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Structure and Bonding

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Aims and Scope

The series *Structure and Bonding* publishes critical reviews on topics of research concerned with chemical structure and bonding. The scope of the series spans the entire Periodic Table and addresses structure and bonding issues associated with all of the elements. It also focuses attention on new and developing areas of modern structural and theoretical chemistry such as nanostructures, molecular electronics, designed molecular solids, surfaces, metal clusters and supramolecular structures. Physical and spectroscopic techniques used to determine, examine and model structures fall within the purview of *Structure and Bonding* to the extent that the focus is on the scientific results obtained and not on specialist information concerning the techniques themselves. Issues associated with the development of bonding models and generalizations that illuminate the reactivity pathways and rates of chemical processes are also relevant.

The individual volumes in the series are thematic. The goal of each volume is to give the reader, whether at a university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to a larger scientific audience. Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years should be presented using selected examples to illustrate the principles discussed. A description of the physical basis of the experimental techniques that have been used to provide the primary data may also be appropriate, if it has not been covered in detail elsewhere. The coverage need not be exhaustive in data, but should rather be conceptual, concentrating on the new principles being developed that will allow the reader, who is not a specialist in the area covered, to understand the data presented. Discussion of possible future research directions in the area is welcomed.

Review articles for the individual volumes are invited by the volume editors.

In references *Structure and Bonding* is abbreviated *Struct Bond* and is cited as a journal.
Mihai V. Putz • D. Michael P. Mingos
Editors

Applications of Density Functional Theory to Chemical Reactivity

With contributions by
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For a long time, chemistry was considered as “ancilla Phisica” due to the commonly accepted hierarchy of scientific disciplines that implied a reduction in rigor from physics to chemistry. In the early twentieth century, following the elucidation of the structure of atoms, it became evident that atoms and molecules with even numbers of electrons were far more numerous than those with odd numbers of electrons. In 1916, G. N. Lewis provided the first comprehensive description of ionic and covalent bonds, when he postulated that atoms tend to hold an even number of electrons in their outer shells and a special stability was associated with eight valence electrons, which he speculated were arranged symmetrically at the eight corners of a cube. In 1919, I. Langmuir suggested that the structure of the periodic table could be rationalized using an extension of Lewis’ postulates. In 1922, N. Bohr updated his model of the atom by assuming that certain numbers of electrons (for example 2, 8, and 18) corresponded to stable “closed shells.” In 1926, Schrödinger established a wave mechanical description of the hydrogen atom which was subsequently extended to polyelectron atoms. Pauli was the first to realize that the complicated numbers of electrons in closed shells can be reduced to the simple rule of one per state, if the electron states are defined using four quantum numbers. For this purpose he introduced a new two-valued quantum number, identified by Goudsmit and Uhlenbeck as electron spin. The resulting Pauli Exclusion Principle states that no two electrons in a single atom can have the same four quantum numbers; if \( n, l, \) and \( m_l \) are the same, \( m_s \) must be different such that the electrons have opposite spins.

The idea of shared electron pairs introduced by Lewis provided an effective qualitative picture of covalent bonding and it still forms the basis of the universal notation for chemical communication, but it was Heitler and London who in 1927 developed the first successful quantum mechanical expression for this bonding model. Initially they provided a description of the bonding in molecular hydrogen, but it was subsequently adapted to more complex molecules and its widespread applications were articulated with great conviction by Linus Pauling. An alternative molecular orbital description of chemical bonding originated from Burarr’s description of the hydrogen molecule ion and this model was subsequently widely
developed by Mulliken and Lennard-Jones. The electrons occupy molecular orbitals which are delocalized over the whole molecule and were filled according to the Aufbau Principle and assigned quantum numbers according to the Pauli Exclusion Principle. The orbitals are calculated in a self-consistent fashion in a manner analogous to those developed previously for atomic orbitals and are based on linear combination of the atomic orbitals of the individual atoms. The number of molecular orbitals equals the number of atomic orbitals in the atoms being combined to form the molecule. A molecular orbital describes the behavior of one electron in the electric field generated by the nuclei and some average distribution of the other electrons. This approximation proved to be more amenable to computer programming than the valence bond model and was widely developed and used in increasingly less approximate forms from 1960 to 1990.

