# Formal Techniques in Real-Time and Fault-Tolerant Systems

# Mathematical Chemistry

Edited by
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# EDITORIAL FOREWORD

This book is the hard-cover version of a comprehensive collection of papers on mathematical chemistry originally published in the *Journal of Mathematical Chemistry*. These papers represent the proceedings of an International Conference on Mathematical Chemistry held at the Galvez Hotel in Galveston, Texas, during the week of March 5–9, 1989. The principal organizers of the Conference were Professors D.J. Klein and W.A. Seitz, both of Texas A&M University at Galveston, Texas. The present book contains refereed versions of most of the papers delivered at the Conference. The considerable task of arranging for the refereeing of all these papers was undertaken by Professors D.J. Klein and M. Randić (Drake University, Des Moines, Iowa). Accordingly, their names appeared as Special Guest Editors of the volume of the *Journal of Mathematical Chemistry* devoted to the Conference, and they also appear as the editors of this book.

The Conference attracted close to one hundred participants from some ten different countries and represented the third in an ongoing series of North-American Conferences on the theme of Mathematical Chemistry. The first two Conferences in this series were held at the University of Georgia in 1983 and 1987; the proceedings of both were subsequently published in book form [1,2]. This hard-cover version appears simultaneously with the special volume of the *Journal of Mathematcal Chemistry.*
It is intended primarily for those interested in our field who wish to have a separate, bound book of the Conference proceedings.

To facilitate the location and study of the papers delivered at the Conference, I have arranged them into five sections. The underlying idea was to group together papers that are somewhat related. The five sections are headed Arenes and Aromaticity, Polynomials and Eigenvalue Equations, Structure–Property Predictions, Treatments of Many-Electron Systems, and Miscellaneous Topics in Mathematical Chemistry. The Conference Theme Address which precedes the papers is based on the Conference banquet speech given by Professor P.-O. Löwdin (University of Florida, Gainesville, Florida; emeritus of Uppsala University, Uppsala, Sweden) on March 7, 1989. This speech has been placed to the fore since is provides an excellent introduction to these Conference Proceedings.

## Editorial foreword

It is interesting to observe that the series of North-American Conferences on Mathematical Chemistry appears to be gradually changing in character. Thus, whereas the first two of these Conferences were devoted almost exclusively to the chemical applications of graph theory, combinatorics and topology, the third has broadened in scope considerably to include topics such as quantum chemistry and solid-state chemistry. It is also worthy of mention that the frequency of the Conferences seems to be increasing: there were five years between the first and second Conferences, but only two years between the second and third Conferences. All of this would appear to support the contention that mathematical chemistry is currently a burgeoning area of international scientific research endeavor.

[1]  R.B. King (ed.), *Chemical Applications of Topology and Graph Theory* (Elsevier, Amsterdam, 1983).
[2]  R.B. King and D.H. Rouvray (eds.), *Graph Theory and Topology in Chemistry* (Elsevier, Amsterdam, 1987).

Dennis H. Rouvray
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## Editorial Foreword

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# Conference Theme Address

# MATHEMATICS IN CHEMISTRY AND IN MATHEMATICAL CHEMISTRY

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Address to the
Third International Mathematical Chemistry Conference

It is certainly a great honour and privilege for me to address the banquet of the Third International Mathematical Chemistry Conference, and – at the same time – it is very difficult, since there are so many themes one could speak about. Today, I have chosen to speak about the different roles of mathematics in theoretical chemistry in general and in mathematical chemistry as defined as the topic of this conference.

