Preface

Chemists consider a molecule as consisting of atoms held together by chemical bonds; physicists treat it as a system of individual particles—nuclei and electrons. From that perspective, most of quantum chemistry is basically a special chapter in computational molecular physics, rather than a branch of chemistry in the traditional sense of the word. Both approaches have their well-established fields and merits. If we need accurate numbers of bond lengths, formation energies, energy barriers, spectroscopic data, etc., then we have to calculate the wave functions (as accurately as we can) which means that we have to deal explicitly with the particles constituting the molecular systems. At the same time, all the enormous amount of chemical knowledge is systematized on the basis of the observation that there are similar molecules having similar atoms and bonds, which in many cases behave similarly both in the laboratory and in the living body. While nobody casts doubt that all these properties in the final count are determined by the behavior of the particles forming the molecule, we often cannot see that connection in any explicit manner. For instance, it would hardly be possible to explain what is, say, a secondary alcohol, referring directly to the electrons and nuclei constituting the molecule in question.

One would like to bridge this gap between the physical and chemical descriptions of molecular systems to make them constituents of a common thesaurus of the knowledge, instead of separate entities. Obviously, it would be best if one could *derive* the basic chemical laws and tendencies from the underlying physical theory (the Schrödinger equation). This seems, however, not realizable at this time, and there seems no real hope that this is to be changed soon. In such a situation one has to refer to the *a posteriori* analysis of the wave functions obtained in the actual calculations, and develop theoretical tools that permit connecting the results of calculations with genuine chemical concepts.

I started to work in this direction more than thirty years ago. My attention has been concentrated on the quantum mechanical meaning of the *bond order* (multiplicity of a chemical bond) and actual *valence* of an atom in a molecule, as well as the different atomic and diatomic *energy components* reflecting the energetics of formation of a molecule. Also, I paid great attention to the interesting problems of *effective atomic orbitals* within a molecule, usually forming an *effective minimal basis*, and more recently to the study of *local spins*.

The results that I obtained are scattered in numerous papers published in different journals, which makes it difficult to assess them, especially if their interrelations are concerned. The main aim of this book is, therefore, to put together these pieces in a systematic manner and to *present all the results with complete derivations.* For that reason, most of the results are obtained by using a common theoretical framework, the "atomic resolution of identity." In accord with my inclination, this book is basically about obtaining formulae, not their applications to actual chemical problems. Nonetheless, I hope that it may be useful for every quantum chemist interested in linking chemical concepts to quantum mechanics.

One of the basic difficulties in connecting the physical and chemical description of molecules is due to the lack of a unique definition of an *atom within a molecule.* As is discussed in the book, there are different definitions, none is perfect. Due to my preferences, most discussions are presented in terms of the so-called "Hilbert space analysis," when the atom is defined by its nucleus and basis orbitals. The great advantage of applying the "atomic resolution of identity" formalism is that it permits the formulae to be rewritten in a trivial manner also to the so-called 3D formalism, in which the physical space is partitioned into atomic domains. Accordingly, the 3D formalism receives less attention in the book.

Reading the book does not require any special knowledge, only materials every quantum chemist may be assumed to be familiar with. An exception is some sporadic use of a special second quantization formalism (use of creation and annihilation operators) for non-orthogonal orbitals. It is explained in detail in the appendix (along with the conventional second quantization for an orthonormal basis).

I use this opportunity to express my sincere gratitude to my coworkers—coauthors of several works discussed in the book—in particular to Drs. Pedro Salvador, Andrea Hamza, and Eduard Matito. Last but not least this book could not have been written without the permanent and crucial backing I receive from my wife, Dr. Márta Révész.