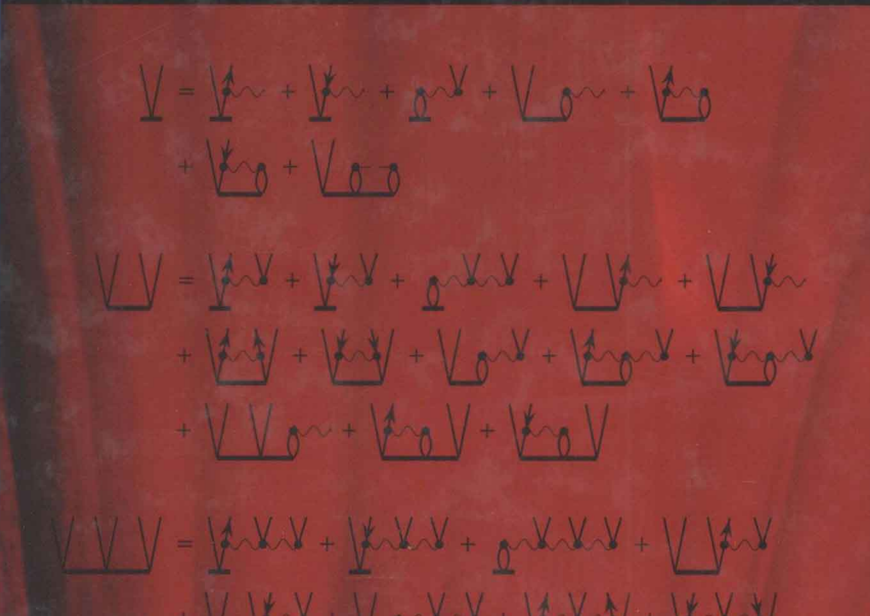
Many-Body Methods in Chemistry and Physics

MBPT and Coupled-Cluster Theory

Isaiah Shavitt and Rodney J. Bartlett



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MBPT and Coupled-Cluster Theory

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MANY-BODY METHODS IN CHEMISTRY AND PHYSICS

Written by two leading experts in the field, this book explores the many-body methods that have become the dominant approach in determining molecular structure, properties, and interactions. With a tight focus on the highly popular many-body perturbation theory (MBPT) and coupled-cluster (CC) methods, the authors present a simple, clear, unified approach to describe the mathematical tools and diagrammatic techniques employed. Using this book the reader will be able to understand, derive, and confidently implement the relevant algebraic equations for current and even new CC methods. Hundreds of diagrams throughout the book enhance reader understanding through visualization of computational procedures, and the extensive referencing and detailed index allow further exploration of this evolving area. This book provides a comprehensive treatment of the subject for graduates and researchers within quantum chemistry, chemical physics and nuclear, atomic, molecular, and solid-state physics.

ISAIAH SHAVITT, Emeritus Professor of Ohio State University and Adjunct Professor of Chemistry at the University of Illinois at Urbana-Champaign, developed efficient methods for multireference configuration-interaction calculations, including the graphical unitary-group approach (GUGA), and perturbation-theory extensions of such treatments. He is a member of the International Academy of Quantum Molecular Science and a Fellow of the American Physical Society, and was awarded the Morley Medal of the American Chemical Society (2000).

RODNEY J. BARTLETT, Graduate Research Professor at the Quantum Theory Project, University of Florida, pioneered the development of CC theory in quantum chemistry to offer highly accurate solutions of the Schrödinger equation for molecular structure and spectra. He is a member of the International Academy of Quantum Molecular Sciences and a Fellow of the American Physical Society (1986). He was awarded a Guggenheim Fellowship (1986), the ACS Award in Theoretical Chemistry (2007) and the Schrödinger Medal of WATOC (2008).

Cambridge Molecular Science

As we enter the twenty-first century, chemistry has positioned itself as the central science. Its subject matter, atoms and the bonds between them, is now central to so many of the life sciences on the one hand, as biological chemistry brings the subject to the atomic level, and to condensed matter and molecular physics on the other. Developments in quantum chemistry and in statistical mechanics have also created a fruitful overlap with mathematics and theoretical physics. Consequently, boundaries between chemistry and other traditional sciences are fading and the term *molecular science* now describes this vibrant area of research.