## In memory of Oskar Polansky

Before I start, I would like to say a few words in memory of our esteemed colleague, Professor Oskar Polansky, who was one of the outstanding pioneers in the field of mathematical chemistry. I first met him when he attended the four-week 1959 Uppsala Summer Institute in Quantum Chemistry and Solid-State Theory at Lidingö outside Stockholm, and he was then a young enthusiastic professor in Vienna, Austria. The institute had many outstanding participants – including Roald Hoffman – but, for some reason, Oskar Polansky was selected by the participants as their spokesman and leader. He obviously had an unusually warm personality and a natural talent for leadership, and thanks to the fine interaction with him, the quality of the institute could be greatly improved. I had also the privilege of visiting him as a guest lecturer in Vienna, and – on this occasion – I learnt about his immense hospitality. Some years later, I was assigned to the little site committee – "Fachbeirat" – which periodically evaluated the research at the Max-Planck Institute for Radiation Chemistry at Mülheim an der Ruhr in West Germany, and I learnt about the excellent research done by Oskar Polansky and his group there, and about his intense international collaboration – particularly with Vienna and the Bulgarian Academy of Science. In spite of the warm recommendations by the site committee to continue the research project in theoretical chemistry in Mülheim even after Oskar's retirement, the leadership of the German Max-Planck Institute decided otherwise, and this also means that the fine journal called

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Match, which he strongly sponsored, probably has to find a new home in the future. Oskar Polansky was not only an outstanding scientist, but also an unusually fine human being with far-reaching interests, and his death in the middle of January 1989 was a great loss for science and mankind. We will miss him. At the same time, his fine scientific results will always stay alive among us.

## Mathematics in chemistry

Let us admit that mathematics has seldom been really popular among chemists in general, and this is probably best illustrated by the quotation from Comte given by Josef Paldus in his fine lecture at this conference. Still, it is very difficult to carry out chemical experiments without having some idea or "theory" in mind, and it is obvious that it would be highly desirable to explain all the various phenomena occurring in chemistry by means of some simple unifying principles. The modern chemists are highly skillful mathematicians and computer experts, as is well illustrated by the work in crystallography by Jerome and Isabella Karle and Herbert Hauptman. Still, it needs to be emphasized that much more good mathematics is needed in the field of theoretical chemistry.

At one of the early Sanibel conferences, Professor John C. Slater made the strong statement that any violation of mathematics could not only give you excellent agreement between theory and experiment, but also that you could prove almost anything. At the luncheon after his lecture, I remember that we were standing in line for the salad when a senior colleague came up to Slater and said: "If you would be permitted to make wrong rounding-off errors in the sixteenth decimal, could you prove that you are the Pope?" Slater thought for a few seconds, and then came his reply: "If $+0.5 \times 10^{-16} = -0.5 \times 10^{-16}$, one could multiply by $2 \times 10^{16}$ and get $+1 = -1$, $4 = 2$, and $2 = 1$. Multiplying by $C$ and $P$, respectively, one would have the two relations $2C = C$ and $P = 2P$, as well as $2C + P = C + 2P$ and $C = P$. If $C$ is John C. Slater and $P$ the Pope, I would certainly be the Pope". Even if there may be some logical objections against this type of reasoning, the senior colleague was certainly astounded and went away to contemplate the consequences.

I remember that, in the Uppsala group in the early 1960's, we had a special one-lecture course called "How to get good results without actually cheating". A typical example could be found in the theory of the intensities of spectral lines, where one could use coordinate, velocity, or acceleration formulas for the transition moment, which would give the same results in the exact theory but usually different results in an approximate theory. However, in the latter case one could – for instance – multiply the coordinate formula by $\lambda_1$ and the velocity formula by $\lambda_2$. As long as $\lambda_1 + \lambda_2 = 1$, the formula gives the correct result in the exact theory, and by giving one of the $\lambda$'s the proper value, it will give the correct result also in the approximate theory. This is a one-parameter formula, and by studying its behaviour for, e.g., a series of related molecules, one may be able to interpolate or extrapolate the transition moments in the series.

However, the main purpose of this course was really to teach the students that they should never be impressed by good agreements with experiments alone. Excellent agreement between theory and experiment is certainly a *necessary* condition for the goodness of a theory, but it is by no means a *sufficient* condition. An exact theory should be internally consistent and have no adjustable parameters, and it should be able to *explain* not only the existing experimental data but also to make *predictions*. It is certainly true that most of the current theoretical chemistry could be improved by strengthening its mathematical background, and the only question is how this should be done.

