MATHEMATICAL AND COMPUTATIONAL CONCEPTS IN CHEMISTRY

Editor:

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This book is dedicated to great Croatian scientists

Rugjer Bošković (1711–1787)
Andrija Mohorovičić (1857–1936)
Lavoslav Ružička (1887–1976)
Božo Težak (1907–1980)

Chemistry in general and its chemical graph theory in particular. We accepted the responsibility, both as an honour and a privilege. We are especially happy that the long standing tradition of Mathematical Chemistry in this country, and in Croatia in particular, has been recognized in this way. Hence, this the first symposium dealing exclusively with topics that constitute Mathematical Chemistry has been organized by our Group with great fervour and enthusiasm.

We selected Dubrovnik as the site of the symposium because it is one of the most interesting Croatian cities with a distinguished historical, cultural and scientific heritage. The famous Croatian scientist Ruđer Bošković, fellow of the Royal Society (London), Professor of Mathematics at Collegium Romarum in Rome, and founder of the Observatory at Brera, was born here (May 18, 1711). Besides Dubrovnik, known for its mild Mediterranean climate, is a frequent site for scientific lectures, and is easily accessible by land, sea and air.

The International Symposium on the Applications of Mathematical (Chemistry to Chemistry) was attended by 121 participants from 21 countries. The Symposium brought together mathematical chemists, computer chemists, theoretical chemists, mathematically and theoretically minded experimental chemists, mathematical physicists and mathematicians, for discussions about the status of Mathematical Chemistry, its perspectives, and its influence on various aspects of Chemistry.

Last day of the Symposium has been dedicated to the memory of the late Professor Andrej Ažman (Celje 1937 - Ljubljana 1980) who in his time was the leading chemical theoretician in Jugoslavia and inspiring supporter of Mathematical Chemistry. Last, but not least, during the Symposium important preliminary steps have been made to establish an International Society of Mathematical Chemistry. We expect that the combination of exciting science, beautiful scenery, warm weather and the hospitality of the local people made the Symposium a memorable experience for all participants.

The lectures and posters covered a significant part of the broad spectrum of problems in Mathematical Chemistry and its interactions with other areas of Chemistry. The Symposium also revealed the permanent need for Mathematics in all branches of Chemistry. In addition, it became evident that Mathematical Chemistry will continue to grow as a part of

Preface

Theoretical Chemistry; other overlapping but distinguishable parts include Quantum Chemistry, Statistical Mechanics and Computational Chemistry.

The contributed papers presented at the Symposium will appear in a special issue of Croatica Chemica Acta, a chemistry journal published by the Croatian Chemical Society.

Zagreb, September 1985.

Nenad Trinajstić

Contents

Contents

Contents

INTRODUCTORY REMARKS

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About 200 years ago Immanuel Kant wrote in his
"Kleinere Schriften zur Naturphilosopie": "Ich be-
haupte, dass in jeder besonderen Naturlehre nur so
viel Wissenschaft angetroffen werden könne, als darin
Mathematik anzutreffen ist". He wrote then: "Solange
also noch)für die chemischen Wirkungen der Materien
aufeinander kein Begriff aufgefunden wird, der sich
konstruieren lässt ....eine Forderung, die schwerlich
jemals erfüllt werden wird - so kann Chemie nichts
mehr als Kunst oder Experimentallehre, niemals aber
eigentliche Wissenschaft werden". Just about the same
time Lavoisier was introducing mathematics into chem-
istry through his use of the balance. The law of de-
finite proportions became the basis of stoichiometry
and every chemist-artist had to learn some arithme-
tic.

The next great step in development of chemistry
was the structural theory, but the pioneers in this
field, Butlerov, Couper and Kekulé did not realize
that the structural formulae are actually mathemati-
cal objects, graphs. It was the mathematician Arthur
Cayley who first became aware of that and he devel-
oped the theory of tree-graphs by trying to calculate

the number of possible constitutional isomers of par-
affin hydrocarbons C_nH_{2n+2}. Later, Georg Polya, in an
encounter with problems of isomerism discovered his
famous theorem which became one of the fundaments of
combinatorics. These mathematical achievements, how-
ever, had very little impact on the daily praxis of
chemists, because their everyday problems were usual-
ly so simple that they could mostly be solved by tri-
al and error.

Soon after the structural theory had been devel-
oped Jacobus Hendricus van't Hoff and Achilles Le Bel
founded organic stereochemistry and Alfred Werner the
stereochemistry of inorganic complexes. Symmetry, di-
symmetry and asymmetry became recognized as important
features of molecules, and although group theory was
clearly the branch of mathematics most appropriate
for treating problems in this area very few chemists
made use of it.

The gate of entrance for more sophisticated
mathematics into chemistry was and still is physical
chemistry. Step by step, methods of mathematical
physics penetrated into chemistry: first calculus, to
deal with problems of chemical thermodynamics and
kinetics, then linear algebra and group theory, as
additional tools of quantum chemistry and molecular
spectroscopy.

