The Growth of Computational Quantum Chemistry from 1950 to 1971

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1 Introduction

In the evolution of a science there are often prolonged periods devoid of dramatic discoveries but rich in rewarding results as the theory is thought through, the techniques tamed, and the applications accumulated. For Quantum Chemistry the past 21 years has been such a period. The foundations, such as the Schrödinger equation and the molecular orbital wavefunction, were already laid in the decade after 1925 as were the principal working tools such as variation and perturbation methods, expansions in atomic functions, and group theory. The years since 1950 have seen the building up of a sound theoretical superstructure on these foundations and the development of methods of calculation sufficiently reliable to be programmed and distributed widely for anyone to use.

The inclusion of 'computational' in the title draws attention to the role of the computer in the subject. Its impact has been crucial, perhaps more so than in any other subject, as calculations that would have taken literally several lifetimes have become feasible. The extension of the subject beyond the limits of one- and two-electron systems to systems of general interest to chemists is really the consequence of having computers. The title is interpreted here as including both *ab initio* and semi-empirical calculations. In this context, since they often use the same methods and even the same programs, the distinction is not important.

Although 1950 is, to some extent, an arbitrary date with which to begin this survey it does represent approximately the point when the subject began its postwar growth by initiating several new approaches. I have also a personal interest in accepting this suggested date since it is the date of my first paper so that I have been involved in the subject throughout the whole of this period.

It is not the intention to deal with the details of the thousands of publications appearing during this period. A bibliography of review articles published since 1950 is provided for those who would like such details. Nor will I be concerned with questions of priority or credit which seem to me foreign to the true spirit of science and a source of many injustices and quarrels.

2 The Situation in 1950

As mentioned above, the basic elements of Quantum Chemistry were already established in 1950. This is shown most obviously in the introductory textbooks by Eyring, Walter, and Kimball and by Coulson which date from that period and are still valuable references. On the other hand, the subject was difficult to learn to the standard required to begin research since there were few appropriate lecture courses and no summer or winter institutes. It was virtually necessary to join, like an apprentice, one of the few existing groups with their 'oral tradition' of how things should be done and their collections of theses to serve as advanced textbooks. Even basic mathematical techniques, such as the calculation of eigenvalues and eigenvectors for a matrix, presented major problems since none of the methods now used was known then and the earlier methods were tedious and numerically unstable.

The electronic computer had not yet arrived in 1950 and desk calculators were heavy and slow. A calculation on a simple diatomic could take a year, as could a Hückel calculation for a hydrocarbon with about a dozen carbon atoms. In these circumstances calculations were performed only when an important principle had to be established. Most of the time, results had to be obtained by making the maximum use of group theory and by appealing to a variety of crude approximations and analogies.

One major factor in the situation which must be mentioned, because of its importance at the time, concerns the status of the subject in most chemistry departments. Apart from such minor matters as the structure of the hydrogen atom and the ultimate nature of the chemical bond, Quantum Theory was thought irrelevant to Chemistry. Chemists, organic chemists in particular, had achieved a systematic synthesis of their subject in terms that seemed final to them and could be seen to have practical point in predicting the properties of complicated compounds, whereas quantum theorists were still in dire trouble over such simple species as water and benzene. Thus Ingold, for example, writing his massive textbook on the 'Structure and Mechanisms of Organic Chemistry' in 1953 can dismiss quantum mechanics in a few pages. The concepts of electron behaviour used in these explanations were usually qualitative and included electronegativity, ionic–covalent resonance, and the mesomeric and electromeric effects. The principal hypothesis was that molecular structure determined molecular reactivities and *vice versa.* Since, consequently, their concepts were based partly on what was known of the structure of the molecule and partly on its susceptibility to reactions of various kinds, it was not possible to relate them all to quantum calculations of the electronic structure of molecules in their ground states. In so far as it seemed to be talking the same empirical language, valence bond theory was thought more relevant to chemistry than molecular orbital theory. The ultimate in theory was represented by Pauling's book on 'The Nature of the Chemical Bond'. The inability of theorists to reply coherently to such simple questions as 'Is the Coulomb energy always 15% of the exchange energy?' and 'Is planarity absolutely necessary for resonance?' showed up how little they could contribute even when the problems were theoretical! In this situation the quantum chemist was tolerated only because he probably knew more statistical mechanics and he could integrate a kinetic equation from time to time!

