

Contents

1. Introduction	1
2. Basis Set	5
2.A. Fundamental Concepts and General Description	5
2.B. Slater-Type Orbitals	11
2.C. Gaussian-Type Functions	17
2.D. Contracted Gaussian Basis Sets	21
2.E. Gaussian Expansion of Slater-Type Orbitals	26
2.F. Polarization Functions	31
2.G. Off-Centered Gaussian Functions	38
2.H. Comparison of Slater-Type and Contracted Gaussian Basis Sets	43
2.I. Remarks on the Selection of the Basis Set	49
3. SCF Calculations	54
3.A. Integrals over Slater-Type Orbitals	56
3.B. Integrals over Gaussian-Type Functions	57
3.C. Computer Time Saving in Evaluation of Integrals	59
3.D. Computer Time Saving in the SCF Procedure	66
4. Correlation Energy	72
4.A. Definition and Origin of the Correlation Energy	72
4.B. Conservation of the Correlation Energy	74
4.C. Empirical Calculations	78
4.D. Configuration Interaction	82
4.E. Independent Electron Pair Approximation	85
4.F. Cluster Expansion of the Wave Function	86
4.G. Many-Electron Theory of Sinanoglu	92
4.H. Coupled-Pair Many-Electron Theory	93
4.I. Coupled-Electron Pair Approximation	97
4.J. Perturbation Calculations	100
4.K. Numerical Treatment of Perturbation Expressions	126
4.L. Basis Set Dependence	131
4.M. Size Consistency	131
5. Applications	134
5.A. Molecular Geometries	135
5.B. Force Constants	142

5.C. Barriers to Internal Rotation and Inversion	146
5.D. Potential Curves	148
5.E. Thermochemistry	151
5.F. Chemical Reactivity	154
5.G. Ionization Potentials	159
5.H. Intermolecular Interactions	170
5.I. Solvation	187
5.J. Presence and Future	201
 Appendix A: Atomic Units	 209
Appendix B: Most Common Computer Programs	211
References	214
Subject Index	242