Edited by Martin Kaupp,
Michael Bühl, Vladimir G. Malkin

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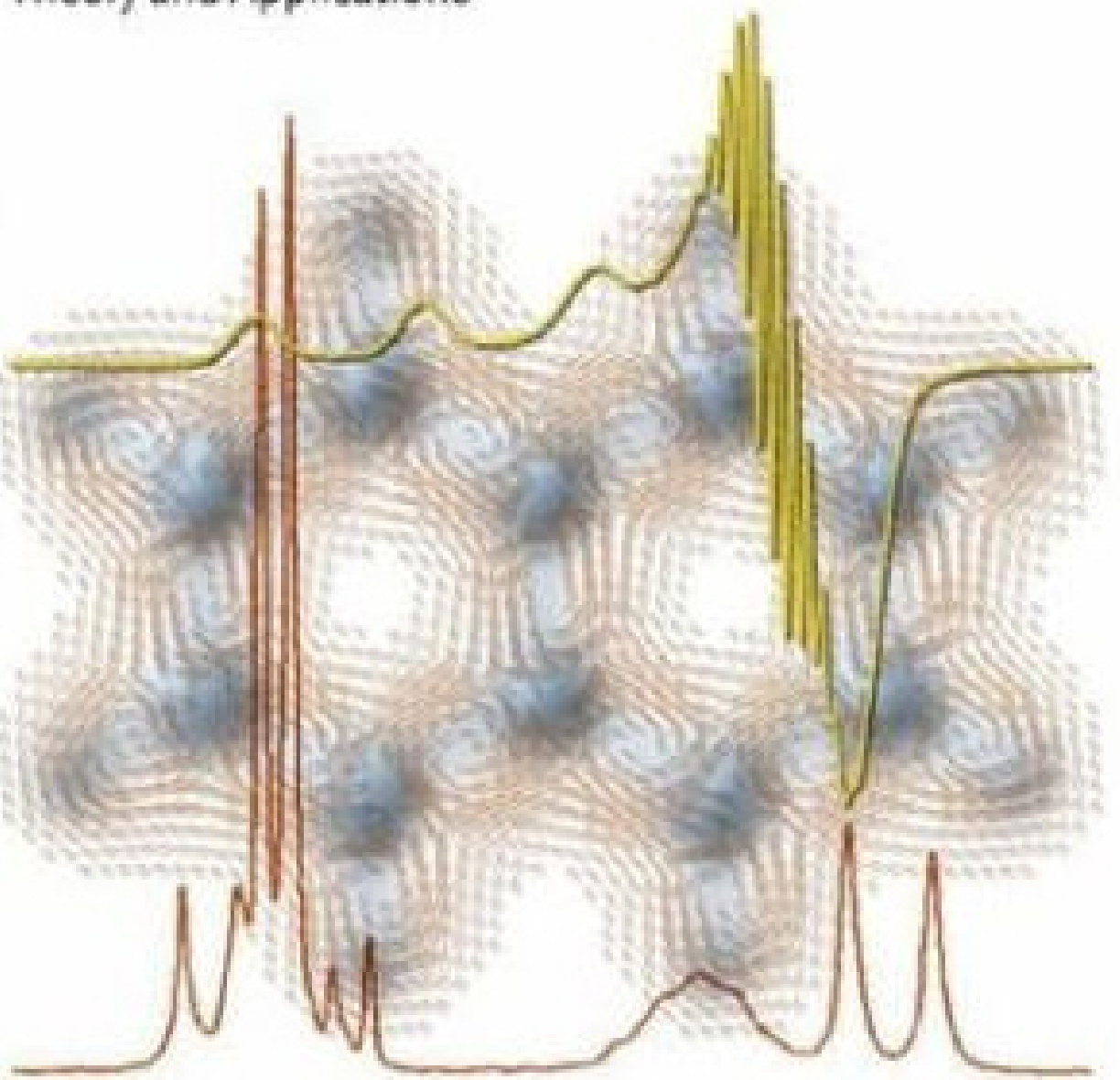
Calculation of NMR and EPR Parameters

