

"CHEMISTRY RESEARCH"

Molecular Structure and Theoretical Chemistry

Report of Committee 15*

Chairman Dr. R. F. W. Bader (Theoretical Chemistry)

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* The data in this report was collected by a survey, conducted by the authors, of the scientists in the fields of spectroscopy, X-ray and neutron diffraction and theoretical chemistry.

There is some measure of disagreement between our data and that tabulated for Committee 15 by the C.I.C. survey. The discrepancy is easily traced to the fact that the field 2709, molecular energy levels and geometry, was taken to imply (along with the general title of molecular structure) the inclusion of pure spectroscopy in the report of Committee 15. Pure spectroscopy is not covered under any other heading in the C.I.C. survey. Unfortunately, the people filling in the questionnaires did not interpret 2709 as spectroscopy and all entries under this heading are blank. Consequently the only information available on pure spectroscopy is that contained in this report.

SPECTROSCOPY

Goals and Boundaries

The present report covers all fields of spectroscopy excluding purely analytical aspects; that is, infrared, Raman, electronic, nuclear spin resonance, electron spin resonance; spectroscopy utilised to determine fundamental properties of molecules, such as structure, geometry, electronic configurations, intermolecular and intramolecular interactions in the gaseous, liquid and solid states, lifetimes of excited states and relaxation processes.

Research and development in this field provides basic information about molecular structures and electronic configurations that is useful in all other branches of chemistry. It enables the transient radicals which occur during chemical reactions to be identified and characterized; for photochemical reactions, many of the intermediate species can be examined by combining flash photolysis techniques with spectroscopic ones, and the detailed reaction mechanisms established. The conformations of organic molecules are of interest to organic chemists, and can be established by nuclear magnetic resonance, infrared and Raman spectroscopy, as well as the effects of solvent interactions and hydrogen bonding. Spectroscopic techniques are widely employed in inorganic chemistry to establish the structures of compounds, especially compounds of the transition metals at present. Comparison of the spectra of molecules in the gaseous and crystalline phases throws light upon the intermolecular forces occurring in the latter. Spectroscopic studies of species produced in the upper atmosphere and by extraterrestrial sources are complemented by studies on the same species in the laboratory, enabling the mechanisms of photochemical reactions above the earth's surface to be understood. Spectroscopic results are the chief source of data with which the theoretical chemist compares his calculations.

Apart from the above, industrial applications include the development of

new laser sources; spectroscopy is used as a basic tool during the synthesis of new compounds and polymers, and is fundamental to applied photochemistry. There are no manufacturers of spectroscopic equipment in Canada at present, all such apparatus being imported from abroad. The demand in Canada is at a sufficient level for equipment to be manufactured here, and, consequently, exported to other countries.

Development and Present Status

Apart from some early academic work, mainly at the University of Toronto, the most important factor in the development of spectroscopy in Canada has been the large growth in work in the field at the National Research Council. This has developed in the Division of Pure Physics, under the leadership of Dr. G. Herzberg, into a group recognized as one of the foremost in the world in electronic spectroscopy. The Division of Pure Chemistry, particularly through the activities of Drs. H. Bernstein and R. N. Jones, has developed a considerable body of spectroscopic talent in the post-war years. In the past decade, spectroscopic work in Canadian Universities has undergone a tremendous increase: almost all Chemistry Departments across the country have at least one spectrometer. Academic schools particularly worthy of note are: nuclear magnetic resonance, University of Manitoba (Dr. T. Schaefer), U.B.C. (Dr. L. W. Reeves), Western Ontario (Dr. J. B. Stothers), McMaster (Dr. R. J. Gillespie); ESR, U.B.C. (Dr. C. A. McDowell), Waterloo (Dr. W. F. Forbes); infrared, University of Toronto (Dr. J. C. Polanyi), Université Laval (Dr. P. A. Giguere), University of Calgary (Dr. P. J. Kreuger); electronic spectroscopy, McMaster University (Dr. G. W. King), Université de Montreal (Dr. C. Sandorfy), U.B.C. (Dr. A. V. Bree). The Ontario Research Foundation also has a strong interest in infrared spectroscopy, and the B.A. Oil Company and Dow Chemical of Canada also are engaged in this field.

