITHMS AND COMPUTER CODES FOR ATOMIC AND MOLECULAR QUANTUM SCATTERING THEROY

June 25-27, Part 1 at Argonne National Laboratory
October 26-27, Part 2 at the NRCC, Lawrence Berkeley Laboratory

Organizers: Prof. John C. Light, NRCC Program Committee and the
Department of Chemistry, University of Chicago
Dr. Lowell D. Thomas, NRCC

The purpose of this workshop was to identify algorithms and codes currently in use, test them against a fixed set of problems, and make the best of them available to the chemistry community through the NRCC software library.

At the Argonne meeting, participants discussed their algorithms and codes, decided on the test problems to be solved on the LBL computer, and were introduced to remote computing at LBL. In the four-month interval between meetings, eight individuals (or groups) working remotely, solved the test problems which were real three-dimensional systems taken from the current literature that proved to be quite demanding of all the programs. At the second meeting, a comparison of results from different codes revealed that further significant improvements could be made by producing true hybrid codes which incorporate two or more algorithms for use in different scattering regions. This was quickly accomplished and a resulting hybrid code, now available through the NRCC, is approximately a factor of two faster than any of the codes previously tested. Thus the workshop not only served to test existing codes, but led directly to the creation of a significantly superior code.

STOCHASTIC MOLECULAR DYNAMICS

July 9-11 at the National Academy of Sciences Woods Hole,
Massachusetts facility

Organizers: Dr. John Tully of Bell Laboratories
Dr. David Ceperley, NRCC

This workshop brought together 25 scientists involved in computer simulations of stochastic systems who discussed methods of ignoring solvent atoms in the simulation of a single molecule in a solvent. The simplest approach, which treats the solvent as an idealized heat bath, leads to the Langevin equation. The workshop focused on practical ways to generalize the Langevin equation, and on such applications as: the dynamics of chain molecules, vibrational relaxation in condensed phases, gas phase collisions and atom-surface scattering. At the final session on the role the NRCC might take in promoting the advancement of this area, the recommendation was made by some that the NRCC should have a first-rate simulation code. It was quickly pointed out by others that the NRCC had such capability in Ceperley's Classical Many Particle Simulation (CLAMPS) program which was already in the NRCC software library. Besides the CDC 7600, this computer code also has been adapted to the VAX 11/780, VAX 11/780 with array processor, and CRAY-1.

SOFTWARE STANDARDS IN CHEMISTRY

July 25-27 at the University of Utah, Salt Lake City

Organizers: Prof. Frank E. Harris and Dr. Nelson Beebe,
University of Utah
Dr. Arthur Olson and Dr. John Wendoloski, NRCC

Twelve quantum chemists, thirteen crystallographers and five computer scientists and applied mathematicians met to discuss and recommend standards for machine-independent, modular, documented software suitable for use on the large minicomputers that are rapidly becoming available to chemists. The crystallographers made several recommendations focused on demonstrating the feasibility of standardized programming systems and data formats through the NRCC's sponsorship of workshops to produce useful crystallographic code. They settled upon a specific preprocessor language and a set of program conventions and data file formats to be used in such pilot demonstrations. A workshop to develop software for macromolecular crystallographic studies was held 10-17 November 1979 at the NRCC (see Cooperative Computer Code Generation for Crystallography, below). The quantum chemists drafted a list of program types and program capabilities which should be included in a software base. They also prepared a preliminary draft of a standard data interface for this software base. They also proposed the formation of a committee composed of authors of major quantum chemistry systems such as GAUSSIAN 7X, ALIS, and MUNICH to make final recommendations on a standard data interface within a year. (A meeting of the data interface committee was held at the NRCC on 15-17 January 1980 organized by Dr. Stanley Hagstrom of the NRCC.)

COMPUTATIONAL METHODS FOR MOLECULAR STRUCTURE DETERMINATION: THEORY AND TECHNIQUES

August 13-24 at the Chemistry Department of Indiana University,
Bloomington

Held jointly with the Quantum Chemistry Program Exchange.

Forty-five participants from academe, industry, and government attended lectures on the theoretical foundation of molecular structure determination, presented by Profs. Norman L. Allinger, Ernest R. Davidson, William A. Goddard, John A. Pople, Michael Zerner, and Dr. Bowen Liu. Remote interactive access to the Lawrence Berkeley Laboratory CDC 7600 was provided in order to give the participants hands-on experience with the NRCC-QCPE software. Fifteen terminals as well as a remote job-entry station were effectively utilized by the participants both to familiarize themselves with the software and to examine molecular systems of chemical interest.

COOPERATIVE COMPUTER CODE GENERATION FOR CRYSTALLOGRAPHY

November 10-17 at the NRCC, Lawrence Berkeley Laboratory

Organizers: Dr. Steven Freer, University of California, San Diego
Dr. Arthur Olson, NRCC

As a direct result of the workshop on software standards held in Salt Lake City in late July, the NRCC initiated a pilot project to develop portable crystallographic software. The crystallographers present at the Utah conference recommended that the NRCC sponsor the development of a code that has a standard data format and is portable from computer to computer. In order to demonstrate the feasibility of the idea, the NRCC held this workshop at which ten invited scientists came together in order to develop and code a multiple isomorphous replacement (MIR) program for distribution among crystallographers. The MIR code, which is used for the phasing of macromolecular structures, was developed on the NRCC's VAX 11/780 and will be tested on other computers to insure its portability. The success of such a project could signal the beginning of a new era in program exchange among computational chemists.

The NRCC is a catalyst for successful workshops because of the involvement of the Policy Board, Program Committee, and in-house staff. Both the Policy Board and the Program Committee make recommendations that guide the selection of workshop topics, leaders, and speakers. The in-house staff bring their expertise to bear on appropriate aspects of workshop planning and implementation. They work with conference coordinators both at LBL and remote sites, and assist in the development of workshop proceedings as technical advisors and as liaison between the NRCC and the LBL Technical Information Department, which publishes the proceedings. The NRCC also has access to the expertise of the LBL support divisions which made possible the remote access computing capability that had such a major role in the success of the novel instructional workshop on molecular structure determination. The NRCC's workshop program is not duplicated by any other organization or agency.

Software

In 1979 the base of the NRCC Software Library was established in the major computational chemistry areas of chemical kinetics, crystallography, macromolecular science, physical organic chemistry, quantum chemistry, and statistical mechanics. Considerable effort went into the preparation of user documentation for the programs. The staff in physical organic and quantum chemistry in particular, concentrated on the development of user documentation and in making most programs in their areas operational for remote use in August in preparation for the molecular structure determination workshop. Similarly, the software in chemical kinetics received special attention because of the workshop on quantum scattering theory. The participants in this workshop agreed to make their codes available for use by others in the course of carrying out the test problems as discussed in the previous section. A listing of NRCC computer programs is contained in the 1979 NRCC Bulletins. Future listings of NRCC software will be found in the NRCC Software Catalog. The first edition is now available upon request.

The NRCC has also developed a software classification policy describing the level of staff support that may be expected for troubleshooting and other assistance on software library holdings.

Many inquiries are received from scientists desiring to carry out computations who are not well informed about the most appropriate methods and software packages to use for a particular application. Because of their scientific backgrounds, and their experience gained in bringing up the software, the staff is able to provide this assistance on a regular basis. Such support is not available, to our knowledge, from any other facility in the world for such a broad range of chemical applications.

The staff has implemented a software distribution system that greatly facilitates responding to requests and can be handled by a technical assistant. We believe that as the quality of our service and assistance becomes better known in the chemistry community, we will see increased interest and activity related to the software library.

It should be noted that the software base for the library is predominantly derived from code made available by workers elsewhere. The interaction of in-house staff with the originating groups has engendered rapid improvements, better testing, and improved user documentation. In some instances, the presence of an in-house staff has made possible the first general accessibility of codes from outside research groups.

Although the focus during the planning stage of the NRCC was primarily on software for large mainframes, the recent change in computing patterns in the U.S. chemistry community with the advent of minicomputers dictated that the NRCC also adapt programs for these smaller machines. The NRCC is now receiving inquiries and requests for software it has modified to run on the VAX. Because of the close similarity of the VAX to IBM equipment, this effort has the immediate benefit of facilitating the removal of non-portable features of the codes.

The successful instructional workshop on computational techniques for molecular structure determination could not have taken place without the existence of the software library.

Cooperative Programs

National Theoretical Effort on Combustion

A collaborative research effort on the chemistry of combustion has been launched by an association of scientists of the nation's leading national laboratories and universities. The participants agreed to pursue a course of research to elucidate the electronic structure and collision dynamics of a system of reactions involving carbon, hydrogen, and oxygen. This extensive and intensive theoretical examination of a processs which is basic to the production of energy will be coordinated by the NRCC.

Two meetings have been held to date. The first meeting on June 28, 1979 at Argonne National Laboratory, and the second on October 9, 1979 at Brookhaven National Laboratory. The issues discussed included:

- What reactions, or classes of reactions, are of general importance in combustion systems?
- What can theoretical studies contribute to the understanding of these reactions?
- How can the participants organize their research programs to ensure that these problems are properly addressed?

At the first meeting the participating scientists resolved to study reaction prototypes, such as CH_n+O, in their search for general principles of importance in all hydrocarbon processes.

Daresbury Laboratory Interactions

A complementary organization to the NRCC has been established by the Science Research Council (SRC) of England, through the Daresbury Laboratory, called the Collaborative Computational Projects (CCP) under the direction of Prof. P. G. Burke. The major aim of this project is to bring together scientists from several different universities and research groups to:

1. Provide for the rapid interchange of information on theory, algorithms, and computer codes;

2. Collect, maintain, and develop relevant items of software;

3. Encourage basic research in the given areas by providing facilities for rapid computer implementation of new methods and techniques;

4. Assess and advise on associated computational needs;

5. Disseminate information among university and other research groups by organizing symposia or workshops.

Recently the SRC and the National Science Foundation (NSF) agreed to support reciprocal visits between NRCC personnel and Daresbury and collaborating university staff. The purpose of these visits is the exchange of relevant computer codes and information on computational techniques.

During June and the first part of July 1979, Dr. Victor Saunders visited the NRCC as part of a staff and software exchange program between the Theory and Computational Science Division of Daresbury Laboratory, England. This Division of the Daresbury Laboratory has a mandate similar to the NRCC's in a number of areas. During his visit Dr. Saunders installed the ATLMOL3 system of programs on the LBL CDC 7600. ATMOL is a sophisticated system for carrying out molecular Hartree-Fock calculations of various types using s, p, and d-type Gaussian and Slater basis orbitals. The system is laboratory documented. ATMOL also runs on IBM systems, for which a CI extension (called SPLICE) based on the bonded function approach of Sutcliff also exists.

Dr. Brian Buckley, Daresbury Laboratory, visited the NRCC for two weeks in September. During this period he adapted the R-matrix program, RMATOM, of Berrington, Burke, LeDourneuf, Robb, Taylor and Vo Ky Lan to the LBL CDC 7600. RMATOM is a suite of three programs for performing electron-atom, electron-atomic ion and atomic photoionization cross section calculations and atomic frequency-dependent polarizability calculations using the R-matrix methods. Extensive modifications were necessary to implement the software here. We are grateful to Dr. Buckley for carrying out this task.

In May and June of 1979, Dr. Stanley Hagstrom, of the NRCC, spent six weeks at the Daresbury Laboratory under the same exchange program. During this visit Dr. Hagstrom installed several NRCC computer codes on Daresbury computers.