Molecular science has made giant strides in recent years. Bolstered both by instrumental and theoretical developments, it covers the temporal scale down to femtoseconds, a time scale sufficient to define atomic dynamics with precision, and the spatial scale down to a small fraction of an Ångstrom. This has led to a very sophisticated level of understanding of the properties of small-molecule systems, but there has also been a remarkable series of developments in more complex systems. These include: protein engineering; surfaces and interfaces; polymers colloids; and biophysical chemistry. This series provides a vehicle for the publication of advanced textbooks and monographs introducing and reviewing these exciting developments.

To Vera and Beverly

Preface

"What are the electrons really doing in molecules?" This famous question was posed by R. A. Mulliken over a half-century ago. Accurate quantitative answers to this question would allow us, in principle, to know all there is to know about the properties and interactions of molecules. Achieving this goal, however, requires a very accurate solution of the quantum-mechanical equations, primarily the Schrödinger equation, a task that was not possible for most of the past half-century. This situation has now changed, primarily due to the development of numerically accurate many-body methods and the emergence of powerful supercomputers.

Today it is well known that the many-body instantaneous interactions of the electrons in molecules tend to keep electrons apart; this is manifested as a correlation of their motions. Hence a correct description of *electron correlation* has been the focal point of atomic, molecular and solid state theory for over 50 years. In the last two decades the most prominent methods for providing accurate quantum chemical wave functions and using them to describe molecular structure and spectra are *many-body perturbation theory (MBPT)* and its *coupled-cluster (CC)* generalizations. These approaches have become the methods of choice in quantum chemistry, owing to their accuracy and their correct scaling with the number of electrons, a property known as *extensivity* (or *size-extensivity*). This property distinguishes *many-body* methods from the configuration-interaction (CI) tools that have commonly been used for many years. However, maintaining extensivity – a critical rationale for all such methods – requires many-body methods that employ quite different mathematical tools for their development than those that have been customary in quantum chemistry. In particular, diagrammatic techniques are found to be extremely powerful, offering a unified, transparent and precise approach to the derivation and implementation of the relevant algebraic equations. For many readers, however, diagrammatic methods have seemed to be used arbitrarily, making it difficult to understand with confidence the detailed one-to-one correspondence between the diagrams and the various terms of the operable algebraic equations.

In order to address this situation, this book presents a unified, detailed account of the highly popular MBPT and CC quantum mechanical methods. It introduces direct, completely unambiguous procedures to derive all the relevant algebraic equations diagrammatically, in one simple, easily applied and unified approach. The ambiguity associated with some diagrammatic approaches is completely eliminated. Furthermore, in order for a quantum-chemical approach to be able to describe molecular structure, excited states and properties derived from expectation values and from response methods, new theory has had to be developed. This book also addresses the theory for each of these topics, including the *equation-of-motion CC (EOM-CC)* method for excited, ionized and electron attached states as well as the *analytical gradient* theory for determining structure, vibrational spectra and density matrices. Finally, the recent developments in multireference approaches, *quasidegenerate perturbation theory (QDPT)* and *multireference CC (MRCC)*, are also presented. All these equations are readily developed from the same simple diagrammatic arguments used throughout the book. With a modest investment of time and effort, this book will teach anyone to understand and confidently derive the relevant algebraic equations for current CC methods and even the new CC methods that are being introduced regularly. Selected numerical illustrations are also presented to assess the performance of the various approximations to MBPT and CC.

This book is directed at graduate students in quantum chemistry, chemical physics, physical chemistry and atomic, molecular, solid-state and nuclear physics. It can serve as a textbook for a two-semester course on many-body methods for electronic structure and as a useful resource for university faculty and professional scientists. For this purpose, an extensive bibliography and a detailed index are included. Useful introductory material for the book, including detailed treatments of self-consistent field theory and configuration interaction, can be found in parts of the book by Szabo and Ostlund (1982). Additional useful sources include, among others, the monograph by Lindgren and Morrison (1986), which emphasizes atomic structure and includes the treatment of angular momentum and spin coupling, and the book focusing on diagrammatic many-body methods by Harris, Monkhorst and Freeman (1992). An interesting historical account of the development of coupled-cluster theory was provided by Paldus (2005), whose unpublished (but widely distributed) Nijmegen lectures introduced many researchers to this methodology.

Many colleagues, students and others have helped us in various ways during the writing of this book. In particular we would like to thank the following: Erik Deumens, Jürgen Gauss, Tom Hughes, Joshua McClellan, Monika Musiał, Marcel Nooijen, Josef Paldus, Steven Parker, Ajith Perera, John Stanton, Peter Szalay, Andrew Taube and John Watts.