Some of the most significant advances are: the production by flash photoly

and identification of numerous triatomic radicals at NRC (Pure Physics Division); non-linear effects in Raman spectroscopy and Brillouin scattering, being examined by Dr. B. Stoicheff at the University of Toronto; work on relaxation processes using a "spin-echo" NMR spectrometer at U.B.C. (Drs. L. W. Reeves and M. Bloom); work on NMR spectra of Group V halides by Dr. W. Schneider's group using superconducting magnets at NRC; theoretical analyses of NMR spectra by Dr. H. Bernstein's group at NRC, and their use of argon ion lasers to excite Raman spectra.

In Chemistry Departments of Universities, there are an estimated 20 faculty members and 100 graduate students engaged primarily in spectroscopic research. In government and industry, there are probably about 50 persons engaged in non-analytical research aspects. The expenditure in this field is difficult to estimate, but is probably around \$1 million per annum at present. The number of Ph.D.'s per annum is around 15, and M.Sc.'s around 5. However, many theses combine spectroscopy with other aspects of molecular structure.

Growth and Future Needs

The amount of research will continue to expand rapidly; a great deal of more highly developed equipment, also more highly priced, will be available and will be purchased as research tools. The number of qualified persons engaged in the area will probably double in the next five years, and the expenditure rise to \$5-10 million per annum. There has been little research in the area of spectroscopy in the industrial field, for the usual reason that such work is undertaken in the U.S.A. rather than by Canadian subsidiaries of U.S. firms. Research in the Universities will increase naturally as more instruments become commercially available as tools. There is already strong activity in the field at the National Research Council.

For the next 5 years, \$10 million would be a satisfactory expenditure in all branches, and 100 trained chemists (B.Sc., M.Sc., and Ph.D.) per annum should

cover requirements of University and industry, allowing for "brain drain" wastage. More large pieces of spectroscopic equipment (costing up to \$100,000 each) will certainly be needed to expedite research in the area, although the number of these required will depend upon the degree of cooperation between different groups that may wish to use them.

- (1) Research and development in the areas of laser Raman spectroscopy and molecular beam techniques applied to spectroscopy should be accelerated. New opportunities are provided by the availability of equipment of increasingly higher resolving power and sensitivity, especially in the NMR field and the increased availability of liquid helium to enable studies on crystals and solutions at 4°K.
- (2) Microwave spectroscopy has received little attention in Canada as far as chemical applications are concerned, and more work in this area should be encouraged.
- (3) There is need for a computer system to store and retrieve the vast mass of spectroscopic data now available at the international level.
- (4) There is a definite shortage of trained personnel, especially at the technician level, to maintain and operate spectroscopic equipment.

X-RAY, NEUTRON AND ELECTRON DIFFRACTION

Goals and Boundaries

The area covered by this report is the determination of structure on a molecular scale by X-ray, neutron and electron diffraction. In the case of X-ray diffraction this report will be confined to single crystal methods.

Structural crystallography provides information regarding atomic arrangements from which details concerning chemical bonding and reactivity can be derived. This information is also of importance in the areas of solid state physics, metallurgy and materials science in such aspects as phase transformations, magnetic and ferroelectric properties, optically and electronically active devices. However, it should be clear that structural crystallography in general provides information which at best can, in the hands of the skilled, be used to guide the development of research and technology in other fields.

Development and Present Status

There was very little activity in the area of electron diffraction until very recently. There has however, been an international awakening to the value of this field to chemistry and this is only beginning to have impact in Canada. This awakening results from the fact that gas electron diffraction determines the molecular structure of molecules containing a modest number of nuclei and electrons and that current research in theoretical molecular calculations of bonding are considered reliable enough to be checked with this structural information. The first and only research group in Canada in this important area is being established by Dr. J. Hencher (Windsor).

Neutron diffraction has played a limited role in chemistry in Canada. The installations at Chalk River and McMaster have been used primarily for exploring solid state problems such as lattice vibrations, hydrogen bonding, and

ferroelectricity.

Structural determination by X-ray on single crystals has been actively pursued by the National Research Council for many years. It is only over the past 5 to 7 years that comparable development has been seen in the University scene. This probably is a result of a substantial reduction, with the advent of digital computers, in the turnover time for the elucidation of a structure. This trend will no doubt increase encompassing more areas of chemistry as automation continues to be used in the field. This time period for a structural study is approaching time periods tolerable on an industrial level.

