Computational Chemistry

Reviews of Current Trends

Volume 3

Computational Chemistry: Reviews of Current Trends

Editor-in-Charge: Jerzy Leszczynski,
Dept. of Chemistry, Jackson State University, USA

Published

Vol. 1: Computational Chemistry: Reviews of Current Trends
Edited by Jerzy Leszczynski

Vol. 2: Computational Chemistry: Reviews of Current Trends
Edited by Jerzy Leszczynski

Computational Chemistry

Reviews of Current Trends

Volume 3

editor

Jerzy Leszczynski

*Department of Chemistry
Jackson State University
USA*

World Scientific

Singapore • New Jersey • London • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 912805

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

COMPUTATIONAL CHEMISTRY: REVIEWS OF CURRENT TRENDS — Vol. 3

Copyright © 1999 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 981-02-3752-9

Printed in Singapore.

PREFACE

Undoubtedly, the predictive power of computational simulations is well recognized by chemists. We do see a continuous growth in the number of chemists using computers as a research tool. This results in an increasing numbers of papers based either entirely or at least partially on applications of computational techniques which are being published in journals devoted to the whole chemical community. It also supplies sufficient data to justify its existence and to support the steady growth of a number of journals intended mainly for computational chemists.

The information obtained from computer simulations is especially attractive when experimental data are not available and a theoretical approach supplies accurate information on par with those of reliable experiments. It has become a common practice in every field of chemical research to use a computational methodology which, if properly incorporated into computer software, could supplement or even replace experimental techniques. Theoretical methods--quantum mechanics, molecular dynamics, and statistical mechanics--have been successfully used to characterize chemical systems and to design new materials, drugs, and chemicals. Proliferation of the Internet has accelerated the rapid and worldwide flow of a large volume of numerical data produced as a result of such calculations. However, due to its uncontrolled and rapid progress, dissemination of computational techniques is nonhomogeneous among different disciplines; the validity of theoretical algorithms has not always being properly evaluated, and software packages are too often commercialized before being adequately developed.

The goal of this book series is to navigate through the rapidly increasing computer-generated bulk of data and to bring to researchers and students working in related areas timely information of the current progress in the theory, practice, and results of computational studies. Each volume includes chapters on the development of methods and the applications of different computational techniques.

Contributions collected in Volume 3 add well to the chapters of the first two volumes in this series, disclosing the results of the current developments in the methodologies and applications of computational chemistry methods. The Coupled-Cluster (CC) Theory has been widely considered as the most accurate approach toward the calculation of the molecular properties of ground state species. This method pioneered by J. Cizek and J. Paldus has gained popularity due to the developments of computationally efficient approaches by Bartlett's group. The current challenges for the CC type methods are predictions for molecules in the excited states. The first chapter by Ivan Hubac, Jozef Masik, Pavel Mach, Jan Urban, and Peter Babinec discusses the recent developments in the Brillouin-Wigner CC Theory. This method is available in its single and multireference versions. The developed theory gives a new approach to a multireference problem. The discussion is augmented by examples of the calculations which illustrate well applications of this method.

Chapter 2 by Mariusz Klobukowski, Sigeru Huzinaga, and Yoshiko Sakai reveals the theory and applications of model core potential. Currently three versions of the model potential method are used: the Model Core Potential (MCP) method, the *ab initio* Model Potential Method (AIMP), and the extensions of the AIMP method. The current review focuses on the first method while the AIMP will be reviewed in Volume 4 of this series. Klobukowski, Huzinaga, and Sakai discuss in detail the development and refinement of the MCP method. Examples of the application of this model core potential in investigations of weakly interacting systems and compounds with transition metals are given. Also applications of the MCP method in Quantum Monte Carlo Methods and Density Functional Theory are covered by the authors.

Gas-phase reactions are among the most important processes which could be accurately predicted by *ab initio* calculations. Such reliability makes *ab initio* methods especially attractive for revealing the different aspects of atmospheric reactions. Certainly, depletion of the ozone layer has been one of the crucial processes studied in detail by atmospheric scientists for the last two decades. Sujata Guha and Joseph S. Francisco devote their chapter to a review of an intriguing aspect of ozone destruction--reactions of O_3 with

bromine-containing species. Detailed computational studies were used to examine the structures and properties of such reaction products, and their results have brought new insights into the associated aspects of atmospheric chemistry.

An interesting extension to the subjects discussed in Chapter 4 is given in Chapter 5 by David C. Young and Michael L. McKee. Among the species important to atmospheric chemistry are radical sulfur compounds. The authors give a detailed description of the electronic structures, energetics, molecular structures, and bonding characteristics of the series of gas-phase radical species. In addition, they tabulated similar information for related molecules.

In contrast to gas-phase reactions there is no certainty in the quantum chemical methods which are used to describe solvent influence. Since most reactions in nature take place in the liquid phase, understanding the limitations of currently available models and their applicability to specific problems is of importance for computational chemists using commercial software packages. Chapter 5 written by Leonid Gorb and Jerzy Leszczynski reviews modern methods for modeling solvent effects. The method overview is supplemented by a discussion of their advantages, accuracy, and restrictions. Specific examples of the interactions of simple molecules and ions with water are given.

I am willing to admit that it is not possible to overestimate the importance of the Internet in research and education. Our expectations have always fallen short of the actual progress of the Internet. Ken Flurchick, Margaret Hurley, Jan K. Labanowski, Gerald H. Lushington, and Theresa L. Windus provide an overview of the currently available World Wide Web chemistry-related sites and the developments therein. Chapter 6 discusses Internet and Web basics as well as information on Internet publishing, chemistry resources, and teaching chemistry on the Internet. A glossary of relevant terms is given at the end of the chapter. This chapter also features the individual views by all coauthors of the current state and future growth of the Internet. I do encourage you to browse through these predictions after five years and to mail to me your comments.

I would like to acknowledge all authors for their great contributions and fecund collaborations. Comments from the readers are always welcome as well as suggestions for future volumes in this series. I do not expect that this audience will be willing to use for such purpose anything but the Internet, so for your convenience my e-mail address is `jerzy@tiger.jsums.edu`.

Jerzy Leszczynski
Jackson, MS
June, 1998

CONTENTS

Preface	v
1. Multireference Brillouin-Wigner Coupled-Cluster Theory <i>Ivan Hubac, Jozef Masik, Pavel Mach, Jan Urban and Peter Babinec</i>	1
2. Model Core Potentials: Theory and Applications <i>Mariusz Klobukowski, Sigeru Huzinaga and Yoshiko Sakai</i>	49
3. Stratospheric Bromine Chemistry: Insights from Computational Studies <i>Sujata Guha and Joseph S. Francisco</i>	75
4. Bonding in Gas-Phase Sulfur Radicals <i>David C. Young and Michael L. McKee</i>	149
5. Chemistry of the Liquid State: Current Trends in Quantum-Chemical Modeling <i>Leonid Gorb and Jerzy Leszczynski</i>	179
6. Chemistry and the Internet <i>Ken Flurchick, Margaret Hurley, Jan. K. Labanowski, Gerald H. Lushington and Theresa L. Windus</i>	215
Index	303