

Structural Chemistry

Mihai V. Putz · Fanica Cimpoesu
Marilena Ferbinteanu

Structural Chemistry

Principles, Methods, and Case Studies

 Springer

Mihai V. Putz
West University of Timișoara & National
Institute of Research and Development for
Electrochemistry and Condensed Matter
Timișoara (INCEMC)
Timișoara
Romania

Marilena Ferbinteanu
Department of Inorganic Chemistry
University of Bucharest
Bucharest
Romania

Fanica Cimpoesu
Institute of Physical Chemistry “Ilie
Murgulescu”
Bucharest
Romania

ISBN 978-3-319-55873-8 ISBN 978-3-319-55875-2 (eBook)
<https://doi.org/10.1007/978-3-319-55875-2>

Library of Congress Control Number: 2017941056

© Springer International Publishing AG, part of Springer Nature 2018

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by the registered company Springer International Publishing AG part of Springer Nature
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Foreword I

This book *Structural Chemistry: Principles, Methods, and Case Studies* represents a very interesting didactical and review work suitable for scientists but especially for students who need an updated view on quantum chemistry. The matter covered by the book is so vast, complete, and rationally ordered that I feel a great respect for the authors, internationally very well-known scientists working on advanced research especially in the boundaries between chemistry and physics represented by the chemical bonds, the chemical topology with forays to the borders between chemistry and biology.

Chapter 1 is dedicated to atomic structure and quantum mechanics with a deeper and updated view of the matter. Chapter 2 is dedicated to quantum chemistry in a bridge from atoms to molecules covering among other topics the Gaussian-type orbitals, and all the key ab initio methods.

Chapters 3 and 4 are dedicated to the Density Functional Theory and computational chemistry of the chemical bonds. With Chap. 5 the fascinating worlds of hybridization, aromaticity, and topology applied to chemical problems are explored. Chapters 6 and 7 are respectively dedicated to coordination bonding and the connection between electronic structure and properties and to the modeling of molecular magnetism. Chapter 8 is dedicated to the bonding in rings and clusters and finally, Chap. 9 presents the theoretical approach to interpretation of the chemical bond through the bondon particle, a really seductive new theory proposed by Prof. M.V. Putz. In the views of Prof. Putz the bondon is a boson, i.e. an exchange particle which represents the interaction and coupling of two electrons. This interpretation may facilitate the understanding of chemical bond formation by the coupling of two electrons. The didactical power of this view is self-evident.

I hope that this book not only will be viewed by the vast audience of chemistry and physicists as a modern and updated review of quantum chemistry but will also be recognized as the springboard of the bondon concept proposed by the eminent Prof. M.V. Putz.

Viterbo, Italy

Prof. Franco Cataldo
Dipartimento di Scienze Ecologiche e Biologiche
Università degli Studi della Tuscia

Rome, Italy

Scientific Director
Actinium Chemical
Research Institute

Foreword II

The underlying law in the molecular world is clear. It is based on quantum mechanics. Theoretical chemistry is firmly based on the study of practical solutions of the Schrödinger equation for a molecule.

Once Paul Dirac said the general theory of quantum mechanics is now almost complete, ... and he continued that “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble” (*Proc Roy Soc (London) A* 123, 714 (1929)).

Chemistry covers a wide range of science, from the birth of the universe to the mysteries of life. Even if the whole chemistry is known in principle, there exist a lot of things we want to know. Theoretical chemists have analyzed the problem carefully and developed theory to obtain the practical solution of the Schrödinger equation for a molecule. Theoretical chemistry has come a long way. Theoretical and computational chemistry have seen significant advances in both methodology and applications in recent years. They have opened up a world of new possibilities and are becoming an integral part of chemistry research.

Today nobody is surprised to see accurate calculations of big molecules, such as carbon nanotubes and proteins. What Paul Dirac could not have in mind is the surprising development of computers. Owing to the help of computers, we can now treat real-world molecules and can deal with real chemistry.

This monograph entitled *Structural Chemistry: Principles, Methods, and Case Studies* is conceived at the midpoint between top research topics and didactic concerns, presenting original innovation and clues for both sides of the discourse. The team of authors develop many well-tempered storylines and detective analyses, where the expertise in theoretical and computational chemistry of Fanica Cimpoesu mediates between the experimental structural case studies proposed by Marilena Ferbinteanu and the physicist’s perspective of Mihai Putz. The book has rich and attractive graphics, rendering a vivid representation of structural chemistry.

The challenging perspective is sketched from the beginning, in the authors' introduction, by analogies between the history of art and the state of the art in computational chemistry.

Chapter 1 starts with the basics of quantum mechanics, putting certain emphases on the history and philosophy of the domain, presenting—for instance—a very interesting reformulation of Schrödinger's cat thought experiment. New artifices and shortcuts are drawn in the exposition of the Schrödinger equation for the hydrogen atom and the introduction of orbitals within the spherical symmetry. The chapter continues with elements of relativistic quantum chemistry, perturbation theory, and Feynman's path-integrals method.

Chapter 2 contains information that can quickly guide the reader toward applied quantum chemistry, some clues and hints being valuable even for experienced practitioners of computational chemistry. The Slater rules for making the matrix elements of many-electron problems are emphasized as a basic protocol in matrix representation of molecular or atomic problems. For the atomic case, emphasizing the symmetry-determined Slater-Condon integrals, the issue of atomic spectra is brought closer to the status of hands-on practical problems. Several difficult topics are dealt with efficiently with the help of computer algebra insets, programmed in the Mathematica language.

The knowledge of atomic electron structure is even more important than understood at first glance from traditional introductions in electron structure or its application in the physics of free atoms. Thus, for many systems with importance in current or future technologies, such as transition metal or lanthanide-based lattices or complexes, the basic optical and magnetic properties are due to atom-localized mechanisms, as will be reiterated in Chaps. 6 and 7.