CECAM Interactions

The Centre European de Calcul Atomique et Moleculaire (CECAM) (The European Center for Atomic and Molecular Calculations) located on the campus of the Universite de Paris Sud, began operation in October 1969 under the direction of Dr. Carl Moser. The purpose of the Centre is to encourage international cooperation in the theoretical and computational aspects of different problems in physics, chemistry, and biology which are of such complexity that advances will likely occur in these fields from bringing together a number of specialists. This is done in three ways:

1. The organization of two- to three-day discussion meetings involving both theorists and experimentalists to attempt the delineation of problems and to discuss the desirability and feasibility of workshops;

2. The organization of four- to eight-week workshops to help initiate new collaborations and projects in defined areas. It is anticipated that the collaborations so started will continue after the workshop period; and

3. The support of occasional individual visitors to Orsay for periods of three months to a year.

In 1979, CECAM and the NRCC agreed to participate in two workshops, one of these was held in France at CECAM and the other in the United States. The workshop designated for joint participation in France was "Simulation of Enzyme Catalysis," which was organized by Drs. P. Th. van Duijen and W. G. J. Hol, Laboratorium voor Chemische, Fysica Chemische Laboratoria der Rijksuniversiteit, Nijenborgh 16, 9747 AG Gronigen, and was held July 2-August 16, 1979. The United States workshop was held jointly with the Quantum Chemistry Program Exchange (QCPE), and was entitled "Computational Methods for Molecular Structure Determination: Theory and Technique," August 13-23, 1979.

Collaborating in the program are 14 quantum chemists and collision theorists supported by the Office of Basic Energy Sciences of the U.S. Department of Energy at Argonne, Brookhaven, Ames, Sandia Livermore, Lawrence Berkeley Laboratories, Princeton University, and the University of California, Berkeley.

RESEARCH BY NRCC STAFF

In 1979 the NRCC grew into a fully operational research organization with the assembly of a multidisciplinary scientific staff of computational chemists. The research areas represented by this core staff of eight scientists include: collision dynamics, crystallography, macromolecular science, quantum chemistry, physical organic chemistry, and statistical mechanics. During the year much of the scientific staff effort was devoted to laying the groundwork for the service and educational functions of the NRCC. This work included the development of the NRCC software library, organizational efforts for NRCC workshops and publications, and consultation for NRCC users and grant awardees. In addition to these activities the scientific staff was able to initiate and carry out research on significant problems in several areas of computational chemistry. The major thrust of the research undertaken at the NRCC has dealt with improving, extending, and developing new methodologies to solve chemical problems through the application of computational technology.

Collisions Dynamics

The focus of research in collision dynamics has been on the inelastic collisions of atoms and molecules. The work falls into three categories:

1. The calculation of inelastic collision cross sections for specific systems. He-CO and Li^+-CO have been studied. Rotational excitations of CO are of fundamental importance in the study of interstellar molecular clouds and much attention has been given in recent years to the He-CO system. Experimental data are available for Li^+-CO collisions and calculations have been done for comparison.

2. The interpretation of rainbow scattering in inelastic atom-molecule collisions. The rainbow structures are very sensitive to the anisotropy of the potential energy surface and hence the theoretical development of them is of fundamental importance to the interpretation of the experimental data.

3. The development of improved numerical methods for quantum mechanical, inelastic collision cross-section calculations. Common to almost all quantum mechanical studies of state-to-state chemistry, whether they are elastic, inelastic or reactive collisions, whether exact or approximate methods are used, is the solution of coupled sets of second-order, differential equations. Improvements in the numerical methods will benefit a broad range of chemical studies.

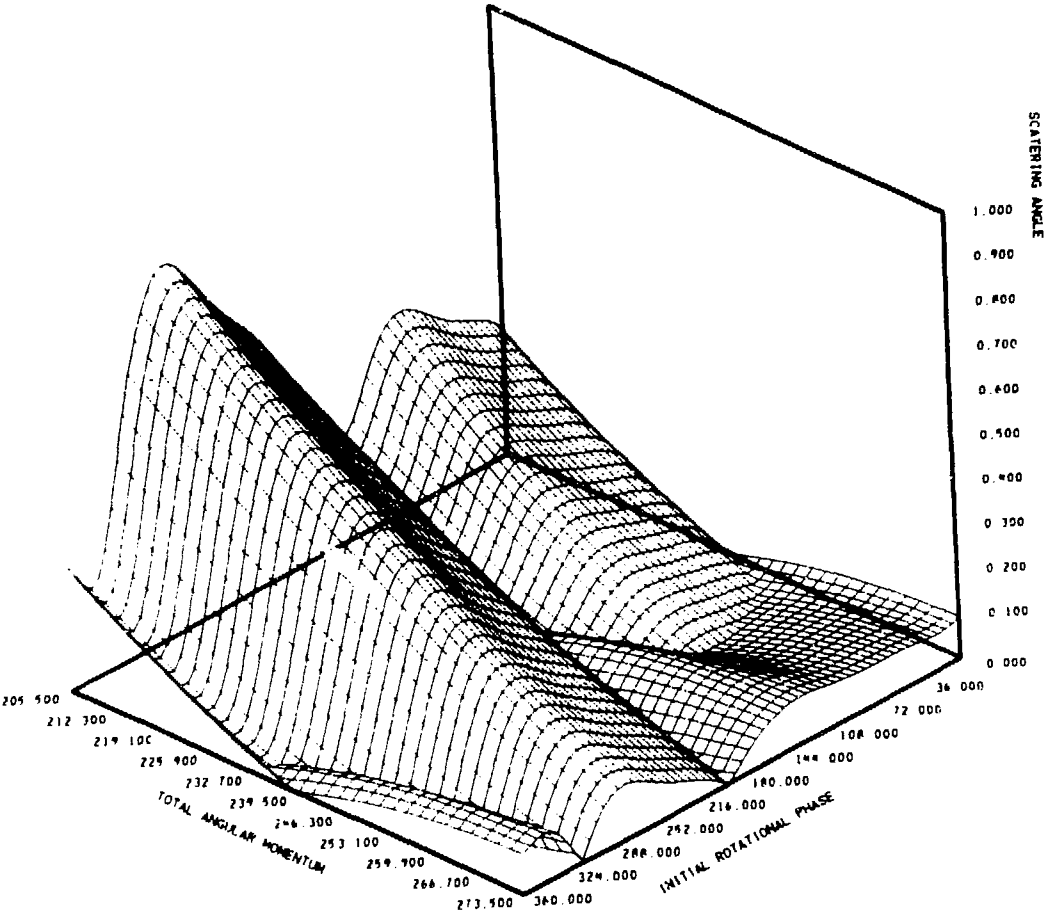

Figure 1. Three-dimensional plot of the classical scattering angle vs the independent trajectory variables for Li^+-CO scattering. Contours of constant scattering angle can be found for any angle by cutting this surface with a plane parallel to the plane of initial trajectory variables. This in turn is used to locate the rotational rainbows.

1. ROTATIONAL EXCITATIONS OF CO BY HE

L. D. Thomas, W. P. Kraemer and G. H. F. Diercksen

Rotational excitations of CO are important in the study of interstellar molecular clouds and much work has been done in this area. W. P. Kraemer and G. H. F. Diercksen (Max-Planck-Institute for

Astrophysics, Munich) have computed a configuration interaction (CI) potential energy surface for the He-CO interaction using a large orbital basis set. A collision study has been done to test the sensitivity of the computed rotational excitation cross sections to the accuracy of the potential energy surface. Converged close coupling calculations have been done on the Kraemer-Diercksen surface and on several other less accurate surfaces. On the most accurate surface, cross sections were also calculated in the infinite-order sudden (IOS) approximation and with the Monte Carlo, quasiclassical method.

The converged close coupling inelastic cross sections computed using the CI and electron gas surfaces showed differences of up to 200 percent. A change of orbital basis set for the CI surface produced differences of up to 30 percent. The differences between the cross sections computed following close coupling, IOS and quasiclassical formalisms using the CI surface were in the range 0-60 percent. A manuscript describing this work has been accepted by Chem. Phys.

2. THE USE OF PRESSURE BROADENING DATA TO ASSESS THE ACCURACY OF CO-HE INTERACTION POTENTIALS

S. Green and L. D. Thomas

Pressure broadening cross sections were computed for an electron gas surface and the Kraemer-Diercksen CI surface for He-CO. These were then compared to experimental data. The comparison indicated that pressure broadening cross sections are not very sensitive to changes in potential energy surface. Both potentials predict essentially the same result for room temperature broadening of the 0 → 1 rotational transition. However, with decreasing temperature the electron gas potential yields an increase in the pressure broadening cross sections whereas the CI potential results in a slight decrease. In both cases, however, the temperature dependence changes by only a few percent, and both surfaces yield pressure broadening cross sections that lie within the experimental error limits. A manuscript has been submitted to J. Chem. Phys.

3. LOW ANGLE SCATTERING OF Li^+ BY CO

L. D. Thomas, W. P. Kraemer and G. H. F. Diercksen

A classical trajectory study of rotational excitation of the Li^+-CO system was carried out to assist analysis of recent low-angle experiments. The center-of-mass cross sections were transformed to the laboratory frame and compared directly to the time-of-flight spectrum. The rotational rainbow structure in the classical cross sections cannot explain the structure observed in the experiment. This result indicates that strong quantum mechanical interference effects may play a dominant role in rotational rainbow structures. A manuscript has been submitted to Chem. Phys. Lett.

4. RAINBOW SCATTERING IN INELASTIC MOLECULAR COLLISIONS

G. Zahr and L. D. Thomas

In a related study of the Li^+-CO system, semiclassical calculations, which do show quantum mechanical interferences, have been done for coplanar scattering and compared to the classical results. It has also been shown that the classification of rotational rainbows commonly used in the literature has no theoretical justification, and a correct classification scheme has been presented. A letter to J. Chem. Phys. has been submitted for publication.

5. NUMERICAL METHODS FOR QUANTUM MECHANICAL COLLISION DYNAMICS

L. D. Thomas

Over the past 15 years there has been a proliferation of numerical methods developed for solving the coupled, second-order differential equations of molecular scattering theory. Over 20 methods are commonly discussed in the literature. The NRCC sponsored a workshop for the purpose of identifying what computer codes are available, testing them against a set of test problems, and making the best of them available to the scientific community.

Ten different methods for solving the coupled equations of inelastic molecular collision theory have been tested against a fixed set of test problems. Analysis of the results has led to the development of a new hybrid program which performs significantly better than any of the individual methods tested. This was a collaborative effort involving M. H. Alexander, B. R. Johnson, W. A. Lester, Jr., J. C. Light, K. McLenithan, G. A. Parker, M. J. Redmon,

T. G. Schmalz, D. Secrest, L. D. Thomas, and R. B. Walker. The results of this study will be published in the Journal of Computational Chemistry.

6. AN ITERATIVE METHOD FOR A SINGLE COLUMN OF THE S-MATRIX

L. D. Thomas

Recently a new method, not tested in the NRCC workshop, was developed by L. D. Thomas for computing a single column of the matrix of transition probabilities. The savings in numerical effort by computing only a single column allows one to solve much larger systems of equations. The method has already been used to solve a problem twice as large as the largest problem solved previously by standard methods.

Improvements to this new method have been developed which hold the promise of a 10-fold increase in the size of the problems which can be treated. The method is based on integral equations and a new algorithm has been developed which uses a matrix Green function in the kernel. A stable numerical method for calculating the matrix Green function has also been developed. This will allow exact quantum mechanical collision studies of atomic and molecular systems which can currently only be studied by approximate methods.

7. PROTON - H_2 SCATTERING ON AN *AB INITIO* CI POTENTIAL ENERGY SURFACE: VIBRATIONAL EXCITATION AT 10 eV

R. Schinke*, M. Dupuis, and W. A. Lester, Jr.

Recent computations of vibrational-rotational excitation cross sections for the H^+-H_2 system deviated significantly from highly resolved experimental data at a collision energy of 10 eV. Previous theoretical investigations of proton-H_2 scattering used the Giese-Gentry (GG) potential function. Concerns regarding the adequacy of the GG surface for describing vibrational motion of the system prompted reexamination.

A complete configuration interaction (CI) ground state surface for the H_3^+ system has been calculated using 5S and 3(P_x, P_y, P_z) basis functions at each center. A total of 650 nuclear geometries has been considered which makes the new surface appropriate not only for scattering calculations, but also for the evaluation of the vibrational-rotational spectrum of the H_3^+ molecule. Vibrational-rotational excitation cross sections have been calculated in the rotational sudden approximation which treats the vibrational degree of freedom exactly by solving seven vibrationally coupled radial equations. The use of the new surface leads to increased vibrational excitation compared to previous calculations utilizing the same scattering formalism and angular distributions in excellent agreement at 10 eV with the measurements of Hermann, Schmidt, and Linder.