The graphics in this book were generated in LaTeX, using the package *pstricks 97*. We are grateful to its author, Timothy van Zandt, and editors, Denis Girou and Sebastian Rahtz, for providing such a versatile graphics facility.

Contents

1
Introduction

1.1 Scope

The book focuses primarily on many-body (or better, many-electron) methods for electron correlation. These include *Rayleigh–Schrödinger perturbation theory (RSPT)*, particularly in its diagrammatic representation (referred to as *many-body perturbation theory*, or *MBPT*), and *coupled-cluster (CC)* theory; their relationship to *configuration interaction (CI)* is included. Further extensions address properties other than the energy, and also excited states and multireference CC and MBPT methods.

The many-body algebraic and diagrammatic methods used in electronic structure theory have their origin in quantum field theory and in the study of nuclear matter and nuclear structure. The second-quantization formalism was first introduced in a treatment of quantized fields by Dirac (1927) and was extended to fermion systems by Jordan and Klein (1927) and by Jordan and Wigner (1928). This formalism is particularly useful in field theory, in scattering problems and in the study of infinite systems because it easily handles problems involving infinite, indefinite or variable numbers of particles. The diagrammatic approach was introduced into field theory by Feynman (1949a,b) and applied to many-body systems by Hugenholtz (1957) and by Goldstone (1957). Many-body perturbation theory and its linked-diagram formalism were first introduced by Brueckner and Levinson (1955) and by Brueckner (1955), and were formalized by Goldstone (1957). Other important contributions to the methodology, first in field theory and then in the theory of nuclear structure, are due to Dyson (1949a,b), Wick (1950), Hubbard (1957, 1958a,b) and Frantz and Mills (1960). Applications to the electronic structure of atoms and molecules began with the work of Kelly (1963, 1964a,b, 1968), and molecular applications using finite analytical basis sets appeared in the work of Bartlett and Silver (1974a,b).

More complete accounts of the history of these methods have been given by Lindgren and Morrison (1986) and by Lindgren (1998).

The coupled-cluster method also has origins in nuclear structure theory, with the seminal papers of Coester (1958) and Coester and Kümmel (1960). It was introduced to electronic structure theory and formalized by Čížek (1966, 1969) and Čížek and Paldus (1971). A historical account of its origins and development was given by Paldus (2005).

Additional references to the development and extensions of the many-body methods are given in the relevant chapters.

The rest of this chapter provides some background material, including a brief discussion of the independent-particle model and the configuration-interaction method. We discuss the limitations of these methods and the need for the perturbation-theoretical and many-body methods that form the subject of the rest of this book. We also provide a preliminary introduction to the cluster ideas that form the basis of coupled-cluster theory. Readers in need of a more extensive introduction are referred to the excellent book by Szabo and Ostlund (1982).

A detailed exposition of formal perturbation theory is given in Chapter 2. A number of different derivations and approaches are included in this exposition in order to provide a broad foundation for the terminology and techniques employed in this field. The many-body technique of second quantization is introduced in Chapter 3, and the diagrammatic representation is described in Chapter 4. The application of the many-body and diagrammatic techniques to perturbation theory is described in Chapter 5, and this is followed by proof of the crucial linked-diagram theorem in Chapter 6 and a discussion of some practical aspects of many-body perturbation-theory calculations in Chapter 7. Open-shell and quasidegenerate perturbation theory is presented in Chapter 8. Coupled-cluster theory is discussed in Chapters 9 and 10, again including several forms of the derivations in order to provide better understanding. The calculation of properties in the coupled-cluster method is described in Chapter 11. Several additional aspects of coupled-cluster theory are discussed in Chapter 12, and the equation-of-motion (EOM) coupled-cluster method for excited-state calculations is described in Chapter 13. Finally, multireference coupled-cluster methods are presented in Chapter 14.

1.2 Conventions and notation

Throughout this book we use atomic units, setting $m = e = \hbar = 1$ where m and $-e$ are the mass and charge of the electron and $\hbar = h/2\pi$ is Planck's

Table 1.1. *Terminology for excitation levels*

Level	Symbol	Name	Alternative
1	S	singles	mono-excited
2	D	doubles	bi-excited
3	T	triples	tri-excited
4	Q	quadruples	tetra-excited
5	P	pentuples	penta-excited
6	H	hextuples	hexa-excited

constant. As is customary in quantum chemistry, these constants are omitted from the expressions in this book but their implied presence is needed for proper dimensionality.

