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.

MANY-BODY METHODS IN CHEMISTRY AND PHYSICS

MBPT and Coupled-Cluster Theory

ISAIAH SHAVITT

Professor Emeritus
The Ohio State University
and
Adjunct Professor of Chemistry
University of Illinois at Urbana-Champaign

and

RODNEY J. BARTLETT

Graduate Research Professor of Chemistry and Physics
University of Florida

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To Vera and Beverly

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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.