The following is a list of X-ray crystallographers in University chemistry departments and government laboratories: Dr. J. Trotter (British Columbia), Dr. H. Lynton (New Brunswick), Dr. C. Calvo (McMaster), Dr. T. Mak (Western), Dr. G. Palenik (Waterloo), Dr. S. Nyburg (Toronto), Dr. O. Knopp (Dalhousie), Dr. R. Heyding (Queens) and Dr. L. Calvert, Dr. F. Ahmed, Dr. W. Pearson and Dr. M. Przybylska (National Research Council). The total number of X-ray crystallographers in Canada is about 40, the remaining workers being members of geology, metallurgy and physics departments. There are in addition about 35 graduate students registered for advanced degrees in the field of crystallography in chemistry departments alone.

Growth and Future Needs

The present annual expenditure on X-ray crystallography in chemistry departments is in the region of 230 thousand dollars for personnel and approximately 120 thousand dollars for their research budgets. Although there will likely be an increase in capital equipment, there will probably be only a modest growth in the number of crystallographers. The new equipment which is now available in the form of an automatic X-ray diffractometer costs in the

region of 70 thousand dollars. In order to be competitive such installations will be mandatory. With the added capital necessary for acquiring the new instruments together with the expected growth, annual expenditures could rise to 2 million dollars.

Increased automation both in electron diffraction and X-ray diffraction studies together with rapid computation techniques has broadened the field considerably. Many researchers with little experience and training in the latter field are becoming attracted to it because of the importance of the data obtainable. Neutron diffraction will always be limited by the availability of a high flux neutron source.

- (1) Very little in the way of electron diffraction studies are currently being pursued in Canada and this area should receive urgent attention. A central neutron diffraction facility should be provided by the government so that scientists throughout Canada will have access to this facility.
- (2) A crisis may occur in the near future if the computational facilities are not up-dated at a rapid enough rate. The rate at which data can be produced by the present automatic X-ray facilities are such that they could easily saturate an installation with a capacity and speed no greater than the IBM 7040.

THEORETICAL CHEMISTRY

Goals and Boundaries

It is the purpose of theoretical chemistry to provide a unified mathematical framework for the prediction, understanding and interpretation of all chemical phenomena. As Dirac pointed out in 1929, quantum mechanics and quantum statistical mechanics provide, in principle, this very framework. Unfortunately, as we appreciate perhaps even better today, the mathematical complexity of the problem precludes our attaining this ultimate goal. Rather than the ideal goal of theoretical chemistry, we shall set down what are at the moment the more attainable goals and present boundaries, boundaries which are dictated by our present mathematical (or perhaps conceptual?) abilities.

All theoreticians agree that their principal task is to aid the experimentalist. Indeed without experimental data there would be no theoretical chemistry, but without the guide of theory, chemistry would be assemblage of sterile facts. Thus it is the goal of the theoretist to correlate and interpret existing data and to suggest new and pertinent experiments. This ideal interaction between theoretist and experimentalist has been best realized in those fields which are considered jointly with theoretical chemistry in this section of the present survey, molecular spectroscopy, X-ray diffraction, electron and neutron diffraction, and nuclear and electron spin resonance. These fields are the experimental source of our knowledge of the structure of atoms, molecules and matter in general.

Many of the most important and pressing problems which lie on the "boundaries" of our present theories occur in these particular fields. For example, the theoretical work concerned with the solid state is resulting in the formulation and application of entirely new theoretical techniques. The most immediate problem in this area is the interaction of electromagnetic

radiation with the solid state, with particular emphasis on molecular crystals and collective excitations. More detailed information could be gained from present day X-ray and electron diffraction experiments if the necessary theories were sufficiently developed. The wealth of structural data, both geometrical and electronic, obtained from nuclear and electron spin resonance experiments could be greatly enhanced if theory could completely account for the various coupling constants and chemical shifts which such experiments provide. Molecular spectroscopy is providing a great deal of information about the structures of the excited states of molecules. Excited states are playing an increasingly important role in many phases of chemistry and theory is needed to account for changes in geometry and chemical reactivity upon excitation. The use of electron scattering to determine the electronic energy levels of molecular systems is a new and promising field, particularly for observing the manifold of triplet states. Theory is here again behind experiment in being able to glean the maximum amount of information from the observed data.

