

TABLE OF CONTENTS

Preface to Revised Edition	ix
Preface	xi
Chapter 1. Mathematical Review	1
1.1 Linear Algebra	2
1.1.1 Three-Dimensional Vector Algebra	2
1.1.2 Matrices	5
1.1.3 Determinants	7
1.1.4 <i>N</i> -Dimensional Complex Vector Spaces	9
1.1.5 Change of Basis	13
1.1.6 The Eigenvalue Problem	15
1.1.7 Functions of Matrices	21
1.2 Orthogonal Functions, Eigenfunctions, and Operators	24
1.3 The Variation Method	31
1.3.1 The Variation Principle	31
1.3.2 The Linear Variational Problem	33
Notes	38
Further Reading	38
Chapter 2. Many Electron Wave Functions and Operators	39
2.1 The Electronic Problem	40
2.1.1 Atomic Units	41
2.1.2 The Born-Oppenheimer Approximation	43
2.1.3 The Antisymmetry or Pauli Exclusion Principle	45
2.2 Orbitals, Slater Determinants, and Basis Functions	46
2.2.1 Spin Orbitals and Spatial Orbitals	46
2.2.2 Hartree Products	47

2.2.3	Slater Determinants	49
2.2.4	The Hartree-Fock Approximation	53
2.2.5	The Minimal Basis H ₂ Model	55
2.2.6	Excited Determinants	58
2.2.7	Form of the Exact Wave Function and Configuration Interaction	60
2.3	Operators and Matrix Elements	64
2.3.1	Minimal Basis H ₂ Matrix Elements	64
2.3.2	Notations for One- and Two-Electron Integrals	67
2.3.3	General Rules for Matrix Elements	68
2.3.4	Derivation of the Rules for Matrix Elements	74
2.3.5	Transition from Spin Orbitals to Spatial Orbitals	81
2.3.6	Coulomb and Exchange Integrals	85
2.3.7	Pseudo-Classical Interpretation of Determinantal Energies	87
2.4	Second Quantization	89
2.4.1	Creation and Annihilation Operators and Their Anticommutation Relations	89
2.4.2	Second-Quantized Operators and Their Matrix Elements	95
2.5	Spin-Adapted Configurations	97
2.5.1	Spin Operators	97
2.5.2	Restricted Determinants and Spin-Adapted Configurations	100
2.5.3	Unrestricted Determinants	104
	Notes	107
	Further Reading	107
Chapter 3.	The Hartree-Fock Approximation	108
3.1	The Hartree-Fock Equations	111
3.1.1	The Coulomb and Exchange Operators	112
3.1.2	The Fock Operator	114
3.2	Derivation of the Hartree-Fock Equations	115
3.2.1	Functional Variation	115
3.2.2	Minimization of the Energy of a Single Determinant	117
3.2.3	The Canonical Hartree-Fock Equations	120
3.3	Interpretation of Solutions to the Hartree-Fock Equations	123
3.3.1	Orbital Energies and Koopmans' Theorem	123
3.3.2	Brillouin's Theorem	128
3.3.3	The Hartree-Fock Hamiltonian	130
3.4	Restricted Closed-Shell Hartree-Fock: The Roothaan Equations	131
3.4.1	Closed-Shell Hartree-Fock: Restricted Spin Orbitals	132
3.4.2	Introduction of a Basis: The Roothaan Equations	136
3.4.3	The Charge Density	138
3.4.4	Expression for the Fock Matrix	140
3.4.5	Orthogonalization of the Basis	142