### Structure of mathematics and deductive theories

Mathematics has a very different structure from chemistry, since it deals with concepts and not experiments. Mathematics is *deductive* in the sense that any part of it starts from a series of *axioms*, which are chosen as building blocks of the theory and only have to fulfill the conditions that they should be non-contradictory and non-redundant. In addition, there may be a series of concepts which are not defined by the axioms – such as, for example, the point, the straight line, and the circle in the Euclidian geometry – and which, in the abstract theory, are referred to as "undefined quantities" without any specific content. When one applies logic to the axioms, one obtains a series of theorems which are characteristic for the *abstract theory*, which is still a content-less structure. The theory may be given a content by giving a definition or realization of the "undefined quantities", and this leads to a *model theory* in which – in addition to the theorems of the abstract theory – one may have model-dependent theorems. It is interesting to observe that, if there are different realizations of the "undefined quantities", one may have model-dependent theorems which are true in one model but false in another. If such theorems can be meaningfully formulated also in the abstract theory, which is often the case, they are examples of theorems which cannot be proven to be true or false within the framework of the abstract theory, and which are, hence, examples of Gödelian theorems.

In theoretical chemistry, one should observe that the physical *observables* – such as, for example, the coordinate $x$ and the momentum $p$ – in the original formulation of modern quantum theory [1] may be considered as "undefined quantities" in the sense of mathematics, which were given three different realizations by the great pioneers: they were interpreted as *operators* by Schrödinger, as *matrices* by Heisenberg, Born, and Jordan, and as *q-numbers* by Dirac. So far, the results to be compared with experiments within the three realizations have been essentially identical.

Another feature of mathematics is that it is historically built up by one building block after another, that every new paper makes reference to all the previous papers, and that a professional mathematician has to know the content of all these papers within a specific field. Most chemists would prefer to see a condensed review on how one may understand the last paper in the chain without going through all the previous papers. Even though such reviews are highly valuable, they are not easily produced. It should

also be observed that there are several levels of *mathematical proofs*: the symbolic or *intuitive proofs*, which give a certain insight into the structure of the theory and some of its most important theorems as conjectures, the *strict proofs*, which convince any reasonable reader, and the *rigorous proofs*, which should convince even the most doubtful ones. The latter usually requires a great deal of space, and most chemists would probably feel satisfied with the intuitive proofs put into a somewhat more strict framework.

## Structure of theoretical chemistry

Let us now briefly review the structure of the field of theoretical chemistry. As I said before, the main purpose of the theory is to explain the enormous number of various chemical phenomena occurring in experiments, in technology, and in industry, etc., by means of a few unifying principles. If one selects a specific sector of experiments, the best type of theory may be a "rule of thumb", which may be used to construct new experiments and to make certain predictions. The next level of theory are the *semi-empirical theories*, where one set of experimental data through the theory are able to predict another set of experimental data. The next level of theory are the *deductive* ones, which have a more mathematical structure: one starts from a series of *axioms* or basic assumptions, and by applying logic and mathematics one derives a series of theoretical results, which may then be compared with the corresponding experimental results. If the agreement is good, one may be satisfied and try to use the theory for predictions. If the agreement is not so good, one tries to go back and modify the basic assumptions and repeats the entire cycle, until one reaches the agreement desired. One of the great teachers and pedagogues of theoretical chemistry is Professor F.A. Matsen here in the audience, and he used to cleverly describe this pragmatic approach as "the six steps to chemical insight". A fine example of this iterative approach has been given at this conference by Mark Johnson, Eric Gifford, and Chung-che Tasai in their study of models for metabolic pathways.

Since the time of Heitler and London [2], one has had good reason to believe that the unifying principle in theoretical chemistry would be provided by modern quantum theory, and Dirac's famous 1929 statement about the laws underlying chemistry has already been quoted at this conference. It should be observed, however, that pure quantum mechanics based on wave functions describes only systems at absolute zero temperature, and that, in theoretical chemistry, one needs the more *general quantum theory* based on the concept of ensembles as described by J. von Neumann [4]. This theory treats also the *statistical mechanics* of interacting particles, as well as the approach to equilibrium. This approach has been illustrated at this conference by the beautiful lecture by Michael Fisher about the statistical mechanics of membranes and vesicles in molecular biology.