The above are some of the important theoretical problems of the moment. They illustrate the inseparability of the development of theory and experiment. Fundamental to the aforementioned fields and to all of chemistry is the theory of the electronic structure of molecules. The most all-embracing, best-developed and widely-used conceptual model which theory has provided for the understanding of chemistry is the orbital model of the electronic structure of atoms and molecules. The scope and limitations of this theory are well defined in terms of Hartree-Fock theory; a Hartree-Fock wave function by definition being the best one-electron or orbital approximation to a many-electron problem. Only relatively recently has it been possible to obtain "the molecular orbitals" and then only for relatively small molecules. For larger systems approximations to the molecular orbitals have been obtained by semi-empirical methods such as

Hückel theory, the Pariser-Parr-Pople method or by LCAO MO self-consistent field methods with basis sets of limited size. These methods have provided the spectroscopist and the experimental chemist with a single conceptual framework on which have been constructed our present theories of chemical bonding, chemical reactivity and our interpretations of the electronic spectra of molecules. No single field of chemistry has benefited more from the advent of the new high-speed computers than has the one concerned with obtaining an orbital description of molecules with Hartree-Fock or near to Hartree-Fock accuracy. The use of Gaussian functions rather than the usual Slater-type atomic orbitals, has extended the size of molecules which can be treated up to molecules such as benzene and pyridine. Hartree-Fock wave functions have many very useful properties. Conceptually they are simple to understand and are well-suited for interpretive studies on molecular structure and properties. They have the remarkable property of generating one-electron distributions which are correct to the second-order. Thus the multipole moments of the molecular charge distribution such as the dipole and quadrupole moments are calculated with some precision.

Since Hartree-Fock theory approximates the many-electron wave function by a simple product of one-electron functions, it specifically neglects the correlative effects which the electrons exert on one another's motion. Methods for the calculation of this remaining contribution to the energy are being actively pursued and wave functions which will account for ninety percent or more of the correlation energy of simple molecules will soon be available.

Doubtless the orbital approximation will remain for some time to come the best single theory which the theoretician can offer to the chemist for the prediction and correlation of chemical phenomena. However, there is an increasing number of theoreticians who feel that the above methods, which we might term the

traditional methods, are inadequate and are not capable of providing an all-encompassing theory of chemical phenomena. The traditional methods are aimed at obtaining solutions to the time independent Schrodinger equation

$$H\psi = E\psi$$

and thus effectively ignore all time dependent processes. New approaches which explicitly include the time dependence are being developed and applied, largely to problems in theoretical physics. There is no reason however, why the same theories of scattering, particle propagators, density matrices and many-body theory in general cannot be applied to the problems of chemistry. In particular, the interaction of electromagnetic radiation with matter, particularly in the solid state, molecular collisions and chemical kinetics are problems which can be handled directly and elegantly by the new formalisms.

One of the main forces behind these new developments is directed at obtaining a theory which is more closely tied to or based on those properties of a system which may be observed directly. A discipline which devotes too much of its effort and energy to determining wave functions and orbitals is in the final analysis not a healthy one as neither of these quantities are physical observables. The new approaches have in common a stress on the calculation of observable quantities in a realistic system, that is, one which includes the radiation field. Attempts are being made to reformulate quantum chemistry in terms of the single particle density, an observable property of the system. The two-particle density matrix has received even more attention as we know that it directly determines all of the observable properties of the system. The conditions which insure that the two-particle density function reflect the antisymmetry requirements imposed on the N-particle wave function have not, however, been formulated in a manner which permits the application of this physically appealing approach.

On the macroscopic, as opposed to the microscopic level, theoretical chemistry has provided a sound basis for equilibrium and steady state transport phenomena of gases and simple fluids. In the realm of irreversible statistical mechanics only the simplest of systems can be handled. For polyatomic systems experiment, as well as theory, is inadequate. Such studies are handicapped by a lack of knowledge of translational-rotational-vibrational energy transfer and sufficiently accurate intermolecular potential energy functions. Theories of chemical kinetics suffer from the same handicaps. However, experimental results from molecular beam experiments, and theoretical attacks using scattering theory and ab initio calculations of potential surfaces should soon result in useful and exciting results in this area.

