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An Algebraic Approach to the Many-Electron Problem

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Preface

The many-electron problem in quantum mechanics is the basis for our understanding of the atomic and molecular structure, the nature of the chemical bond, the rates and mechanisms of chemical reactions, and so on. The Hartree-Fock (HF) method reduces the many-electron problem to the problem of one electron moving in an effective field of nuclei and other electrons. Although the HF method explains semi-quantitatively the main features of the problem, for instance, it is able to explain Bohr's Aufbau Principle for filling electron shells in the atoms, it does not suffice for a quantitative comparison with experiment. That is, the HF method does not provide a predictive, and whence useful, theory. To obtain such a theory, one has to take into account what is called the dynamical correlation between electrons. This brings us to the realm of so-called post-HF approaches. Among those, the coupled-cluster (cc) method plays a prominent role due to its correct scaling behavior with increasing the number of electrons, the so-called size-extensivity.

This book grew out of the author's dissatisfaction with the usual presentation of cc method. There are two common ways to present it. The first route, see for instance [1] [1], is to stay within the framework of ordinary quantum mechanics. This means to use Slater determinants to fulfill the requirement of the antisymmetry of the many-electron wave function. Proceeding in this way, one encounters very early rather formidable combinatorics [2]. So at some point, the authors stop and only indicate a general strategy how to proceed. The second route is to use field methods. The authors derive the rules for construction of Feynman-like diagrams and their evaluation. This was the original presentation of the cc method by its inventor Jiří Čížek [3]. This route is followed for instance in [4, 5, 6, 7]. We do not find this diagrammatic approach illuminating either, but this is clearly a matter of taste. In this book, we follow the third route, pioneered by Josef Paldus [8]. We use field methods, but we proceed in an algebraic, not diagrammatic, manner. In our view, and also in our teaching experience, this is the most simple and understandable way

[1] We strongly recommend this excellent textbook to reader's attention.

to derive and use the cc method. Once one absorbs the formalism of a quantized electron field, everything else is straightforward.

As it is customary in most ab initio calculations and as was alluded to above, we start from the independent particle model, the HF method. We assume throughout the most of the book that the HF solution exists and is unique. This covers nearly all neutral closed-shell molecules not very far from equilibrium geometry. Thus we restrict ourselves to what is considered as standard and firmly established. The situations where this is not the case are certainly interesting from both the methodological and practical point of view, but they are outside the scope of this introductory treatment. For a not so too out-of-date state of the affairs and a guide to literature we refer reader to [4]. For a fascinating account of the history of the cc method, see Josef Paldus's essay [9].

This book is organized as follows. In Chap. 1 we introduce the notion of the quantized electron field and show how the N-electron Hamiltonian can be expressed in its language. In the following Chap. 2 we introduce the notion of the Fermi vacuum and derive the Hartree-Fock equations and conditions for the stability of their solutions. These two chapters are preparatory for Chap. 3. There, we first discuss the so-called method of configuration interaction, which is commonly used for accounting for dynamical correlation between electrons. We point out the size-extensivity problem and show how this problem is solved within the cc approach. We then proceed to derive the cc equations in spin-orbital form. Chapter 4 mostly deals with practical aspects of the cc method. We show how one can take advantage of the permutational and spin symmetries, and how to practically solve cc equations. We illustrate this whole approach on the Hubbard model of benzene, the simplest quasi-realistic model of electron correlation. Finally, we briefly discuss the use of the cc method for one-electron open-shell systems.

Prerequisites

Knowledge of quantum mechanics on the level of standard courses, see, e.g., [10, 11, 12, 13], is assumed.

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