A ground-breaking message is brought in Sect. 2.4 of Chapter 2 entitled "Back to the Basis", dealing with a systematic introduction and analysis of the atomic bases. Although everyone from applied computational chemistry knows that Gaussian Type Orbitals (GTOs) are approximations, these are yet regarded as convenient and acceptable, certified by their intensive and extensive use. However, very few realized the caveats launched here. For instance, all the s-type primitives are produced with simple $\exp(-\alpha r)$ exponentials, lacking the use of general terms like $r \cdot \exp(-\alpha r^2)$, $r^2 \exp(-\alpha r^2)$, ... $r^n \exp(-\alpha r^2)$. This makes the account of orbits with large quantum numbers (such as 3s for hydrogen) a difficult task, poorly resolved, and acting as a hidden burden in the actual settings of calculations with rich basis sets. After such a revolutionary stand, the book proposes alternative options, such as plane wave or numeric bases as rather good choices and possible future paths in quantum chemistry.

Chapter 2 ends with a brief exposition of Self-Consistent Field (SCF) methods: Hartree-Fock (HF) and multi-configuration procedures, such as Complete Active Space (CAS), whose applications will be detailed in the following chapters.

Chapter 3 is dedicated to the Density Functional Theory (DFT), honoring its privileged place in today's public attention, on central stages of conceptual and applied chemistry. The introduction to DFT objects (exchange-correlation hole and self-interaction terms) is done in an unprecedented maieutic way. Recalling that

DFT provides quantities valuable to the chemical language: electronegativities—as first-order derivatives of energy of population, and the so-called chemical hardness (measure for strength of Lewis’s definition of acids and bases)—as related to second-order derivatives, the authors are proposing to rename chemical hardness as electrorigidity, potentially more suggestive of its nature and of the fact that it is a legitimate companion of electronegativity.

Chapter 4 brings a basket of applications with various computational techniques, in a consistent arrangement. The power of *ab initio* methods to reinvent nature from first principles is illustrated on small molecules, pointing also to the tools and methods required for more complex cases. The experiment is, indisputably, the ultimate check and guide for theoretical constructs. However, in certain instances, the experiment is poorer in information or less precise than the instrumental measurements. Along the lines of Einsteinian thought, that the theory decides what experiment measures, the red-line of this book advocates for an equal footing between experiment and theory.

As a distinct feature, the book presents a passionate emphasis on the Valence Bond (VB) theory, both as phenomenology (by Heisenberg effective Hamiltonian) and as realization by modern computation tools, paying the deserved tribute to the very first theory of chemical bonding.

The second part of Chap. 4 goes beyond the usual Born-Oppenheimer situation of frozen nuclei, briefly discussing potential energy surfaces, molecular dynamics and the Jahn-Teller and pseudo Jahn-Teller effects. The interplay between vibrational and electronic degrees of freedom (the vibronic coupling) is advocated as a powerful paradigm, presenting also an original conceptualization of this domain.

Chapter 5, “New Keys for Old Keywords”, deepens the insight, debating how concepts dear to the heuristic language, such as hybridization and aromaticity, can be retrieved in the course of or after calculations. The classical aromaticity on benzenoid systems is debated with tools of quantum chemical calculations and model Hamiltonians, extending the discussion to the 3D cluster aromaticity. A very interesting proof of hybridization as an effective engine of stereochemistry is presented, combining experimental and theoretical reasons.

Chapter 6 treats the coordination bonding and ligand field theories, a domain less often treated in usual monographs of computational chemistry, while having its own classic textbooks, not well updated in conjunction with today’s *ab initio* techniques. This book fills these gaps. It is interesting to draw attention to the authors’ reinterpretation of the so-called Ligand Field Stabilization Energy (LFSE) correlations.

A special emphasis is put on the special issue of lanthanide systems, where the f-shell electrons are inducing special electronic structure features, with important implications in magnetic and optical properties. The authors of this book have made pioneering breakthroughs in this domain.

Molecular magnetism, the topic of Chap. 7, is one of the new lands in modern chemistry, the field being developed in last decades in a symbiosis of experiment and theory. Two of the authors (Fanica Cimpoesu and Marilena Ferbinteanu) review this domain from the heights of their own contribution with rationales on the

hot research topics, such as the investigation of ferromagnetic and anti-ferromagnetic coupling mechanisms in d-f complexes.

The magneto-structural considerations are completed at advanced level by the treatment of magnetic anisotropy, for which powerful and transparent tools are presented: the polar maps of state-specific magnetization functions. The virtues of calculations and modeling are illustrated, serving as guidelines to explanation or prediction and even as leverage for property design.

Chapter 8 debates the bonding in rings and clusters, revisiting with modern tools the principles of qualitative theories, like Tensor Surface Harmonics (TSH), used to catch the electronic structure specifics of such systems in the era preceding the availability of applied quantum chemistry.

Chapter 9 exposes the bondonic concept, by Mihai Putz, translating the idea of electron pairing in terms of quantum field theories.

I myself cooperated with two of the authors (Fanica Cimpoesu and Marilena Ferbinteanu) in a first state-of-the-art *ab initio* account of the non-trivial aspects of electron structure in lanthanide complexes, being able to certify their broad views and actions in holding a vivid dialogue between the realms of experimental and theoretical chemistry, using structural ideas as trading currency.

By the large horizons of this book and the density of new ideas in representing the domain together with its borderline junctions, I predict that the monograph will stir fresh impetus in the ongoing paradigms of structural chemistry.

Chūō-ku, Kobe, Japan

Dr. Kimihiko Hirao
Director

RIKEN Advanced Institute for Computational Science

Preface

The fact that the properties and, ultimately, the practical utility of different material systems are determined by their structure is well understood and firmly stated as a general principle of knowledge and action. The experiment is glorified, on good reasons, as the main source of knowledge, chemistry being probably the science most clearly perceived in this sense. However, the theory is equally important for setting the working paradigms. Einstein said that the theory decides what experiment measures. Let us imagine how awkward chemistry would look without concepts like atomic and molecular orbitals, ground and excited states, molecular geometry, which help understanding large amount of data, from spectroscopy and electrochemistry to reactivity. The revolution in the availability of powerful computers, even in domestic environments, and the creation of user-friendly codes has brought a “few clicks away” access to parts of a once impenetrable world of quanta. A graphic interface helper, available in many quantum chemistry programs, can make computational modeling no more difficult than operating a spectrometer, for instance. Either at routine level, or in advanced operating mode, the experimental solving of structure by X-ray diffraction, via specialized codes and interfaces, demands know-how comparable with the control of a quantum chemical package, at its modules of different complexity.

