

MANY-BODY METHODS FOR ATOMS AND MOLECULES

Rajat Kumar Chaudhuri
Sudip Kumar Chattopadhyay



CRC Press
Taylor & Francis Group

A CHAPMAN & HALL BOOK

**MANY-BODY
METHODS FOR
ATOMS AND
MOLECULES**



Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

MANY-BODY METHODS FOR ATOMS AND MOLECULES

Rajat Kumar Chaudhuri

Indian Institute of Astrophysics
Bangalore, India

Sudip Kumar Chattopadhyay

Bengal Engineering and Science University
West Bengal, India



CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

A CHAPMAN & HALL BOOK

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2017 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper
Version Date: 20160517

International Standard Book Number-13: 978-1-4822-1190-0 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

Contents

| | |
|---|-----------|
| List of Figures | xii |
| List of Tables | xiii |
| Preface | xv |
| 1 Introduction | 1 |
| 1.1 Background | 1 |
| 1.2 Born–Oppenheimer approximation | 3 |
| 1.3 Approximate methods | 6 |
| 1.3.1 Variational method: Linear variation principle | 6 |
| 1.4 Independent particle model | 8 |
| 1.4.1 Hartree product | 8 |
| 1.4.2 Slater determinant | 9 |
| 1.4.3 Slater’s rule | 10 |
| 1.4.4 Hartree–Fock method | 11 |
| 1.4.5 Hartree–Fock–Roothan method | 13 |
| 1.4.6 Brillouin’s theorem | 14 |
| 1.4.7 Koopmans’ theorem | 14 |
| 1.5 Configuration interaction | 15 |
| 1.6 Electron correlation | 19 |
| 1.7 Size extensivity and consistency | 20 |
| 2 Occupation Number Representation | 23 |
| 2.1 Background | 23 |
| 2.2 Creation and annihilation operators | 24 |
| 2.3 Occupation number representation of operators | 28 |
| 2.4 Evaluation of matrix elements | 29 |
| 2.4.1 Number operators | 29 |
| 2.4.2 Overlap matrix elements | 29 |
| 2.4.3 Matrix elements between vacuum states | 30 |
| 2.5 Normal order product of ordinary operators | 31 |
| 2.5.1 Wick’s theorem for ordinary operators | 32 |
| 2.6 Hole-particle formalism and Fermi vacuum | 34 |
| 2.7 Evaluation of Hamiltonian elements between reference states | 36 |
| 2.8 Normal order product for a Fermi vacuum | 37 |

| | | |
|----------|---|------------|
| 2.9 | Normal product form of quantum mechanical operators | 40 |
| 2.9.1 | Evaluation of matrix elements between states | 43 |
| 2.9.2 | Vacuum expectation value of composite operators | 44 |
| 2.10 | Graphical representation of normal product operators | 44 |
| 3 | Perturbation Theory | 49 |
| 3.1 | Background | 49 |
| 3.2 | Rayleigh–Schrödinger perturbation theory: Traditional approach | 50 |
| 3.2.1 | Systematic derivation of order by order perturbation expansion | 50 |
| 3.2.2 | Wigner’s $(2n + 1)$ rule | 53 |
| 3.2.3 | Hylleraas variation principle | 54 |
| 3.3 | Projection operator based formulation of perturbation theory | 56 |
| 3.4 | Brillouin–Wigner perturbation theory | 58 |
| 3.5 | Rayleigh–Schrödinger perturbation theory | 59 |
| 3.6 | Wave operator based formulation of Rayleigh–Schrödinger perturbation theory | 61 |
| 3.7 | Choice of zero-order Hamiltonian \mathcal{H}_0 | 64 |
| 3.8 | Intruder state problems in Rayleigh–Schrödinger perturbation theory | 65 |
| 3.9 | Comparison of Brillouin–Wigner and Rayleigh–Schrödinger perturbation theories | 69 |
| 4 | Multireference Perturbation Theory | 73 |
| 4.1 | Introduction | 73 |
| 4.2 | Choice of Fermi vacuum and the hole-particle states | 75 |
| 4.3 | Multiconfiguration self-consistent field method | 78 |
| 4.4 | Improved virtual orbital complete active space configuration method | 81 |
| 4.4.1 | Closed-shell ground state | 81 |
| 4.4.2 | Restricted open-shell doublet state | 82 |
| 4.5 | Classification of perturbative methods | 83 |
| 4.6 | Formal multireference perturbation theory for complete model space | 84 |
| 4.6.1 | Order by order expansion of the wave operator | 87 |
| 4.6.2 | Linked cluster theorem | 91 |
| 4.7 | Multireference perturbation theory for incomplete model space | 92 |
| 4.8 | Intermediate Hamiltonian methods | 97 |
| 4.8.1 | Generalized degenerate perturbation theory | 99 |
| 4.9 | Effective valence shell Hamiltonian method | 100 |
| 5 | State-Specific Perturbation Theory | 107 |
| 5.1 | Background | 107 |

