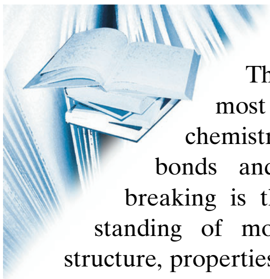


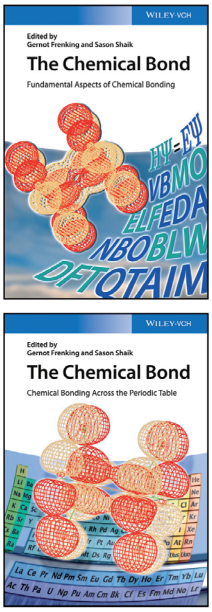
The Chemical Bond

The chemical bond is the most central concept of chemistry: the existence of bonds and their formation and breaking is the basis for our understanding of molecules, including their structure, properties, and chemical reactions. While the definition of the chemical bond given by the IUPAC Gold Book is undoubtedly correct (“When forces acting between two atoms or groups of atoms lead to the formation of a stable independent molecular entity, a chemical bond is considered to exist between these atoms or groups.”), it is not particularly useful for our understanding, as it does not address the origin of a bond, which is the interaction of nuclei and electrons in a molecule. The two-volume text The Chemical Bond, edited by Frenking and Shaik, with contributions by many distinguished experts in the field, tackles the task of substantiating and extending our understanding of this subject. The first volume, *Fundamental Aspects of Chemical Bonding*, covers the basic principles, while the second one, *Chemical Bonding across the Periodic Table*, places the focus on examples. Although the work is rather expensive for most chemistry students, it should in fact be considered as part of the interested modern chemist’s personal library. Indeed, these two volumes should be part of every well-chosen chemistry library, for the sake of its state-of-the-art textbook-style components, as well as for its review of modern bonding analysis techniques and well-chosen examples.

However, this work suffers from the typical drawback of edited books: different authors prefer different styles. This is particularly evident here, as Wiley has introduced some new and useful means for improving the readability of books. One is the possibility to print formulas in color, which, if used consistently, allows the reader to easily keep track of the different terms in long equations; another is the option of inserting text boxes that give an encyclopedia-style explanation of a term without disturbing the flow of the text. These tools have been appreciated differently by the authors—some take advantage of them and some ignore them. This gives the books a somewhat inconsistent appearance, and requires a different reading style in the individual chapters.

In chemistry, which is one of the most traditional scientific disciplines, the chemical bond has been a subject of intensive research and controversial debate over many years. Early quantum mechanics allowed one to rationalize the principal bonding types by analyzing the distribution or redistribution of electrons in a molecule or solid. The impossibility of exactly solving the Schrödinger equation for any chemically relevant system, and the need to project the complex many-particle information onto easily digestible single-particle (i.e., single electron or electron pair) pictures in order to predict new structures by analogies, experience, and/or intuition, resulted in different approaches to the problem of chemical bonding. Obviously, all such approaches are necessarily simplifications, which work well in some areas but less well in others, and controversies that arose in the scientific community are still evident in the present volumes. A striking example is a heated debate that occurred between Richard F. W. Bader and Gernot Frenking, one of the editors of this work. Bader rationalized the chemical bond by considering the only easily accessible many-particle quantity, the electron density, whereas Frenking’s arguments are based on the necessity to understand the interaction between individual orbitals (the single-particle picture). Similar controversies have arisen between the two common single-particle pictures, namely the valence bond (VB) and molecular orbital (MO) theories. In this work, an attempt is made to bridge the divide, by applying each of these pictures—including derived concepts—in its appropriate place. The global, electron density, approach is reflected in a chapter that discusses the Bader theory (or quantum theory of atoms in molecules, QTAIM), the electron delocalization function (ELF) theory, and the conceptual density functional theory (CDFT). On the other hand, a chapter on the single-particle picture attempts a bridging between the apparently contradictory VB and MO theories and, paying tribute to more recent developments, also discusses rigorous partition schemes such as the natural bond orbitals (NBO) and block-localized wave function (BLW) methods. The energy decomposition analysis (EDA) method, combined with the frozen density approximation, is perhaps the most elegant way to offer a bridge between the two main approaches, and it is also the subject of this work.

Volume 1 deals with the fundamental aspects of describing chemical bonding, which are clearly associated with the distribution (or redistribution) of electrons in the molecule. Unfortunately, here we sadly miss Bader and his personal viewpoint on the topic with regard to the electron density and its connection with the chemical bond. According to the Hohenberg–Kohn theorem, the electron density distribution is sufficient to describe any molecular system, and thus it is the origin of the chemical bond. Consequently, it should provide a sufficient explanation for any type of chemical bonding. Bader theory is included in the excellent Chapter 8, where the quantum theory of atoms in molecules (QTAIM) is introduced—including a historical excursion with a critical discussion of the different stages of Bader theory. In Chapter 9, it does indeed



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become evident that this theory offers a straightforward comparison of the computed electron density and its descriptors with state-of-the-art experiments.

Volume 2 consists of 18 chapters and collects applications of quantum-chemical theories across the Periodic Table to give a detailed insight into the nature of the chemical bond. Of course, the number of interesting examples is unlimited, and it is difficult to divide them into well-defined sections. The first six chapters deal with molecules containing main-group elements, and they are followed by four on transition metal complexes. Compounds of lanthanides and actinides are reviewed in detail in Chapter 11. Chemical bonding in clusters, in solids, and on surfaces is also discussed in separate sections. The final part of the book is devoted to dispersion interactions, hydrogen bonding, and halogen bonding.