A shortcut to the chemistry would be the plain statement that molecules are made by atoms, linked by forces that can be figured like sticks, building edifices with certain shapes and different stabilities. At a bit more advanced level of knowledge, experimental chemists will acquire the intuition about qualitatively different sorts of bonding and mutual affinities of atoms in building molecules, or between whole molecules, to go to the supramolecular level, while the theoretical chemist will find advanced tools and descriptors of such features in analyzing the energy and electronic density distributions of the considered systems. If the experimental and theoretical (computational) chemists share a common background about grasping the sense of chemical formulas, recognizing the taxonomy of chemical species and reactions, then the communication over the borders of specializations is possible in the paradigm of molecular structures and correlated properties. A synthetic work often ends with a crystallographic characterization

concretized in a file (cif-type: crystallographic information format) from where the basic modeling can start, e.g. with an affordable and well received calculations in the frame of Density Functional Theory. As after synthesis the samples can undergo some instrumental, e.g. optical or magnetic measurements, the theoretical models can advance toward the account of such properties, after having a molecular structure and some orbitals to rely on. As the experiment, on its own, claims often to provide rules of thumb for acquiring a certain desirable property by tailored synthesis, the theoretical approach can naturally and consistently align with such goals. The causal understanding of structure–property relationships and even the rational design of useful features is the holy grail of structural chemistry, with its instrumental and theoretical branches.

Most of the properties can be defined as various sorts of derivatives from energy, under the variation of external parameters (e.g. electric or magnetic fields), so that the atomic or molecular energies are the primary subject of the calculations. Whether the vibrational spectroscopy concerns states with energy in the range of hundreds to thousands of wave numbers (reciprocal centimeters, cm^{-1}), or in the domain of 10^4 – 10^5 cm^{-1} , as is the case of optical manifestations, the magnetism is related with a subtler scale of a few, up to tens, of wave numbers. The quantum chemistry methods, which, in their varieties, depend also on the building ingredients (the basis sets), can determine the energies with good (yet limited) precision. This accuracy should be regarded merely in relative respects. With a good setting, the calculations can account, let us say, in a generous and optimistic estimation, about 20–30% from the relative positioning of states or parameters, in the given scale of the concerned properties. A calculation can be wrong, and yet acceptable in semi-quantitative respects, by several thousands of wave numbers if the peaks from the ultraviolet spectrum are targeted, but at the same time, the error bars for the match with the experimental vibrational spectrum can be in the range of tens of reciprocal centimeters. Thus, fortunately, the numeric precision in the first-principles quantum approach is not on a unique absolute scale and is not necessary to achieve the level of centi-calories per mol when calculate the formation energy, to have good computational retrieval of certain parameters of molecular magnetism.

The possibility to simulate the atomic and molecular structures from scratch, or in other words, in *ab initio* manner (from the very beginning, without presupposed particularized ingredients) was one of the appeals of quantum chemistry. Actually, there are several levels of approximations and basic ingredients (like basis sets) even in the classes of *ab initio* methods, but yet the flavor of having the molecule, *de novo*, reborn along with the run of the computer, is kept. We mentioned previously the experimental molecular structure (from X-ray diffraction) as starting point, but the computation can reinvent the molecule by itself, using geometry optimization routines. This fact, aside being helpful in cases when experimental structure is not directly known, having only guesses from spectroscopy hints, also confers to computational chemistry a sort of autonomy, long with the self-determination of theoretical goals.

As an art in itself, quantum chemistry is still marked by its filiation from quantum mechanics, born about a century ago as a revolutionary act of the human spirit, entering a world where the rules of games are completely changed, not benefitting from the guidance offered by intuition and common sense, or by the equations of classical mechanics. The perplexity in the face of quantum world has not yet receded, being even more excited by modern experiments and possible applications, such as quantum entanglement and particle teleportation. Besides, we have learnt recently that the matter we can describe as made of molecules, atoms, or their known particle substructures, constitutes only about 4% of the energy-mass content of the whole universe. We are not going to touch even marginally such topics, but we would point out that, aside from learning the rather well established principles and methods of atomic and molecular structures, one may secretly hope to have new fundamental discoveries that may affect this domain in the future. The actual quantum chemistry does not question what is space and time, directly using them as variables in the fundamental Schrödinger equation and its approximated offsprings. However, if we would have an intimate knowledge of such things, it will be possible to see a “proof” for wave-mechanics in the very fabric of space-time. At the same time, in a very practical sense, the computer revolution may bring some new openings in the customary aspects of quantum mechanics. For instance, for decades, most of quantum chemistry is done with so-called Gaussian-type orbitals (GTOs) as atomic basis sets, that replaced, by reasons of computing efficiency, the initially envisaged Slater-type orbitals (STOs), which in some sense were rational approximations originating from the known hydrogen-type solutions of the Schrödinger equation. However, GTOs, although very popular, show some intrinsic limitations and since computers have evolved spectacularly it is perhaps possible to return to STO bases. One may also opt for other routes, such as numeric bases, which are reproducing the atoms and molecules without predefined ingredients.

