RECENT ADVANCES IN THE THEORY OF CHEMICAL AND PHYSICAL SYSTEMS

Progress in Theoretical Chemistry and Physics

VOLUME 15

The titles published in this series are listed at the end of this volume.

Recent Advances in the Theory of Chemical and Physical Systems

Proceedings of the 9th European Workshop on Quantum Systems in Chemistry and Physics (QSCP-IX) held at Les Houches, France, in September 2004

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Progress in Theoretical Chemistry and Physics

A series reporting advances in theoretical molecular and material sciences, including theoretical, mathematical and computational chemistry, physical chemistry and chemical physics

Aim and Scope

Science progresses by a symbiotic interaction between theory and experiment: theory is used to interpret experimental results and may suggest new experiments; experiment helps to test theoretical predictions and may lead to improved theories. Theoretical Chemistry (including Physical Chemistry and Chemical Physics) provides the conceptual and technical background and apparatus for the rationalisation of phenomena in the chemical sciences. It is, therefore, a wide ranging subject, reflecting the diversity of molecular and related species and processes arising in chemical systems. The book series *Progress in Theoretical Chemistry and Physics* aims to report advances in methods and applications in this extended domain. It will comprise monographs as well as collections of papers on particular themes, which may arise from proceedings of symposia or invited papers on specific topics as well as initiatives from authors or translations.

The basic theories of physics – classical mechanics and electromagnetism, relativity theory, quantum mechanics, statistical mechanics, quantum electrodynamics – support the theoretical apparatus which is used in molecular sciences. Quantum mechanics plays a particular role in theoretical chemistry, providing the basis for the valence theories which allow to interpret the structure of molecules and for the spectroscopic models employed in the determination of structural information from spectral patterns. Indeed, Quantum Chemistry often appears synonymous with Theoretical Chemistry: it will, therefore, constitute a major part of this book series. However, the scope of the series will also include other areas of theoretical chemistry, such as mathematical chemistry (which involves the use of algebra and topology in the analysis of molecular structures and reactions); molecular mechanics, molecular dynamics and chemical thermodynamics, which play an important role in rationalizing the geometric and electronic structures of molecular assemblies and polymers, clusters and crystals; surface, interface, solvent and solid-state effects; excited-state dynamics, reactive collisions, and chemical reactions.

Recent decades have seen the emergence of a novel approach to scientific research, based on the exploitation of fast electronic digital computers. Computation provides a method of investigation which transcends the traditional division between theory and experiment. Computer-assisted simulation and design may afford a solution to complex problems which would otherwise be intractable to theoretical analysis, and may also

provide a viable alternative to difficult or costly laboratory experiments. Though stemming from Theoretical Chemistry, Computational Chemistry is a field of research in its own right, which can help to test theoretical predictions and may also suggest improved theories.

The field of theoretical molecular sciences ranges from fundamental physical questions relevant to the molecular concept, through the statics and dynamics of isolated molecules, aggregates and materials, molecular properties and interactions, and the role of molecules in the biological sciences. Therefore, it involves the physical basis for geometric and electronic structure, states of aggregation, physical and chemical transformations, thermodynamic and kinetic properties, as well as unusual properties such as extreme flexibility or strong relativistic or quantum-field effects, extreme conditions such as intense radiation fields or interaction with the continuum, and the specificity of biochemical reactions.

Theoretical chemistry has an applied branch – a part of molecular engineering, which involves the investigation of structure–property relationships aiming at the design, synthesis and application of molecules and materials endowed with specific functions, now in demand in such areas as molecular electronics, drug design or genetic engineering. Relevant properties include conductivity (normal, semi- and supra-), magnetism (ferro- or ferri-), optoelectronic effects (involving nonlinear response), photochromism and photoreactivity, radiation and thermal resistance, molecular recognition and information processing, and biological and pharmaceutical activities, as well as properties favouring self-assembling mechanisms and combination properties needed in multifunctional systems.

Progress in Theoretical Chemistry and Physics is made at different rates in these various research fields. The aim of this book series is to provide timely and in-depth coverage of selected topics and broad-ranging yet detailed analysis of contemporary theories and their applications. The series will be of primary interest to those whose research is directly concerned with the development and application of theoretical approaches in the chemical sciences. It will provide up-to-date reports on theoretical methods for the chemist, thermodynamician or spectroscopist, the atomic, molecular or cluster physicist, and the biochemist or molecular biologist who wish to employ techniques developed in theoretical, mathematical or computational chemistry in their research programmes. It is also intended to provide the graduate student with a readily accessible documentation on various branches of theoretical chemistry, physical chemistry and chemical physics.