| | | |
|----------|---|------------|
| 5.2 | Multireference Möller–Plesset second-order perturbation theory | 109 |
| 5.3 | Multiconfiguration quasi-degenerate perturbation theory | 113 |
| 5.4 | Complete active space second-order perturbation theory | 114 |
| 5.4.1 | General formulation | 114 |
| 5.4.2 | Connection with effective Hamiltonian based method | 117 |
| 5.5 | Multistate complete active space second-order perturbation theory | 118 |
| 6 | Coupled Cluster Method | 121 |
| 6.1 | Introduction | 121 |
| 6.2 | Single-reference coupled cluster method | 122 |
| 6.3 | Separability | 124 |
| 6.4 | Relation with full configuration interaction method | 125 |
| 6.5 | Coupled cluster equation for doubles and singles-doubles approximations | 127 |
| 6.5.1 | Coupled cluster doubles method | 127 |
| 6.5.2 | Coupled cluster singles-doubles method | 131 |
| 6.6 | Evaluation of the matrix elements for coupled cluster doubles equations | 133 |
| 6.6.1 | Evaluation of correlation energy matrix elements | 139 |
| 6.7 | Diagrammatic representation of coupled cluster doubles matrix elements | 140 |
| 6.7.1 | Generation of coupled cluster diagrams | 140 |
| 6.7.2 | Diagram rules and evaluation of matrix elements | 145 |
| 6.8 | Emergence of many-body perturbation theory from CC method | 147 |
| 6.9 | Other variants of CC theory | 149 |
| 7 | Fock Space Multireference Coupled Cluster Method | 151 |
| 7.1 | Background | 151 |
| 7.2 | Choice of wave operator for multireference systems | 153 |
| 7.3 | Connectivity of the effective Hamiltonian | 155 |
| 7.4 | Fock space coupled cluster theory for energy difference | 156 |
| 7.4.1 | Hierarchical generation of coupled cluster equations | 160 |
| 7.4.2 | Quadratic nature of Fock space coupled cluster equations | 162 |
| 7.5 | Systematic generation of cluster equations for various valence sectors | 163 |
| 7.5.1 | Coupled cluster equations for the (1,0) valence sector | 163 |
| 7.5.2 | Coupled cluster equations for the (0,1) valence sector | 165 |
| 7.5.3 | Coupled cluster equations for the (1,1) valence sector | 167 |
| 7.6 | Equation of motion coupled cluster method | 172 |
| 7.7 | Relationship between FSMRCC and EOMCC | 175 |
| 7.8 | Numerical examples | 178 |

| | | |
|----------|---|------------|
| 7.8.1 | Ionization potential of Be I and Na I isoelectronic sequence | 178 |
| 7.8.2 | Ionization potential of Yb I | 179 |
| 7.9 | Intermediate Hamiltonian based multireference coupled cluster theory | 180 |
| 7.9.1 | Similarity transformation based formulation | 182 |
| 7.9.2 | Eigenvalue independent partitioning based coupled cluster formulation | 184 |
| 8 | Hilbert Space Coupled Cluster Theory | 187 |
| 8.1 | Introduction | 187 |
| 8.2 | State universal multireference coupled cluster theory | 188 |
| 8.2.1 | State universal multireference perturbation theory | 190 |
| 8.3 | Development of state-specific theories | 192 |
| 8.3.1 | State-specific Brillouin–Wigner multireference coupled cluster theory | 193 |
| 8.3.2 | State specific MkMRCC theory | 195 |
| 8.3.3 | State-specific multireference perturbation theory | 197 |
| | Index | 217 |