Development and Present Status

Theoretical chemistry is a very young discipline in Canada. Aside from some then-original statistical mechanical calculations of the thermodynamic properties of polyatomic molecules by Professor Gordon^{A.P.} (Toronto) in 1930, there was no theoretical work in Canada until 1954, at which time Professor C. Sandorfy established the first theoretical chemistry group in Canada at the University of Montreal. This group made contributions to the field of semi-empirical calculations, which included the first application of LCAO MO methods to saturated hydrocarbons. This work was the forerunner of the more recent studies of Fukui, Klopman, Hoffman and Pople. By 1959 only five Canadian Universities listed a theoretical chemist among their staff members. This picture has changed rapidly since 1962. There are now over 30 theoretical chemists in Canada and almost every chemistry department has at least one theoretician on their permanent staff.

The research interests of Canadian theoreticians cover the complete range of current fields outlined in the introduction. Semi-empirical calculations on

molecules of moderate size are performed by Dr. C. Sandorfy (Montreal), Dr. S. Moffat (Waterloo), Dr. L. McEwen (Saskatchewan), Dr. M. Whitehead (McGill), Dr. N. Baird (Western), Dr. D. Chong (British Columbia) and Dr. D. Santry (McMaster). These calculations attempt to relate observed spectral behaviour, spectroscopic constants, molecular geometry and chemical reactivity to theoretically determined quantities.

A growing number of workers are concerned with obtaining accurate wave functions for small molecules. Most of this work is within the framework of the Self-Consistent Field method with goals of Hartree-Fock or near Hartree-Fock accuracy. Dr. D. Bishop (Ottawa) and Dr. T. Dingle (Victoria) use one-center expansion techniques. Dr. I. Csizmadia (Toronto) employs a Gaussian basis set in an SCF approach. Dr. R. McEachran (Department of Physics, York) is developing methods for obtaining accurate analytic two-center wave functions for small molecules. Dr. C. Lin (Windsor) is investigating three-electron atomic and molecular systems. Dr. F. Birss (Edmonton, Alberta) has made contributions to the Self-Consistent Field method. Dr. F. Grein (New Brunswick) does work on electron correlation and on positron-electron correlations in atoms and molecules.

A number of workers are concerned with the calculation of molecular properties. Dr. S. Fraga (Edmonton, Alberta) and Dr. G. Malli (Simon Fraser) employ Hartree-Fock wave functions in the calculation of the expectation values for a variety of operators. Dr. G. Hunter (York) is concerned with the calculation of electronic energy curves and their associated rotational-vibrational energy levels. Dr. M. Benston (Simon Fraser) has investigated various methods for the calculation of molecular force constants. Dr. R. Bader (McMaster) employs the molecular charge distributions obtained from Hartree-Fock wave functions for an interpretation of chemical bonding and molecular properties. Dr. D. Hutchinson (Queens) is concerned with the theory of optical rotation. Dr. J. Coope (British

Columbia) does work in various fields of molecular physics including studies of the relationships between valence-bond and molecular orbital theory.

A number of workers are concerned with chemical reaction rates from various points of view. These are Dr. H. Pritchard (York), Dr. B. Eu (McGill) and Dr. W. Laidlaw and Dr. R. Paul (Calgary). Dr. W. Meath (Western) is interested in the calculation of inter- and intramolecular forces with a view to studying collision processes.

A number of theoretical chemists in Canada are applying the newer and more formal theoretical techniques, which include many-body theory and the quantum mechanical Green's Functions, particularly to problems involving interactions of electromagnetic fields with the solid state. Workers in these areas are Dr. C. Mavroyannis, Dr. W. Siebrand and Dr. R. Somorjai (all at N.R.C.) and Dr. R. Wallace (Manitoba), whose particular interests are in multiphoton transitions. Dr. V. Smith (Queens) is investigating the role of electron correlation through an analysis of accurate wave functions by means of the natural spin orbitals. Dr. A. Coleman (Queens) is one of the prime instigators of the use and development of the second-order density matrix in molecular quantum mechanics. (Dr. Coleman is a mathematician but his work in quantum mechanics has led to his adoption by the international body of chemical theoreticians.) The research of Dr. F. Peat (Queens) is also concerned with the N-representability problem.

