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Mathematical Models and Methods for Ab Initio Quantum Chemistry

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Foreword

On the occasion of the fourth International Conference on Industrial and Applied Mathematics[1], we decided to organize a sequence of 4 minisymposia devoted to the mathematical aspects and the numerical aspects of Quantum Chemistry. Our goal was to bring together scientists from different communities, namely mathematicians, experts at numerical analysis and computer science, chemists, just to see whether this heterogeneous set of lecturers can produce a rather homogeneous presentation of the domain to an uninitiated audience.

To the best of our knowledgde, nothing of this kind had never been tempted so far. It seemed to us that it was the good time for doing it, both because the interest of applied mathematicians into the world of computational chemistry has exponentially increased in the past few years, and because the community of chemists feels more and more concerned with the numerical issues.

Indeed, in the early years of Quantum Chemistry, the pioneers (Coulson, Mac Weeny, just to quote two of them) used to solve fundamental equations modelling toy systems which could be simply numerically handled in view of their very limited size. The true difficulty arose with the need to model larger systems while possibly taking into account their interaction with their environment. Hand calculations were no longer possible, and computing science came into the picture. Today, the challenge is twofold: improving the formalism (both from a physical viewpoint and from the mathematical viewpoint), and speeding up rigorously founded numerical methods. From this originates the revival of interest in the communities of chemists and applied mathematicians.

From what we heard from the audience of our series of minisymposia, the result of our enterprise was beyond our hope. So the idea came out to translate that in a written manner. We therefore suggested that each of the nineteen lecturers should give a written account on his view on the subject. The topic of the written contribution need not be exactly the same as that of the talk, but it has to be related with the interplay between Mathematics, Numerical Analysis and Quantum Chemistry. The volume the two of us planned to edit was not a proceedings volume. It was rather an outgrowth of the series of talks, and an attempt to bring together this heterogeneous population this time in the written mode. The only constraint we imposed to the contributors was the following rule of the game: the mathematicians had to write in a language understandable by chemists, and *vice-versa*. Thirteen lecturers out of nineteen played the game until the end. The result is in the reader's

[1]ICIAM99, held in Edinburgh, Scotland, July 5-9th, 1999,

hands. It consists of eleven chapters devoted to various aspects of Computational Chemistry.

This volume is divided into three parts. The first part deals with topics of general interest, the second one is devoted to the modelling of the condensed phases, the third one focuses on the relativistic aspects.

The book opens with a contribution by Brian Sutcliffe on questions of symmetry in Quantum Mechanics. We find it symbolic that the first chapter of such a volume is written by such an eminent chemist, who is known to have had a constant interest into the mathematical aspects.

The first part continues with a chapter by Eric Cancès on the numerical analysis of SCF algorithms for HF calculations. Eric Cancès is one of the representatives of this new generation of applied mathematicians who are very much involved in Computational Chemistry. He presents a rigorous analysis of the existing SCF algorithms and introduces new ones.

Chapter 3 is written together by a chemist and a mathematician, Michel Caffarel and Roland Assaraf. It is devoted to Quantum Monte-Carlo methods. Their contribution, that we consider in some sense as an instance of what should be done in order to enhance the links between the two communities, has been deliberately written on a pedagogical tone. They are to be thanked for that (unfortunately unusual but so much useful) intention.

The last chapter of the first part is due to Gabriel Turinici, who introduces the reader to the very important issue of exact control of quantum systems.

As announced above, the second part of this volume deals with the modelling of the condensed phases. In Chapters 5 to 8, the crystalline solid phase is of concern. Chapter 9 is devoted to the liquid phase.

Chapters 5 and 6 rather stand on the theoretical side. The former, due to Isabelle Catto, Pierre-Louis Lions and one of us (CLB), reports on a series of works devoted to the rigorous derivation of the models of the solid phase, a topic not so often addressed in the physical literature. The latter, written by Olivier Bokanowski, Benoît Grébert and Norbert Mauser, follows the same vein. It discusses the rigorous foundations of some well accepted approximations of Quantum Chemistry, such as the Xα method.

In Chapter 7, Xavier Blanc, a young mathematician, presents his personal view on the models in use for the simulation of the crystalline phase. It may be interesting for a chemist expert at this topic to see the presentation of it by someone of the "outer world".

Chapter 8, from Vanina Louis-Achille and one of us (MD), is the logical sequel of Chapter 7; it develops the practical numerical aspects encountered in solid quantum chemistry calculations which are hidden in usual scientific papers.

Chapter 9 by Benedetta Mennucci is an overview of liquid state methods of calculations. It provides the theoretical framework for the various methods currently used in Quantum Chemistry codes.

The third part, devoted to the relativistic models, features two contributions.

Chapter 10 is due to Jean Dolbeault, Maria Esteban and Eric Séré. It reports on the works of the authors that give a sound mathematical ground to the Dirac-Fock model. By their contribution to the field, they bring the mathematical understanding of the Dirac-Fock model to the level to that of the Hartree-Fock model.

Trond Saue and H. J. Aa. Jensen introduce in Chapter 11 the various concepts of quaternion symmetry appearing in the Dirac Equations as they are implemented in the 4-component relativistic molecular calculations (DIRAC code).

Let us end this foreword by emphasizing we strongly believe that the two communities of applied mathematicians and chemists can take benefit of an interaction. At least we hope that our endeavour towards the challenge to bring together applied mathematicians and chemists will stimulate other ones. As we are tenacious, we are currently working on another project in the same vein.

Needless to say, we encourage every interested reader to contact us.

M. D. & C. L. B.
Paris, April 2000.