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8. COUPLED-CHANNEL STUDY OF HALOGEN (^2P) + RARE GAS (^1S) SCATTERING

C. H. Becker,*† P. Casavecchia,*‡ Y. T. Lee,* R. E. Olson,§ W. A. Lester, Jr.

Quantum mechanical coupled-channel (CC) scattering calculations were performed using realistic adiabatic potentials for the ^2P + ^1S interaction of F-Ar, F-Xe, and Cl-Xe. Differential cross sections $d\sigma/d\omega$ derived from a simple elastic approximation appropriate for large spin-orbit interactions accurately reproduced all the gross features computed by the coupled-channel method. This finding supports the extraction of interaction potentials from laboratory differential cross sections $I(\theta)$ via an elastic analysis. Integral inter and intramultiplet changing cross sections were expressed conveniently in terms of Grawert's $B(j,j';g)$ coefficient. Information on the collision dynamics was extracted by following the partial wave dependence of selected $B(j,j';g)$. Classical turning point analysis, based on the values of the large ℓ-waves for which these partial wave contributions $B_\ell(j,j';g)$ begin to rise above zero, led to the conclusion that both intermultiplet and first-order forbidden intramultiplet transitions were caused by a single localized nonadiabatic coupling region at the position of complex crossing of the $\Omega=1/2$ adiabatic potentials. Small amplitude oscillations or perturbations in the CC calculated $d\sigma/d\omega$ and in the experimental $I(\theta)$ are thought to be examples of Stuekelberg oscillations, though quantitative agreement between these quantities was not obtained. The energy dependence and interference structure of the computed $B(j,j;g)$ were explored, as was the approximation of constant spin-orbit interaction over the experimentally accessible range of internuclear distances.

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Crystallography

Crystallographic research at the NRCC has focused in the area of macromolecular structure determination and interpretation. The application of diffraction techniques in this realm has grown dramatically in the past decade and is demanding increasing computer resources. The computational methodology used in analysing molecular structures of this size is still very much in the development stage. By concentrating effort on virus structure — among the largest crystallographic problems yet to be undertaken — not only will important information be gained about basic molecular biological processes but also new computational techniques will be developed that will have considerable impact on future crystallographic investigations that are at the frontier of structural knowledge.

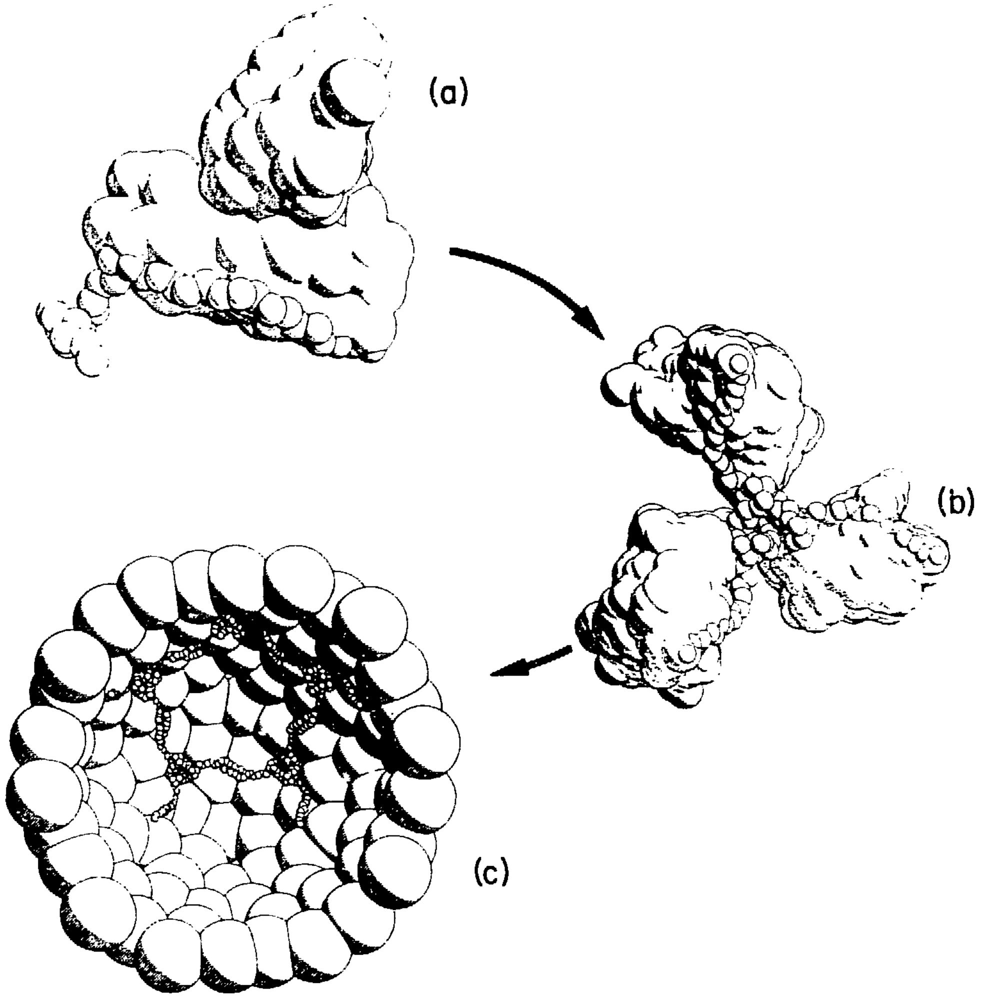

Figure 2. Computer generated drawings representing three aggregation states of tomato bushy stunt virus. (a) View of a single viral coat protein molecule. (b) View of three coat protein molecules linked together. (c) Cut-away view showing interior surface of completely assembled protein coat which contains 180 protein molecules — 90 shown in this view. (XBL 8010-12284)

1. INTERPRETATION OF MACROMOLECULAR STRUCTURAL ASSEMBLIES

A. Olson

Crystallographic research has been, since its inception, one of the most computationally intensive branches of experimental chemistry. Present crystallographic techniques allow investigation of macromolecular structures such as proteins and nucleic acids. Analyses of structures of this size present very demanding tasks to the crystallographer. The interpretation of complex structural information is one task that can be greatly facilitated by the appropriate scientist-computer interface. Work is presently underway at the NRCC to develop graphical methods for examining assemblies of macromolecular structures.

The atomic level interpretation of supra-molecular aggregates such as viruses, multi-subunit enzymes, and organelles, is critical to a detailed understanding of fundamental cellular processes such as self-assembly, regulation and recognition. Work has been initiated to develop software for a highly interactive vector refresh graphics device interfaced to the NRCC's VAX 11-780 computer. The emphasis of this developmental work is on general methods for generating symmetry related elements of assemblies (both crystallographic and non-crystallographic), and techniques for the most effective representation and analysis of intermolecular contacts and the global structures resulting from assembly.

2. THE STRUCTURE OF TOMATO BUSH STUNT VIRUS AT 2.9 ANGSTROMS RESOLUTION

A. Olson and S. Harrison

The structure of tomato bushy stunt virus (TBSV) has now been solved to near atomic resolution.[1] By several measures this is the largest crystal structure to be solved to date (600,000 daltons in the crystallographic asymmetric unit, 383 angstrom cubic unit cell axis). Work is presently underway on the refinement and interpretation of the structural results. The size of the structure necessitates new developments in the techniques of structure interpretation. Concurrent work is proceeding along these lines.

As analysis progresses, we are learning more about the nature of flexibility of proteins in supra-molecular assemblies. In the TBSV structure, 180 chemically identical proteins pack to form the icosahedrally symmetric coat of the virus particle. As a result of the particle geometry, the proteins occupy three distinct symmetry environments. Important structural and functional differences exist between the three distinguishable versions of the coat protein molecule. The virus structure thus gives three distinct pictures of the same molecule, and shows the flexibility that has been built in by evolution to enable the process of self-assembly. Work is continuing on the complete analysis of structural differences shown in the coat protein and on the nature of the protein-protein interfaces.

Reference

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3. PORTABLE CRYSTALLOGRAPHIC CODE, MULTIPLE ISOMORPHOUS REPLACEMENT PHASING

A. Olson

There has been a great deal of duplicate time and effort spent in individual laboratories implementing complex programs written elsewhere. Even within a single laboratory, when a computer has been changed, much work has gone into revising working programs to enable them to run in the new environment. A pilot project in portable crystallographic code generation has been undertaken at the NRCC in order to help alleviate this burden from the individual research groups. By bringing concepts of computer science to bear on problems of chemical computation, we can simplify both the process of program generation and utilization.

A cooperative crystallographic code project involving ten scientists[1] has produced a new multiple isomorphous replacement (MIR) program for the phasing of macromolecular crystal structures. Because the programming system, XTAL80, and the preprocessor language, RATMAC, that were used are modular as well as portable, the participants were able to develop the code in a short time by effectively working in parallel. In addition, the program structure allowed two distinct algorithms for MIR phasing[2,3] to be easily incorporated into the same program with little additional overhead.

References

1. The participants were: Richard Alden and Steven Freer, University of California at San Diego; Robert Munn and James Stewart, University of Maryland; George Reeke, Jr., Rockefeller University; Steven Sheriff, University of California at Los Angeles: Jurgen Sygush, University of Sherbrooke, Canada; Lynn TenEyck, University of Oregon; Keith Watenpaugh, University of Washington; Sid Hall, University of Western Australia; and Arthur Olson, NRCC.

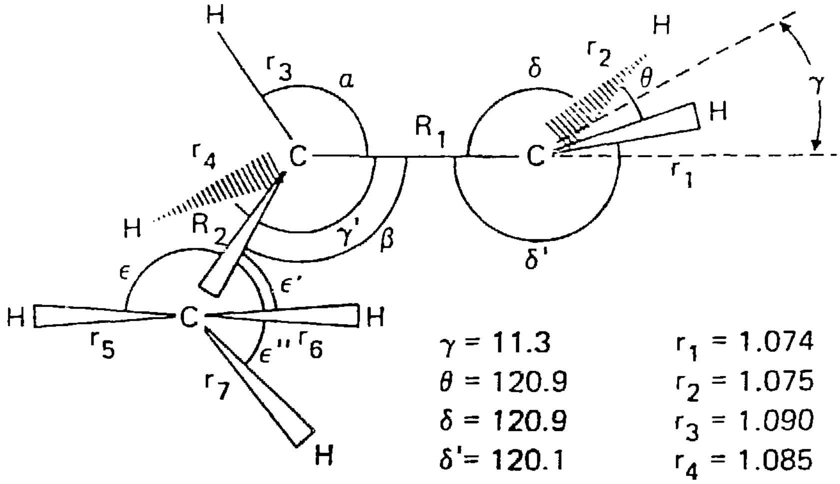
2. F. TenEyck and A. Arnone, J. Mol. Biol., Vol. 100, pp. 3-11 (1976).

3. Sygush, Acta Cryst., Vol. A33, pp. 512-518 (1977).

Quantum and Physical Organic Chemistry

Research activities in quantum chemistry at NRCC fall into the general areas of methodology and applications. The methodology studies are concerned with applied mathematical problems (e.g., integral evaluation, diagonalization, science problems (sorting, operations on large randomly sparse matrices), and with various high-level computational models for studying real chemical systems (Hartree-Fock, Generalized Valence Bond, Configuration interaction). The goal in developing these new methods is to both increase the efficiency of existing calculations and extend the scope of chemical applications that can be studied by quantum chemical techniques.

In the applications area, a number of real chemical systems are under active investigation ranging from simple atoms to large molecular complexes and reaction intermediates. In addition to providing data about the chemical system which may be useful in experimental identification and problem design, applications to real systems increase understanding of the chemical models employed. A more detailed presentation of the activities is given below.



$\gamma = 11.3$

$\theta = 120.9$

$\delta = 120.9$

$\delta' = 120.1$

$\alpha = 110.0$

$\alpha' = 109.2$

$\beta = 113.6$

$\epsilon = 110.8$

$\epsilon' = 111.22$

$\epsilon'' = 110.9$

$E = -117.463447$ a.u.