At present there are only four theoretical chemists in Canada whose primary interests lie in statistical mechanics. These workers and their fields are: Dr. R. Snider (British Columbia) and Dr. J. Valleau (Toronto), kinetic theory of gases; Dr. N. Snider (Queens), study of fluids and reaction rate theory and Dr. R. Paul (Calgary), statistical mechanics of electrolyte transport phenomena and studies in chemical kinetics.

A research group at the University of Toronto has initiated a theoretical programme on the calculation of the rates of simple gas phase chemical reactions. These calculations are classical in nature and at the moment rely on potential energy surfaces derived in a semi-empirical fashion. However, with the rapid advance of ab initio calculations of molecular energy surfaces, the solution to the equations of motion on such surfaces will provide valuable information regarding the basic assumptions of reaction rates and mechanisms.

The theoretical field most frequently cited as being neglected in Canada is statistical mechanics and the related subject of the theory of reaction rates. In actual fact the whole field of theoretical chemistry in Canada has been neglected. While the number of workers interested in the microscopic aspects of the properties of matter at present outweigh those interested in the macroscopic, a steady state has not been reached. A number of the more recent additions to the body of Canadian theoretical chemists are interested in reaction rate theory and time-dependent phenomena in general. The present proportion of workers engaged in work on equilibrium and irreversible statistical mechanics is to some extent a reflection of the present state of theoretical chemistry, as is the present surge of interest in reaction rate theory and scattering processes in general. However, with a number of theoretical groups already established, it is to be hoped that more emphasis will be placed on statistical mechanics in the future.

Another criticism which has been voiced concerning the state of theoretical chemistry in Canada is that overemphasis has been placed on the computational aspects of the subject. This is however, rapidly changing (whether true or not) and again reflects the changing attitude of theoretical chemistry in general. The original theoretical chemistry carried out in Canada was largely semi-empirical in nature. The rise of the computer saw the beginnings of a number of groups interested in ab initio calculations, as occurred elsewhere. Finally, the dis-

enchantment by some with the traditional methods is reflected in the interests of many of the more recently appointed theoretical chemists. In short, Canadian theoreticians present a sampling of the current interests in theoretical chemistry. All of the approaches have important contributions to make and all are in need of growth. Only the semi-empiricists can provide useful guides concerning the structure and reactivity of relatively large molecules in their ground and excited states. The ab initio calculations must continue and be expanded if we are to test the semi-empirical theories at the small molecule limit, if we are to have accurate values for many molecular properties which are difficult to measure and finally, if we are to have reasonable potential surfaces and potential functions for intermolecular interactions. The application of scattering theory and other time-dependent methods all require accurate potential functions before any useful results can be obtained.

Growth and Future Needs

The very rapid increase in the number of theoretical chemists in Canada since 1962 does not reflect the true growth rate, or one which can be expected to continue. The sudden increase in numbers was caused by many Universities hiring their first theoretician. There had been a marked reluctance in many chemistry departments to consider theoretical chemistry as a discipline in itself, worthy of pursuing for its own sake. This attitude has now changed partly as a result of the necessity for instruction in quantum and statistical mechanics at the undergraduate level. The need for such instruction is itself a measure of the change which theoretical chemistry has brought about in the basic concepts of chemistry. This trend in undergraduate instruction can only increase and will generate a constant demand for new theoretical chemists. About eight departments with one theoretician have plans to hire another in the near future and two

departments have initiated plans to form centers of theoretical research consisting of about six staff members. Perhaps no single member of a chemistry department can feel as isolated professionally as a theoretical chemist, at least if his interests tend heavily toward fundamental studies. The fact that Canadian theoretical chemists have been isolated in the past has been recognized. The National Research Council conducts a two month summer session to which a number of Canadian and foreign theoreticians are invited for discussions and the exchange of ideas.