In the early 1970s, a new electronic structure approach emerged from the physics community and was described as density functional theory (DFT). The total energy of a molecule was expressed as a functional of the total electron density. Hohenburg and Kohn proved the unique relationship between electron density and energy, and Kohn and Sham put forward a practical variational DFT approach. Although calculations in solid-state physics had been reported since the 1970s, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were refined to more accurately describe the exchange and correlation interactions. Computational costs for \textit{ab initio} DFT calculations are relatively low when compared to the valence bond and molecular orbital methods. DFT thus began to approach the goals of computational thermochemistry to calculate the energetic properties of chemical processes to an accuracy of 1 kcal mol\(^{-1}\). The widespread acceptance of these methodologies by the chemical community led to Kohn and Pople sharing the Nobel Prize in Chemistry in 1998.

When in 2004 Volumes 112 and 113 of Structure and Bonding were devoted to the “Principles and Applications of Density Functional Theory in Inorganic Chemistry” the editors N. Kaltsoyanis and J.E. McGardy noted “It is difficult to overestimate the impact that Density Functional Theory has had on computational quantum chemistry over the last two decades. Indeed, this period has seen it grow from little more than a theoretical curiosity to become a central tool in the computational chemist’s armory.” In these volumes they described recent applications in inorganic and biochemistry and addressed key issues in spectroscopy, mechanistic studies, and magnetism.

As a tribute to the continuing success story of DFT, the current two volumes mark the fundamental advances made in the first decade of the twenty-first century and the first volume provides an appropriate global view of its applications to chemical reactivity. It is apparent that the DFT methodology has acquired new and significant insights into modeling chemical phenomena which will have implications for at least the next decade and the chapters highlight some of the most exciting current directions of DFT. The first chapter reviews how Bose–Einstein condensation may be modeled by extension of DFT models, leading to a generalization of chemical bonding by employing the recently proposed
advanced bondon—the quantum particle in the chemical bonding field. Then, the ideas central to information theory have been used to advance new concepts in molecular orbital theory, which leads to the prediction of the chemical interactions by means of “cascade” probability propagations through atomic orbital intermediates and these results are discussed in the second chapter. In the next chapter “conventional” high-priority classes of molecular systems such as “soft” metal clusters or weakly bonded molecules are analyzed and classified from polarizability and hyperpolarizability perspectives and this has been facilitated with the aid of new graph and pattern recognition techniques. It is followed by a chapter amenable to specialist and nonspecialist alike about different chemical reactivity descriptors such as electronegativity, chemical hardness, chemical softness, and Fukui functions. The combination of these concepts is conceptually responsible for helping chemists understand chemical stability and reactivity. The final chapter is dedicated to a historical view of the chemical indices and allied principles, with special references to hard and soft acids and bases (HSAB). This principle which was discussed at some length in early volumes of Structure and Bonding ultimately plays an important unifying role in qualitative descriptions of Lewis acid–base interactions and for rationalizing the rates of chemical reactions.

In summary, the volume critically reviews the applications of DFT to chemical reactivity from a structural and bonding perspective and aims to undermine those historical differences between physics and chemistry which were mentioned in the opening sentence.

We thank the contributors to this volume for the consistent efforts they have made in writing high-class scientific reviews and for providing the readers with a broad perspective which has revealed the widespread uses of DFT in interpreting chemical reactivity. MVP acknowledges the research and editing facilities provided for the present volume by the Romanian Education and Research Ministry within the project CNCS-UEFISCDI-TE-16/2010-2013. MVP and DMPM sincerely thank the Springer team and in particular Marion Hertel, Ursula Gramm, Elizabeth Hawkins, and Tanja Jaeger for professionally supervising the production of the Structure and Bonding series in general and of this volume in particular.

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