# Additions and Corrections

**An *in*-Fluorosilaphane: The Largest *in*-Functional Group Is a Uniquely Encapsulated Fluorine Atom** [*J. Am. Chem. Soc.* **1998**, *120*, 6421−6422]. STEVEN DELL, NANCY J. VOGELAAR, DOUGLAS M. HO, AND ROBERT A. PASCAL, JR.*

The $^{19}$F NMR spectra of tri(*o*-tolyl)fluorosilane (**15**) and the *in*-cyclophane **2** were incorrectly (and differently) referenced. Their correct chemical shifts are $\delta$ −160.6 and $\delta$ −155.3, respectively, relative to $CFCl_3$; therefore the chemical shift of the *in*-fluorine of compound **2** is not unusual. We thank Professor Ludger Ernst for alerting us that such an error was likely.

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# Book Reviews

**Chemistry, Structure, and Bonding of Zintl Phases and Ions**. Edited by Susan M. Kauzlarich (University of California−Davis). VCH Publishers, Inc.: New York, Weinheim and Cambridge. 1996. $ 125.00. xxx + 306 pp. ISBN 1-56081-900-6.

The interest in Zintl phases and ions has significantly increased in the last 10 years. This is manifested by the increase in the number of research publications related to the synthesis, structure, properties, and chemical bonding of these unusual materials. The significant interest in this field has workers in this field desire an in-depth review of the current state of affairs in Zintl phases. Moreover, new researchers wanting to initiate work in the field have relied heavily on many reviews and individual articles and papers, mostly published in the early 1980s to early 1990s. The publication of *Chemistry, Structure, and Bonding of Zintl Phases and Ions*, edited by Professor S. M. Kauzlarich, fulfills the need for an in-depth review of the current research directions in the area of Zintl phases that would be useful to both novices and experts.

The book is a compilation of chapters written by individual experts in research areas that range from syntheses, properties, chemical bonding models, and reactivity of Zintl phases. The book begins with an introduction fittingly written by Professor R. Kniep, director of the Eduard-Zintl-Institute at Darmstadt, on the short but very productive life of Eduard Zintl. The introduction contains many historical details in the scientific career of E. Zintl relevant to the development of the solid state and solution chemistry of Zintl phases and ions. The introduction also includes facsimiles of some of the original works of Eduard Zintl which provides a useful historical perspective to the rest of the chapters. The first three chapters, which take more than half of the book, focus on the current and useful chemical bonding−crystal structure models, as well as the wide variety of Zintl phases and related polar intermetallics which illustrate the successes and limitations of the currently accepted bonding models. The first chapter by Miller also provides unique perspectives pertaining to future developments in chemical bonding theory as applied to intermetallics. The second and third chapters nicely illustrate the diverse structural patterns and topologies exhibited by complex Zintl phases. These chapters also show the successful application of the Zintl concept to complicated intermetallic structures. The last four chapters present new directions and opportunities in the area of Zintl phases, namely, liquid ionic alloys, transition metal Zintl ions and phases, and the chemical reactivity of Zintl phases. Although the synthesis, crystal structure, and characterization of Zintl phases are well established, their chemical reactivity is often perused. These four well-presented chapters cover the nontraditional areas of Zintl phases. Except for the well-developed area of transition metal Zintl phases, the rest of the later chapters describe the early state of these research areas as well as a unique perspective for future research.

A minor observation which long-time researchers in this field will notice is the absence of any contribution from Stuttgart (Max Planck Institute) and Zurich (ETH) groups which have been major players in this field. Their absence, though unfortunate, does not significantly diminish the impact and value of this book to beginning and experienced solid state researchers.

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**Relativistic Effects in Chemistry Part A: Theory and Techniques**. By Krishnan Balasubramanian (Arizona State University). Wiley Interscience: New York. 1997. xiii + 301 pp. $145.00 (paperback $84.95). ISBN 0-471-30400-X.