List of Figures

| | | |
|-----|---|----|
| 2.1 | Non-interacting Fermi system where the dashed line represents the Fermi level. The single particle energies are denoted by k_i . | 34 |
| 2.2 | Graphical representation of hole-particle creation-annihilation operators. The Fermi vacuum is represented by the horizontal dashed line. | 45 |
| 2.3 | Graphical representation of one-particle and two-particle operators in normal product form. The interaction vertex is represented by the dashed line with a cross. | 46 |
| 2.4 | Graphical representation of a two-particle operator in normal product form. The dashed line represents the interaction vertex. | 46 |
| 2.5 | Graphical representation of two-particle operators and their contractions. | 47 |
| 3.1 | Plot of five lowest 1S state full configuration interaction (FCI) energies of a Be atom as a function of perturbation parameter z for MP-type partitioning. States corresponding to the model (virtual) space at $z = 0$ are represented by the solid (dashed) lines. | 67 |
| 3.2 | The squared amplitudes of the configuration state functions $ 1s^22p^2\rangle (^1S)$ and $ 1s^22s3s\rangle (^1S)$ of a Be atom as a function of perturbation parameter z for MP-type partitioning. | 68 |
| 4.1 | (a) The bonding ($1\sigma_g$) and anti-bonding ($1\sigma_u$) orbitals of an H_2 molecule from the linear combination of atomic orbitals (LCAO) to molecular orbitals (MO) theory. (b) The energy of the H_2 molecule with electrons in the bonding and anti-bonding orbitals. | 74 |
| 4.2 | Classification of orbitals into hole (occupied), particle (unoccupied), core, valence, and excited (virtual) categories. | 77 |
| 4.3 | Diagrammatic representation of core, valence, and virtual orbitals. | 77 |
| 4.4 | Diagrammatic representation of a wave operator for the multi-dimensional model space. | 79 |
| 4.5 | Illustration of the rules for operating on a wave operator Ω diagram by the V interaction. | 87 |
| 4.6 | Examples of <i>closed</i> , <i>open</i> , <i>linked</i> , and <i>unlinked</i> diagrams | 88 |

| | | |
|------|--|-----|
| 4.7 | Formation of unlinked and folded diagram(s) from V- Ω contraction. | 91 |
| 4.8 | Typical products of disconnected quasi-open (q-op) diagrams generating closed operators for hole-particle incomplete model space. The squares around a vertex denote the denominators encompassing the open lines. | 95 |
| 4.9 | Diagrammatic representation of zero- and one-body diagrams (without exchange) in the \mathcal{H}^ν Hamiltonian. | 101 |
| 4.10 | Diagrammatic representation of two- and three-body diagrams in the \mathcal{H}^ν Hamiltonian. | 101 |
| 4.11 | Core, valence, and excited orbitals energies resulting from (a) V^N potential (Hartree-Fock potential), (b) V^{N-1} multi-Fock operator, and (c) democratic averaging of the valence orbital energies. | 105 |
| 6.1 | Graphical representation of one-, two-, and three-body cluster operators. | 125 |
| 6.2 | Diagrammatic representation of (top) the <i>ket</i> state $\langle \Phi_{\alpha\beta}^{pq} = \langle \Phi_0 \{a_\alpha^\dagger a_\beta^\dagger a_q a_p\}$, (middle) the cluster operator $t_{\gamma\delta}^{rs} \{a_r^\dagger a_s^\dagger a_\delta a_\gamma\}$, and (bottom) the one-electron operators $\langle i f j \rangle \{a_i^\dagger a_j\}$. The excitation levels of the operators are shown in parentheses. | 141 |
| 6.3 | Diagrammatic representation of the two-electron operators $\langle ij kl \rangle \{a_i^\dagger a_j^\dagger a_l a_k\}$. The excitation levels of these terms are shown in parentheses. | 141 |
| 6.4 | Graphical representation of the matrix elements $\langle \Phi_{\alpha\beta}^{pq} V_N \Phi_0 \rangle$ contributing to the coupled cluster doubles equation. | 142 |
| 6.5 | Diagrams resulting from $\{F_N T_2\}_c$ contraction. Diagrams for $j = s$ and $i = \delta$ are not shown here for convenience. | 143 |
| 6.6 | Diagrams resulting from $\{V_N T_2\}_c$ contraction. Diagrams for $j = s$ and $i = \delta$ are not shown here for convenience. | 143 |
| 6.7 | Graphical representation of $\{V_N T_2^2\}_c$ contraction. | 144 |
| 6.8 | Contribution of non-linear terms other than that shown in Figure 6.7 to coupled cluster double equations. Additional diagrams arising from the permutation of in-equivalent hole and particle lines are not shown here. | 144 |
| 6.9 | Correlation diagram for coupled cluster doubles. | 145 |
| 7.1 | (a) Schematic classification of particle and hole orbitals into active and inactive categories. (b) Diagrammatic representation of inactive holes (\downarrow inside the circle), active holes (double down arrow), active particles (double up arrow), and inactive particles (\uparrow inside the circle). General hole-particle orbitals are represented by lines with down-going and up-going arrows. | 157 |