$r_1 = 1.074$

$r_2 = 1.075$

$r_3 = 1.090$

$r_4 = 1.085$

$r_5 = 1.083$

$r_6 = 1.083$

$r_7 = 1.082$

$R_1 = 1.499$

$R_2 = 1.531$

Figure 3. Calculated conformation of the n-proply radical (4-31G basis set). (XBL 8010-12283)

1. SOFTWARE FOR THE DIAGONALIZATION OF SYMMETRIC MATRICES

D. Spangler and C. Moler*

The diagonalization of symmetric matrices has often represented a considerable portion of the effort required to computationally investigate chemical systems. In certain problems in quantum chemistry and in chemical kinetics, the diagonalization is the most time-critical process. For instance, in the performance of semi-empirical calculations on large systems, as much as 80 percent of the computer time is consumed in this operation. To address the problem of diagonalization, the subroutine GIVENS was written by Franklin Prosser of Indiana University in the early 1960's and has become a standard in theoretical chemistry. Since then, several variants have been developed and propagated. Also, significant improvements in both the matrix diagonalization algorithms and in their software implementation have been incorporated in EISPACK, a large collection of FORTRAN subroutines, most of which are translations of the efficient ALGOL procedures developed by J. H. Wilkinson and his colleagues.

The goal of this study was the elucidation and development of a program that meets the following criteria: 1) the computational effort is minimized, 2) the resulting eigenvectors are highly accurate and orthogonal to each other, 3) the computer memory requirements are limited, and 4) the software is highly portable and machine requirements clearly specified.

The diagonalization of a symmetric matrix can readily be divided into two sections: 1) finding the eigenvalues, and 2) finding the eigenvectors. To find the eigenvalues, the matrix is first reduced to tridiagonal form using Householder transformations and second reduced to diagonal form using the QR algorithm. There are two major algorithms for finding the eigenvectors. 1) the QR method -- accumulation of the transformations used by the QR algorithm, and 2) inverse iteration — solution of a system of equations to determine the eigenvectors of the tridiagonal matrix and then backtransformation to produce the eigenvectors of the original matrix.

To compute all the eigenvectors, the QR method (the suggested method in EISPACK), requires of the order of 16/3 N^3 operations where each operation includes one floating point multiply, one floating point add, a fetch from memory, a store to memory, and some indexing operations. The inverse iteration method (which is used by GIVENS) requires of the order of 8/3 N^3 operations. Therefore, inverse iteration is clearly faster. However, care must be taken in the production of the eigenvectors to guarantee orthogonality between eigenvectors.

To take advantage of the speed of inverse iteration while maintaining eigenvector orthogonality, a new program called GIVEIS was developed. First, the inverse iteration path through EISPACK was selected. This involved using the EISPACK subroutines TRED3, IMTQLV, TINVIT, and TRBAK3. Second, branching operations were eliminated in critical loops to increase efficiency. Thirdly, calls to the Basic Linear Algebra Subroutines SDOT and SAXPY were inserted in place of time critical vector operations. Since these FORTRAN callable subroutines are written in assembly language for many machines, they are portable and achieve a large increase in speed.

To test the loss of orthogonality for inverse iteration versus the QR method, a matrix was devised that would produce arbitrarily close eigenvalues. For this matrix, the subroutine GIVENS lost 8 places of orthogonality with respect to the more stable QR method while the subroutine GIVEIS lost only 2 places of orthogonality. At the same time, for a 150 X 150 matrix the GIVEIS subroutine took only half the time that either the QR method or GIVENS required. Therefore, this new subroutine should replace either of the two currently used subroutines. Also, because of the portable nature of the EISPACK subroutines, GIVEIS should be easily convertible to any computer with only small adjustments in machine dependent parameters.

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2. THEORETICAL STUDY OF C_2 AND C_2

M. Dupuis and B. Liu*

Traditionally electron affinities (EA) have been difficult to calculate accurately by *ab initio* methods as the energy difference between the neutral and negative species. The purpose of this study was to determine what level of computational effort is necessary to calculate accurately the EA of C_2 and similar molecules.

Potential energy curves of the ground states of $C_{\bar{2}}(X^1\ \Sigma_g^+)$ and $C_{\bar{2}}(X^2\ \Sigma_g^+)$ have been calculated using SCF, MCSCF and CI methods. Close agreement with experimental dissociation energies, bond lengths, and spectroscopic constants is obtained by a CI calculation including all single and double excitations from the restricted Hartree-Fock configuration, with corrections for the quadrupole excitations estimated by a formula due to Davidson. The restriced Hartree-Fock method overestimates the electron affinity of C_2, giving a value 4.33±0.02 eV, which is to be compared with the experimental value of 3.54±0.05 eV. The effect of higher excitations on the calculated electron affinity has been investigated, and some general conclusions regarding the computation of molecular electron affinity have been drawn.

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3. AB INITIO STUDY OF ALKYL RADICALS: THE N-PROPYL AND ISOPROPYL RADICALS

J. Pacancky* and M. Dupuis

The matrix isolation technique coupled with infrared spectroscopy has increased the understanding of the molecular structure of reactive species. Ab initio techniques may help in the determination of molecular structure and normal coordinate analysis of organic radicals. With these calculations and the infrared spectra, it was intended to obtain a consistent analysis of the structure and dynamics of radicals larger than those normally encountered in low temperature matrices.

Ab initio calculations were carried out for three possible conformations of the n-propyl radical. The completely optimized geometry and total energy for each conformation was found by using the gradient method. The theoretical results show that the conformations are energetically very close to each other. This agrees with experimental studies on the n-propyl radical in rare gas matrices but disagrees with experiments performed in solutions.

Calculations were performed on seven conformations of the isopropyl radical. For each conformation all of the geometric parameters were optimized using the gradient method. The calculations show that the planarity of the radical center and the potential energy required to distort the radical is quite different for each conformation although the conformations are separated from each other by very small differences in energy.

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4. AB INITIO QUANTUM MECHANICAL CALCULATIONS: THE HONDO PROGRAM

M. Dupuis, D. Spangler, J. Wendoloski

HONDO is a computer code written for *ab initio* quantum mechanical calculation. Originally the code featured the Rys quadrature method, an algorithm specially efficient for high angular momentum basis functions, for the computation of the ubiquitous electron repulsion integrals.

Over the past year new capabilities have been incorporated into the code. The goal is to set up a general program for molecular structure determination using wavefunctions of various accuracy. The present features of the program are:

a. Use of cartesian gaussian functions of s, p, and d-type.

b. Calculation of closed-shell Hartree-Fock wavefunctions, restricted open-shell Hartree-Fock wavefunctions,* spin unrestricted Hartree-Fock wavefunctions, and generalized valence bond perfect pairing wavefunctions.*

c. Calculation of CI wavefunctions using the Graphical Unitary Group Approach (GUGA)[1] computer code of *Schaefer, et al.**†

d. Calculation of molecular properties with the wavefunctions listed above, including dipole moments, spin density, and population analysis.

e. Calculation of the analytic energy gradient with respect to the nuclear coordinates for the wavefunctions listed in b, above.

f. Automatic geometry optimization by taking advantage of the energy gradient.

g. Calculation of the complete vibrational spectra of molecules by differencing numerically the energy gradient.

Footnotes and Reference

*Previously not available.

†Substantial interface modifications have been made. In addition, the Distinct Row Table program has been modified to allow for a wider class of CI wavefunctions, including First-Order, Second-Order wavefunctions, POL-CI wavefunctions.

1. B. R. Brooks, Ph.D. Thesis, University of California, Berkeley, 1979

5. GEOMETRY AND ELECTRONIC STRUCTURE OF $(CO)_3NiCH_2$: A MODEL TRANSITION METAL CARBENE

D. Spangler, J. J. Wendoloski, M. Dupuis, M L. Chen*, and H. F. Schaefer, III*

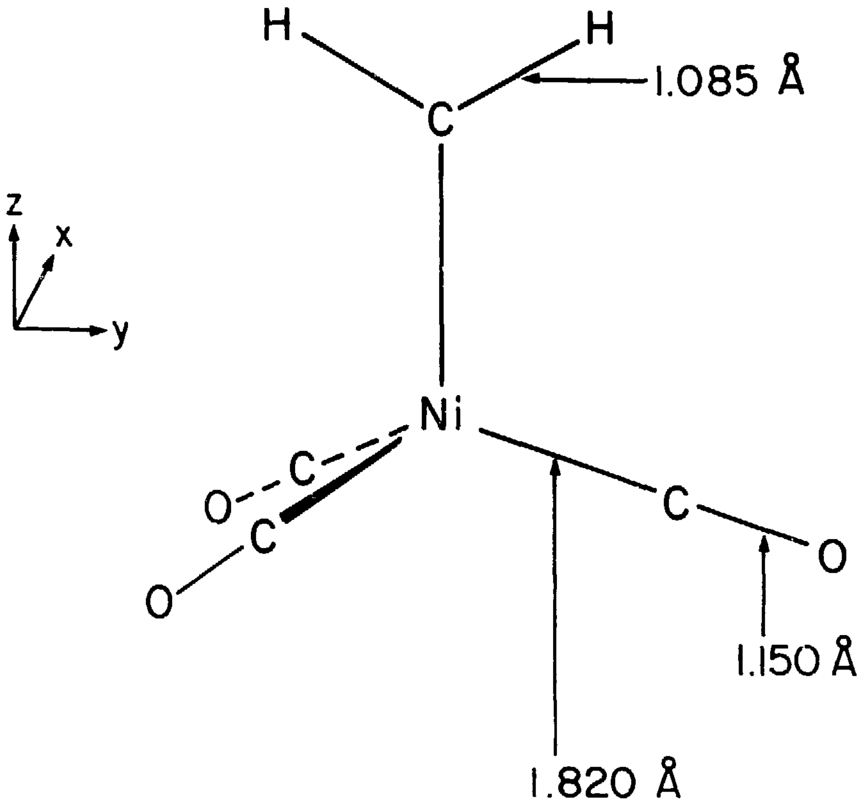
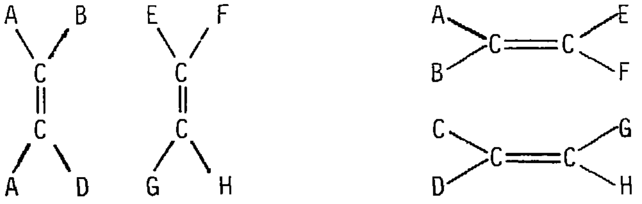


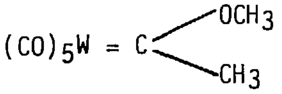
Figure 4. Structural assumptions for the prototype nickel carbene complex. The three CO ligands are assumed to be tetrahedrally coordinated about the nickel atom. (XBL 803-8756)

It has become clear over the past five years that transition metal carbenes play a critical role in the olefin metathesis reaction



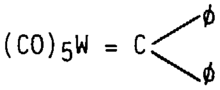
(1)

Although transition metal carbenes have been known since Fischer and Maasbol's pioneering synthesis of



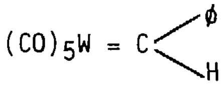
$$(CO)_5W = C\begin{matrix} OCH_3 \\ CH_3 \end{matrix} \qquad (2)$$

in 1964, those which catalyse the olefin metathesis reaction are not of the general type (2), which typically involve an alkoxycarbene. Instead, as shown by Casey in 1973, molecules such as



(3)

for which the carbene substitutes (R in CR_2) are composed of only C and H atoms. are the critical catalytic species. In more recent work Casey has synthesized the simpler compound,



(4)

which is also effective in the homogeneous metathesis of olefins. One of the limiting steps to further progress in understanding the metathesis reaction is that molecules such as (4) have been difficult to prepare, and almost no information concerning their structure and energetics is available.

The three simplest prototype transition metal carbenes are

$(CO)_5Cr = CH_2$ (5)
$(CO)_4Fe = CH_2$ (6)
$(CO)_3Ni = CH_2$ (7)

The first application of non-empirical molecular electronic structure theory to a realistic transition metal carbene complex is reported. The system chosen was $(CO)_3NiCH_2$, methylene (tricarbonyl) nickel(0). All studies were carried out at the self-consistent-field (SCF) level. A large and flexibly contracted basis set was chosen labeled Ni(15s 11p 6d/11s 8p 3d); C,O(9s 5p/4s 2p); H(5s/3s). In addition, the importance of methylene carbon d functions was investigated. The critical predicted equilibrium geometrical parameters are R[Ni-C (methylene)] = 1.83 Å, (HCH) = 108°. The sixfold barrier to rotation about the Ni-C (methylene) axis is small, 0.2 kcal. The electronic structure of $(CO)_3NiCH_2$ is analysed and features useful for identification of the species discussed.