Along with computer evolution, quantum chemistry, aside from being widely available, has reached new heights in the race to acquire better precision in reproducing spectral or thermochemical data. Having an atomic basis set defined, the sky, usually unreachable, except for very small systems, can be touched in the full-configuration interaction (CI), which means considering all the possible permutations of the electrons in all the orbitals, and resolving matrices of astronomic size. With an appropriate mixing of atomic orbitals into molecular ones, by defining mean fields, the problem can be reduced to fewer configurations, even to a single one. Certain problems, such as optical spectroscopy, demand multi-configuration methods, where a restricted CI is performed, altogether with optimization of orbitals, but for most cases the single configuration limit is a fair, satisfactory, approximation. Such a single-configuration limitation is, in the *ab initio* frame, the so-called Hartree-Fock (HF) method. It is regarded nowadays as obsolete, but is still in use as the starting point of improved techniques. Actually, the HF can give a reasonable performance, regarded from a particular perspective. It can reproduce some parameters, like optimized bond lengths and angles, or even some relative thermochemical scales, with precision amounting, roughly, even to 95% with respect of some trusty reference (experiment or higher level methods). In some

circumstances this can be enough, but in other respects, not. Consider that the gorilla has a DNA overlapping with about 98% of the human one. This is a good reason to look with modesty at the whole of nature, but also a hint that tiny details matter. The HF lacks so-called correlation effects, namely certain details of the electron-electron interactions, e.g. their avoiding to come too close to each other, while the HF designed a mean field by equally smearing the inter-electron encounters. Discarding, for this concise story, the multi-configuration methods (which are, of course, superior to HF), there are some ways to bring corrective increments to a Hartree-Fock background, one of the best routes being the so-called Coupled Cluster techniques.

We dare an analogy between art and the state-of-the-art in computational chemistry, with respect of “accuracy” level, in Fig. 1. For art, the accuracy will be roughly defined as the realism in rendering the visual details of the portrait or landscape. Of course, in the modern sense, this is not a parameter of the art itself, but throughout its history, veracity functioned as an intrinsic goal. Consider, for instance, that the Greek word for art is “*techne*”, a recognizable root of the “*technique*” keyword, suggesting initial utilitarian and methodological concerns of the art. Thus, in this construction, the art of the earliest socially organized humans achieved a rather low resolution, looking for instance at drawings from ten

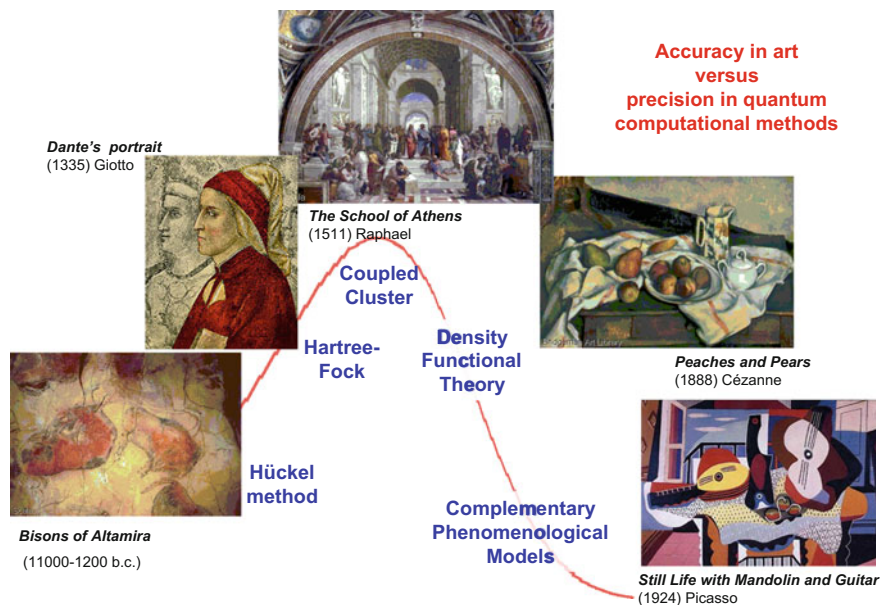


Fig. 1 Indulging ourselves a parallel between accuracy of image rendering in art and the trend to numeric precision in quantum chemistry. In a loosely defined analogy, based on single configuration-type methods, the Hückel theory can be proposed as the ancestor with poorest numerical sophistication, and the Coupled Cluster as higher in reliability, while the Density Functional methods represent a trend toward the simplification of the computational engine

thousand years ago, in the Altamira caves. We compare, in parallelism to this beginning, the empirical Hückel method, because it is really simple and offered a very convincing sketch about what quantum chemistry would become. Actually, the Hückel method was born almost at the same time as the Hartree-Fock principles, in the 1930s, but clearly the HF was not immediately tractable, so that we give priority to Hückel, on our scale. Since in its initial evolution the art clearly longed for better resolution, we conventionally assign the level reached at Giotto's time, around 1300, as a match for Hartree-Fock. Then, the peak attained at the Renaissance, by masters like Raphael, can be compared with the present-day upper limit of the Coupled Cluster-type performances. The drawing techniques and principles continued to be enriched along the centuries after 1500, until they reached a plateau from where no new achievement was possible in the age of academicism and mannerism in painting. What happened after? The newcomers, such as Impressionists, started to challenge the clamp on rigor. For instance, Cézanne intentionally disobeyed the rules of perspective in his *Still Life with Peaches and Pears* picture, where the table is rectangular, not trapezoidal elongated in the deeper fundal. Things became more revolutionary with the cubists and other modernist artists, who completely gave up and severely mocked the realism and accuracy desiderata in the art of painting. Art and science cannot be completely parallel, of course, although some chemists may be tempted to regard their domain as very akin to that of art. However, we suggest that when the dream of having enough precision in the calculations is satisfied, quantum chemistry will transmute itself in finding its non-trivial goal in simpler truth sequences, behind heavy modeling engines.