With a few exceptions, lower-case letters ($a, b, \ldots, \phi, \psi, \ldots$, etc.) are used for one- and two-particle entities, and upper-case letters ($A, B, \ldots, \Phi, \Psi, \ldots$, etc.) are used for many-particle entities. Operators are designated by a caret over a roman letter ($\hat{a}, \hat{\imath}, \hat{F}, \hat{H}$, etc.), by a script upper-case letter ($\mathcal{H}, \mathcal{P}$, etc.) or by an Greek upper-case letter (Λ, Ω, etc.). Vectors and matrices are represented by boldface lower- and upper-case letters, respectively.

The acronyms used to specify excitation-level combinations included in the different computational models have evolved, first in configuration interaction (CI) and then in coupled-cluster (CC) theory, using a mixture of English, Greek and Latin roots, in view of the need to provide a unique initial letter for each level, as listed in Table 1.1. For example, a CI calculation that includes all single, double and triple excitations is described as CISDT. The fourth column in Table 1.1 lists some alternative excitation-level names that have been used.

1.3 The independent-particle approximation

In this section we briefly summarize several aspects of the procedures used to obtain starting approximations for correlated molecular electronic structure calculations. For more complete discussions and detailed derivations the reader is referred to other sources, such as Szabo and Ostlund (1982) or standard textbooks.

Most electronic structure calculations begin with a relatively simple approximation based on the independent-particle model. The wave function for such a model is a single Slater determinant (SD),

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix} = \mathcal{A}\psi_1\psi_2\ldots\psi_N, \quad (1.1)$$

where $\psi_i(\mu)$ is a spinorbital, a function of the space and spin coordinates of the μth electron (typically a product of a spatial orbital and a spin function), and $\mathcal{A}$ is the antisymmetrizer. The most commonly used independent-particle model is the *Hartree–Fock (HF)* or *self-consistent field (SCF)* wave function,† in which the spinorbitals are varied to minimize the energy expectation value of the single-determinant wave function. The minimization can be achieved by solving a set of coupled one-electron eigenvalue equations for the spinorbitals,

$$\hat{f}\psi_i = \varepsilon_i\psi_i\,, \quad (1.2)$$

in which the Fock operator $\hat{f}$ depends on all the spinorbitals (this dependence is given explicitly later in this section). Iterative procedures are required to obtain consistency between the spinorbitals used to define $\hat{f}$ and the spinorbitals obtained as its eigenfunctions.

Because a determinant is invariant to unitary transformations of its columns or rows, the SD wave function (1.1) is invariant under unitary transformations of the occupied spinorbitals $\{\psi_i, i = 1, 2, \ldots, N\}$ among themselves. Therefore, any unitary transformation of the occupied spinorbitals provides an alternative representation of the *same SD wave function*. The particular representation of the wave function in which the spinorbitals are solutions of (1.2), i.e., are eigenfunctions of $\hat{f}$ (so that the matrix representation of $\hat{f}$ in terms of these spinorbitals is diagonal, $\langle\psi_i|\hat{f}|\psi_j\rangle = \varepsilon_i\delta_{ij}$), is called the *canonical HF wave function*; the corresponding spinorbitals (including

† It was common to distinguish between the original type of *Hartree–Fock* solution, which achieves the absolute minimum of the energy of an SD wave function (1.1) with respect to any variation of the spinorbitals (subject only to appropriate restrictions in the restricted HF case) and usually require numerical (finite difference) methods of solution as employed by Hartree and others for atomic wave functions, and the *self-consistent field* form (also known as *Hartree–Fock–Roothaan* or *matrix Hartree–Fock*), in which the spinorbitals are expanded in a basis set and the lowest energy solution within the space generated by that basis set is sought. This second approach converts the operator eigenvalue equation (1.2) to a matrix eigenvalue equation for the eigenvectors of expansion coefficients. The HF solution is thus the limiting result (the *HF limit*) of the self-consistent field procedure as the basis set approaches completeness. In current usage, however, the distinction has unfortunately been lost, and the terms Hartree–Fock and self-consistent field are used interchangeably, both commonly referring to the basis-set expansion approach. We shall follow this practice in this book.