

## PREFACE

### ATOMS, MOLECULES AND CLUSTERS IN ELECTRIC FIELDS. THEORETICAL APPROACHES TO THE CALCULATION OF ELECTRIC POLARIZABILITY

#### **Homage to D.M.Bishop's contribution.**

This volume presents a collection of papers focusing on the theoretical determination of the electric polarizability of atoms, molecules and clusters. This is currently a vigorously expanding research field. The book aims at a wide readership, ranging from specialists and workers in field to graduate and undergraduate students in the molecular sciences. All chapters are written by scientists with extensive experience in the field. Thus, this volume offers a comprehensive account of recent progress in the field, and the trends and emerging perspectives.

Electric polarizability is routinely associated with fundamental characteristics of atomic and molecular systems: hardness, softness and hypersoftness, stiffness and compressibility. The basic theory of electric polarizability and hyperpolarizability is of central importance to the rational approach to the description and interpretation of a wide range of phenomena. These include nonlinear optics, scattering and phenomena induced by intermolecular interactions. It is also present as a key element in the rigorous analysis of spectroscopic observations. In recent years the theoretical determination of electric polarizability and hyperpolarizability is making decisive contributions to new fields with important potential for advanced technological applications. Such fields are the molecular simulation and modeling of fundamental processes and the search for new optical materials. One should also add here the powerful emergence

of pharmacology, where electric polarizability and hyperpolarizability is used as descriptors in QSAR and drug design studies.

It is easily understood that the increasing demand for accurate polarizability and hyperpolarizability values has resulted in intense investigations on all computational aspects of their determination. At a relatively early stage the agreement between theory and experiment for these quantities was a major issue. The careful analysis of the observed discrepancies has brought about an effective rapprochement between theory and experiment. The development of theoretical methods of high predictive capability and reliable computational strategies has transformed computational quantum chemistry into a true vehicle of progress for modern molecular science.

In his review of the atomic static dipole polarizabilities Schwerdtfeger offers a critical evaluation of the available values for all elements from  $Z = 1$  to 119. His compilation of data is certainly a valuable reference and will be of great help to working scientists.

Quinet, Champagne and Kirtman present detailed analysis of the zero-point vibrational averaging (ZPVA) correction to the first hyperpolarizability of mono-substituted benzenes. Reliable estimates of the ZPVA correction are relatively rare for polyatomic systems. Their study offers valuable insights into the determination of this important quantity.

Pouchan, Zhang and Bégué propose a computationally advanced studied of the polarizability and hyperpolarizability of small silicon clusters. There are several studies of the polarizability of these important systems, but very little is known of their hyperpolarizability.

Fuentealba's contribution focuses on the calculation of the static polarizability of lithium, sodium, silicon and copper clusters. The polarizability of copper clusters has been a matter of some controversy in recent years.

The extensive review of Gu, Imamura and Aoki presents in detail a very promising contribution to the field. The elongation method for polymers paves the way to a new type of investigation with important potential applications to nonlinear optics.

Torii discusses the response of molecular vibrations to intermolecular electrostatic interactions. The author presents a

comprehensive account of their effects. Illustrative examples conclude this important review.

The following chapter treats in an exemplary manner the highly non-trivial problem of the determination of the polarizability and hyperpolarizability of liquid water. Kongsted, Osted, Mikkelsen and Christiansen rely on Coupled Cluster/Molecular Mechanics response theory. The determination of electric properties of molecules in condensed phases constitutes a major challenge to Computational Quantum Chemistry.

Jensen and van Duijnen present the Discrete Solvent Reaction Field Model. This powerful QM/MM based method offers a promising tool for the determination of the electric properties of molecules in condensed phases.

Wu, Li, Li and Sun show that dipole bound anions as  $(HF)_n^-$ ,  $n=2, 3, 4$ , are characterized by very large first hyperpolarizabilities.

The long review of Nakano reports an extensive investigation of the hyperpolarizability of open-shell molecules. Very little is known about the electric properties of such systems. This comprehensive review offers an invaluable account of this difficult subject, illustrated by many examples.

Coutinho and Canuto present a sequential Monte Carlo/Quantum Mechanics approach to the dipole polarizability of atomic liquids. Their treatment of liquid argon shows that the polarizability in the liquid is slightly larger than in the gas phase.

Bancewicz, Le Duff and Godet show that the analysis of interaction-induced light-scattering spectra can lead to the determination of multipolar polarizabilities of the interacting molecules. Their results for  $CH_4$ ,  $CF_4$  and  $SF_6$  are in very good agreement with the available *ab initio* values.

Buldakov and Cherepanov have obtained polarizability functions for  $N_2$  and  $O_2$ . Their method allows the determination of polarizability curves for a wide range of internuclear separations. In addition, they present dipole polarizabilities for the dimers  $(N_2)_2$  and  $(O_2)_2$ .

A critical compilation of atomic polarizabilities and hyperpolarizabilities is offered by Thakkar and Lupinetti. With the notable exception of the work of Stiehler and Hinze (Numerical Hartree-

Fock hyperpolarizabilities for atoms from  $Z=1$  to 36), critical presentations of atomic hyperpolarizability data are very rare in the literature.

Yan, Zhang and Li present a review of accurate methods for the calculation of the polarizability of few-body atomic and molecular systems. They also review polarizability data for He, Li, Be,  $H_2^+$ ,  $H_2$  and the positronic system PsH.

Wu reviews recent theoretical advances in the calculation of electric hyperpolarizabilities of transition metal clusters. His review presents novel results, shows clearly the computational difficulty of similar investigations and offers valuable insights into this promising subject.

Maroulis and Haskopoulos present new results for the interaction polarizability and hyperpolarizability in the complexes of  $N_2$ ,  $CO_2$ ,  $H_2O$ ,  $(H_2O)_2$  and  $O_3$  with He.

Chandrakumar, Ghanty and Ghosh review recent theoretical results for the polarizability of lithium and sodium clusters. Due to the extensive experimental investigations reported in recent years, the electric properties of these systems have been extensively studied. This important review will be of great value to future investigations.

Last, Senet, Yang and van Alsenoy present a study of the charge distribution and polarizability in water clusters up to the icosamer. With the exception of the monomer, no experimental values are known for the polarizability of water clusters.

*This Book is dedicated to David M. Bishop in celebration of his contribution to the field, on the occasion of his 70<sup>th</sup> birthday.*

**George Maroulis**  
Department of Chemistry  
University of Patras  
Patras, Greece