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6. COMBINED CI-HYLLERAAS CALCULATIONS ON ATOMS

S. Hagstrom and E. Plute*

Over the last several years I have been exploring, for atomic systems, the combination of the conventional configuration interaction (CI) method and the Hylleraas (Hy) approach, which uses interelectronic coordinates explicitly in the wavefunction. This combined CI-Hy method has been used to carry out very accurate calculations on several 2-, 3-, and 4-electron systems, namely, for the ground and excited states of Be and Be-like ions, Li^-, Li, and He. The effects of basis set size, CI expansion lengths, types of correlation factors, etc., on calculated energies, transition probabilities, and polarizabilities have been studied. Of particular interest have been the calculation of rigorous upper and lower bounds on transition probabilities and lower bounds on the polarizability using Weinhold's method.

The goal in the present work is to extend the CI-Hy method to atoms with more than four electrons. The early programs were designed with a maximum of 4 electrons in mind and have served well for exploring the general features of the CI-Hy method. A basic restructuring of these codes is needed in order to go up to 10 electrons and beyond and to handle states of any symmetry. In addition, it has been decided to switch from a non-orthogonal basis to an orthogonal basis formulation of the CI-Hy method. The orthogonal basis formulation has the special advantage that it will permit a direct, detailed comparison of CI-Hy with conventional CI, e.g., one can systematically study various natural orbital truncations of the INO-CI function in conjunction with the several types of CI-Hy correlation factors (i.e., interpair, intrapair, K-shell, etc.).

The problem of constructing matrix elements of the Hamiltonian is also simplified with an orthonormal basis. The r_{ij} integrals on the other hand become more difficult, especially for the 3- and 4-electron cases. The integral problem has been attacked by using a new charge-distribution based numerical method that promises to reduce computation time by an order of magnitude or more. Essentially, the new method evaluates integrals over orthonormal orbitals in terms of charge distribution quantities that occur over and over again in many different integrals. The method is an adaptation of the Ruedenberg scheme (J. Chem. Phys., 19, 1459 (1951)); 57, 2575 (1969)) for doing two-center exchange integrals to the 3- and 4-electron, one-center r_{ij} integral cases. It is also possible to use piecewise polynomial representations for INO-CI natural orbitals as recently formulated by Harris Silverstone instead of linear combinations of STO's. This is a much more flexible basis set for atomic calculations and has the advantage that the integrals can be done exactly with an appropriate choice of Gaussian quadrature points and weights.

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7. COMBINED CI-HY CALCULATIONS FOR DIATOMIC MOLECULES

S. Hagstrom

Except for the greater difficulty of doing the integrals, CI-Hy calculations on small diatomics are similar to those for atoms. Test programs for the simpler 3- and 4-electron integrals were written in 1977 at Indiana University for the case of non-orthogonal basis orbitals and showed that 10 digit accuracy was possible with reasonable average integral times. The method of integral evaluation being used is similar to that used for atoms except that elliptical coordinates are employed. Work on this program has continued during the past year. There are still some analytic problems to be overcome for certain integrals, however, before this problem can be said to be 'solved' from the point of view of practical calculations. Initially we will study simple 3- and 4-electron diatomics, namely, H_2, He_2 (long range), He_2 excited states, and LiH.

8. MOLECULAR INTEGRALS OVER SLATER ORBITALS USING THE FOURIER TRANSFORM METHOD

H. Partridge* and S. Hagstrom

Development has continued on a comprehensive program package for doing 3- and 4-center electron repulsion integrals over s-, p-, and d-type Slater type orbitals using the Bonham-Peacher-Cox Fourier transform method. Major improvements have been made in the algorithms to both speed up the integrations as well as improve accuracy. This work is in the process of being submitted for publication.

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9. DIATOMIC SLATER INTEGRALS

S. Hagstrom and H. Partridge*

The diatomic integral package DERIC has been substantially modified and improved. The most important enhancements are 1) the ability to handle principle quantum numbers up through 8f, which is important in the study of heavy atom diatomics; 2) a refined numerical quadrature selection scheme that routinely permits 8-10 decimal place accuracy to be achieved for the most difficult integrals; 3) the capability to handle very large blocks of integrals without a substantial increase in I/O overhead, and 4) extensive vectorization of the code for improved performance on vector machines such as the CYBER 203 and CRAY-1.

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10. DIAGRAMMATIC MANY-BODY PERTURBATION THEORY

S. Wilson*, D. Silver†, and S. Hagstrom

A study of quasi-degeneracy effects in non-degenerate diagrammatic many-body perturbation theory as applied to Be and Be-like ions and Ne and Ne-like ions is in progress. Extensive CI calculations on these systems are currently underway using the same "universal" even-tempered basis set used in corresponding diagrammatic many-body perturbation calculations carried out at Daresbury on the

CRAY-1 computer. The program being used for these calculations is the ATOMCI atomic CI program of Sasaki and Yoshimine as modified for CDC computer by Sasaki and Hagstrom.

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†Address: Applied Physics Laboratory, Johns Hopkins University

11. CI STUDY OF THE VALENCE STATES OF Ti AND Ti IONS

S. Hagstrom, Y. Lee*, and K. Freed*

The purpose of these calculations is to explore the role of electron correlation in Ti and Ti ions at the atomic level prior to looking at the more complicated molecular case. The results obtained thus far indicate that correlation effects, including core valence interactions, are quite important for calculating excitation energies correctly due especially to the presence of the 3d valence electrons. The calculations are being carried out using a number of different basis sets, including the basis set used in recent second-order _ab initio_ effective valence shell Hamiltonian calculations on Ti and Ti ions by Prof. Karl Freed and co-workers at the University of Chicago. This will permit a detailed comparison of the CI and effective valence shell Hamiltonian approaches. Calculations of transition probabilities as a function of the level of CI approximation are also under way.

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12. ANALYSIS OF THE STRUCTURE AND ENERGY OF MOLECULES BASED ON CHARGE DISTRIBUTION

J. Wendoloski

The relationship between molecular geometry and energy was examined by studying both the static charge distribution and changes in the charge distribution in a vibrating molecule. Comparisons between the picture presented by the conventional delocalized molecular orbital description and localized valence bond description were also made. As a result of these investigations, models for the partitioning of charge into chemically meaningful "fragments" were developed, and an improved description of the effect of local geometry on energy was obtained. Detailed information on individual projects follows.

The charge distribution along the CH bonds of methane, ethylene and acetylene were obtained by numerical integration of 6-31G**[1] wavefunctions. Several criteria for assigning electron populations to carbon and hydrogen led to negative charge on H for methane and ethylene and a positive charge on H for acetylene. These results were compared with the charges derived from the effective bond dipole moment obtained from infrared intensity measurements. The difference between the electron population determined from infrared intensities and from the electron density calculations was shown to result from incomplete orbital following in the molecular deformation and the creation of a "bent-bond" moment. (Joint research with Professor K. B. Wiberg, Yale University)

Wavefunctions for a series of ethyl derivatives have been converted into electron density distributions. Bader's criterion was used to partition the charge distributions into atomic regions, which were then numerically integrated to give atomic charges. Charge shifts relative to ethane were determined and split into sigma and pi components and correlated with the σ- or π-acceptor/donor nature of the substituent. (Joint research with Professor K. B. Wiberg)

The nature of the charge distribution and charge rearrangement in methane, ethylene, and acetylene was examined using restricted Hartree-Fock methods plus Boys localization, and also within the generalized-valence bond (GVB) framework. It was found that the intensities could not be explained by considering the magnitude of the atomic charge shifts themselves. Instead, account had to be taken of the vector direction both of the bond dipoles and the lone pair-like atomic dipoles which form during vibration. Mulliken population results were found to lead to misleading conclusions about the nature of the infrared intensities.

Energy-optimized geometries for methane, ethylene, and acetylene were calculated using analytic energy gradients (Force Method) within the GVB perfect pairing framework. The full force field and normal mode frequencies were then calculated using the GVB Force Method. The infrared intensities associated with each normal mode were also obtained from the numerical differencing of the GVB dipole moments. Basis set dependencies for all of these quantities were also examined. The frequencies and force constants calculated using GVB provided much better agreement with experiment than the RHF values. The GVB infrared intensities for stretching modes were comparable to the RHF values, while those for bending modes gave poorer agreement with experiment.

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Statistical Mechanics and Macromolecular Science

The research in statistical mechanics has been concentrated in two areas: simulation of quantum mechanical systems at zero temperature and the simulation of concentrated polymer systems. The motivation for the first effort is to develop, for quantum mechanical systems, the powerful simulation methods similar to those that have been applied to classical systems for many years. The principle difficulty to overcome is to relate the antisymmetry of the wavefunction to the boundary conditions of the simulation. Substantial progress has been made this year on this problem. We anticipate these simulation methods will have wide applicability in computing the properties of many electron systems and, in particular, quantum chemistry. The second effort has been to develop simulation methods capable of efficiently modelling concentrated systems of polymers and then to understand the effect of entanglements on the statistical dynamic properties of these systems.

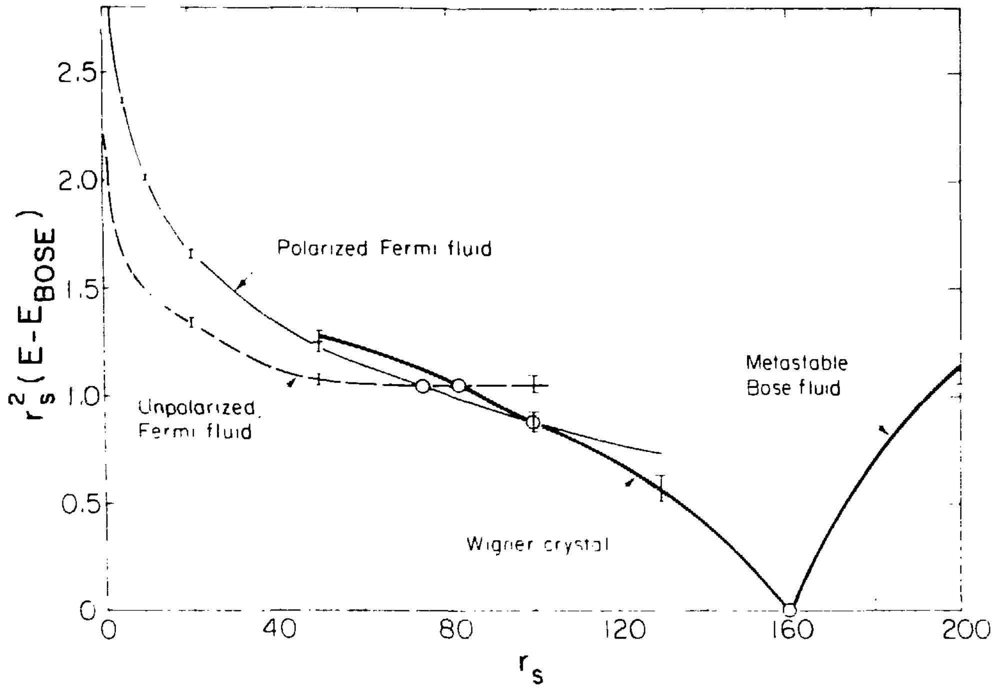

Figure. 5. The energy of the four phases studied relative to that of the lowest Boson state times r_s^2 in Rydbergs version r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect of $r_s = 75$. The polarized (ferromagnetic) Fermi fluid will be stable between $r_s = 75$ and $r_s = 100$
(XBL 803-526)

1. SIMULATION OF QUANTUM MANY-BODY SYSTEMS

D. Ceperley and B. Alder*

In the past decade stochastic simulation methods[1] have been used to calculate properties of many particle Boson systems, most notably liquid helium. This year we have generalized these Monte Carlo methods to Fermion systems and carried out such a simulation on a model problem, the electron gas.[2] The simulation consists of constructing an ensemble of systems on the computer, each system is composed of several hundred electrons with periodic boundaries. The Schroedinger equation is interpreted as a diffusion equation. In this process, the electrons within each system diffuse under the influence of an importance function. In addition, systems are removed or created in the ensemble depending on the potential energy and the importance function. After the process has stabilized, the probability density of a system is proportional to the exact ground state wavefunction. The antisymmetry of the eigen-state is achieved by changing the sign of the contribution of a given system to any average when a system moves across the nodes of a trial antisymmetric function. With the use of importance sampling, very precise ground state energies can be obtained from the Monte Carlo simulation. This method is promising for quantum chemical calculations since the computational time is proportional to the number of electrons (N) in contrast to the N^4 dependence of traditional quantum chemical methods.