Part A of Krishnan Balasubramanian's two volumes on relativistic effects in chemistry is an invaluable resource for researchers in electronic structure theory and molecular spectroscopy of heavy-element molecules and clusters. It is composed of five chapters that address the theoretical underpinnings and methodology required for the in-depth understanding of their bonding and spectra. The first chapter is more of a directed review of important relativistic effects in chemistry than an introduction to the chapters that follow. The author has chosen a set of examples that show the importance of relativity in understanding the anomalous behavior in such molecules as $Au_2$, $Hg_2$, PtH, $Pt_4$, $PbH_2$, and others, as well as the qualitative nature of such phenomena. The specific relativistic effects introduced in the first chapter, although reviewed more extensively by Balasubramanian himself, as well as other authors over the past 10 or so years, provide a good backdrop for the importance of the detailed theoretical developments to follow.

The second chapter presents the underlying principles of special relativity in a clear and concise manner. This chapter was written with the audience of molecular scientists in mind and is a chemist's perspective of the subject. The references cited at the end of the chapter can be consulted for more comprehensive developments. Chapter 3 addresses relativistic quantum mechanics and is also a good re-expression of the existing physics literature as interpreted by a chemist. This reviewer has become aware of at least two volumes in preparation that address the use of relativistic quantum mechanics in molecular structure and spectra that are more detailed and expansive than the presentation comprising the 21 sections of Chapter 2. However, the author has done a commendable job of including the salient aspects of the Klein−Gordon equation, Dirac equation, and various transformations and perturbation expansions therefrom in this chapter. The review of material that is discussed more comprehensively in the volume by Bethe and Salpeter and in Moss' text is extremely useful in the context of establishing the forms of relativistic wave functions and the specific relativistic effects as defined by the Breit−Pauli approximation.

The fourth chapter begins with the presentation of the relativistic Hamiltonian operator appropriate for use in calculations on molecular systems. The second section presents relativistic effective core potentials (RECPs) and their use in representing the core electrons and core- and valence-electron interactions. The author then shows in Section 3 how the RECPs provide the point of departure for the computational electronic structure methods that he and others have developed over the past 20 years. Clearly, the author has chosen to present the methods he has used in his extensive list of published studies on molecules and clusters. Alternative methods developed by other groups using RECPs, model potentials, and all-electron procedures are largely neglected, although some are referenced at the end of the chapter. Readers especially interested in all-electron relativistic methods will not find this volume useful as a resource in gaining an in-depth understanding of these approaches. The works alluded to above will address these areas and should be available soon. It is this reviewer's opinion that the basic philosophy behind the research directions of Balasubramanian and his colleagues has been one belonging to a chemist and molecular spectroscopist; viz., core electrons do not play a role in chemical bonding and spectra and, consequently, can be removed from the problem, as long as an accurate, first-principles method such as that underlying RECPs can be employed. Major advances in all-electron methods, together with technological advances in supercomputing, may make them competitive with pseudopotential-based methods in the future. However, concomitant advances in the latter raise questions regarding the necessity for incorporation of the additional cost and complexity mandated by all-electron approaches. In this context, the present volume presents techniques that will be in use for the foreseeable future, and it provides one of the best sources for detailed background material. The last section of Chapter 4 discusses two approximate methods that are becoming more generally used: the local density functional and semiempirical approaches.

The last chapter is the jewel of the volume and the one of most value to active researchers in the field. Entitled Double-Group Symmetry and the Classification of Relativistic Electronic States, it fills an enormous void in the available reference literature. Theoretical chemists and molecular spectroscopists will be pleased to have access to the development presented here. That the electron angular momentum coupling of molecular electronic states, especially those of molecules containing one or more heavy elements, is intermediate in nature is a fact not generally appreciated nor understood by the chemical and molecular physics community. Balasubramanian admirably develops this problem, beginning with discussions of double group symmetry in the first five sections. The 12 tables comprised of double group character tables, electronic states derived from separated atoms, molecular term symbols, nonrelativistic−relativistic correlations, and direct products are invaluable for the construction and analysis of relativistic molecular wave functions for diatomics. The same information is presented for polyatomics in Sections 6 and 7. The section includes double group character tables for all of the important molecular point groups. The chapter concludes with a section on symmetry-adapted spin functions for electronic states. This subject is especially important in the context of the increasingly popular spin−orbit configuration interaction and related methods whereby initial (active-space) wave functions are defined in terms of nonrelativistic angular momentum coupling, i.e., molecular orbitals built as linear combinations of atomic spin orbitals, and the final Hamiltonian matrix is constructed in the presence of spin−orbit coupling operators. (This method is to be contrasted with those employing atomic basis sets of four- or two-component spinors.) The author shows how double group symmetry-adapted configuration sets are constructed for polyatomic systems using the proper combinations of $\alpha$ and $\beta$ spin functions. This chapter is of practical value to the researcher involved with the calculation and analysis of electronic states of molecules that contain heavy elements.