Theory and Applications



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Foreword

It is difficult to overemphasize the importance of magnetic resonance techniques in chemistry. Experimental spectra can usually be successfully interpreted empirically, but more difficult cases require a prediction based on the electronic structure. In the last 25 years the calculation of magnetic resonance parameters from first principles has become a powerful research tool that can significantly enhance the utility of magnetic resonance techniques when empirical interpretations are insufficient. This can be crucial even for NMR spectra of organic molecules, where the interpretations are the simplest and where empirical material has been collected for half a century. Examples can be found in such diverse fields as the identification of new fullerenes, the use of calculated chemical shifts as probes of peptide conformation, and the study of hydrogen bonding. Calculations play an even more important role in the inorganic and organometallic fields, where empirical interpretations are far more difficult. The ability to calculate NMR and EPR parameters also increases the efficacy of electronic structure calculations. Computed energies of different structures are often too close to allow a unique identification of the stable isomer. Calculated NMR spectra, however, are often significantly different, so that even simple calculations can lead to unambiguous identification in such cases.

The unprecedented improvement in the cost-effectiveness ratio of computers (about six orders of magnitude over the last 20 years), and the continuing fast pace of development, together with improved computational techniques, will certainly make the calculation of NMR and EPR parameters more routine and more widespread in the future.

This book, then, is particularly timely, edited as it is by three researchers of the younger generation who have themselves played an important role in the development and application of theoretical techniques. The author list includes many of the original developers of improved theoretical methods, as well as a number of leaders in chemical applications, offering a comprehensive coverage of the field.

The calculation of NMR and EPR parameters is less straightforward than the calculation of most other molecular properties. Understanding the source of these difficulties led ultimately to their successful solution. In the theory of NMR chemical shifts, for instance, Hameka has clarified many of the concepts, paving the way to Ditchfield's seminal work on Gauge-Independent (later Gauge-Including) Atomic Orbitals (GIAOs). However, computers and programs in the early seventies were

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not yet ready for calculations on chemically relevant larger molecules. A renaissance in NMR chemical shift calculations began around a decade later, with the Individual Gauge for Localized Orbitals (IGLO) method developed by Kutzelnigg and coworkers, with a parallel development by Hansen and Bouman. It took a few more years to show that the currently preferred GIAO method can achieve similar computational efficiency.

The calculation of hyperfine coupling parameters suffers from two major difficulties. Firstly, electron correlation is important, particularly when the direct effect – due to the spin density of the unpaired orbital – vanishes for reasons of symmetry. Much of our understanding of this problem is due to Davidson's analysis. The other problem is high basis set sensitivity, due to the local nature of the interaction. A possible solution for Gaussian basis sets was calculated early on by Meyer; alternative methods are discussed in the present volume.

The calculation of spin-spin coupling constants has a long history but until very recently has received less attention than NMR shieldings, and therefore a summary of recent progress in the field is particularly welcome. Another timely topic, both for chemical shifts and for spin-spin couplings, is the effect of relativity. Because of its importance in inorganic chemistry, this has been in the forefront of recent theoretical work, and is well covered in several chapters. The calculation of electric field gradients, necessary for predicting nuclear quadrupole coupling constants, complements the calculation of NMR parameters. Some other recent topics of high interest include the theory of NMR in paramagnetic systems, and the calculation of EPR *g*-tensors and zero-field splittings. The interpretation of resonance parameters in terms of chemical concepts, although necessarily a somewhat arbitrary procedure, is important for the chemical community; its inclusion here fills a void.

The book covers a wide range of methods, from semi-empirical through density functional to highly accurate correlated wave functions where vibrational corrections become important. The chapter on extended systems will no doubt help bridge the gap between the chemistry and the physics communities in this area. The introductory chapters, written by distinguished scholars, will be particularly useful for anybody entering the field. Finally, the application chapters provide broad coverage, and will be a valuable guide to future work.

In summary, this book promises to become the standard reference for the calculation of NMR and EPR parameters, and will undoubtedly stimulate research in this fascinating and important field.

Peter Pulay Jan. 2004

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Part A
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