Let us now return to pure quantum mechanics. In order to solve the time-dependent Schrödinger equation, as well as the eigenvalue problem associated with the time-independent Schrödinger equation, one needs many valuable tools from pure

mathematics: particularly the theory of solution of partial differential equations of first- and second-order of a large number of variables. A nice application of the theory of differential equations was given here in the lecture by Carl Wulfman. The standard solution today of the time-dependent problem involves the use of evolution operator techniques.

As to the eigenvalue problem, the main tool for finding approximate solutions seems to be the Rayleigh–Ritz *variation principle* [3], and it is even today the main basis for the various computational techniques. However, there are also many important results which can be obtained without numerical calculations, and which are connected with the *constants of motion* of the Hamiltonian under consideration. Since the unitary constants of motion always form a group, they are conveniently handled by *group theory* involving the symmetric group, the point groups, as well as the unitary group itself. The importance of the unitary group has been nicely demonstrated at this conference in the lectures by Josef Paldus and Al Matsen – by the latter in connection with the Hubbard model. The groups form a natural tool for the classification of states, but today they are also of importance in the pure computational schemes – like GUGA – and I will return to this later.

## Graph theory

Many years ago, at a Sanibel Symposium, Milan Randić convinced me that the natural tool for the classification of all the isomers of the organic hydrocarbons would be *graph theory*, and in these efforts he has over the years been strongly supported at the Sanibel conferences by Leo Klasinć and Nenad Trinajstić. Since then, we have published many important papers on chemical graph theory in the International Journal of Quantum Chemistry (IJQC). A few years later, I received a nice letter from Professor Frank Harary – Editor of the Journal of Graph Theory (JGT) – who pointed out that not all the graph theory papers published in IJQC were of sufficiently high mathematical quality and offered to serve as an additional mathematical referee, if we so desired. Since Professor Harary is present in the audience, I would like to take this opportunity to thank him for his effort to improve the quality of IJQC. In this connection, I wrote to Milan and suggested that, in the future, the main bulk of the papers in pure graph theory should perhaps be submitted to JGT.

There have been many nice papers on graph theory and related subjects presented at this conference by Soteros, Janse, van Rensburg, Herndon, Rouvray, Sumners, King, Klasinć, Poshusta, Kiang, Harary, Dias, Trinajstić, and others. They are all characterized by the fact that the chemical formulas for the hydrocarbons are represented by graphs, which are labelled by matrices which also arise in the Hückel approach or in the molecular-orbital methods in general. These graphs or matrices have different invariants, such as the characteristic polynomial or its eigenvalues. There are, apparently, chemical formulas which have the same invariants and which have to be distinguished in other ways. In this connection, I wonder whether there are any structural formulas

which are not represented by Hermitian matrices and which have multiple eigenvalues characterized by the orders of the Jordan blocks involved, i.e. by the so-called Segré characteristics.

I was deeply impressed by the aesthetical beauty of the concealed non-Kekuléan graphs presented by Cyvin, and by the powerful theory developed by Hosoya. It is evident to me that most of the molecules represented by these graphs will never be chemically synthesized, and sometimes I wonder how many could be synthesized, at least in principle. Then I realize that, at least for the moment, this is a rather irrelevant question at this part of the conference, which has more emphasis on the graphs themselves than on chemistry. It should still be remembered, however, that many of the results obtained one day could be highly useful in making predictions about the stability of certain chemical structures. I was also fascinated by the theory of knots and entanglements, and – even if my own practical experience in this field is limited to the handling of ropes in sailing and mountaineering – I realize that one day it may be of essential value in the treatment of the folding and tertiary structure of proteins and nucleic acids of importance in understanding their structure–activity relationship.