This book can be used as an introduction to relativistic quantum chemistry for advanced graduate students. I would be inclined to use it as a text for such a graduate course. In particular, the material contained in Chapter 3 condenses much of the subject matter presented in advanced treatises or relativistic quantum mechanics texts into a form appropriate for the classroom. The detailed solution of the relativistic hydrogen atom is especially well-conceived. The incorporation of some of the language of relativistic quantum chemistry is, at long last, finding its way into new physical chemistry, inorganic chemistry, and even general chemistry textbooks. The insightful work of such pioneers as Kenneth Pitzer and Pekka Pyykkö inspired the quantitative developments that are in extensive use today. This book is a good introduction to the general subject and presents, together with Balasubramanian's second volume (*Part B: Applications*), an extensive treatise on the methods used by the author and his applications to a vast number of molecules and clusters containing heavy elements. This book is a valuable addition to the literature dealing with relativistic quantum chemistry and is highly recommended.

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**HPLC and CE: Principles and Practice**. By Andrea Weston (Dionex) and Phyllis R. Brown (University of Rhode Island). Academic Press: San Diego. 1997. xiv + 280 pp. $69.95. ISBN 0-12-136640-5.

This book is unique in that it covers the basic principles, instrumentation, method development, and applications of both HPLC and capillary electrophoresis. (Similar books invariably deal with either a single technique or several.) Although the coverage of this volume is supposedly aimed at both novices and users, it is particularly suitable for use in teaching upper level undergraduate courses in analytical chemistry and instrumental analysis, and for individuals from other scientific disciplines who need to do separations but have no previous experience or basic knowledge of chromatography or capillary electrophoresis.

The first three chapters deal with HPLC. Chapter 1 covers fundamentals and principles. Chapter 2 deals with the different types of separations and the different modes of LC (affinity, chiral, hydrophobic interaction, reversed phase, and so on). Chapter 3 covers all the components of instrumentation (solvent delivery system, inlet, the column, and the various detectors), and also includes a rather extensive section on trouble-shooting. Trouble-shooting information is always very useful, but it is usually found only in handbooks intended for use in the laboratory.

The next three chapters, 4, 5, and 6, cover CE following the same organization as for HPLC, i.e., principles, modes of separation, and instrumentation. Again, each chapter concludes with a summary of major concepts, and the instrumentation section ends with several pages on trouble-shooting.

The final two chapters, 7 and 8, cover data manipulation and miniaturization for both HPLC and CE. Data manipulation in this case deals with the various methods of peak identification (by retention factors, UV and MS libraries, spiking with standards, etc.), and also includes methods of quantitative measurement. Miniaturization covers the various practical aspects of designing an HPLC or CE system based on chips, micromachining, and so on.

The material in each chapter is presented in a well-organized and easy to understand style. Everything is expressed in a manner that makes it easy for the reader to follow, to learn, and to remember. At the end of each chapter there is a section summarizing the major concepts. Because this is a compact book, it tends to provide information that is mainly of immediate and practical use to the practitioner (or the student). At the same time the book takes no shortcuts to provide the "reason why" in addition to the "how to". For example, in describing MECC (micellar electrokinetic capillary chromatography), it explains why this technique is commonly performed with anionic surfactants and why SDS (sodium dodecyl sulfate) is the preferred surfactant.

*HPLC and CE: Principles and Practice* is a well-organized and well-written handbook useful to anyone, but the expert, who is doing or planning to do HPLC or CE analysis.

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