Computational Chemistry

Reviews of Current Trends

Volume 1

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Volume 1

editor

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PREFACE

Since the mid-1980's, computational chemistry has been one of the fastest growing areas of chemistry. This is due to both a vast increase in the number of computing platforms and to efficient high-performance computational algorithms. The chemical community has already accepted high-quality theoretical data not as an addition to the experimental findings, but as a reliable, independent source of information about molecular structures, properties, and reactivity. Interest in applying computational methods to different problems in chemistry, biochemistry, and physics is growing remarkably.

In 1992, a Conference on Current Trends in Computational Chemistry (CCTCC) was organized in Jackson, Mississippi. This conference has become an annual event in the intervening years. It has given us a unique opportunity to bring together distinguished experts from different areas of computational chemistry and to survey the impact of their presentations on a broad audience consisting of both professionals and students. Many of our previous and prospective speakers appreciate the idea of sharing their expertise and the results of their current research with a larger group, and from our discussions and interactions evolved the concept for this volume. Two crucial prerequisites were considered during the development of this project: affordability of the book and fast publication in order to bring to the readers truly current information. World Scientific Publishing recognized the value of this book and has done an outstanding job of making sure it is inexpensive and up-to-date.

In this volume, an overview of recent progress in computational techniques, as well as examples of the application of existing computational methods in different areas of chemistry, physics, and biochemistry, is given. In the first chapter, Yasuyuki Ishikawa and Uzi Kaldor present a survey of current methods for computing atomic and molecular structures based on the relativistic quantum mechanics of many-body systems. Following discussion of the many-electron Hamiltonian and the matrix Dirac-Fock SCF method, they describe how to prevent the variational collapse associated with basis-set expansion methods. Recent work on relativistic Many-Body Perturbation Theory and Coupled Cluster Methods is reviewed. The authors give extensive examples of applications of different methods for treating relativistic effects for atoms and molecules.

Chapter 2, by Matt Challacombe, Eric Schwegler, and Jan Almlöf, presents their new developments in overcoming the computational limit of N^2 (where N is

the number of basis functions) for Coulomb matrices. A number of new methods for accelerating constructions of the Coulomb matrices, based on simplified representation of the electron charge density, is presented. Also, projection methods, which may be used to approximate the density by combination of auxiliary basis functions, are reviewed. A suggested fast Gauss transform and Barnes–Hut method are shown to be very competitive and scale as $N^{1.6}$ in calculations on large peptides and water clusters.

Paul G. Mezey explains in Chapter 3 how to generate molecular fragment densities within molecules using the fuzzy electron density fragmentation principle. Several methods (MEDLA (Molecular Electron Density Lego Assembler), ALDA (Adjustable Local Density Assembler), and ADMA (Adjustable Density Matrix Assembler)) are introduced. He also discusses how to study local interactions by means of local shape analysis, using *ab initio*-quality approximate density matrices generated using the ADMA method.

An efficient way of describing and predicting solute–solvent interactions is proposed by Jean-Louis Rivail and Daniel Rinaldi in Chapter 4. After a discussion of the physical basis of the solvation process used to evaluate the electrostatic, cavitation, and dispersion terms, they introduce the Self Consistent Reaction Field equations, which allow for multicentric expansion of the solute's charge density and selection of an arbitrary cavity shape. A program offering the possibility of fast *ab initio* calculations using the discussed models and including post-Hartree-Fock and analytical energy derivatives is under development. Selected examples of chemical applications are given (free energy of solvation, solvent effect on molecular properties, and chemical reactions).

In Chapter 5, Eluvathingal D. Jemmis and Boggavarapu Kiran explore an intriguing, novel way to stuff fullerenes. The resulting structures might exhibit interesting properties. The elemental boron route is discussed and developed for fullerene and its higher analogues. A proposed concept is supported by results of preliminary semiempirical calculations.

Computational methods are becoming more applicable to biomolecules. In Chapter 6, Jiří Šponer, Pavel Hobza, and Jerzy Leszczynski describe the results of recent *ab initio* calculations on the structure and interactions of DNA bases. Applying results from high-level *ab initio* calculations predicting non-planarity of the amino groups in DNA bases, the authors discuss how this nonplanarity and flexibility contribute to the stabilization of different interactions in DNA. Base-stacking and hydrogen bonding in different basis pairs are discussed and compared. For the cytosine dimer, predictions were obtained at the electron correlated level and compared with results from different empirical-potential models.

Traditionally of industrial importance, drug design processes are also sparking the interest of computational medicinal chemists. In Chapter 7, Nicholas Bodor and Ming-Ju Huang share their expertise in “rationally” designing effective drugs with minimal side effects. The authors explain a “soft drug” approach and automate it through use of computer programs that starting from an AM-optimized structure provide information on the tested species ranging from estimation of its solubility, partition coefficients and isostericisoelectronic comparisons to the lead compound and metabolic rates of the predicted enzymatic degradation.

I express my gratitude to all the authors for their splendid contributions and for their pleasant cooperation. The very efficient assistance of Ms. Liqun Wong and Mr. Michael Stewart in putting together this volume is greatly appreciated.

Jerzy Leszczynski
Jackson, Mississippi
September 1995

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