In the following, we summarize the contents of the two volumes, and describe selected chapters in more detail.

Volume 1

The single-particle picture is given a very strong focus. Orbitals, either in canonical form (MOs) or transferred to valence bond orbitals (VBs), are the essential means to describe chemical bonding. Indeed, the single-particle model allows one to provide both an intuitive and a mathematically rigorous picture of what happens if an electron is subject to the effective potential of a molecular environment. The analysis of electron delocalization from the viewpoint of the kinetic energy and the virial theorem are fundamental (Chapter 1). A great deal of effort is devoted to bridging between the apparently contradictory viewpoints of the MO and VB theories, and we consider that to be a highly valuable contribution of this work (Chapters 2 and 5). An important tool that helps in understanding bonding concepts is the natural bond orbitals (NBO) concept discussed in Chapter 3, where, besides the fundamental theory, many tricks of the trade are shared with the reader. Similarly, the energy decomposition analysis (EDA) method is explained in great detail in Chapter 4, with useful reference molecules as examples. Another important analysis tool is the electron localization function (ELF), which is introduced and applied to molecules and solids in Chapter 10.

The charge shift is a fundamental quantity in VB theory, in particular in classifying systems as polar or donor–acceptor. The three concepts, VB theory, Bader theory, and ELF, are compared and found to be convergent in their conclusions and complementary in providing valuable details for the analysis of the chemical bonding in a molecule. The treatment of VB theory is completed by a chapter on the BLW approach, which is probably the simplest and most efficient VB method based on first principles. The theory is still in its infancy, and thus is not applicable to all situations. However, it is currently being extended to form a generalized BLW method, which will allow a much wider range of applications (Chapter 6).

In the didactically excellent Chapter 7, conceptual DFT is derived from the DFT standard formulation, and molecular reactivity is introduced, including global and local descriptors of reactivity, Pearson's hard–soft–acid–base (HSAB) model, and related quantities such as the Fukui function.

Finally, Chapter 11 is devoted to the effect of relativity on the chemical bond. Scalar relativistic effects, taking into account the change of inertial mass of the electrons at high velocities, are discussed, and their importance for valence bonds is illustrated by describing, for example, the contraction of the s-shell in metals and effects on ionization potentials. The role of relativistic effects, including spin–orbit coupling, is then illustrated for a series of molecules and solids. Thus, Volume 1 offers a complete overview of the modern theory of the chemical bond, describing methods and theories and attempting to reconcile them as far as possible.

Volume 2

Key principles of chemical bonding in main-group elements and of important trends in the Periodic Table are reviewed by Kaupp, with special attention to the hybridization defects of s- and p-valence electrons of orbitals with disparate sizes, to account for the most common trends in chemistry, such as the dependence of the inert-pair effect on the electronegativity of the ligands, or multiple bonds between heavy main-group elements. Even hypervalency can be rationalized in terms of the effects of "primogenic repulsion". The role of the outer d-orbitals in bonding and relativistic effects is also discussed.

The energy decomposition analysis (EDA) method gives, in principle, a quantitative account of the strength of σ- and π-bonding, without the need for a reference compound. As in any energy partitioning scheme, the main problem is to define the proper fragments. Of course, the molecule does not care about that; it will make whatever electron shift it needs to maximize bonding between the fragments. Frenking has compiled, in three chapters, the contributions of his group on EDA-based bonding analysis of main-group elements and transition metal compounds.

The Hückel rule, the octet rule, the 18-electron rule, and Wade's rule are some of the most powerful tools to understand, classify, and predict the structure and electronic properties of molecules and solids. Thus, electron-counting rules are attempts to simplify the complexity of the chemical

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world. It is fascinating to learn that a simple modification to Wade's rule (called the "mno rule") can explain the bonding in boron systems where multicenter bonds are dominant in macropolyhedral boranes, metallaboranes, boron-rich solids, and polyhedral metal complexes (Chapter 5).

In theory, a diatomic transition metal system can form up to six bonds. But the correct description of bonding in molecules containing quintuple or sextuple bonds needs very sophisticated quantum-chemical computations using, for example, multi-reference methods. In Chapter 9, Gagliardi explains in detail how to analyze the chemical bond of these fascinating systems. In particular, the effective bond order (EBO) concept can be used to quantify the degree of multiple bonding in systems such as $Re_2Cl_8^-$, or complexes containing M_2 units ($M = Cr, Mo, W$). In the same vein, advances in quantum chemistry allow us to understand the bonding in the f-block of elements. However, there are several technical problems in the computational chemistry of f-shell elements, because they show strong electron correlation and relativistic effects at the same time. Thus, several different approaches may be required to obtain a deeper description of the bonding character in compounds of the f elements. These technical problems are discussed in Chapter 11, and examples of the use of different theoretical approaches are described.

London dispersion bonds and hydrogen bonds are weaker than the main types of chemical bonding discussed in these two volumes, but they should not be regarded as unimportant. These weak interactions are responsible for the spatial organization of molecules, and are crucial to understanding many biological processes. In Chapter 16, Grimme discusses the importance of dispersion bonds in chemistry, and describes different theoretical methods to treat them. In Chapter 17, Hirao and Wang review the many ways to describe hydrogen bonding theoretically.

In these volumes, Frenking and Shaik present an excellent summary of the state of the art in the theory of the chemical bond (Volume 1), and complement it with a well-chosen series of applications (Volume 2), where modern concepts are applied to timely questions of this fascinating research field.

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