Almost fifty years ago Wigner[3] predicted that the electron gas would crystallize at sufficiently low density. The crystallization density has proved elusive to reliably calculate; estimates vary over several orders of magnitude. With our quantum Monte Carlo method we have been able to determine that the crystallization density is $r_s=100\pm10$ where r_s is the Wigner-Seitz sphere radius in units of Bohr radii. Our correlation energies in the metallic density regime are in reasonable agreement with other many body theories. The Monte Carlo results are significantly more accurate for $r_s > 4$ when electronic correlation becomes more important.

Footnote and References

*Collaborator from Lawrence Livermore Laboratory

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2. D. M. Ceperley and B. J. Alder, "Ground State of the Electron Gas by a Stochastic Method", submitted to Phys. Rev. Letts (1980).

3. E. P. Wigner, Phys. Rev. 46, 1002 (1934).

2. SIMULATION OF POLYMERIC SYSTEMS

D. Ceperley, M. Bishop*, M. Kalos[†], and H. Frisch[‡]

We have been performing simulations of concentrated polymer melts in order to understand the entanglement mechanism and the equilibrium conformations as the density and length of the polymers become larger. The usual Monte Carlo and molecular dynamics methods require an excessively large amount of computer time to simulate these systems. Our initial efforts were to generalize the Monte Carlo method so that polymer can "snake" around very rapidly through configuration space thus reducing, by several orders of magnitude, the time needed to complete equilibrium properties. We have shown[1] that as the polymer density increases the properties of an individual polymer do approach the ideal chain limit, as Flory[2] predicted many years ago, but there remain significant discrepancies. We have also performed dynamical simulations with both Brownian dynamics and molecular dynamics. That work is still in progress. These simulations were done in collaboration with M. Bishop (Fordham), M. Kalos (New York University), and H. L. Frisch (SUNY Albany).

Footnotes and References

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†Collaborator from New York University, Courant Institute of Mathematical Science, 251 Mercer Street, New York, New York 10012

‡Collaborator from State University of New York at Albany, Department of Chemistry, Albany, New York 12222

1. M. Bishop, D. M. Ceperley, H. L. Frisch, and M. H. Kalos, J. Chem. Phys. 75, 3228 (1980).
2. P. J. Flory, "Principles of Polymer Chemistry" (Cornell University, New York (1953)).

PROPOSAL PROGRAM

The NRCC's proposal program is directed toward the advancement of new computational methods, the innovative use of existing methods, the study of problems of significant scientific merit, the resolution of intradisciplinary computational issues and the development of interdisciplinary approaches to forefront problems in chemistry. In response to the two 1979 Calls for Proposals, 43 proposals were received and 22 approved. The cost of the computer time allocated for these proposals is $257,100. This aspect of the NRCC's program is growing and publications have already been received that document research advances supported by the NRCC.

Proposals Funded

RELATIVISTIC MOLECULAR ELECTRONIC STRUCTURE CALCULATIONS

David A. Case, Department of Chemistry, University of California, Davis.
Cary Y. Yang, Stanford/NASA Ames Joint Institute for Surface and Micro-structure Research, NASA Ames Research Center.

Construction of computer codes to perform self-consistent Dirac-Slater multiple-scattering calculations for molecules, evaluation of expectation values of one-electron operators over the resulting wave functions, and applications to important heavy-atom-containing systems. ($3,800 for 12 months)

KINETICS OF PROTEIN-NUCLEIC ACID AND OTHER LARGE LIGAND-LATTICE INTERACTIONS

Irving R. Epstein, Department of Chemistry, Brandeis University.

Development and improvement of programs for simulating various models of ligand-lattice interaction processes. ($6,000 for 18 months)

COMPUTER STUDIES OF EFFECTIVE VALENCE SHELL HAMILTONIANS

Karl F. Freed, Department of Chemistry, University of Chicago.

Ab initio computation of the exact effective valence shell Hamiltonian for atomic and molecular systems. ($7,500 for 24 months)

COMPUTER SIMULATION OF MOLECULAR LIQUIDS AND SOLUTIONS

William L. Jorgensen, Department of Chemistry, Purdue University.

Monte Carlo simulations for the solvents liquid water, ammonia, hydrogen fluoride; and for the solvation of carbonium ions in liquid hydrogen fluoride and of carbanions and neutral molecules in water. ($20,000 for 24 months)

REACTIVE SCATTERING OF HYDROGEN ISOTOPIC SYSTEMS

John C. Light, Department of Chemistry, University of Chicago.
Ellen B. Stechel, Department of Chemistry, University of California, Los Angeles.
Robert B. Walker, Los Alamos Scientific Laboratory.

Benchmark quality quantum close-coupling calculations of the related assymmetric reactions of the H_2D and HDT systems in the same energy range. ($15,000 for 12 months at the University of Chicago)

STUDIES OF ELECTRONIC SPECTRA OF HEME PROTEINS AND CHARGE TRANSFER IN CATIONIC INTERACTIONS WITH NUCLEIC ACID COMPONENTS

Gilda Loew, Department of Genetics, Stanford University.
George Pack, Department of Biomedical Sciences, Rockford School of Medicine.

Test of a new INDO-type computer program including configuration interaction written for transition metal complexes by its use to assign the single crystal polarized optical absorption spectra of oxy and carboxy hemoglobin. ($7,500 for 12 months)

CLASSICAL TRAJECTORY STUDIES OF STATE TO STATE ENERGY TRANSFER AND CHEMICAL REACTIONS INVOLVING TRIATOMIC MOLECULES

George C. Schatz, Department of Chemistry, Northwestern University.

Development of general computer codes which use the quasiclassical trajectory method to study collisional energy transfer and chemical reactions involving triatomic molecules. Unique to these codes will be the accurate treatment of anharmonic and Coriolis coupling effects, including Fermi resonance effects), in determining the semiclassical stationary states of the triatomics before and after each collision. ($6,000 for 18 months)

POLARIZATION POTENTIALS AND PSEUDOSTATES FOR ELECTRON SCATTERING CALCULATIONS

Donald G. Truhlar and David A. Dixon, Department of Chemistry, University of Minnesota.

Use of a test-charge self-consistent-field method to calculate adiabatic polarization potentials and polarized pseudostates for electron scattering by small hydrocarbons as a function of geometry. ($4,500 for 12 months)

A NEW APPROACH TO THE DETERMINATION OF ATOMIC CHARGES

Leland C. Allen, Department of Chemistry, Princeton University.

Development and testing of a new scheme for obtaining the charges on atoms in a molecule using an implementation and extension of the Hirshfeld definition. ($5,000 for 12 months)

DYNAMIC AND STATIC PROPERTIES OF CONCENTRATED POLYMER SOLUTIONS

Marvin Bishop, Division of Science and Mathematics, Fordham University at Lincoln Center.
Harry L. Frisch, Department of Chemistry, State University of New York at Albany.
Malvin H. Kalos, Courant Institute of Mathematical Sciences, New York University.

Extension of earlier work on the static properties of concentrated polymer solutions to include such properties as the diffusion coefficient, the viscosity, and the dependence of relaxation times of various correlation functions upon polymer length and density. ($20,000 for 12 months)

ELECTROSTATIC POTENTIALS FROM ACCURATE DIFFRACTION DATA

Philip Coppens and Grant Moss, Department of Chemistry, State University of New York at Buffalo.

Development of algorithms for the calculation of the electrostatic potential along the periphery of a molecule which are then used to calculate mechanisms of protonation of metal clusters, pathways of reaction of sulfur containing molecules, and protonation of biochemically important molecules. ($12,450 for 12 months)

CI CALCULATIONS

Ernest R. Davidson, Department of Chemistry, University of Washington.

Ab initio calculations of reaction pathways of several carbenedioxolane systems using moderate size configuration interaction (CI). ($40,000 for 24 months)

CRYSTALLOGRAPHIC REFINEMENT OF GLYCOGEN PHOSPHORYLASE *a*

Robert Fletterick, Department of Biochemistry and Biophysics, University of California, San Francisco.

Crystallographic refinement of approximate atomic coordinates for glycogen phosphorylase *a* using a recently developed fast Fourier transform (FFT) procedure as suggested by R. Agarwal and modified by A. Jack. ($5,550 for 18 months)

PREPARATION AND TESTING OF SOFTWARE FOR COMPLEX CHEMICAL KINETICS

David Garfinkel, Department of Computer and Information Science, University of Pennsylvania.

Developing, testing, and applying to current research three computer programs for the computation of the kinetics of complex chemical and biochemical systems. ($3,000 for 12 months)

DETERMINATION OF SURFACE STRUCTURE BY CLASSICAL TRAJECTORY STUDIES OF ION BOMBARDMENT OF SOLIDS

Barbara J. Garrison, Department of Chemistry, The Pennsylvania State University.

Investigate the details of ion impact phenomena in solids as they relate to yielding information about the structure of atoms and molecules on surfaces. ($25,200 for 24 months)

GENERALIZED MOLECULAR ORBITAL THEORY

Michael B. Hall, Department of Chemistry, Texas A & M University.

Implementation of the newly developed Generalized Molecular Orbital (GMO) multiconfiguration self-consistent-field technque; applications of the GMO method to several inorganic systems. ($40,000 for 24 months)

SIMULATION OF DYNAMIC PROPERTIES OF A POLYMER SOLUTION AS A FUNCTION OF CONCENTRATION

David E. Kranbuehl, Department of Chemistry, College of William and Mary.

Monte Carlo lattice model simulation studies on the dynamic behavior of nondilute polymer solutions. ($11,400 for 24 months)

MOLECULAR APPLICATIONS OF PERTURBATIVE CORRECTIONS TO AN INCOMPLETE BASIS SET

Keith McDowell, Department of Chemistry, Clemson University.

Designed to begin quantitative studies of molecular applications of the (corrections to an incomplete basis set) CIBS. In particular, benchmark computations on H_2 and H_2O using a version of the GAUSSIAN molecular orbital program are proposed. ($3,000 for 12 months)

A MOLECULAR DYNAMICS SIMULATION OF THE CAGE EFFECT WITH MULTIPLE POTENTIAL ENERGY SURFACES

Mark G. Sceats, Department of Chemistry, University of Rochester.

Perform molecular dynamics simulations of the cage effect following the photodissociation of iodine in dense rare gases. ($5,000 for 12 months)

CHARGE DISTRIBUTIONS IN ORGANIC EXCITED STATES

Andrew Streitwieser, Jr., Department of Chemistry, University of California.

Develop a modification of existing "PROJ" program and associated graphics to determine integrated electron distributions from ab initio SCF-MO-CI excited states. ($3,000 for 12 months)

HARTREE-FOCK-SLATER CALCULATIONS OF SPECTROSCOPIC PROPERTIES FOR HEAVY METAL CLUSTER COMPLEXES

William C. Trogler, Department of Chemistry, Northwestern University.

Elucidate the electronic structural features of trinuclear metal cluster complexes by employing a joint experimental-theoretical approach. The theoretical approach will make use of relativistic self-consistent-charge discrete variational X_α or Hartree-Fock-Slater methods. ($3,000 for 24 months.)

THEORETICAL AND COMPUTATIONAL STUDIES OF MULTICONFIGURATIONAL

Danny L. Yeager, Department of Chemistry, Texas A & M University.