It is quite non-trivial to recover from the black box of complex calculations intuitional constructs of chemistry, such as hybridization, aromaticity, or even reaction mechanisms (when there are so many evolution channels and lots of scenarios in molecular dynamic runs). In our parallelism with the history of painting we place the Density Functional Theory (DFT) on the other side of the curve, after the peak of accuracy assigned to the post-Hartree-Fock method of Coupled Cluster type. Aside from being recommended and increasingly popular, by its tractability, the DFT method can be regarded as a revolutionary way of challenging the extreme technical effort in climbing the HF-CC difficult slope, adopting a simpler central paradigm. Theoretically, it is possible to keep the single-configuration simplicity, adding the secret ingredient of a functional alleviating the correlation effects in a simple cut. The theorem allowing such a construction, enunciated by Walter Kohn in 1964, received the Nobel Prize in 1998, when the rising of DFT on the scene became visible. Because the rigorous formulas for these functionals are not yet known, people adhering to this paradigm rely on some empirical approximations, a fact that makes other "factions", loyal to "traditional" wave function methods consider that the DFT does not belong to the *ab initio* branch. The terminology limits are not so severe, however, and in many respects the DFT can be considered as quite akin to the *ab initio* sense. Regarding therefore the DFT as a bit of an outcast aside the growth trend line in accuracy, we opine that the appeal of this theory is not only due to reasonable numeric performances at

affordable costs, but, subtly, also to its fresh and simple perspective, beyond the Coupled Cluster type academicism. In its capacity to describe instants of chemical reality, though incompletely accurate, the DFT can be compared with the Impressionists' breakthrough in favor of sketched landscapes rather than photographically detailed ones. After all, we should not turn our computers into spectrometers, aiming for the full virtual reproduction of physical reality.

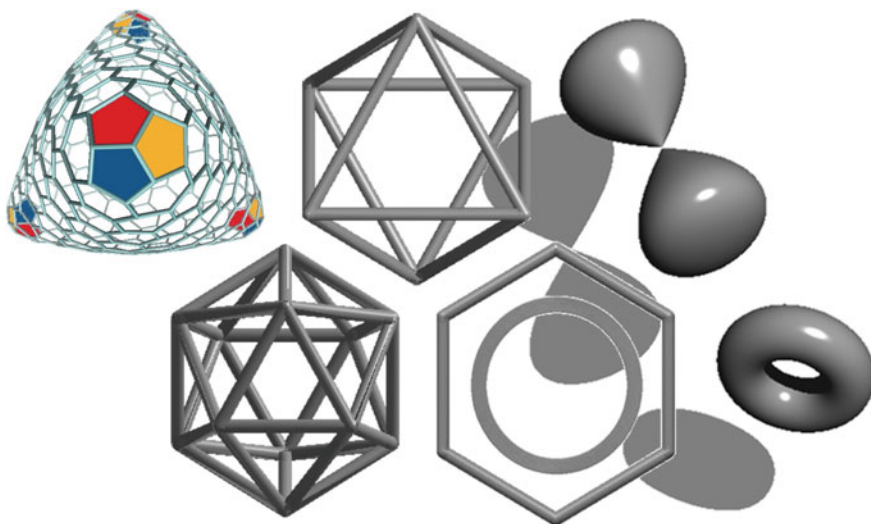


Fig. 2 A logo suggesting the interests of authors and content of the book. In the central part, the objects encased in the three hexagonal contours are suggesting different branches of structural chemistry. The plain hexagon stands for the organic chemistry (with a hint on aromaticity issues). The octahedron is suggesting the coordination compounds, while the icosahedron the cluster chemistry. The two-lobe and toroidal shapes from the right side are symbols for symmetry, orbital patterns and magnetic anisotropy. The large carbon cluster from the left side suggests the topological theories

A compromise between a realistic and sketched drawing of the chemical world is the duty and inner longing of the structural chemist. We rate as less important the demand for higher and higher numerical precision, indulging a certain amount of ignorance (regarded as freedom) in respect to complex quantum numerical increments, in favor of simplified methods. However, we do not want to be misunderstood. The reliability in the account of correlation effects matters enormously. We can draw another parallel with other fields. Recently, the world has passed through a severe economic crisis, not predicted by the vast majority of scientists or players in this field. We dare to suppose here that the actual economic models lack the effect of correlation. Using monetary values, which are defined by protocols similar to a mean-field model, we guess that the actual economic models are somewhat similar to the Hartree-Fock level in quantum chemistry. With this parabola we want

to underline our respect for those designing complex and accurate models in any science. In this work we have tried to follow a middle path, illustrating state-of-the-art structural ancillary tools and also keeping a simplified perspective at the level of modeling apparatus.

The contents of this book reflect the authors' perspectives on current fundamental topics in structural chemistry. Accordingly, the theoretical discourse is always exemplified and extended with cutting-edge chemical themes, often not clarified in most standard quantum chemistry textbooks.

We hope this work will be a useful guide scrutinizing the structural chemistry and quantum modeling landscape.

Timișoara, Romania
Bucharest, Romania
Bucharest, Romania
Autumn 2017

Mihai V. Putz
Fanica Cimpoesu
Marilena Ferbinteanu

Acknowledgements

Parts of this book *Structural Chemistry: Principles, Methods, and Case Studies* were realised with resources from the following funding grants, awarded through the UEFISCDI-Romanian Executive Agency for Higher Education, Research, Development and Innovation Funding, which are heartily acknowledged hereby: MVP by the reaserch project PED123/2017; FC by the research projects “IDEAS” PN2-PCE 14/2013 and PN3-PCE 108/2017 and MF by the exploratory research projects “COMPLEX IDEAS” PN2-PCCE 9/2010 and European COST Action 1305, ECOSTBIO; respectively.

Contents

1	Atomic Structure and Quantum Mechanics	1
1.1	The Long Road from Democritus to Bohr	2
1.1.1	Arcadian Antiquity	2
1.1.2	Along the Centuries, to the Positivist Era	4
1.1.3	Bohr's Atomic Model: <i>Natura Facit Saltus!</i>	5
1.2	The Dawn of Quantum Theory and the Founding Fathers	11
1.2.1	The Revolutionary Milieu and Quantum Mechanics	11
1.2.2	<i>Modus Operandi</i> : Waves and Operators	12
1.2.3	The Schrödinger Equation and Schrödinger's Cat	17
1.2.4	The Heisenberg Equations: Uncertainty and Matrix Mechanics	19
1.2.5	Hamiltonian Matrices, Non-orthogonal Bases, Variational Methods	23
1.3	Atomic Shell Structure and the Spherical Harmonics	27
1.3.1	Atomic Orbitals and Quantum Numbers: The Radial-Angular Factorization of the Atomic Wave Functions	27
1.3.2	Intuitive Primer on the Pattern of Atomic Orbitals	29
1.3.3	Toward Setting the Schrödinger Equation in Atoms	34
1.3.4	The Schrödinger Equation for the One-Electron Atom: The Radial Part	36
1.3.5	A Qualitative Analysis of the Radial Nodal Structure of the Atomic Orbitals	40
1.3.6	The Complete Analytic Formulas of the Atomic Orbitals	42
1.3.7	A Philosophical Divagation	44
1.4	Elements of Relativistic Quantum Mechanics	45
1.4.1	The Electronic Spin, the Missing Link Between Atomic Shell Scheme and Chemical Systematics from the Periodic Table of Elements	45
1.4.2	First Principles of Relativistic Quantum Mechanics: Klein-Gordon and Dirac Equations	49