The more recent general impact of computers on
chemistry and on chemists cannot be overestimated.
Without computers theoretical chemistry, structural
analysis by diffraction methods, molecular mechanics,
etc. could not have developed far, and the collec-
tion, retrieval and classification of the terrifying
multiplicity of chemical data would be almost impos-
sible . The design of syntheses and analyses of reac-
tion pathways are other promising applications.

Last but not least topological aspects of chemi-
cal concepts such as e.g. aromaticity, should be men-
tioned. Thus the progress of chemistry depends more
than ever on applications of mathematics.

The important aims of such conferences as this
one are to bring together scientists who use the many
different branches of mathematics in chemistry and to
bridge existing gaps between them, to learn about the
new work of pioneers and about the progress in estab-

lished fields. The titles in the programme indicate that almost all mentioned topics will be covered.

In summary one can say that chemistry today includes quite enough mathematics to be considered a respectable science from the Kantian point of view, but let us also not forget what Lord Kelvin said about physics: "It is as dangerous to let mathematics take charge of physics as to let an army run a government."

Chapter 2

THE MATHEMATICAL
TRAINING OF CHEMISTS

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I was recently a member of an appointing committee for a
university lectureship in mechanical engineering and was
struck by the fact that none of those interviewed had dirty
fingernails.   I should put it less glibly;   everyone that
was seriously considered for the post was involved in the
computer simulation of structures rather than the building
and testing of rigs.   Of course, one can understand why
this is so;   it is far cheaper to do a computer simulation
of an oil rig than to build one and test it to
destruction.   I assume that somewhere in the background
there must be engineers with oily hands who are still
building and testing, because one can only confidently use
mathematical models to extend empirical knowledge by small
amounts.   Nevertheless, the balance between the
mathematical model builders, and the rig builders and
testers, seems to have swung far towards the clean handed
people in recent years.

I do not think this situation has occurred yet in chemistry
which is still predominantly an empirical subject.   In
fact, I would go as far as to say that the mathematical
models used in chemistry still have rather poor predictive
performance.   How often does an experimental chemist ask
for the results of a calculation before, deciding whether an
experiment is likely to prove fruitful?   In part this is

because chemical experiments are still generally cheap and
not too time consuming.   It is quite often quicker to do a
good experiment than a poor calculation.

However, the situation is bound to change in the future and
one can see already that this is beginning in some of the
more expensive fields such as the pharmaceutical industry.
It costs several million pounds to bring a new drug to the
market so that any model which can narrow the field of
likely candidates is very useful.

The point of this preamble is to stress that what has in the
past been found adequate by the chemical community for their
models may not be adequate for the future.   I am not saying
that our chemistry courses should ignore the Friedel-Craft's
reaction in favour of more time for the Schrödinger
equation.   Rather that we should move our theoretical
studies a little away from conceptual models towards more
quantitative models.

I have for many years been struck by the fact that chemists
and physicists seem to have different approaches to
theoretical problems.   Physicists like to solve approximate
models exactly and chemists prefer to solve good models
approximately.   Think how far the physicist has gone with
the particle-in-a-box.   In fact. I believe that most
physicists are by training or inclination even less inclined
to seek the help of quantitative mathematical models than
are chemists.

You might justly ask whether I practice what I preach.
Well. with my close colleagues Sydney Kettle and John Tedder
I have written two undergraduate textbooks on the theory of
the chemical bond.   The first of these. Valence theory. was
written in 1965 and is quite firmly based on mathematical
skills.   For example. the book shows how to derive the
ligand field matrix for p^2 in the intermediate (weak-strong)
coupling regime. which I think is quite tough for an
undergraduate text.   We assumed that the reader had a prior
knowledge of vector. operator and matrix algebra and
possessed a spirit which was not overawed by mathematical
manipulations.   However, Valence theory is essentially a
book that deals with concepts.   In a later edition we
derived the Hartree-Fock-Roothaan equations but there were
few references to the results which could be obtained from
them.

Our second book. The Chemical Bond. was published in 1978
and is much less mathematically demanding; nothing more is
required than the ability to expand a secular determinant.

However. the principles underlying the ab-initio SCF
approach are explained and the results of such calculation
are used to establish the validity of the qualitative MO
approach.   For example, the concept of a molecular orbital
is developed not only by arguments based on the LCAO
approximation but also by examining the actual ab-initio
results for H_2^+.   Our view in 1978 was that students could
appreciate the basis of quantitative calculations without
having the mathematical ability to follow the problems
encountered in. say. integral evaluation.   In a new edition.
of the book. soon to appear. we are more expansive on the
mathematical basis of the ab-initio method and on the
general structure of the commonly available black-box SCF
programs.   I stress my belief that one can get students to
understand the basis of the ab-initio method and to
appreciate the results of such calculations even though
their mathematical background is poorer than is required to
follow many of the conceptual models of valence theory.