It must be confessed that Quantum Chemistry in 1950 had also some unfortunate legacies from its own past which retarded its progress. Earlier, imprecise arguments based on Hartree product wavefunctions had suggested that molecular orbital theory was inappropriate for the description of excited states and consequently this area of application was neglected. On the other hand, the prediction of resonance energies and dissociation energies was given top priority without a clear appreciation of the complications involved in their definition, both theoretically and experimentally, because of the changes in nuclear geometry. Semi-empirical theories suffered also from the absence of any clear statement of the approximations on which they were based so that no checking of the theories was possible and many of the derivations were suspect since their first principles were obscure.

3 Progress made since 1950

Perhaps the most obvious change since 1950 is in the status of the subject. Quantum chemistry now has an honoured place in most chemistry departments and a share in the teaching programme. There are many textbooks propounding the subject and regular Institutes where the interested amateur can receive a concentrated professional training. The subject owes a great deal to those, like Coulson and Löwdin, who pioneered this instructional effort. We have also our own journals, *The International Journal of Quantum Chemistry*, *Theoretica Chimica Acta*, and *Advances in Quantum Chemistry* though it is still true that papers are scattered through almost every Physics and Chemistry journal and sometimes even wider.

This acceptance of Quantum Chemistry is closely related to its use in the analysis and interpretation of molecular spectra of various kinds. Classical descriptions of electronic structure and categories of explanation of electronic behaviour, derived inductively from ground-state observations, did not extend to excited or ionized states whereas explanations and predictions based on simple wavefunctions were remarkably successful. As n.m.r. and e.s.r. apparatus moved into experimental laboratories so it became patently obvious that there were some essential techniques of chemical analysis that could be comprehended only in terms of quantum variables and concepts. It also became intolerable, as Chemical Physics expanded, that the laws governing electrons in chemistry should differ from those governing electrons in physics.

In Quantum Chemistry itself perhaps the greatest advance has been in the status of molecular orbital theory. It is now accepted that this theory can be made rigorous and amenable to practical calculations. Its predictions of molecular structure and of one-electron properties have been demonstrated in many examples to be substantially correct and, with a moderate use of configuration interaction, it can also account for electronic spectra. Predictions of two-electron properties and properties depending on a differencing of energies are not yet reliable. While it is the computer with its power and speed which has been the main factor in reaching this situation, it is also the result of careful analysis of the equations and of the methods of evaluating the integrals involved in them. The use of Gaussian basis functions, too, as well as the traditional exponentials has opened up several new ways of solving integral problems.

An important achievement which can be ascribed to this period is the derivation of theoretical expressions for a large number of molecular properties. Some of these arise from the small relativistic terms in the Hamiltonian of the molecule itself and some from the interaction of the molecule with radiation or other external fields. For the lighter atoms some form of Breit Hamiltonian is sufficient for this purpose and for heavier atoms a radical change in approach is indicated but has not yet been established. In several instances new, specialized forms of perturbation theory have been required for the practical calculation of the properties. Even if the expressions have remained difficult to evaluate accurately, it has been important to trace the origin of each effect to specific terms in the Hamiltonian and to indicate the circumstances in which it will be very large or very small as well as the form of its dependence on such variables as the nuclear spin or the external field.

A theoretical subject also advances by recognizing the limitations of some of its approaches. It is now clearly recognized that the arguments originally used to justify the Hückel form of molecular orbital theory are imprecise and inadequate. The theory does have some justification as an approximate treatment though it is not yet clear what limitations must be placed on this since its use of empirical quantities often means that correlation and other effects are implicitly included. Similarly, valence bond theory, in its original form, has been abandoned though not so much because the theory is imprecise or inaccurate as because the proper inclusion of all the overlap integrals produces an unwieldy formalism ill-adapted to calculation and with no natural definition of localization which would lead to a unique semi-empirical interpretation. The essence of the theory persists in localized geminal and pair theories. The use of one-centre expansions for polyatomic molecules has been widely investigated and, while they continue to have a substantial attraction when considering hydrides, their rates of convergence for large molecules are too slow for practical calculations. Numerical analysis has contributed too since it has produced eigenvalue procedures so fast and reliable that earlier methods based on desk machines are superseded and some pieces of theory whose only purpose was to avoid an eigenvalue problem can now be eliminated.