1.4.3	The Quantum Numbers of Dirac Relativistic Equations . . .	52
1.4.4	The Two Quantum Worlds of Dirac Equations: Small and Large Spinor Components.	53
1.4.5	Toward the Relativistic Atom: Electromagnetism Instead of Electrostatics.	55
1.4.6	Concluding the Types of Relativistic Hamiltonian Terms: Zeeman, Spin–Orbit, Mass-Correction, Darwin, Breit, Breit-Pauli.	58
1.4.7	The Spin–Orbit Coupling: A Term to Remember	60
1.5	Perturbation Theory Application: Quantum Polarizability.	65
1.6	Atomic Stability: The Proof by Quantum Path Integrals.	75
1.6.1	Schrodinger Equation by Quantum Path Integral.	75
1.6.2	Feynman-Kleinert Effective Density Formalism	79
1.6.3	Quantum Smeared Effects and the Stability of Matter.	84
1.6.4	Ground State ($\beta \rightarrow \infty$, $T \rightarrow 0$ K) Case	90
1.7	Free and Observed Quantum Evolution: Extended Heisenberg Uncertainly Relationship (HUR) by Path Integrals	93
1.7.1	HUR by Periodic Paths	94
1.7.2	Wave-Particle Ratio Function	97
1.7.3	Extended HUR	99
1.8	Conclusions	103
	References.	104
2	Wave Function Theories and Electronic Structure Methods:	
	Quantum Chemistry, from Atoms to Molecules	107
2.1	Poly-electronic Wave Functions from Spin-Orbitals	108
2.1.1	Indiscernible Electrons and Anti-symmetric Wave Functions with Slater Determinants.	108
2.1.2	Matrix Elements in a Basis of Slater Determinants: The Slater Rules	113
2.1.3	The Atomic Integrals: The Slater–Condon Symmetry Factorization of the Two-Electron Integrals.	119
2.1.4	Orbital and Spin Quantum Numbers in the Poly-electronic Atom: The Spectral Terms	122
2.1.5	Slater Rules at Work: A Hands-On Example on the Helium Atom	129
2.2	Atoms with Many Electrons: A Guided Tour Through Selected Examples	137
2.2.1	Spectral Terms of Main Group Elements: The Li, B, C, N, O, F, Ne Series	137
2.2.2	Spectral Terms of Transition Metal Ions.	144
2.2.3	Other Notes: Racah Parameters for Real-Type d Orbitals. Calculation of Slater–Condon Parameters. Approximate Ratios in the Series of Slater–Condon or Racah Parameters.	148

2.3	Atomic Spectra in Practical Applications: From Neon Tubes to Warm White Light	152
2.3.1	Fiat Lux! Sunlight and Black Body Radiation	152
2.3.2	Generating Light from Atoms Excited in Plasma	153
2.3.3	Converting the Light Wavelength with Solid-State Phosphors	157
2.4	Back to the Basis! Atomic Basis Sets: Slater versus Gaussian Orbitals and Other Options.	162
2.4.1	Deconstructing the Hydrogen-Type Analytic Atomic Orbitals and Recomposing the One-Electron Atom from Slater-Type Primitives.	162
2.4.2	A Test with Slater-Type Orbitals (STOs)	170
2.4.3	The Gaussian-Type Orbitals (GTOs): The “Steel and Concrete” of the Massive Development of Quantum Chemistry	172
2.4.4	Caveats on Gaussian-Type Basis Sets	180
2.4.5	Other Options: Plane Waves and Numerical Bases	186
2.5	Ab Initio Methods	194
2.5.1	Hartree–Fock Method: The Simplest Level of Electronic Structure Calculations in Atoms and Molecules	194
2.5.2	Multi-configuration Self-consistent Field Methods: Closer to the Physical Truth and Chemical Realism.	200
2.5.3	Valence Bond: A Tribute to the Historical Roots of Bond Theories and Yet a Promising Land	208
2.6	Conclusions	215
	References.	216
3	Density Functional Theory: From Conceptual Level Toward Practical Functionality	221
3.1	Background and Principles	222
3.1.1	The Deep Roots of Density Functional Theory	222
3.1.2	The Hohenberg–Kohn Theorems and the Problem of Universals in Electronic Structure	223
3.1.3	A Bit of Maieutics on Exchange and Correlation Holes	227
3.1.4	An Illustration of Density Functional Issues	230
3.1.5	Methods and Concepts in DFT: Kohn–Sham Self-consistent Field, Fractional Occupations, Electronegativity and Chemical Hardness (Electrorigidity).	234
3.1.6	The Chemical Relevance of DFT: Electronegativity Equalization, Maximum Hardness Principle, Hard and Soft Acids and Bases (HSAB)	238

