Methods of Molecular Quantum Mechanics

An Introduction to Electronic Molecular Structure

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To my Quantum Chemistry students

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Preface

The structure of this little textbook is essentially methodological and introduces in a concise way the student to a working practice in the *ab initio* calculations of electronic molecular structure, giving a sound basis for a critical analysis of the current calculation programmes. It originates from the need to provide quantum chemistry students with their own personal instant book, giving at low cost a readable introduction to the methods of molecular quantum mechanics, a prerequisite for any understanding of quantum chemical calculations. This book is a recommended companion of the previous book by the author, *Elementary Methods of Molecular Quantum Mechanics*, published in 2007 by Elsevier, which contains many worked examples, and designed as a bridge between Coulson's *Valence* and McWeeny's *Methods of Molecular Quantum Mechanics*. The present book is suitable for a first-year postgraduate university course of about 40 hours.

The book consists of 12 chapters. Particular emphasis is devoted to the Rayleigh variational method, the essential tool for any practical application both in molecular orbital and valence bond theory, and to the stationary Rayleigh–Schroedinger perturbation methods, much attention being given to the Hylleraas variational approximations, which are essential for studying second-order electric properties of molecules and molecular interactions, as well as magnetic properties. In the last chapter, elements on molecular symmetry and group theoretical techniques are briefly presented. Major features of the book are: (i) the consistent use from the very beginning of the system of atomic units (au), essential for simplifying all mathematical formulae; (ii) the introductory use of density matrix techniques for interpreting the properties of many-body systems so as to simplify calculations involving many-electron wavefunctions; (iii) an introduction to valence bond methods, with an explanation of the origin