

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 N -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	3.4.6	The SCF Procedure	145
2.2.4	The Hartree-Fock Approximation	53	3.4.7	Expectation Values and Population Analysis	149
2.2.5	The Minimal Basis H ₂ Model	55	3.5	Model Calculations on H ₂ and HeH ⁺	152
2.2.6	Excited Determinants	58	3.5.1	The 1s Minimal STO-3G Basis Set	153
2.2.7	Form of the Exact Wave Function and Configuration Interaction	60	3.5.2	STO-3G H ₂	159
2.3	Operators and Matrix Elements	64	3.5.3	An SCF Calculation on STO-3G HeH ⁺	168
2.3.1	Minimal Basis H ₂ Matrix Elements	64	3.6	Polyatomic Basis Sets	180
2.3.2	Notations for One- and Two-Electron Integrals	67	3.6.1	Contracted Gaussian Functions	180
2.3.3	General Rules for Matrix Elements	68	3.6.2	Minimal Basis Sets: STO-3G	184
2.3.4	Derivation of the Rules for Matrix Elements	74	3.6.3	Double Zeta Basis Sets: 4-31G	186
2.3.5	Transition from Spin Orbitals to Spatial Orbitals	81	3.6.4	Polarized Basis Sets: 6-31G* and 6-31G**	189
2.3.6	Coulomb and Exchange Integrals	85	3.7	Some Illustrative Closed-Shell Calculations	190
2.3.7	Pseudo-Classical Interpretation of Determinantal Energies	87	3.7.1	Total Energies	191
2.4	Second Quantization	89	3.7.2	Ionization Potentials	194
2.4.1	Creation and Annihilation Operators and Their Anticommutation Relations	89	3.7.3	Equilibrium Geometries	200
2.4.2	Second-Quantized Operators and Their Matrix Elements	95	3.7.4	Population Analysis and Dipole Moments	203
2.5	Spin-Adapted Configurations	97	3.8	Unrestricted Open-Shell Hartree-Fock: The Pople-Nesbet Equations	205
2.5.1	Spin Operators	97	3.8.1	Open-Shell Hartree Fock: Unrestricted Spin Orbitals	206
2.5.2	Restricted Determinants and Spin-Adapted Configurations	100	3.8.2	Introduction of a Basis: The Pople-Nesbet Equations	210
2.5.3	Unrestricted Determinants	104	3.8.3	Unrestricted Density Matrices	212
Notes		107	3.8.4	Expression for the Fock Matrices	214
Further Reading		107	3.8.5	Solution of the Unrestricted SCF Equations	215
Chapter 3. The Hartree-Fock Approximation		108	3.8.6	Illustrative Unrestricted Calculations	216
3.1	The Hartree-Fock Equations	111	3.8.7	The Dissociation Problem and its Unrestricted Solution	221
3.1.1	The Coulomb and Exchange Operators	112	Notes		229
3.1.2	The Fock Operator	114	Further Reading		229
3.2	Derivation of the Hartree-Fock Equations	115	Chapter 4. Configuration Interaction		231
3.2.1	Functional Variation	115	4.1	Multiconfigurational Wave Functions and the Structure of the Full CI Matrix	233
3.2.2	Minimization of the Energy of a Single Determinant	117	4.1.1	Intermediate Normalization and an Expression for the Correlation Energy	237
3.2.3	The Canonical Hartree-Fock Equations	120	4.2	Doubly Excited CI	242
3.3	Interpretation of Solutions to the Hartree-Fock Equations	123	4.3	Some Illustrative Calculations	245
3.3.1	Orbital Energies and Koopmans' Theorem	123	4.4	Natural Orbitals and the One-Particle Reduced Density Matrix	252
3.3.2	Brillouin's Theorem	128	4.5	The Multiconfiguration Self-Consistent Field (MCSCF) and Generalized Valence Bond (GVB) Methods	258
3.3.3	The Hartree-Fock Hamiltonian	130	4.6	Truncated CI and the Size-Consistency Problem	261
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			

Notes	269
Further Reading	269
Chapter 5. Pair and Coupled-Pair Theories	
5.1 The Independent Electron Pair Approximation (IEPA)	271
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 by M.C. Zerner	437
Appendix D. Molecular Integrals for H_2 as a Function of Bond Length	459
Index	461