3.1.7	Ways to Approximated Density Functionals	241
3.1.8	Other Issues Related to Density Functional Theory: The DFT+U Methods and an Atomic Model Based on the Interpolation of Spectroscopic Configuration Energies	248
3.1.9	A Phenomenological Model: Energy of Atoms as Continuous Function of Valence Shell Populations.	254
3.2	Density Functional Theory in More Detail	266
3.2.1	Density Functionals of Kinetic Energy	266
3.2.2	Density Functionals of Exchange Energy	269
3.2.3	Density Functionals of Correlation Energy	274
3.2.4	Density Functionals of Exchange-Correlation Energy	280
3.3	Conclusions	284
	References.	285
4	Bond! Chemical Bond: Electronic Structure Methods at Work. . . .	291
4.1	Molecular Structure by Computational Chemistry: A Brief Synopsis	293
4.2	Hartree–Fock Versus Density Functional Theory Computation Simple Samples	297
4.3	Orbitals, the Building Blocks of Electronic Structure	304
4.4	The H ₂ Molecule: The Simplest Bond Prototype. Phenomenological Models and Calculation Methods	309
4.4.1	The Spin-Coupling Phenomenology of the Chemical Bond	309
4.4.2	Model Calculations on H ₂	313
4.5	Computational and Conceptual Valence Bond: The Spin Coupling Paradigm at Work	323
4.5.1	Overture to the Valence Bond Calculations.	323
4.5.2	Benzene: Valence Bond Versus Complete Active Space	325
4.5.3	Playing with Graphic Rules for Setting a VB Modeling	332
4.6	<i>Mobilis in Mobile</i> : Electrons Moving Around Mobile Nuclei. Floppy Molecules, Unstable Systems, and Chemical Reactions . .	341
4.6.1	Jahn–Teller and Related Effects. Vibronic Coupling	341
4.6.2	A Simple Approach of the H ₃ Prototypic System. Example for Reaction Potential Energy Surfaces and E ⊗ E-Type Jahn–Teller Effect.	344
4.6.3	The Computational Approach of the Pseudo Jahn–Teller Effect (Second-Order Vibronic Coupling)	351
4.6.4	The Vibronic Orbitals	357
4.6.5	More on the Usage of Vibronic Modeling	362

4.7	Breaking Symmetry in Quantum Chemistry	373
4.7.1	The Symmetry Breaking of Chemical Field Generation . . .	373
4.7.2	The Inverse Quantum Chemical Problem	377
4.8	Conclusions	382
	References.	384
5	New Keys for Old Keywords: Hybridization and Aromaticity, Graphs and Topology	389
5.1	Introduction	390
5.2	The Concept of Hybridization	391
5.2.1	Hybrids with s and p Orbitals: A Good Basis of Discussion.	391
5.2.2	The Natural Hybrids Orbitals from Natural Bond Orbital Analysis of Electronic Density	396
5.2.3	Are the Hybrids with s, p, and d Composition Realistic?.	399
5.2.4	Hybrids in the Isolobal Analogy	403
5.3	Aromaticity as Resonance.	408
5.3.1	Criteria of Aromaticity	408
5.3.2	Iconic Prototypes: Aromaticity in Benzene Versus Anti-aromaticity in Cyclobutadiene, from Valence Bond Perspective	411
5.3.3	Resonance Structures Without a Valence Bond Frame	423
5.3.4	The Spherical Aromaticity in Inorganic Clusters: The Icosahedral Borane.	429
5.3.5	Aromaticity and Anti-aromaticity in Non-organic Systems.	433
5.4	Aromaticity by Chemical Reactivity.	436
5.4.1	Modeling Molecular Aromaticity with Electronegativity and Chemical Hardness.	436
5.4.2	Modeling Absolute Aromaticity of Atoms-in-Molecules . . .	440
5.4.3	Modeling Compact Aromaticity of Atoms-in-Molecules . . .	447
5.5	Chemical Bonding by Coloring Reactivity	464
5.5.1	Reactivity Coloring of Topological Distance Matrix	464
5.5.2	Reactivity Coloring of Topological Adjacency Matrix	475
5.6	Conclusions	494
	References.	495
6	Coordination Bonding: Electronic Structure and Properties	503
6.1	The Ligand Field Theory: An Evergreen Field.	504
6.1.1	The Puzzle of Supra-valent Coordination Numbers and Werner's Clear Cut Theory	504
6.1.2	Generalities on Ligand Field Modeling.	505
6.1.3	The Effective Electrostatic Formalism of Ligand Field Theory	508

6.1.4	The General Formulation of the Ligand Field Potential in Spherical Harmonics Basis	510
6.1.5	Particular Ligand Field Hamiltonians in Selected Symmetries	515
6.1.6	Limitations of Ligand Field Modeling: The Holohedrization Effect.	522
6.1.7	Ligand Field Potential Maps: A Picturesque Representation of Multi-parametric Systems	526
6.2	The Angular Overlap Model (AOM): Angling for Chemical Meaning in Ligand Field Parameterization	529
6.2.1	Principles and Techniques of AOM: Chemists Believe in Orbital Overlapping	529
6.2.2	The AOM Parameterization in Prototypic Cases	533
6.2.3	Meaning and Estimation of AOM Parameters	535
6.3	Bonding Schemes and Ligand Field Stabilization Energy in Transition Metal Complexes	539
6.4	Modeling Electronic Spectroscopy of Transition Metal Complexes	543
6.4.1	Taking a Case Study: The $[\text{Ni}(\text{Phen})_3]^{2+}$ Complex. Preamble: Molecular Geometry of the Complex Electronic Structure of the Free Metal Ions	543
6.4.2	Calculation of the Ligand Field Spectra by Multi-configuration Methods	545
6.4.3	The Advanced Level: Guiding the Calculations and Handling the Results to Meet the Ligand Field Phenomenology	547
6.4.4	The Time Dependent Density Functional Theory (TD-DFT) Calculation of Electronic Spectra in Coordination Compounds: Limitations and Advantages . . .	558
6.5	The Thermochromism of Coordination Compounds	564
6.5.1	A Colorful Topic	564
6.5.2	Thermochromic Behavior by Linkage Isomerism: The Nitro-nitrito Isomerization	566
6.5.3	The Thermochromism of the Tetrahalocuprates: Tetrahedral-Square Planar Switching	571
6.6	The Specifics and Subtleties of the Electronic Structure of Lanthanide Complexes. Ligand Field + Spin-Orbit = Magnetic Anisotropy	585
6.6.1	The Puzzle of the f Orbitals in Molecule	585
6.6.2	An Intermezzo on Magnetic Anisotropy	586
6.6.3	The Non- <i>aufbau</i> Nature of the f-Shell in the Molecular Orbital Pictures	588

