

Preface

This book is primarily intended as a textbook introducing to the reader the basic elements of the quantum theory of the electronic structure of molecular systems, including in its first two parts the basic axioms of the nonrelativistic quantum mechanics and rudiments of the wave function and density based theories. Its remaining two parts, of a more monographic character, contain the *Information Theory* (IT) description and some elements of the modern theory of chemical reactivity, respectively. The basic aim of this book is to present in a single text alternative outlooks on the molecular electronic structure, including the basic principles and techniques of the contemporary conceptual and computational quantum chemistry, covering also the insights provided by IT. Together these complementary perspectives enhance the depth of our understanding of the electronic/geometric structure of molecules and provide a full “vocabulary” to tackle diverse conditions, which influence their reactivity behavior. Indeed, only the insights from several different point of view amount to a real understanding of the problem. The emphasis is on the concepts involved and the key ideas encountered in these alternative approaches in the molecular quantum mechanics, and on the interpretation of calculated results in chemical terms: the bonded atoms and molecular fragments, the chemical bonds that connect these building blocks of molecules, and on their responses in a changing environment, which shape the reactivity preferences of reactants.

Explanation and understanding of chemical phenomena ultimately call for the quantum mechanical description provided by the modern quantum chemistry. The latter uses ideas and concepts that differ substantially from their classical analogs. A precise formulation of these generalized physical concepts, which requires some new mathematical tools, is the subject of Part I of this book. The depth and rigor of this physical/mathematical supplement have been dictated by the main didactic purpose of this text: to introduce all tools necessary for understanding the abstract ideas of the modern theory of the molecular structure and chemical reactivity. The foundations of quantum mechanics are covered using the familiar axiomatic approach, with only an introductory summary of the key experiments that led to their formulation.

The reader can familiarize himself with these novel ideas in the simplest problem of the stationary (bonded) states of the hydrogen-like atom presented in the part closing chapter.

The main theories of the molecular electronic structure are presented in Part II. In its opening chapter it examines available techniques of reducing the complexity of solving the molecular Schrödinger equation. In particular, the rudiments of the adiabatic separation of the electronic and nuclear motions are given and the elements of the approximate perturbational and variational approaches for determining the electronic quantum states are outlined. This brief overview also covers the basics of the orbital approximation and the idea of a pseudopotential, which effectively removes the chemically inactive electrons of the atomic inner shells from an explicit treatment in molecular calculations. The subsequent exposition of the principal *Wave Function Theories* (WFT), in which the system wave-function (probability amplitude) defines the quantum state of the molecule, covers the *Self-Consistent-Field Molecular Orbital* (SCF MO) theory, major *Configuration-Interaction* (CI) techniques for dealing with the Coulomb correlation problem, and rudiments of the *Valence Bond* (VB) treatment, which gives a more chemical understanding of molecules compared to its chief rival, the *Molecular Orbital* (MO) description and currently experiences a notable revival.

The following presentation of theoretical basis of the modern techniques of the *Density-Functional Theory* (DFT), in which the electron density or the density matrix constitute the system basic *state*-variables, covers the famous *Hohenberg-Kohn* (HK) theorems and some of their refinements/extensions, the basic elements of the ground-state *Kohn-Sham* (KS) theory and the associated ensemble approach to excited states. The theory of the density functional for the exchange-correlation energy is summarized, including the rudiments of the adiabatic connection and some more recent developments in the field of the density-matrix and orbital-dependent functionals, time-dependent DFT and alternative approaches to the molecular *van der Waals* (vdW) interactions. This short exposition also introduces the main concepts of the density-based reactivity theory: the hardness and softness responses of the electron distribution in molecules in the complementary *electron-following* (EF) and *electron-preceding* (EP) perspectives.

The additional insights from IT are presented in the monographic Part III of this textbook. Its dominating theme is the electron distribution as a source and carrier of information in molecules. First, the basic elements are summarized in the part opening chapter, to be followed by a brief exposition of the information principles in molecular quantum mechanics. The local IT probes of the presence of the direct chemical bonds are formulated and the importance of the nonadditive (interference) information tools is emphasized. In particular, the *Electron Localization Function* (ELF) and the *Contra-Gradiance* (CG) bond criterion are used to explore the molecular electronic structure and the IT variational principles are used to derive the so called stockholder scheme for dividing the molecular electron density into the associated atomic pieces. Various *Charge Transfer* (CT) and *Polarization* (P) displacements accompanying the formation of chemical bonds in molecular

systems are examined, including the equilibrium redistribution of electrons among the bonded *Atoms-in-Molecules* (AIM) and the molecular promotion of the latter.