3.4.6	The SCF Procedure	145
3.4.7	Expectation Values and Population Analysis	149
3.5	Model Calculations on H_2 and HeH^+	152
3.5.1	The $1s$ Minimal STO-3G Basis Set	153
3.5.2	STO-3G H_2	159
3.5.3	An SCF Calculation on STO-3G HeH^+	168
3.6	Polyatomic Basis Sets	180
3.6.1	Contracted Gaussian Functions	180
3.6.2	Minimal Basis Sets: STO-3G	184
3.6.3	Double Zeta Basis Sets: 4-31G	186
3.6.4	Polarized Basis Sets: 6-31G* and 6-31G**	189
3.7	Some Illustrative Closed-Shell Calculations	190
3.7.1	Total Energies	191
3.7.2	Ionization Potentials	194
3.7.3	Equilibrium Geometries	200
3.7.4	Population Analysis and Dipole Moments	203
3.8	Unrestricted Open-Shell Hartree-Fock: The Pople-Nesbet Equations	205
3.8.1	Open-Shell Hartree Fock: Unrestricted Spin Orbitals	206
3.8.2	Introduction of a Basis: The Pople-Nesbet Equations	210
3.8.3	Unrestricted Density Matrices	212
3.8.4	Expression for the Fock Matrices	214
3.8.5	Solution of the Unrestricted SCF Equations	215
3.8.6	Illustrative Unrestricted Calculations	216
3.8.7	The Dissociation Problem and its Unrestricted Solution	221
	Notes	229
	Further Reading	229
Chapter 4.	Configuration Interaction	231
4.1	Multiconfigurational Wave Functions and the Structure of the Full CI Matrix	233
4.1.1	Intermediate Normalization and an Expression for the Correlation Energy	237
4.2	Doubly Excited CI	242
4.3	Some Illustrative Calculations	245
4.4	Natural Orbitals and the One-Particle Reduced Density Matrix	252
4.5	The Multiconfiguration Self-Consistent Field (MCSCF) and Generalized Valence Bond (GVB) Methods	258
4.6	Truncated CI and the Size-Consistency Problem	261

Notes	269
Further Reading	269
Chapter 5. Pair and Coupled-Pair Theories	271
5.1 The Independent Electron Pair Approximation (IEPA)	272
5.1.1 Invariance under Unitary Transformations: An Example	277
5.1.2 Some Illustrative Calculations	284
5.2 Coupled-Pair Theories	286
5.2.1 The Coupled Cluster Approximation (CCA)	287
5.2.2 The Cluster Expansion of the Wave Function	290
5.2.3 Linear CCA and the Coupled Electron Pair Approximation (CEPA)	292
5.2.4 Some Illustrative Calculations	296
5.3 Many-Electron Theories with Single Particle Hamiltonians	297
5.3.1 The Relaxation Energy via CI, IEPA, CCA, and CEPA	303
5.3.2 The Resonance Energy of Polyenes in Hückel Theory	309
Notes	318
Further Reading	319
Chapter 6. Many-Body Perturbation Theory	320
6.1 Rayleigh-Schrödinger (RS) Perturbation Theory	322
*6.2 Diagrammatic Representation of RS Perturbation Theory	327
6.2.1 Diagrammatic Perturbation Theory for 2 States	327
6.2.2 Diagrammatic Perturbation Theory for N States	335
6.2.3 Summation of Diagrams	336
6.3 Orbital Perturbation Theory: One-Particle Perturbations	338
*6.4 Diagrammatic Representation of Orbital Perturbation Theory	348
6.5 Perturbation Expansion of the Correlation Energy	350
6.6 The N -Dependence of the RS Perturbation Expansion	354
*6.7 Diagrammatic Representation of the Perturbation Expansion of the Correlation Energy	356
6.7.1 Hugenholtz Diagrams	356
6.7.2 Goldstone Diagrams	362
6.7.3 Summation of Diagrams	368
6.7.4 What Is the Linked Cluster Theorem?	369
6.8 Some Illustrative Calculations	370
Notes	378
Further Reading	379

Chapter 7. The One-Particle Many-Body Green's Function	380
7.1 Green's Functions in Single Particle Systems	381
7.2 The One-Particle Many-Body Green's Function	387
7.2.1 The Self-Energy 389	
7.2.2 The Solution of the Dyson Equation 391	
7.3 Application of the Formalism to H_2 and HeH^+	392
7.4 Perturbation Theory and the Green's Function Method	398
7.5 Some Illustrative Calculations	405
Notes	409
Further Reading	409
Appendix A. Integral Evaluation with 1s Primitive Gaussians	410
Appendix B. Two-Electron Self-Consistent-Field Program	417
Appendix C. Analytic Derivative Methods and Geometry Optimization <i>by M.C. Zerner</i>	437
Appendix D. Molecular Integrals for H_2 as a Function of Bond Length	459
Index	461

ATTILA SZABO
NEIL S. OSTLUND