
Theoretical Models of Chemical Bonding

Part 4

Theoretical Treatment of Large Molecules and Their Interactions

Editor: Z. B. Maksić

With contributions by

J. G. Angyán, A. van der Avoird, E. J. Baerends,
R. Bonaccorsi, Ch. L. Brooks, III, R. Cammi,
R. E. Christoffersen, P. Ch. Hiberty,
G. M. Maggiora, V. Magnasco, R. McWeeny,
G. Náray-Szabó, J. D. Petke, R. A. van Santen,
S. Scheiner, S. Shaik, A. J. Stone, O. Tapia,
J. Tomasi

With 104 Figures and 52 Tables



Springer-Verlag

Berlin Heidelberg New York

London Paris Tokyo

Hong Kong Barcelona

Budapest

Professor Dr. Zvonimir B. Maksić
Theoretical Chemistry Group
The "Rudjer Bošković" Institute
41001 Zagreb, Bijenička 54, Croatia/Yugoslavia
and
Faculty of Natural Sciences and Mathematics
University of Zagreb
41000 Zagreb, Marulićev trg 19, Croatia/Yugoslavia

ISBN 3-540-52253-0 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-52253-0 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data
Theoretical treatment of large molecules and their interactions /
editor, Z. B. Maksić; with contributions by J. G. Ángyán ... [et
al.].

p. cm. — (Theoretical models of chemical bonding; pt. 4)

ISBN 3-540-52253-0. — ISBN 0-387-52253-0

1. Macromolecules. 2. Molecular association. I. Maksić, Z. B.
(Zvonimir B.) II. Ángyán, János, 1956- . III. Series.

QD381.T43 1991

541.2'2—dc20 91-14223 CIP

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and a copyright fee must always be paid.

© Springer-Verlag Berlin Heidelberg 1991

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Th. Müntzer, Bad Langensalza; Printing: Heenemann, Berlin;

Bookbinding: Lüderitz & Bauer, Berlin

VA51/3020-543210 — Printed on acid-free paper

*To the memory of my parents
Olivera and Branko Maksić*

Preface

The French chemist Marcellin Berthelot put forward a classical and by now an often cited sentence revealing the quintessence of the chemical science: “La Chimie cree son objet”. This is certainly true because the largest number of molecular compounds were and are continuously synthesized by chemists themselves. However, modern computational quantum chemistry has reached a state of maturity that one can safely say: “La Chimie Theorique cree son objet” as well. Indeed, modern theoretical chemistry is able today to provide reliable results on elusive systems such as short living species, reactive intermediates and molecules which will perhaps never be synthesized because of one or another type of instability. It is capable of yielding precious information on the nature of the transition states, reaction paths etc. Additionally, computational chemistry gives some details of the electronic and geometric structure of molecules which remain hidden in experimental examinations. Hence, it follows that powerful numerical techniques have substantially enlarged the domain of classical chemistry. On the other hand, interpretive quantum chemistry has provided a conceptual framework which enabled rationalization and understanding of the precise data offered either by experiment or theory. It is modelling which gives a penetrating insight into the chemical phenomena and provides order in raw experimental results which would otherwise represent just a large catalogue of unrelated facts. One should point out here that by models we imply simple physical models, obtained in a controlled way, which reflect the essence of systems under study. It is also noteworthy that models can be developed in a completely ab initio fashion without any resort to experiment thus supporting once more a previous statement that theoretical chemistry creates its own object of research. However, modern investigations of the structure and properties of matter at the molecular level require joint efforts of computational and interpretive quantum chemistry combined with empirical chemical research. Concomitantly, the main impetus for the Series „Theoretical Models of Chemical Bonding” was a need to increase understanding and the cooperation of researchers of these con-

ventionally and traditionally separated disciplines of chemical investigation.