6.6.4	The Multi-configurational Methods of the f-Element Complexes: The First-Principles Route to Ligand Field Phenomenology and ab initio Magnetic Anisotropy	590
6.6.5	Other Ways of LF Modeling: Stevens Equivalent Operators Technique, Exemplified in Axial Symmetry	601
6.7	Conclusions	606
	References.	608
7	The Modeling in Molecular Magnetism.	613
7.1	Phenomenological Models in Magnetochemistry	615
7.1.1	The Spin Coupling Hamiltonian	615
7.1.2	Other Effective Magnetic Components: Zeeman Hamiltonian and Zero Field Splitting	617
7.1.3	Magnetic Susceptibility	619
7.2	Fit to Experiment of Spin Coupling Parameters: Some Non-trivial Issues	622
7.3	The CASSCF and Broken Symmetry DFT Methods, Face to Face, in the Estimation of Exchange Coupling Parameters.	626
7.4	The Broken Symmetry Approach to Poly-nuclear Systems.	629
7.5	The Complexity of Structure-Property Relationships Poly-nuclear Systems Within Lanthanide Ions: Spin Coupling, Ligand Field, and Spin-Orbit Factors.	633
7.5.1	Generic Mechanisms for Ferromagnetic and Antiferromagnetic d-f Exchange Couplings. The Case of Cu-Gd Complexes	633
7.5.2	Exchange Coupling in d-f Complexes with Degenerate Ground Terms of Lanthanide Ions	638
7.5.3	The Ligand Field Analysis of the CASSCF Results	641
7.5.4	The Angular Overlap Modeling of the Ligand Field in Lanthanide Complexes	646
7.5.5	Magnetic Anisotropy of the Lanthanide Ions in Ground and Excited States. State-Specific Magnetization Polar Maps. The Ab Initio Simulation of the Magnetic Properties	648
7.6	The Spin Crossover Phenomena.	656
7.6.1	Generalities	656
7.6.2	A Simple Modeling of the Ligand Field Versus Spin Coupling Balance	658
7.6.3	Adding the Vibrational Factors	662
7.6.4	Illustration of the Spin Crossover in Prototypic Fe(II) Complexes	665
7.6.5	The Rare Cases of Spin Crossover in Mn(III) Complexes	670
7.7	Conclusions	674
	References.	676

8 Bonding in Rings and Clusters	681
8.1 Clues for Heuristic Insight in the Structure of Quasi-symmetric Systems	682
8.1.1 Symmetry as Ancillary Tool	682
8.1.2 Point Groups in a Nutshell	683
8.1.3 Orbital Symmetry in Ring Systems	686
8.2 Tensor Surface Harmonics (TSH) Theory	689
8.2.1 Orbital Patterns in Quasi-spherical Clusters	689
8.2.2 Modeling Clusters by Vector Surface Harmonics	704
8.2.3 Complex Structures MO Diagrams by TSH Theory	710
8.3 Special Bonding in Adjacencies by Topological Isomers	713
8.4 Conclusions	721
References	721
9 Add on. The Bondon: A New Theory of Electron Effective Coupling and Density Ensembles	725
9.1 The Need for Bondonic Theory in Quantum Chemistry	726
9.2 The Analytical Roots of Bondonic Theory	728
9.3 The Gravitational Side of Bondonic Theory	737
9.4 Modeling Graphene Systems by Bondonic Theory	752
9.5 Bondons on Graphene by Symmetry Breaking Modeling	766
9.5.1 Symmetry Breaking Phenomenology in Quantum Nanochemistry	766
9.5.2 Bondons by Symmetry Breaking	769
9.5.3 Goldstone Bondons on Graphene with Topological Defects	774
9.6 Conclusions	778
References	779
Appendix: Atomic Two-Electron Integrals	783
Index	799

About the Authors

Mihai V. Putz is currently Full Professor of theoretical and computational physical chemistry at the West University of Timisoara, Romania. He has an interdisciplinary training and research experience in physics, chemistry, and spectroscopy and has been involved in numerous postdoctoral projects at the University of Calabria, Italy and at the Free University of Berlin, Germany. He has made valuable contributions to computational, quantum, and physical chemistry through seminal works published in numerous international journals. He is also a member of many professional societies and has received several national and international awards. In 2010 Mihai V. Putz was declared through a national competition the Best Researcher of Romania, while in 2013 he was recognized among the first Dr.-Habil. in Chemistry in Romania. From 2014 he became a full member of International Academy of Mathematical Chemistry.

Fanica Cimpoesu graduated from the University of Bucharest. His Ph.D. work, under the guidance of I.B. Bersuker, was dedicated to the orbital models of vibronic effects. Self-didactically, he approached several other topics such as organometallic stereochemistry and molecular magnetism, continuously enlarging his research area. The trademark of Fanica Cimpoesu's work is finding new methodological clues and heuristic viewpoints at the borderline between theory, computation, and experimental chemistry. Research stages at the universities of Leuven (Prof. A. Ceulemans), and Tokyo (Prof. K. Hirao) are acknowledged as emulative events in his curriculum vitae.

Marilena Ferbinteanu is an Associate Professor at the University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Department. She graduated and received her M.S. and Ph.D. degrees in inorganic chemistry, at the same university. In 1999 she was awarded with the Alexander Von Humboldt fellowship (Prof. Herbert Roesky) and in 2004 with the Japan Society for Promotion Science fellowship (Prof. Masahiro Yamashita). She had several postdoctoral stages in

Germany (Institute of Inorganic Chemistry, Göttingen, 2001) and in Japan (Ochanomizu University, Prof. Yutaka Fukuda, 2002; Tokyo Metropolitan University, Prof. Masahiro Yamashita and Hitoshi Miyasaka, 2003). She promoted advanced structural-property correlations combining the experiment, structural and applied coordinative chemistry, magnetic and optic properties with theory.