Alternative bond-multiplicity descriptors and the electron localization criteria are introduced and molecules are interpreted as communication systems. This concept, developed within the standard SCF MO description, gives rise to the *Orbital Communication Theory* (OCT) of the chemical bond (Nalewajski 2010) an extension of the bond Communication Theory in atomic resolution (Nalewajski 2006). They both use the standard entropic descriptors of information channels in exploring patterns of the chemical bonds in molecules and their constituent parts, as well as the bond covalent/ionic composition.

The molecularly promoted AIM are only slightly modified, compared to their free (separated) analogs, mainly in the outer (valence) shell of electrons. These “external” electrons are responsible for the AIM chemical behavior and the equilibrium bonding pattern they exhibit in the field exerted by the framework of the practically unchanged atomic-cores. This bonding shell of the (delocalized) electrons is also crucial for the propagation of information in the molecule among the system constituent AIM and the *Atomic Orbitals* (AO) the latter contribute to the bonding subspace of the occupied MO, which ultimately determine the system network of chemical bonds. Using the standard tools of IT (summarized in the opening chapter of Part III) in treating these information scattering phenomena due to “communications” via the system chemical bonds provides a novel perspective on the origins and multiplicity of the system chemical bonds, as well as on the entropic nature of their covalent and ionic composition. In particular, the IT multiplicities of the localized chemical bonds are generated, the bond-coupling phenomena in molecular subsystems are discussed and the interference effects due to the multiple information scattering in molecules are examined. The new indirect (*through-bridge*) bonding mechanism is identified, which complements the familiar direct (*through-space*) chemical interactions in molecular systems, and its origins due to the implicit dependencies between AO in the molecular bonding subspace are explored.

The chemical concepts are discussed in a more depth in Part IV. It first provides a survey of alternative perspectives on diverse phenomena conditioning the chemical reactivity, stressing the importance of the conceptual approaches for a more chemical understanding of these bond-forming/bond-breaking processes. The distinction between the “horizontal” (involving displacements of the system electron density) and “vertical” (for the fixed electron distribution) changes in the molecular electronic structure is made and the responses of molecular fragments in the fragment-constrained equilibria are described in terms of the subsystem charge sensitivities. These perturbation–response relations are summarized for all admissible representations of the molecular/subsystem states, covering both the EF perspective of the Born–Oppenheimer approximation and the complementary EP picture, in the spirit of modern DFT. The illustrative case of the bimolecular reactive system is discussed in a more detail and alternative measures of the adiabatic coupling between the electronic and geometrical degrees-of-freedom of

the molecular and reactive systems, including the novel compliant theoretical framework, are identified and modeled.

Finally, several qualitative approaches to reactivity phenomena are summarized. They cover recent IT probes of the elementary reaction mechanisms, chemical reactivity indices provided by the alternative hardness/softness (Fukui function) descriptors of molecules and their fragments, e.g., reactants in the *Donor–Acceptor* (DA) systems, as well as the associated equilibrium and stability criteria of molecules and the maximum hardness and the *Hard/Soft Acids and Bases* (HSAB) principles of chemistry. The importance of the complementary internal and external eigenvalue problem of quantum-mechanical observables for a compact description of the electronic processes in molecules and reactants is stressed and alternative hardness-decoupling schemes are examined.

This joint exposition of a variety of perspectives on the electronic structure of molecular systems, which are usually presented in separate texts, aims at comparing these diverse philosophies of treating the subject in the unifying language of the (nonrelativistic) molecular quantum mechanics and IT. Such presentation should help in uncovering the mutual relations between the specific concepts and techniques of these complementary approaches by extracting their common roots in the molecular quantum mechanics, in the frameworks of both the molecular states involved and the associated probability/density distributions.

The book may serve as both the classroom and reference text of the classical and modern ideas in the field of the chemical bond and reactivity theories. This text has evolved from teaching both the graduate and undergraduate courses in quantum chemistry, density-functional and reactivity theories, as well as the IT of molecular systems. It is intended for graduate and advanced undergraduate students and chemical researchers interested in the new ways of looking at the subject. It is hoped that a significant diversity of the student backgrounds have been accommodated in this textbook/monograph of the contemporary ways of thinking about classical issues in the theory of the electronic structure and reactivity behavior of molecules.

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