The fourth volume deals with giant molecular systems of biological interest and their interactions. Since they are out of grasp of the rigorous *ab initio* methods, penetrating wisdom and suitable models are the only means in exploring their properties. This is not necessarily a drawback because an approximate picture offered by an easy to understand model may be more useful than a very accurate but obscure solution provided by a plain quantum theory of numbers. Consequently, the emphasis in the book is laid on the qualitative aspects of the theory which does not imply that necessary mathematics is avoided. The chapters are intended to give "the state of the art" survey of the most important scientific findings in the respective fields. Their overlapping is not zero, which is a desirable feature because it increases the readability of the text. In particular, the interested reader will find that electrostatic interactions are an essential ingredient of several chapters. This is not surprising since electrostatics is, figuratively speaking, Ariadne's thread which enables a pathway to be traced through a labyrinth of a large number of interactions and degrees of freedom in extended (almost infinite) systems like biopolymers, molecular crystals, solutions etc.

The present volume begins with an extensive description of the important fragmentation approach in studying gigantic chemical systems. The underlying idea is a reduction of the insoluble problems involving perhaps thousands of atoms to a problem of interactions of small units or building-blocks. The choice of the (transferable) basic units is not unique, meaning that their definition is a delicate decision. Attention is focused here mainly on the functional groups since other possibilities were discussed in detail in vol. 2 of the Series.

A brief chapter is devoted to a combined quantum and classical (semiclassical) approach in investigating structure, motion and reactivity of proteins and nucleic acids which in turn provide a key to understanding biological systems. This is followed by the molecular fragment FSGO basis set methodology applied to examining the electronic excited states of individual biomolecules (chlorophyll, porphyrin etc.) and their aggregates.

The long range molecular interactions, their classical electrostatic components and a general partitioning of weak interactions into meaningful physical contributions are then considered in great detail. The formalism is illustrated by applications to some simple VdW and hydrogen-bonded dimers. Then a review of accurate *ab initio* procedures suitable for description of hydrogen-bonded systems is given.

The following block of chapters is dedicated to chemical reactivity. It commences with the concept of extramolecular

electrostatic potential which yields important clues in locating reactive sites in molecules. Then the model of curve-crossing/avoided crossing diagrams based on the VB approach is scrutinized illustrating a power of a proper mixture of qualitative ideas and particular quantitative procedures in considering chemical reactivity. This block is concluded by a survey of theoretical treatments of chemisorption and in particular by a discussion of bonding between metal particles and metal adsorbents. A deep analysis reveals a key role of the symmetry principles and rehybridization which are of utmost importance for understanding chemical reactivity on boundary surfaces.

The last part of the book addresses the questions of bulk and spectral properties of molecular crystals and the chemically extremely important problem of solvent effects involving their influence on molecular properties and reactivity.

To reiterate, if this book and the whole Series contribute to a better understanding of the modern theoretical chemistry and to an increased collaboration between molecular scientists working in different fields, then our efforts will be greatly rewarded.

Finally, it is my pleasant duty to thank all authors for their scholarly written articles. I am also grateful to the Alexander von Humboldt-Stiftung for financial support since a part of editing has been performed during my stay at the Organisch-chemisches Institut der Universität Heidelberg. Thanks go to Professor R. Gleiter too for his hospitality and stimulating discussions.

Z. B. Maksić

Table of Contents

Chemical Fragmentation Approach to the Quantum Chemical Description of Extended Systems	
J. G. Angyán and G. Náray-Szabó	1
Semiclassical Methods for Large Molecules of Biological Importance	
Ch. L. Brooks, III	51
Electronic Excited States of Biomolecular Systems: Ab Initio FSGO-based Quantum Mechanical Methods with Applications to Photosynthetic and Related Systems	
G. M. Maggiora, J. D. Petke and R. E. Christoffersen	65
Classical Electrostatics in Molecular Interactions	
A. J. Stone	103
Weak Interactions Between Molecules and Their Physical Interpretation	
V. Magnasco and R. McWeeny	113
Ab Initio Studies of Hydrogen Bonding	
S. Scheiner	171
The Extramolecular Electrostatic Potential. An Indicator of the Chemical Reactivity	
J. Tomasi, R. Bonaccorsi and R. Cammi	229
Curve Crossing Diagrams as General Models for Chemical Reactivity and Structure	
S. Shaik and P. Ch. Hiberty	269
Orbital Interactions and Chemical Reactivity of Metal Particles and Metal Surfaces	
R. A. van Santen and E. J. Baerends	323
Intermolecular Forces and the Properties of Molecular Solids	
A. van der Avoird	391
Theoretical Evaluation of Solvent Effects	
O. Tapia	435