4 Progress still being made

There are several areas of Quantum Chemistry where substantial progress has been made but where the issues are not yet finally resolved. The most obvious of these is 'the correlation problem'. The only generally successful method of obtaining wavefunctions whose accuracy exceeds the single-determinant wavefunctions has been the multi-determinant (polydetor) or configuration interaction method. This gives part of the correlation relatively easily but its convergence in energy is slow and the labour required for extra accuracy increases rapidly. The interpretation and use of the complicated wavefunctions that emerge from the computer is also a problem, though analysis into natural orbitals and geminals has simplified part of this problem by making the expressions much more compact and providing entities which can be understood physically. Of the alternative approaches, the strongly orthogonal geminal and pair-function theories try to allow for local forms of correlation, the trans-correlated wavefunction introduces r_{12} terms into the wavefunction and there are several methods based on field-theoretic techniques of organizing and evaluating the series expansions of perturbation theory. It is still possible that a direct variation of the two-electron density matrix will be the method of the future, though many of us despair of finding conditions for N-representability in a form suitable for molecular calculation. Much of this trying out of techniques and initiating of new and more sophisticated forms of wavefunction may seem futile to a practical chemist who believes 'helium chemistry' to be uninteresting but it is an essential part of the theoretician's professional concern to be building up his stock of methods, and the helium atom has been our most valuable benchmark.

Despite considerable progress, and the discovery of a number of practical algorithms, the calculation of molecular integrals remains a significant technical problem. As the number of basis functions in a calculation increases, the number of molecular integrals increases as its fourth power so that, in many calculations, the evaluation of integrals and the collection of them in various ways into matrix elements are the rate-determining steps. The possibility of numerical quadrature is very attractive since it could reduce the fourth power to the second and would allow the use of any type of basis function. Unfortunately, none of the numerical methods yet suggested has sufficiently rapid convergence to be an accurate and reliable procedure. The problem of collecting and sorting integral lists is fundamentally a list-processing problem and will be solved as programs for handling highly structured lists become generally available.

The proper treatment of large molecules is still being debated. For many people the only procedure which is advocated as able to give worthwhile results is the semi-empirical one because its severe restrictions on the number of variables in the equations and its elimination of the worst of the integral problems through the use of experimental data make calculations feasible on moderately large molecules. Contemporary methods of this type are much more securely founded than the older methods, but there are still arbitrary features in these methods that have not yet been examined critically enough in circumstances where more exact treatments are available to give standards for comparison. We are still in the situation where each of us has his own semi-empirical method in which he believes but none of us has any trust in anyone else's method. It has recently become apparent, however, that *ab initio* calculations can be extended to large systems using an almost minimal basis set of Gaussian functions. In terms of total energy these wavefunctions are poor ($\sim 95\%$) but they do seem to give some properties, especially structural properties, with good accuracy by a balancing of errors and they do not require any experimental data. Perhaps it is a good thing that we should have several modes of attack on the difficulties of large molecules.

The quantum mechanical study of the reactions of molecules lags far behind the study of their structure. Few reaction surfaces have been calculated and little is known about how to proceed economically from the shape of the surface to the reaction rate itself. The use of indices calculated from the ground-state wavefunction and based on a simplified treatment of one feature of the surface is no longer convincing though some of these indices may retain some empirical value.

5 Prospects for the Future

Although it is not the intention of this paper to predict the future of Quantum Chemistry it is appropriate in the light of the past to suggest problems that will have to be faced in the near future.

It is to be expected that technical problems will dominate the scene for some time yet. The search for better wavefunctions, for better methods of evaluating integrals and better treatments of molecular properties, including reactivities, will certainly continue. Nevertheless, the continued strengthening of computing facilities and the invention of more adequate list-processing algorithms may in the end be more significant than most of our present numerical experiments.

I believe that the greatly improved status of Quantum Chemistry now, as compared with 21 years ago, is recognition of the fact that we have become professionals committed to our subject and convinced of its value instead of amateurs whose first interests are elsewhere. We have developed our techniques to the point where we can tell whether or not a property of a particular molecule can be calculated and, if so, with what functions and what expenditure of effort. In this sense we have an analytical tool which should be applied without further hesitation to solve genuine chemical problems which are difficult to study experimentally, such as structure problems for excited states and short-lived species. We ought also, in my opinion, to be paying more attention to the other uses of theory. Thus, for example, we should be concerned with the finding of molecules which have some property in extreme form. The search for a molecular superconductor is one example of this. We should be designing new molecules for specific purposes. An example of this might be a molecule to catalyse a specific reaction rather as an enzyme does. We cannot know that we have really understood the action of an enzyme until we have successfully invented a new one. Molecules which can store information in such a form that it can be read in and out without being destroyed could even lead to molecular memories in computers and would stimulate interest in the memory systems used by insects and small animals. I am convinced, by the evidence of molecular biochemistry, that, as we move to large molecules, more elaborate molecular 'systems' become possible with many interesting co-operative properties that have no analogue in smaller molecules. It should be one of the aims of Quantum Chemistry to lead the way into this fascinating area by suggesting the properties and by investigating them using simplified models.

This paper was first presented at the NATO summer school on 'Computational Quantum Chemistry' held at Ramsau in September, 1971. The author would like to thank the organisers for their invitation and for their permission to publish this lecture.

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