## Mathematical foundation of modern quantum chemistry

Let us now return to the *eigenvalue problem* and its formulation in terms of the Rayleigh–Ritz variation principle. The equivalence of the three formulations of modern quantum theory is best illustrated by the theory of the *abstract Hilbert space* as formulated by Jonny von Neumann [4]. It is perhaps interesting to observe that, in current molecular theory based on a Coulombic Hamiltonian, the problem is usually formulated in terms of the wave mechanics due to Schrödinger, whereas the computational problem is solved in terms of matrices and vector calculus of the type introduced by Heisenberg, Born, and Jordan. The alphabetic symbols HF, MCSCF, CI, GUGA, CC-MBPT, . . . characterize various approximation schemes which are currently in use over all the world and are solved by means of various types of computers. I will return to the computational problem later.

All these computational schemes are based on Hilbert space methods, and Hans Primas in Zürich has pointed out that it is conceptually difficult to generalize these methods to systems with an infinite number of degrees of freedom – as, for example, in radiation theory – and that one may instead have to resort to the *modern algebras* constructed in mathematics, particularly the C*- and W*-algebras. In this beautiful abstract approach to theoretical chemistry, the main problem is then how one should practically perform the necessary computations.

Some interesting topological properties of Banach spaces having a norm with no corresponding binary product have been pointed out here by Ernst Ruch, and we are looking forward to the applications in theoretical chemistry.

Schrödinger proved by partial integration that the Coulombic Hamiltonian for a system of atomic nuclei and electrons is Hermitian symmetric, but it would take until 1951 before Kato [5] could rigorously prove that it is also *essentially self-adjoint*. Even

if the proof is rather long, it is well worth studying. Even though the Coulombic Hamiltonian $H$ is limited from below, it is still an unlimited operator, and this is one of the reasons why one instead often considers the *resolvent* operator $R(z) = (z \cdot l - H)^{-1}$, where $z$ is a complex variable, and its kernel – the Green function – or the associated propagators. Connected with the resolvent methods is the partitioning technique and the infinite-order perturbation theory, as well as the theory of the wave and reaction operators, which have played a fundamental role both in theoretical physics and in quantum chemistry.

Some authors claim that the standard perturbation theory had an almost degenerating influence on theoretical physics, but – even if this may have been at least partly true – perturbation theory was finally given a strict mathematical foundation by Rellich [6] and by Kato [7]. Since then, there has been an enormous development of this particular field in nuclear physics as well as in quantum chemistry, and at least part of the proofs is fairly strict.

The Coulombic Hamiltonian describes a system of electrons and atomic nuclei, but – since it does not assign the electrons to specific nuclei – it does not describe the atoms and molecules involved. Since this Hamiltonian is translationally and rotationally invariant, it is essential to separate the motion of its center of mass as well as the rotation of the system as a whole. Some of the topological and symmetry problems of the associated energy surface – as a function of the nuclear coordinates involved – have been discussed at the conference by Paul Mezey, and some other general aspects by Klaus Ruedenberg and Michael Zerner. The long way from the Coulombic Hamiltonian to the electronic structure of molecules has also been discussed elsewhere by myself [8].

A few years ago, I agreed to give a lecture about the subject "The mathematical definition of a molecule and molecular structure" at an international conference in Paris, in honour of Professor Raymond Daudel [9]. In this connection, I found that all calculations of atomic and molecular ground states so far carried out were based on the conjecture that, if one could find an approximate trial function for which the expectation value of the Coulombic Hamiltonian was lower than the energy of all possible separated clusters, then the system had a closed ground state with a discrete energy. That this conjecture is really true is proven by the *WHVZ theorem*, named after Weyl, Hunziker, Van Winter, and Zhislin (see [9]). The theorem by Weyl from 1909 says – in modern language – that if one can find a trial function for which the expectation value of the Hamiltonian is below the bottom of the essential spectrum, then the system has a discrete ground state. It has taken a great deal of work by mathematicians in the 1970's and 1980's to prove that the bottom of the essential spectrum of the Coulombic Hamiltonian corresponds to the lowest energy of all possible separated clusters, which represent scattering states with continuous spectra. There are, of course, many examples of Coulombic systems without a ground state, e.g. the system consisting of one proton and three electrons. In connection with the WHVZ theorem, many important contributions have been made by Barry Simon, Elliot Lieb, Erik Baslev, and others, and for a bibliography, the reader is referred to ref. [9].