We have been struggling for many years to produce students
who are literate and numerate.   We should now also require
them to be computerate.   I do not much like the word but I
am sure it will not be long before it appears in the Oxford
English Dictionary.

I had originally intended to start this essay with a list of
the mathematical tools that all chemists should know.   On
further reflection I decided that was not very useful.   I
am sure that most of us would take the view that almost any
mathematical skill can be valuable.   Putting this the other
way round: I would be most reluctant to pick out any
mathematical topic as being unworthy of study or as being of
no use to chemists.   The reason that we are at this
conference rather than the Burgenstock conference on Natural
Products (I know a few of us go to both) is not that we know
a great deal of mathematics but that we have an appreciation
for the mathematical approach.   I would even say that most
of us would find some joy in the proof that the square root
of two is not a rational number - and I cannot think that
has much relevance to theoretical chemistry.

However. I will finish by telling you what mathematics is
known by one of our most eminent organic chemists.   I told
Professor John Cornforth that I was to give this talk and in
order to see what was the minimum requirement for a good
organic chemist I asked for the things he knew.   This was
his list:

   (i)   Elementary arithmetic
  (ii)   Two-dimensional geometry including analytical

                        geometry
    (iii)   Plane trigonometry and trigonometric functions
     (iv)   Conic sections
      (v)   Elementary algebra
     (vi)   Simultaneous equations
    (vii)   Permutations and combinations
   (viii)   Differential calculus
     (ix)   Integral calculus
      (x)   Differential equations (including partial)
     (xi)   Theory of probability
    (xii)   Theory of errors
   (xiii)   Exponential functions
    (xiv)   Binomial theorem

He regretted not knowing:

     (i)   Prime numbers
    (ii)   Diophantine equations
   (iii)   Topology
    (iv)   Symmetry

Well, I suspect we do not have a typical case here.   I am
certain that if he had sought my opinion on what organic
chemistry a theoretician needed to know my list would have
been much less impressive.

Chapter 3

THE EFFECT OF ELECTRO-NEGATIVITY ON BOND LENGTHS IN MOLECULAR MECHANICS CALCULATIONS

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ABSTRACT

The attachment of an electronegative atom or group to a carbon-carbon bond causes that bond to have a reduced length. The magnitude of the reduction is roughly proportional to the electronegativity of the attached atom. The substitution of multiple electronegative atoms on the same bond leads to a further reduction of the bond length, unless the size and number of the groups is sufficient so that steric effects outweigh the electronegativity effect. Carbon-hydrogen bonds and carbon-halogen bonds behave similarly, except that the degree of shrinkage differs, depending upon the particular bond. Attachment of an electropositive atom causes a bond lengthening. Within the context of molecular mechanics, these changes in bond length occur in the "natural bond length", or l_o value for the bond, and whatever other effects may be present in the bond due to its particular environment also occur as usual, giving a resulting bond length which may be smaller or larger than the usual value by as much as 0.050 Å or so.

INTRODUCTION

The energy of an electron in a 2s orbital on carbon is much lower than that of an electron in the corresponding 2p orbital. Hence, if a hydrogen atom in an alkane is replaced by an electronegative atom, the carbon bonded to that electronegative atom responds by donating electron density to the electronegative atom, which means the bond to that atom contains more p character than it did in the alkane. If one bond to a carbon has the amount of p character in it increased, the other bonds to that carbon must between them have an increased amount of s character. Considering carbon-carbon bonds in general, an increase in s character (from an sp^3 hybridization) will give a shorter bond, while increased p character will give a longer bond. Thus the attachment of an electronegative atom in, say, ethane, to give fluoroethane, yields a molecule with a shorter carbon-carbon bond than in ethane itself. And attachment of an electropositve atom would yield a longer carbon-carbon bond, for analogous reasons. Experimentally these changes in bond length have long been known, as has the interpretation given.[1-5]

The molecular mechanics treatment of hydrocarbons has been worked out in considerable detail. While it cannot be said that all problems have been solved in this area, most of them have been, at least to a reasonably good approximation. Thus for ordinary saturated hydrocarbons, one can calculate good structures by what are now standard methods.[6]

When one adds other atoms onto the hydrocarbon framework, then the situation is somewhat different. Depending on the type and number of the substituents on the hydrocarbon, the geometries as now calculated by molecular mechanics may be appreciably in error. Since most organic molecules contain various kinds of functionalized substituents, it is also important to be able to deal with the effects of these substituents accurately.

We have been interested in refining the MM2 force field[7] so as to obtain more accurate structures for functionalized molecules. As a prelude to this, we gathered a large amount of representative experimental data so as to quantitatively study this electronegativity effect. We have also carried out ab initio calculations on this effect, and in particular on the torsional dependence of the effect. Some of these calculations have been published previously.[8]

As far as molecular ground states, theory and experiment show substantially the same thing, namely that a given bond will be shortened if an electronegative atom or substituent is attached to it, and lengthened if an electropositive atom is attached to it.[1-5,8] The amount of shortening or lengthening is roughly proportional to the electronegativity of the