CONTENTS

PREFACE

This volume contains twenty-six papers selected from the scientific contributions to the *Ninth European Workshop on Quantum Systems in Chemistry and Physics (QSCP-IX)*, which was held at *Les Houches*, France, in September 2004. About sixty scientists from twenty countries attended the meeting, which addressed the state of the art; they identified new trends and considered future evolution of both methods and applications in the field.

The *QSCP-IX* workshop took place at the world-renowned conference centre of *Les Houches*, which is owned and operated by the *Université Joseph-Fourier Ecole de Physique*. The *Les Houches* facility is situated in the French Alps, overlooking the famous winter resort of *Chamonix*, with stunning views of Europe's tallest mountain, *Mont-Blanc*: http://lepes.grenoble.cnrs.fr/QSCP9/.

The *QSCP-Les Houches* workshop was divided into five morning and four afternoon plenary sessions, during which a total of 46 lectures, each of 30 min, were delivered by leading experts. There were also two evening sessions where 32 posters were presented, each being first described in a 3-min oral presentation. We are very grateful to both oral speakers and poster presenters, for their energy and enthusiasm made the workshop the stimulating experience that it was.

The *QSCP-IX* workshop followed a format that has evolved over the eight previous *QSCP* meetings, beginning with that organised by Pr Roy McWeeny at *San Miniato*, near Pisa, in 1996. At the *QSCP-Les Houches* workshop there were sessions on:

"Density matrices and density functionals",
"Electron correlation treatments: CI and MB methods",
"Relativistic formulations and effects",
"Valence theory; chemical bonding and bond breaking",
"Nuclear motion; vibronic effects, flexible molecules",
"Response theory; properties and spectra",
"Atoms and molecules in strong electric and magnetic fields",
"Condensed matter; clusters and crystals, surfaces and interfaces",
"Molecular electronics; molecular materials",
"Reactive collisions and chemical reactions",
"Computational chemistry, biochemistry and chemical physics".

The *QSCP* workshops have created a unique forum in Europe for open discussion and exchange of ideas. They facilitate cooperation on the development of advanced methods for the description of quantum systems and their applications in chemistry, physics, and the molecular sciences. Workshops since 2000 have been organized by Professor Aristides Mavridis (Athens) on the *Island of Spetses*, Greece, in September 2003; Professor Ivan Hubač (Bratislava) at *Casta Papiernicka*, Slovakia, in September 2002; and Doctors Yavor Delchev and Alia Tadjer (Sofia) in the *Boyana Presidential Residence*, Bulgaria, in April 2001.

The twenty-six papers collected in this volume have been divided into four sections, each addressing different aspects of the study of quantum systems in chemistry and physics. These are:

Part I: Quantum Chemical Methods
Part II: Relativistic and Heavy-Element Systems
Part III: Complexes and Clusters
Part IV: Complex Systems.

We are pleased to acknowledge the support given to the *QSCP-Les Houches* workshop by the *Centre National de la Recherche Scientifique* (*CNRS), Départements Chimie et SPM*, the *Région Rhône-Alpes*, the *Conseil Général de Haute-Savoie* and the *City of Grenoble*.

The efforts of all members of the Local Organizing Committee were very much appreciated, especially the invaluable work of Mrs Karen Guibreteau, Conference Secretary. The supportive help of the team of *Les Houches* centre, particularly Brigitte Rousset and Isabelle Lelièvre, is also gratefully acknowledged. Special thanks are due to Martial Ducloy, Director of the *Les Houches* facility, for offering us the opportunity to hold *QSCP-IX* in this prestigious location.

Professor Daudel acted as Honorary President of the *Centre de Mécanique Ondulatoire Appliquée* (*CMOA)* for the award of the *Promising Scientist Prize*, which was won by Professor Piotr Piecuch (Michigan State University, USA). An impressive ceremony took place at the meeting banquet, held in the restaurant *La Calèche* at *Chamonix-Mont Blanc*. The Prize was awarded at the headquarters of *UNESCO* in Paris: http://www.ccr.jussieu.fr/lcpmr/prize.html.

We hope that, in this volume, we have captured some of the stimulating developments described during the *QSCP-IX* workshop, and that the readers will be fired with as much enthusiasm in consulting these proceedings as were the workshop participants during their time at *Les Houches*.

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