Techniques for Electronic States of Atoms and Molecules Theoretical and calculational development of second order procedure for MCSCF with emphasis on convergency studies for excited states. ($16,200 for 12 months)

HARDWARE DEVELOPMENTS

NRCC Minicomputer

NRCC's Digital Equipment Corporation VAX-11/780 minicomputer arrived at LBL during the first week in June and was officially turned over to NRCC on July 3. The system has virtual memory architecture and is configured with .5M bytes of error correcting MOS memory, a Floating Point Accelerator Unit, one single access 176M byte disk drive, a 45 ips 9-track 1600 bpi magnetic tape drive, a Versatec 1000 lines/minute (pm), 200 dots/inch electrostatic printer/plotter, and eight asynchronous EIA terminal lines operating at up to 9600 baud. Four VADIC VA-317S/P direct connect 300 BPS modems are available for remote access over the dial-up telephone networks. Terminal access to the VAX is by means of a computerized digital switch that also allows access to the CDC 6000's and the PDP 11/70 UNIX text editing system.

The standard VAX/VMS Operating System is used. This system features multiuser timesharing concurrent with background batch. Languages available are FORTRAN, BLISS, and assembly language. Dr. John Wendoloski and Dr. Dale Spangler are acting as the installation managers.

The VAX is being used primarily for software development in chemical kinetics, crystallography, quantum chemistry, and statistical mechanics. Many of the major packages currently running on the CDC 7600 are being converted to the VAX. Already converted are the programs MULTAN (crystallography), CLAMPS (macromolecular science and statistical mechanics), ALIS (quantum chemistry), and a general Slater integrals package for molecules (DERIC, ERIC). A number of other programs are nearing completion. In the area of systems support software, a Fortran NAMELIST processor has been written for the VAX, since VAX Fortran does not provide this useful feature. This software will enable the user interface for NAMELIST directed codes to be preserved when moving programs to the VAX.

Researchers at other laboratories are collaborating with the NRCC in the joint development of minicomputer-based codes. Two such efforts are currently underway. One is an experiment in networking involving a DECNET link (4800 baud dial-up) between NRCC's VAX and a VAX in Prof. John Pople's group at Carnegie-Mellon University. The second involves an adaptation by Dr. David Ceperley of his CLAMPS (Classical Many Particle Simulation) program to a Floating Point Systems Array Processor connected to a VAX-11/780 in Prof. Bruce Berne's group at Columbia University.

A substantial hardware upgrade of the NRCC's VAX is planned for the Spring of 1980. This will involve an additional 2M bytes of memory, a second disk drive, a conventional 600 ℓpm printer, eight additional asychronous terminal lines, and a state-of-the-art real-time interactive graphics system. A high-speed DECNET connection from the VAX to the LBL CDC 7600/6600/6400 complex of machines should also be a reality sometime early in 1980. This should eliminate the present need to carry tapes back and forth between the VAX and the CDC 6600.

Array Processors

As part of its educational function, the NRCC has initiated a study of the use of attached scientific processors ("array processors") for chemical computations. Although each commercially available array processor has its own architectural features, in most cases the array processor is a special purpose "box" which is attached to an existing minicomputer (or mainframe computer) to provide high speed processing of floating point operations in vector- or matrix-oriented applications. For certain restricted classes of calculations, array processors appear to have the possibility of providing cost-effective computation. The use and programming of current products, however, presents difficulties beyond those normally encountered by computational chemists. Initially, this project of the NRCC involves an investigation of the state-of-the-art in array processing and the preparation of a corresponding report.

Prof. Neil Ostlund, Department of Chemistry, University of Arkansas, is serving as a consultant to the NRCC on the project. He spent the month of July 1979 at the NRCC preparing a report on array processors which was distributed by the NRCC to interested members of the chemistry community. This report provides a pedagogical introduction to array processors, describes selected commercially available array processors, and presents the experiences of a number of researchers now using array processors for applications related to computational chemistry.

In conjunction with this report and the NRCC's investigation into array processors, a small one-and-one-half day meeting was held July 19-20, 1979 at the NRCC. This meeting, with the title "Array Processors for Chemical Computations," brought together a small number of invited speakers to describe their direct experience with array processors to the NRCC staff and interested local scientists. A considerable amount of open discussion was generated concerning the advantages and disadvantages of using an array processor. The possible role of the NRCC in advancing this mode of computation was also discussed. Prof. Ostlund's report contains the agenda and the resulting abstracts of this meeting.

The NRCC is considering a continuing assessment of array processors, and interested members of the community have been invited to contribute their ideas on this subject to the NRCC Director, Dr. William A. Lester, Jr. It appears that more general purpose 64-bit array processors will be appearing in the near future and one possibility that has been raised is that the NRCC consider acquiring an array processor to attach to its VAX-11/780.

APPENDIX A

Seminars in 1979

January 8: ROTATIONAL ENERGY TRANSFER IN MOLECULAR COLLISIONS
Prof. Millard H. Alexander, University of Maryland

February 14: IMPLEMENTATION AND PRELIMINARY APPLICATIONS OF THE GRAPHICAL UNITARY GROUP APPROACH TO CONFIGURATION INTERACTIONS CALCULATIONS
Mr. Bernard Brooks, University of California, Berkeley

February 26: WHAT EVERYONE SOLVING DIFFERENTIAL EQUATIONS NUMERICALLY SHOULD KNOW
Dr. Lawrence F. Shampine, Sandia Laboratories, Albuquerque

February 28: IS THERE A BRIDGE BETWEEN SEMI-EMPIRICAL AND AB INITIO THEORIES OF VALENCE
Prof. Karl Freed, University of Chicago,

March 1: R-MATRIX-PROPAGATION METHODS FOR QUANTUM SCATTERING
Prof. John C. Light, University of Chicago

March 6: USE OF RELATIVISTIC EFFECTIVE POTENTIALS IN MOLECULAR CALCULATIONS
Dr. Yoon Lee, Lawrence Berkeley Laboratory

March 22: HYDROGEN IN METAL AND METAL HYDRIDES: ELECTRONIC STRUCTURE AND MOBILITY
Dr. Carl Melius, Sandia Laboratories, Livermore

April 9: INFRARED LASER INDUCED CHEMICAL REACTIONS IN MATRICES*
Dr. J. J. Turner, Cambridge University

April 10: REGULAR AND IRREGULAR SEMI-CLASSICAL QUANTUM STATES*
Dr. M. V. Berry, University of Bristol

April 16: INFORMATION CONTENT IN ROTATIONAL RELAXATION EXPERIMENTS
Dr. S. Green, Goddard Space Flight Center, New York

April 23: THEORETICAL PREDICTIONS OF ELECTRONIC SPECTRA FOR SMALL POLYATOMIC MOLECULES INCLUDING VIBRATIONAL STRUCTURE AND RADIATION LIFETIME*
Prof. S. Peyerimhoff, University of Bonn

April 25: EXOTIC MOLECULES IN SPACE*
Dr. S. Green, Goddard Space Flight Center, New York

May 4: QUANTUM RESONANCE STRUCTURE IN THE THREE-DIMENSIONAL F + H_2 REACTION*
Dr. R. E. Wyatt, University of Texas

May 9: COLLISIONAL ELECTRONIC EXCITATION*
Prof. R. Anderson, University of California, Santa Cruz

May 21: LASER SPECTROSCOPY FOR PHOTOCHEMISTS*
Prof. J. Wiesenfeld, Cornell University

May 30: MCSCF BY EXPANSION - THE LAST WORD
Prof. C. C. J. Roothaan, University of Chicago

June 5: KINETIC ANALYSIS OF FLASH PHOTOLYSIS DATA THE BACTERIORHODOPOS IN PHOTOCYLCE
Dr. R. Lozier, University of California, San Francisco,

June 6: INFRARED LASER INDUCED UNIMOLECULAR REACTIONS*
Prof. E. I. Yablonovitch, Harvard University

July 5: STERIC EFFECTS ON REACTIONS BY MOLECULAR MECHANICS
Prof. DeLos DeTar, Florida State University

July 17: COMPUTER SIMULATIONS OF POLYMERIC SYSTEMS
Dr. Marvin Bishop, Fordham University at Lincoln Center, New York, New York

October 5: CLASSICAL TRAJECTORY STUDIES OF POLYATOMIC MOLECULE COLLISION DYNAMICS
Dr. George Schatz, Northwestern University, Evanston, Illinois,

October 15: A DISCUSSION OF RESONANCE STRUCTURES OF ATOM-DIATOM STSTEMS. EXAMPLES: He-H_2/HD, Xe-HD, H-CO

and

October 16: TESTS OF AB INITIO CALCULATED INTERACTION POTENTIALS
Dr. Joachim Schaefer, Max-Planck-Institut für Physiks und Astrophysik

October 17: NEWTON-RAPHSON MCSCF PROGRAM ARCHITECTURE
Prof. Clemens C. J. Roothaan, University of Chicago

October 31: REACTION DYNAMICS OF OXYGEN ATOMS WITH HYDROCARBONS*
Dr. Alan Luntz, IBM Research Laboratory, San Jose

November 2: NON-NUMERICAL METHODS IN CHEMISTRY--ONE PERSON'S VIEW
Prof. W. Todd Wipke, University of California, Santa Cruz

November 19: OPTICAL PUMPING OF MOLECULES*
Dr. J. Vigue, Laboratoire de Spectroscopie Hertzienne,
de L'Ecole Normale Superieure

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*Joint seminar with the Materials and Molecular Research Division, Lawrence Berkeley Laboratory and the Department of Chemistry, University of California, Berkeley.

Visitors

Prof. M. Alexander, University of Maryland, January 8

Prof. J. Anderson, Pennsylvania State University, February 27

Dr. R. Attalla, Institute for Paper Chemistry, Madison, Wisconsin, February 26

Dr. C. Bauschlicher, NASA Langley, January 2-11

Dr. M. Bishop, Fordham University, January 4-25

Prof. C. E. Dykstra, University of Illinois, January 4-14

Prof. K. Freed, University of Chicago, March 1

Prof. M. Kalos, New York University, February

Dr. S. Kato, Institute for Molecular Science, Japan, March 23

Prof. J. C. Light, University of Chicago, February 28 March 3

Prof. G. Loew, Stanford University, January 12

Dr. C. Melius, Sandia Laboratories, Livermore, March 22

Dr. B. H. O'Connor, Western Australian Institute of Technology, South Bentley, Australia, February 27

Dr. H. Partridge, NASA Ames, January 11

Dr. L. F. Shampine, Sandia Laboratories, Albuquerque, February 26-27

Dr. L. Snyder, Bell Laboratories, January 29

Dr. E. Soulie, Commissariat a l'Energie Atomique, Saclay, France, January 30, 1979, on sabbatical at LBL.

Prof. D. R. Yarkony, Johns Hopkins University, January 2-11

Dr. Sheldon Green, NASA Institute for Space Studies, New York, visited the NRCC October 30 through November 9. During this period he made several improvements to his molecular scattering program, MOLSCAT. He added atom-asymmetric rotor collisions to its capabilities and created a second version which utilizes the large core memory of the CDC 7600. This version permits the solution of much larger sets of coupled equations than the small core version. We are grateful to Dr. Green for his effort and contribution to our software library.

Dr. Frank Rebentrost, Project Group for Laser Research, Max-Planck Society for the Furtherance of Science, Garching, Wes Germany, June 1-July 31

Dr. Glen T. Evans, Department of Chemistry, University of Oregon, June 11-15

Dr. Victor R. Saunders, Daresbury Laboratory, England, June 12-July 6

Dr. Chiakao Kawabuta, Okuyama University, Japan, June 14

Dr. Clair Cheer, Department of Chemistry, University of Rhode Island, June 15

Dr. Russell Pitzer, Department of Chemistry, Ohio State University, June 19-July 17

Prof. DeLos DeTar, Department of Chemistry, Florida State University, June 26-July 10

Prof. Marvin Bishop, Department of Chemistry, Fordham University at Lincoln Center, June 27-July 30

Prof. Neil S. Ostlund, Computer Department, Carnegie-Mellon University, July 3-31

Dr. Stephen T. Elbert, Ames Laboratory, Iowa State University, July 16-24

Prof. Reed A. Howald, Department of Chemistry, Montana State University, July 27-August 7, and September 24-26

Dr. Larry McMurchie, Department of Chemistry, University of Washington, Seattle, Washington, August 6-8

Prof. William Jorgensen, Department of Chemistry, Purdue University, August 17, 24-26

Prof. V. Renugopalakrishnan, Department of Physiology Biophysics, University of Illinois at the Medical Center, Chicago, Illinois, September 5-26

Dr. George F. Adams, U.S. Army Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland, September 6-14

Dr. Brian D. Buckley, Daresbury Laboratory, England, September 10-24

Prof. George C. Schatz, Department of Chemistry, Northwestern University, October 5-8

Prof. Gerald M. Maggiora, Department of Biochemistry, University of Kansas, October 8

Dr. Joachim Schaefer, Max-Planck-Institut für Physik und Astrophysik, Munich, West Germany, October 15-16

Dr. Sheldon Green, Institute for Space Sciences, NASA, New York, New York, October 30-November 10, 1979.