| | | |
|-----|---|-----|
| 7.2 | Schematic depiction of the one- and two-body cluster operators for (1,0) and (0,1) valence sectors. The one- and two-body cluster operators for (0,0) valence are nothing but the cluster operators T_1 and T_2 (see Figure 6.1 for the graphical representation). | 158 |
| 7.3 | Schematic depiction of the one- and two-body cluster operators for (1,1) valence sectors. The prime on the summation sign indicates the exclusion of the case in which both indices in the upper vertex refer to valence orbitals. | 158 |
| 7.4 | Schematic depiction of cluster equations for (1,0) valence sector. Here the thick lines represent \bar{F} and \bar{V} , and the effective Hamiltonian $\bar{\mathcal{H}}_{\text{eff}}$ is denoted by a box. | 165 |
| 7.5 | Schematic depiction of cluster equations for the (0,1) valence sector. Here the thick lines represent \bar{F} and \bar{V} , and the effective Hamiltonian $\bar{\mathcal{H}}_{\text{eff}}$ is denoted by a box. | 166 |
| 7.6 | Schematic representation of $S_1^{(1,1)}$ determining equations. The square and rectangular boxes represent the effective Hamiltonian for the (0,1)/(1,0), and (1,1) sectors, respectively, and the thick line denotes the one-electron dressed operator \bar{F} . The incoming and the outgoing lines are valence types. | 167 |
| 7.7 | Schematic representation of $S_2^{(1,1)}$ determining equations in which the boxes represent the effective Hamiltonian for the (1,1) and lower valence sectors. The one-electron and two-electron dressed operators \bar{F} and \bar{V} are depicted by a thick line. . . . | 168 |
| 7.8 | Schematic representation of $\tilde{\mathcal{H}}^{(1,1)}$ where all the free lines are valence types. | 168 |
| 7.9 | Schematic depiction of the excitation operator R_k^\dagger for generating (a) singly ionized $N_c - 1$, (b) singly ionized $N_c + 1$, and (c) hole-particle excited states. | 172 |
| 8.1 | Redundancy problem Jeziorski–Monkhorst ansatz based formulations. The excitations due to T_1^μ and T_2^ν lead to the same excited configurations. | 195 |



Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

List of Tables

| | | |
|-----|---|-----|
| 6.1 | Interpretation of diagrams D1–D11 (see Figures 6.4–6.9) and their matrix elements. | 146 |
| 7.1 | The first ionization potential (in cm^{-1}) of Be I isoelectronic sequence. Quantum electrodynamic (QED) contributions are shown in the parentheses. | 179 |
| 7.2 | The first ionization potential (in cm^{-1}) of isolated Li I and Na I isoelectronic sequences. | 179 |
| 7.3 | The first ionization potential of Yb and ${}^2S_J (J=\frac{1}{2}) \rightarrow {}^2F_J^o (J=\frac{5}{2}, \frac{7}{2})$ excitation energies (in cm^{-1}) of Yb II from EOMCC calculations with $34s32p28d20f15g4h2i$ uncontracted Gaussian basis. | 180 |



Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

Preface

The development of quantum mechanics in the 1920s, coupled with the genesis of advanced computational algorithms and techniques, culminated in a solid foundation for the development of quantum chemistry, aimed at solving problems associated with atomic and molecular systems, in a wide range of contexts. The problem becomes non-trivial since the many-body Schrödinger equation is not solvable exactly even for the smallest of systems, and one has to resort to techniques of approximation. The prime focus of quantum chemists is toward the development of accurate, formally simple, computationally tractable, and consistently applicable methods of approximation that can be applied to a plethora of systems having arbitrary levels of complexity and generality.

Thus, electronic structure theorists are confronted with the challenge of dealing with the electron correlation problem for many-particle systems. The present book deals with two major classes of theories of electron correlation, namely, the many-body perturbation theory and coupled cluster methods. In the parlance of modern strategies dealing with electronic structure, both methods have withstood the test of time and proved to be of great importance in chemical physics. While the linked cluster theorem takes care of single reference situations, both in the context of coupled cluster and perturbation theories, the corresponding multireference analog is yet to be realized with full-fledged generality. Multireference situations appear in many cases in the domain of chemistry and physics, in general, where the traditionally accepted single reference techniques seem to be inadequate, or at times formally wrong, and often lead to an incomplete physical insight. In view of this, recent decades have witnessed a tremendous methodological development in the realm of multireference electronic structure methods, both in coupled cluster and perturbative contexts, and have created a profound impression in the arena of modern electronic structure theories. Such a set of multireference developments in the realm of perturbation theories sets the tone of the present book.

This book primarily aims to discuss the issues related to the formal development and the consequent numerical implementation of the multireference coupled cluster and perturbation theories from the standpoint of a practicing theoretician. The theoretical nitty-gritty associated with such developments has been emphasized amply, and the related algebraic (and many times diagrammatic) derivations have been put forth in a comprehensive manner to

assist the reader to have a grip on the subject. It has been assumed, throughout this work, that the reader is acquainted with the fundamental nuances of quantum chemistry. There are, nevertheless, numerous textbooks dealing with quantum chemistry at the beginner's level, like the one by Szabo and Ostlund, and a good number of professionally written monographs, like the one by Shavitt and Bartlett [Many-Body Methods in Chemistry and Physics: MBPT and Coupled Cluster Theory] that pave the foundation to the modern nuances of electronic structure. This book is more like an advanced reference text, that would carry forward the reader from the doorstep of modern research to the very frontier of it.

The book is organized as follows. The opening chapter, [Chapter 1](#), attempts to introduce the reader, in a very succinct manner, to a set of issues relevant to the development of explicitly correlated many-body methods in general. We initiate this chapter by formally dealing with the basic issues like the Born–Oppenheimer approximation and general treatment of approximation methods, and proceed to discuss atomic/molecular electronic structure methods by setting the tone with the trivial-most independent particle model. We move ahead, in a very concise fashion, to discuss advanced methods like configuration interaction. As we have already pointed out, since this book is not a beginner's guide to modern electronic structure and is attuned more toward advanced readers, we have given extensive bibliographical support to augment the issues that we have left out of this book.

[Chapter 2](#) is a formally rigorous treatment of the issues that pave the foundation toward the theoretical development of methods attuned to tackle the problem of electronic correlation in a balanced and systematic manner. This chapter is somewhat technical in the sense that here we have developed the pivotally crucial hole-particle formalism through the normal ordering of the creation-annihilation operators using Wick's theorem. In addition, we have also introduced the diagrammatic representation of the involved operator expansions, which eventually leads to the diagrammatic simplification of the working equations (in the chapters that follow), as compared to their complete algebraic form.

