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.

Series editors

Professor Richard Saykally
University of California, Berkeley

Professor Ahmed Zewail
California Institute of Technology

Professor David King
University of Cambridge
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
To Vera and Beverly
# Contents

<table>
<thead>
<tr>
<th>Preface</th>
<th>page</th>
<th>xi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Scope</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Conventions and notation</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>The independent-particle approximation</td>
<td>3</td>
</tr>
<tr>
<td>1.4</td>
<td>Electron correlation</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>Configuration interaction</td>
<td>9</td>
</tr>
<tr>
<td>1.6</td>
<td>Motivation</td>
<td>10</td>
</tr>
<tr>
<td>1.7</td>
<td>Extensivity</td>
<td>11</td>
</tr>
<tr>
<td>1.8</td>
<td>Disconnected clusters and extensivity</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>Formal perturbation theory</td>
<td>18</td>
</tr>
<tr>
<td>2.1</td>
<td>Background</td>
<td>18</td>
</tr>
<tr>
<td>2.2</td>
<td>Classical derivation of Rayleigh–Schrödinger perturbation theory</td>
<td>18</td>
</tr>
<tr>
<td>2.3</td>
<td>Projection operators</td>
<td>27</td>
</tr>
<tr>
<td>2.4</td>
<td>General derivation of formal time-independent perturbation theories</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>Similarity transformation derivation of the formal perturbation equations and quasidegenerate PT</td>
<td>46</td>
</tr>
<tr>
<td>2.6</td>
<td>Other approaches</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>Second quantization</td>
<td>54</td>
</tr>
<tr>
<td>3.1</td>
<td>Background</td>
<td>54</td>
</tr>
<tr>
<td>3.2</td>
<td>Creation and annihilation operators</td>
<td>55</td>
</tr>
<tr>
<td>3.3</td>
<td>Normal products and Wick’s theorem</td>
<td>67</td>
</tr>
<tr>
<td>3.4</td>
<td>Particle–hole formulation</td>
<td>71</td>
</tr>
<tr>
<td>3.5</td>
<td>Partitioning of the Hamiltonian</td>
<td>75</td>
</tr>
</tbody>
</table>
3.6 Normal-product form of the quantum-mechanical operators 80
3.7 Generalized time-independent Wick's theorem 85
3.8 Evaluation of matrix elements 86

4 Diagrammatic notation 90
4.1 Time ordering 90
4.2 Slater determinants 91
4.3 One-particle operators 92
4.4 Two-particle operators 111

5 Diagrammatic expansions for perturbation theory 130
5.1 Resolvent operator and denominators 130
5.2 First-order energy 131
5.3 Second-order energy 131
5.4 Third-order energy 132
5.5 Conjugate diagrams 134
5.6 Wave-function diagrams 135
5.7 Fourth-order energy 138
5.8 Linked-diagram theorem 152
5.9 Numerical example 153
5.10 Unlinked diagrams and extensivity 156

6 Proof of the linked-diagram theorem 165
6.1 The factorization theorem 165
6.2 The linked-diagram theorem 172

7 Computational aspects of MBPT 177
7.1 Techniques of diagram summation 177
7.2 Factorization of fourth-order quadruple-excitation diagrams 180
7.3 Spin summations 182

8 Open-shell and quasidegenerate perturbation theory 185
8.1 Formal quasidegenerate perturbation theory (QDPT) 185
8.2 The Fermi vacuum and the model states 192
8.3 Normal-product form of the generalized Bloch equations 194
8.4 Diagrammatic notation for QDPT 195
8.5 Schematic representation of the generalized Bloch equation 198
8.6 Level-shift and wave-operator diagrams 203
8.7 Incomplete model space 227

9 Foundations of coupled-cluster theory 251
9.1 Coupled-cluster theory for noninteracting He atoms 251
9.2 The coupled-cluster wave function 254
9.3 The coupled-cluster doubles (CCD) equations 258
9.4 Exponential Ansatz and the linked-diagram theorem of MBPT 272
9.5 Diagrammatic derivation of the CCD equations 279

10 Systematic derivation of the coupled-cluster equations 292
10.1 The connected form of the CC equations 292
10.2 The general form of CC diagrams 295
10.3 Systematic generation of CC diagrams 297
10.4 The coupled-cluster singles and doubles (CCSD) equations 299
10.5 Coupled-cluster singles, doubles and triples (CCSDT) equations 308
10.6 Coupled-cluster singles, doubles, triples and quadruples (CCSDTQ) equations 321
10.7 Coupled-cluster effective-Hamiltonian diagrams 328
10.8 Results of various CC methods compared with full CI 340

11 Calculation of properties in coupled-cluster theory 347
11.1 Expectation value for a CC wave function 347
11.2 Reduced density matrices 352
11.3 The response treatment of properties 361
11.4 The CC energy functional 366
11.5 The Λ equations 367
11.6 Effective-Hamiltonian form of the Λ equations 376
11.7 Response treatment of the density matrices 381
11.8 The perturbed reference function 385
11.9 The CC correlation-energy derivative 396

12 Additional aspects of coupled-cluster theory 406
12.1 Spin summations and computational considerations 406
12.2 Coupled-cluster theory with an arbitrary single-determinant reference function 411
12.3 Generalized many-body perturbation theory 415
12.4 Brueckner orbitals and alternative treatments of $\hat{T}_1$ 418
12.5 Monitoring multiplicities in open-shell coupled-cluster calculations 422
12.6 The A and B response matrices from the viewpoint of CCS 425
12.7 Noniterative approximations based on the CC energy functional 427
12.8 The nature of the solutions of CC equations 429

13 The equation-of-motion coupled-cluster method for excited, ionized and electron-attached states 431
13.1 Introduction 431
13.2 The EOM-CC Ansatz 432
13.3 Diagrammatic treatment of the EE-EOM-CC equations 437
13.4 EOM-CC treatment of ionization and electron attachment 445
13.5 EOM-CC treatment of higher-order properties 449
13.6 EOM-CC treatment of frequency-dependent properties 454

14 Multireference coupled-cluster methods 462
14.1 Introduction 462
14.2 Hilbert-space state-universal MRCC 465
14.3 Hilbert-space state-specific MRCC 471
14.4 Fock-space valence-universal MRCC 475
14.5 Intermediate-Hamiltonian Fock-space MRCC 490

References 496
Author index 521
Subject index 524
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
Preface

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.
Preface

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 Musial, 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 \texttt{pstricks} \texttt{97}. We are grateful to its author, Timothy van Zandt, and editors, Denis Girou and Sebastian Rahtz, for providing such a versatile graphics facility.