Canadian industry carries out no purely theoretical research and probably will not initiate any in the near future. However, theoreticians with a broad grasp of fundamental theory from valuable members of research and development teams. As basic research and development expands in Canadian industry, a need for specialists in theory will certainly appear. When this demand will come is impossible to predict.

For the present, and for some time to come, theoretical research will be confined to the University and Government laboratories. No arguments will be presented as to the necessity of research in a field whose task it is to unify and interpret all chemical phenomena. The rate of growth of theoretical chemistry in Canada will be determined almost entirely by the importance which individual departments attach to the field. At present there are 16 students proceeding towards the degree M.Sc. and 33 towards the Ph.D. in theoretical chemistry.

Aside from costs involved in connection with the procurement and use of high-speed computers, a subject which will receive special comment, the monetary needs in theoretical chemistry are very modest. The present average yearly operating budget and salary for a theoretician stands at \$25,000. The only major expenses are the salaries for graduate students and post doctoral fellows. More money should ideally be allotted for post doctoral fellows, particularly in those cases where the number of permanent staff members in theory is only one or

two. Thus with the present number of staff members and the increasing rate at which students are choosing to do a thesis problem in theory, one can estimate that the present level of support of approximately one million dollars should ideally be raised over the next few years to one and one-half million dollars. (These estimates do not include any computer costs, costs which are budgeted separately by N.R.C. to the Universities in any event).

Electronic Computers

Electronic computers are essential to the development and practice of all the fields covered in this section of the report, the determination of molecular structure and theoretical chemistry. Computers are used in the analysis of X-ray and electron diffraction data. In spectroscopy, the computer is employed in normal coordinate analysis, in the analysis of vibration-rotation spectra and the spectra of nuclear magnetic resonance and electron spin magnetic resonance. In theoretical chemistry the computer is used in the calculation of the equilibrium and transport properties of gases and in statistical mechanics for model calculations on the properties of fluids and solutions. In the calculation of the electronic structure and properties of molecules the computer reigns supreme. The results of such calculations are just beginning to have an impact on chemistry. Accurate molecular wave functions for simple systems are now available and methods for the treatment of larger systems of more direct chemical interest are being rapidly developed. No fundamentally new problems are encountered in the extension of such calculations to the determination of potential energy surfaces which are required for the study of chemical reactions. Given a potential surface one is still faced with the complex task of solving the equations of motion of a many-particle system on such a surface for the determination of the rate of a chemical reaction. Problems of this nature cannot be attempted without the aid of computers.

The solution to the computational problems involved in the theoretical study of the electronic structure of large molecules and reaction rate theory demands very large and very fast computers, larger and faster than those now available in Canada. If these studies are to proceed, greatly expanded computing facilities must be made available.

It is the opinion of some theoretical chemists that the computer will open up a new era in theoretical chemistry; not in the sense that it will change our very basic concepts, but in the sense that it will become a predictive tool of real value. The necessary techniques and methods are already available to make this a reality in the fields of molecular electronic structure and chemical kinetics. What is missing is a very large computer. The type of computer envisaged and necessary for these calculations will be of such a large size that Canada could afford only one or two such installations. Such centers would of course, be of enormous benefit to many other fields as well. The need for the establishment of such a computation center or centers in Canada has been voiced by others as well. Dr. R. Uffen, Chairman of the Defense Research Board, has proposed the establishment in Canada of one or two centers in Pure and Applied Mathematics. In actual fact, the establishment of such a center would require a relatively modest outlay of funds. It is a general feeling that by the establishment of such a central computational facility, Canada could, for a nominal amount, be in the forefront of a number of critical areas in scientific research and development. We have now a number of very competent people in the fields of molecular calculations and reaction rate theory and with the proper facilities, Canada could become a center for investigations into these fields. Inasmuch that the monetary requirements for the rest of theoretical chemistry are so nominal, the establishment of such a center would in no way curtail the work of theoreticians engaged in the non-computational aspects of theoretical chemistry.

- (1) The number of theoretical chemists should be increased if the growing impact which theory is having on the development of chemistry is to be adequately reflected in Canadian science. More effort should be placed on studies in statistical mechanics.
- (2) It is the opinion of some theoretical chemists that a major computer installation should be established. Such a computer would be of great predictive value in the fields of molecular electronic structure and chemical kinetics.