In [Chapter 3](#) we consider the perturbation theory, initially in the philosophy of a typical textbook pattern to set the tone of the development. As we progress, we deal with the projection operator route to the perturbation theory, and the Rayleigh–Schrödinger and the Brillouin–Wigner variants in the realm of a completely single-reference situation. In doing so, we discuss in detail the underlying issues that lead to intuitively intelligent partitioning of the Hamiltonian, and have ultimately compared and contrasted the relative performance of the variants under different sets of conditions.

We carry forward the ideas developed in [Chapter 3](#) to deal with perturbation theory in the multireference domain in [Chapter 4](#) by invoking the idea of an appropriate multiconfiguration space and suitably redefine the orbital space as being tailored into core, active, and valence. We bring to the fore the issue of improved virtual orbitals and discuss the formal issues associated with

multireference perturbation theories in both complete and incomplete model spaces.

In [Chapter 5](#) we formally introduce the idea of state-specific theories by discussing the second-order state-specific multireference perturbation theory in the context of a Möller–Plesset partitioning. Various other multiconfiguration and multistate variants are also addressed in this chapter.

[Chapter 6](#) is dedicated to the development and application of the traditional coupled cluster techniques in the single-reference context. In this chapter, we address the crucial issue of the size-extensive nature of the computed energies, and compare the coupled cluster method with the traditional configuration interaction technique. We put forth a detailed survey of the methods to represent the working equations in a diagrammatic format, leading to the extensive simplification of the algebraic forms involved. We also show the method to develop perturbation theories starting from a coupled cluster equation. Numerical applications are provided to supplement the theoretical discussion in this chapter.

[Chapter 7](#) deals with Fock-space based multireference coupled cluster methods. In this chapter we delineate the issues of the choice of the wave operator for multireference systems, the connectivity of the effective Hamiltonian, and the systematic generation of cluster equations for various valence sectors. We deal with the equation of motion coupled cluster method, and its relation to the Fock-space-based multireference coupled cluster technique. Numerical illustrations form a major attraction of this chapter, since these provide a suitable window for the reader to judge the efficacy of the different methods discussed here and the preceding ones.

We conclude this book with [Chapter 8](#), which deals with *state-of-the-art* methods of modern electronic structure. We emphasize the state-universal and the state-specific methods in the contexts of perturbation and coupled cluster theories, and assess their relative performances. This chapter discusses the frontier areas of explicitly correlated methods and provides the reader with a scope to push the frontier ahead.

We want to thank all the people who have made it possible for this book to reach your hands. First, we are deeply indebted to Professor Debashis Mukherjee and Professor Karl F. Freed for the training that they bestowed upon us. We are thankful to Professor A. Satyanarayan and Professor R. Ramesh for their advice and constructive criticism on the entire manuscript. Finally, we express our deep sense of gratitude and thankfulness to the editorial team of Taylor & Francis for providing us this opportunity.



Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

Chapter 1

Introduction

| | | |
|-------|--|----|
| 1.1 | Background | 1 |
| 1.2 | Born–Oppenheimer approximation | 3 |
| 1.3 | Approximate methods | 6 |
| 1.3.1 | Variational method: Linear variation principle | 6 |
| 1.4 | Independent particle model | 8 |
| 1.4.1 | Hartree product | 8 |
| 1.4.2 | Slater determinant | 9 |
| 1.4.3 | Slater’s rule | 10 |
| 1.4.4 | Hartree–Fock method | 11 |
| 1.4.5 | Hartree–Fock–Roothan method | 13 |
| 1.4.6 | Brillouin’s theorem | 14 |
| 1.4.7 | Koopmans’ theorem | 14 |
| 1.5 | Configuration interaction | 15 |
| 1.6 | Electron correlation | 19 |
| 1.7 | Size extensivity and consistency | 20 |

1.1 Background

Perturbation theory, in the arena of quantum mechanics, refers to a set of physically motivated and intuitive approximations engineered by mathematical perturbation to describe and explore the properties of a complicated system. The philosophy of perturbation theory is to begin with a simpler system, whose mathematical solution is known to the best of one’s knowledge, and then “perturb” the system by means of an externally tunable influence. For a disturbance that is not too strong, the physical quantities associated with the perturbed system can be expressed in terms of the “corrections” of the corresponding quantities of the simpler (unperturbed) system. For small perturbation, the magnitudes of these correction terms are really small in light of the magnitude of the quantities themselves and are therefore subject to treatments by approximations like the asymptotic series. The accuracy of the evaluated physical quantity, among other factors, depends on the extent to which such correction terms are incorporated. Therefore, perturbation theory is a useful avenue to explore the properties of a complicated system, where the exact (analytic) solution of the system is either difficult or impossible to achieve.