Dr. Jack Tossell, Department of Chemistry, University of Maryland, November 8-9, 1979.

Dr. John J. C. Mulder, University of Leiden, The Netherlands, November 13, 1979.

APPENDIX B

List of Publications

Research Papers

C. H. Becker, P. Casavecchia, Y. T. Lee, Lawrence Berkeley Labortory; R. E. Olson, SRI International; and W. A. Lester, Jr., Lawrence Berkeley Laboratory; "Coupled-Channel Study of Halogen (^{2}P) + Rare Gas (^{1}S) Scattering," *J. Chem. Phys. 70*, 5477 (1979).

Marvin Bishop, Fordham University at Lincoln Center; David M. Ceperley, Lawrence Berkeley Laboratory; Harry L. Frisch, State University of New York at Albany; M. H. Kalos, New York University, "Computer Simulations of Chains in Solution and Bulk State," Symposium on Statistical Approaches to Micro-Molecular Systems, July 1979.

Marvin Bishop, Fordham University at Lincoln Center; David M. Ceperley, Lawrence Berkeley Laboratory; Harry L. Frisch, State University of New York at Albany; M. H. Kalos, New York University, Investigations of Static Properties of Concentrated Polymer Solution," submitted to *J. Chem. Phys.*

D. M. Ceperley, Lawrence Berkeley Laboratory; G. V. Chester, Cornell University; M. H. Kalos and P. Whitlock, New York University, "Helium in the Close Packed Phase," submitted to *Phys. Rev. B* (1979).

Paul L. DeVries, C. H. Chang, and Thomas F. George, University of Rochester; Bernard Laskowski and James R. Stallcop, NASA-Ames Research Center; "Production of Na*(4s) by Collision of Na(3s) with Xe in the Presence of Two Nonresonant Lasers."

Paul L. DeVries, C. H. Chang, and Thomas F. George, University of Rochester; Bernard Laskowski and James R. Stallcop, NASA-Ames Research Center; "Na + Xe Collisions in the Presence of Two Nonresonant Lasers," *Chem. Phys Lett.* (in press).

G.H.F. Diercksen, W. P. Kraemer, Max-Planck-Institut für Astrophysik, and L. D. Thomas, Lawrence Berkeley Laboratory, "Low-angle Scattering of Li$^+$ by CO," submitted to *Chem. Phys. Lett.*

B. J. Garrison, Purdue University, "Theory of Ion Scattering from Single Crystals," submitted to Surface Sci.

B. J. Garrison and N. Winograd, Purdue University and D. E. Harrison, Jr., Naval Postgraduate School, "Mechanisms of CO Ejection from Ion Bombarded Single Crystal Surfaces," submitted Phys. Rev. B.

B. J. Garrison and N. Winograd, Purdue University, D. E. Harrison, Jr., Naval Postgraduate School, "Ejection of Molecular Clusters from Ion-bombarded Surfaces," J. of Vac. Sci. and Technol. (in press).

B. J. Garrison and N. Winograd, Purdue University and D. E. Harrison, Jr., Naval Postgraduate School, "Classical Trajectory Calculations of the Energy Distribution of Ejected Atoms from Ion Bombarded Single Crystals," submitted to Surface Sci.

James H. Goble and John S. Winn, University of California, Berkeley, "Estimation of the Dissociation Energy of Weakly-Bound Molecules from Spectroscopic Data," submitted to J. Chem. Phys.

James H. Goble and John S. Winn, University of California, Berkeley, "Analytic Potential Functions for Weakly-Bound Molecules: The X and A States of NaAr and the A State of NaNe," submitted to J. Chem. Phys.

A. P. Hickman, SRI International, "Theory of Angular Momentum Mixing in Rydberg-Atom-Rare-Gas Collisions," Phys. Rev. A, 18, 1339 (1978).

William L. Jorgensen, Purdue University, "The Structure and Properties of Liquid Methanol," submitted to the J. Am. Chem. Soc.

William L. Jorgensen, Purdue University, "Monte Carlo Results for Hydrogen Bond Distributions in Liquid Water."

Zeki C. Kuruoglu and David A. Micha, University of Florida, "Diatomic Transition Operators: Results of L^2 Basis Expansions," submitted to J. Chem. Phys.

W. A. Lester, Jr., Lawrence Berkeley Laboratory, "Recent Developments in Computational Chemistry in the U.S.: The NRCC," presented at the International Symposium on Computational Methods in Chemistry, West Germany, 1979, to appear in symposium proceedings, Plenum Press.

Robert R. Lucchese and Vincent McKoy, California Institute of Technology, "Application of the Schwinger Variational Principle to Electron-Molecular Ion Scattering," J. Phys. B: Atom. Molec. Phys., 12, No. 14.

G. C. Schatz and T. Mulloney, Northwestern University, "Classical Perturbation Theory of Good Action-Angle Variables: Applications to Semiclassical Eigenvalues and to Collisional Energy Transfer in Polyatomic Molecules," J. Phys. Chem. (in press).

G. C. Schatz and T. Mulloney, Northwestern University, "Collisional Energy Transfer in Polyatomic Molecules: A Study of Anharmonicity Effects in Kr + CO_2," submitted to J. Chem. Phys.

R. Schinke, Universitaet Kaiserslautern; M. Dupuis, and W. A. Lester, Jr., Lawrence Berkeley Laboratory, "Proton-H_2 Scattering on an Ab Initio CI Potential Energy Surface I: Vibrational Excitation at 10 eV," accepted by J. Chem. Phys.

Arthur E. Stillman, Gary P. Zientara, and Jack H. Freed, Cornell University, "The Variational Method and the Stochastic-Liouville Equation: II. ESR Spectral Simulation via Finite Elements," J. Chem. Phys., July 1979.

K. B. Wiberg, Yale University, and J. J. Wendoloski, Lawrence Berkeley Laboratory, "The Electrical Nature of C-H Bonds and its Relation to Infrared Intensities," submitted to J. Comp. Chem.

N. Winograd and B. J. Garrison, Purdue University, and D. E. Harrison, Jr., Naval Postgraduate School, "Mechanisms of CO Ejection from Ion Bombarded Single Crystal Surface," Phys. Rev. B, (October 16, 1978 issue).

Gary P. Zientara and Jack H. Freed, Cornell University, "The Variational Method and the Stochastic-Liouville Equation. III. Infinite Elements for CIDN(E)P," J. Chem. Phys., July 1979.

Gary P. Zientara and Jack H. Freed, Cornell University, "Spin-Echoes for Diffusion in Bounded, Heterogeneous Media: A Numerical Study," J. Chem. Phys., July 1979.

Abstracts

M. H. Alexander, University of Maryland and P. J. Dagdigian, The Johns Hopkins University, "Recent Studies of Rotational Energy Transfer," (abstract) presented July 1979 at the 6th International Conference on Molecular Energy Transfer, Rodez, France).

W. A. Lester, Jr., Lawrence Berkeley Laboratory, "NRCC Developments and Theoreticians Ad Hoc Group," (abstract) presented at the Basic Sciences Combustion Research Contractor's Meeting, Brookhaven National Laboratory, 1979.

A. J. Olson, Lawrence Berkeley Laboratory, "Crystallography, Computers, and the Coming Decade: What Role for the NRCC," (abstract) presented at the American Crystallographic Association, Boston, 1979.

. Workshop Proceedings

Computational Methodology in Crystallography: Evaluation and Extension Proceedings, LBL-7939, 1979.

The Minicomputer and Computations in Chemistry Proceedings, LBL-8157, 1979.

Numerical Algorithms in Chemistry: Algebraic Methods Proceedings, LBL-8158, 1979.

Post Hartree-Fock: Configuration Interaction Proceedings, LBL-8233, 1979.

Periodicals

NRCC Computers in Crystallography Newsletter, Vol. I, No. 1, Winter 1979.

NRCC Bulletin, Vol. II, No. 1, April 1979.

NRCC Bulletin, Vol. II, No. 2, July 1979.

APPENDIX C

NRCC Staff and Directorate

William A. Lester, Jr., Director
George E. Towns, Division Administrator

Scientific Staff

David M. Ceperley
Michel Dupuis
Stanley A. Hagstrom
Arthur J. Olson
Larry V. Johnson
Dale P. Spangler
Lowell D. Thomas
John J. Wendoloski

Administrative Staff

Carolyn E. Bryant
Tim R. Clark
Jane E. Greer
JoAnn Kim
Maudie Noyd

NRCC Policy Board

Terms of Appointments
October 1, 1977 - December 31, 1980

Prof. James A. Ibers, Chairman
Department of Chemistry
Northwestern University

Prof. Bruce J. Berne
Department of Chemistry
Columbia University

Dr. Charles Bender
Lawrence Livermore Laboratory

Prof. Mary L. Good
Division of Engineering Research
Louisiana State University

Prof. William Guillory
Department of Chemistry
University of Utah

Dr. Carroll J. Johnson
Oak Ridge National Laboratory

Prof. Martin Karplus
Department of Chemistry
Harvard University

Prof. William A. Miller
Department of Chemistry
University of California,
Berkeley

Prof. John A. Pople
Department of Chemistry
Carnegie-Mellon University

Dr. Annessur Rahman
Argonne National Laboratory

Prof. Kenneth Wiberg
Department of Chemistry
Yale University

NRCC Program Committee

Dr. W. A. Lester, Jr., Chairman
National Resource for Computation
in Chemistry
Lawrence Berkeley Laboratory

Prof. Richard Bernstein
Department of Chemistry
Columbia University
Term of appointment:
June 1978 - June 1981

Prof. Ernest Davidson
Department of Chemistry
University of Washington
Term of appointment:
June 1978 - June 1981

Prof. John C. Light
Department of Chemistry
University of Chicago
Term of appointment:
June 1978 - June 1981

Prof. Josef Michl
Department of Chemistry
University of Utah
Term of appointment:
June 1978 - 1980

Prof. Robert Parr
Department of Chemistry
University of North Carolina
Term of appointment:
June 1978 - June 1980

Prof. Stuart Rice
The James Franck Institute
The University of Chicago
Term of appointment:
June 1978 - June 1980

Prof. David Templeton
Department of Chemistry
University of California,
Berkeley
Term of appointment:
June 1978 - June 1980

Prof. W. Todd Wipke
Department of Chemistry
University of California,
Santa Cruz
Term of appointment:
June 1978 - June 1980

NRCC User Association Executive Committee

Term of appointments: May 1979-February 1980

Prof. Gerald M. Maggiora
Chairperson
Department of Biochemistry
University of Kansas

Prof. Barbara J. Garrison
Chairperson-Elect
Department of Chemistry
Pennsylvania State University

Term of appointments: May 1979-February 1981

Prof. Stanley A. Hagstrom
NRCC
Lawrence Berkeley Laboratory

Prof. Gilda Loew
Department of Genetics S009
Stanford University Medical

Dr. David Silver
Johns Hopkins Applied
Physics Laboratory
Johns Hopkins University

Prof. George Schatz
Department of Chemistry
Northwestern University

Dr. John J. Wendoloski
NRCC Liaison
Lawrence Berkeley Laboratory

APPENDIX D

Financial Summary Report

FY 1979
($K)

Staff Wage Expenses (12.5 FTE)	355	
Supplies, Services and Miscellaneous Expenses	260	
Computer Recharges	230	
Technical Support	8	
Total Direct Expenditures		853
Total Indirect Expenditures		332
Total Expenditures FY 1979		1185