In early 1950s, Löwdin [1, 2, 3] and others [4] demonstrated that the “partitioning technique” can be used to develop perturbation theory for many-

particle systems. A series of seminal works by P. O. Löwdin [5] entitled “Studies in Perturbation Theory” during 1963–1971 led to a deep insightful understanding of the expansions of perturbation theory. These explorations also provided pivotal knowledge of the interrelations among the various forms of such expansions, and their immediate consequence and capabilities in tackling quantum mechanical problems pertaining to chemistry.

The perturbation theory for many-electron closed-shell systems [the so-called many-body perturbation theory (MBPT)] was formally developed during the 1950s by Brueckner [6, 7], Goldstone [8], Hugenholtz [9] and Hubbard [10]. Kelly [11] was probably the first to apply this method to the atomic structure problem. These applications used the numerical solutions of the Hartree–Fock equations, which are available for atoms, because of the special coordinate system. Kelly also reported applications to some simple hydrides in which the hydrogen atom nucleus is treated as an additional perturbation. Historically, the diagrammatic representation of MBPT was first introduced by Brueckner [6, 7] and by Brueckner and Levinson [12] in nuclear physics. On the other hand, Bethe [13], Bethe and Goldstone [14] and Rodberg [15] introduced the concepts of “wave” and “reaction” operators to extend this method to study the nuclear many-body problem. Goldstone [8] derived the completely linked (to all order) diagrammatic MBPT using the field theoretic form of the time-dependent perturbation theory and adiabatic hypothesis [16]. Hugenholtz [9] arrived at the same conclusion via a time-independent resolvent approach, leading to the emergence of the famous “linked cluster theorem” (LCT) for closed-shell systems. An early attempt on a degenerate case was made by Morita [17]. The first complete proof of this theorem for a degenerate situation was provided by Brandow [18] using the time-independent approach and later by Lindgren [19].

The closed-shell coupled cluster (CC) method, which is an all-order version of the MBPT, was first introduced by Coester [20] and Coester and Kümmel [21] in nuclear physics. Coester and Kümmel [21] pioneered the use of the exponential ansatz in formulating a quantum mechanical many-body theory in the realm of nuclear physics, although the origin of the cluster expansion approach to many-fermion systems dates back to the early 1950s through attempts to understand the correlation effect in nuclear matter and electron gas by Bethe [13] and Gell-Mann and Brueckner [22]. At about the same time, Čížek [23] developed the formalism of the CC approach for use in the context of molecular electronic structure theory. With the advent of computing methodologies and algorithms during the 1970s, both CC and MBPT were implemented numerically for molecular systems having a reasonably high degree of complexity. Applications of the *ab initio* CC theory using finite basis set expansions were put forth in 1972 by Paldus, Čížek and Shavitt [24], and in the following year Kaldor [25] came up with his application of the MBPT to the hydrogen molecule ground state by invoking the algebraic approximation. The development of high-speed computers, the refinement of algorithmic techniques, and a plethora of fundamental formal advancements during the 1970s

and early 1980s culminated in a rapid and vivid understanding of electron correlation problems in atomic and molecular systems.

1.2 Born–Oppenheimer approximation

It is well known that particles at the atomic or subatomic scale, like electrons and the nucleus in atoms and molecules, must be treated quantum mechanically, as Newtonian mechanics fails to provide the correct description of the behavior of these particles. The quantum mechanical methodology finds one of its most important domains of application in the evaluation of atomic and molecular properties. The method is nowadays applied to almost all branches of physics and chemistry. It also finds its applications in atomic and nuclear physics to characterize spectral lines and nuclear structure.

In this methodology, a wave function is needed to explain the kinematics of electrons in atoms and molecules, where the wave function Ψ defines the quantum state of a system. The wave function Ψ generally depends on time and has the physical interpretation that $|\Psi(\zeta, t)|^2$ represents the probability density of finding the system at position ζ at the instant of time t . The quantum state Ψ is governed by the Schrödinger equation, which is the first-order differential equation in t of the form

$$i\hbar \frac{d\Psi(\zeta, t)}{dt} = \mathcal{H}\Psi(\zeta, t) \quad (1.1)$$

where \mathcal{H} is the Hamiltonian of the system. The fundamental task is to partition Equation (1.1) into space (ζ) and time (t) and solve the time-independent part of the Schrödinger equation

$$\mathcal{H}|\Psi(r, R)\rangle = \mathcal{E}|\Psi(r, R)\rangle \quad (1.2)$$

In atomic units, the Hamiltonian \mathcal{H} for N electrons and M nuclei is given by

$$\mathcal{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{i < j}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{A < B}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.3)$$

in which M_A is the ratio of the mass of nucleus A to the electron mass. The first two terms in the above equation represent the kinetic energies of the electron and the nucleus. The third term refers to the electrostatic interaction between the nucleus and the electrons, while the last two terms denote the electron-electron and nucleus-nucleus repulsions. This Hamiltonian is universal in the sense that it describes all of everyday matter from biological macro molecules, such as proteins, enzymes and nucleic acids, to metals and semiconductors to

synthetic materials such as plastics. Thus, if we could solve for the eigenvalues and eigenfunctions of this Hamiltonian, we could predict any property we wished of a given system. This fact led the physicist P. A. M. Dirac to comment that all of chemistry is a solved problem, at least in principle. Of course, the problem cannot actually be solved exactly, so approximations are needed and it is the development of reliable approximate methods on which quantum chemistry is focused.

Electrons, being lighter than the nuclei, move faster than the nuclei, and hence, to a good approximation one can assume the nuclei to be stationary. The large separation in the time scales of electronic and nuclear motions is rationalized by the fact that the energy separation between the electronic energy levels is much larger than the rotational and/or the vibrational energy levels. This is akin to a situation where one might contemplate that the electrons are being dragged along with the nuclei. From a dynamical perspective, this is equivalent to stating that electrons follow the motion of the nuclei in an adiabatic manner. This is the so-called Born–Oppenheimer (BO) approximation [26, 27]. In this approximation, the nuclear kinetic energy terms are neglected and the nuclear repulsion energy terms are considered to be constant. The reason it is an approximation is because, in principle, one cannot ignore the role of the non-adiabatic effects such as spontaneous and instantaneous motion of the electrons along with the nuclei. Nevertheless, in the case of many-electron systems, the adiabatic approximation is an excellent idea to work with. The mass difference between the nuclei and the electrons in molecules generates yet another effect. The nuclear components of the wave function are seen to be much more localized, spatially, in comparison to electronic wave functions (making the nuclear wave functions rise more steeply than the corresponding electronic counterparts). This effect, in the classical limit, allows one to treat the nuclei as classical point masses. Thus, the electronic Hamiltonian or the Hamiltonian describing the motion of N electrons in a field of M point charges can be expressed as

$$\mathcal{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{i < j}^N \frac{1}{r_{ij}} \quad (1.4)$$

Assuming the eigenfunction of the Hamiltonian \mathcal{H} to be product separable

$$\Psi(r, R) = \Phi_e(r, \{R\}) \Phi_n(R) \quad (1.5)$$

the Schrödinger equation for the electronic Hamiltonian can be written as

$$\mathcal{H}_e \Phi_e(r, \{R\}) = \mathcal{E}_{\text{elec}}(r, \{R\}) \Phi_e(r, \{R\}) \quad (1.6)$$

in which the parametric dependence of the eigenvalue $\mathcal{E}_{\text{elec}}(r, \{R\})$ and the eigenfunction $\Phi_e(r, \{R\})$ on the nuclear coordinate is explicitly acknowledged. The total energy of the system at a given geometry can then be obtained by