Contents

Preface *XV*
List of Contributors *XIX*

1 Chemical Bonding of Main-Group Elements *1*
Martin Kaupp
1.1 Introduction and Definitions *1*
1.2 The Lack of Radial Nodes of the 2p Shell Accounts for Most of the Peculiarities of the Chemistry of the 2p-Elements *2*
1.2.1 High Electronegativity and Small Size of the 2p-Elements *4*
1.2.1.1 Hybridization Defects *4*
1.2.2 The Inert-Pair Effect and its Dependence on Partial Charge of the Central Atom *7*
1.2.3 Stereo-Chemically Active versus Inactive Lone Pairs *10*
1.2.4 The Multiple-Bond Paradigm and the Question of Bond Strengths *13*
1.2.5 Influence of Hybridization Defects on Magnetic-Resonance Parameters *14*
1.3 The Role of the *Outer* d-Orbitals in Bonding *15*
1.4 Secondary Periodicities: Incomplete-Screening and Relativistic Effects *17*
1.5 "Honorary d-Elements": the Peculiarities of Structure and Bonding of the Heavy Group 2 Elements *19*
1.6 Concluding Remarks *21*
References *21*

2 Multiple Bonding of Heavy Main-Group Atoms *25*
Gernot Frenking
2.1 Introduction *25*
2.2 Bonding Analysis of Diatomic Molecules E_2 (E = N – Bi) *27*
2.3 Comparative Bonding Analysis of N_2 and P_2 with N_4 and P_4 *29*
2.4 Bonding Analysis of the Tetrylynes HEEH (E = C – Pb) *32*

2.5 Explaining the Different Structures of the Tetrylynes HEEH (E = C – Pb) *34*
2.6 Energy Decomposition Analysis of the Tetrylynes HEEH (E = C – Pb) *41*
2.7 Conclusion *46*
Acknowledgment *47*
References *47*

3 The Role of Recoupled Pair Bonding in Hypervalent Molecules *49*
David E. Woon and Thom H. Dunning Jr.
3.1 Introduction *49*
3.2 Multireference Wavefunction Treatment of Bonding *50*
3.3 Low-Lying States of SF and OF *53*
3.4 Low-Lying States of SF_2 and OF_2 (and Beyond) *58*
3.4.1 $SF_2(X^1A_1)$ *58*
3.4.2 $SF_2(a^3B_1)$ *59*
3.4.3 $SF_2(b^3A_2)$ *61*
3.4.4 $OF_2(X^1A_1)$ *62*
3.4.5 Triplet states of OF_2 *62*
3.4.6 SF_3 and SF_4 *63*
3.4.7 SF_5 and SF_6 *64*
3.5 Comparison to Other Models *64*
3.5.1 Rundle–Pimentel 3c-4e Model *64*
3.5.2 Diabatic States Model *66*
3.5.3 Democracy Principle *67*
3.6 Concluding Remarks *67*
References *68*

4 Donor–Acceptor Complexes of Main-Group Elements *71*
Gernot Frenking and Ralf Tonner
4.1 Introduction *71*
4.2 Single-Center Complexes EL_2 *73*
4.2.1 Carbones CL_2 *73*
4.2.2 Isoelectronic Group 15 and Group 13 Homologues $(N^+)L_2$ and $(BH)L_2$ *82*
4.2.3 Donor–Acceptor Bonding in Heavier Tetrylenes ER_2 and Tetrylones EL_2 (E = Si – Pb) *88*
4.3 Two-Center Complexes E_2L_2 *94*
4.3.1 Two-Center Group 14 Complexes Si_2L_2 – Pb_2L_2 (L = NHC) *95*
4.3.2 Two-Center Group 13 and Group 15 Complexes B_2L_2 and N_2L_2 *101*
4.4 Summary and Conclusion *110*
References *110*

5 Electron-Counting Rules in Cluster Bonding – Polyhedral Boranes, Elemental Boron, and Boron-Rich Solids *113*
Chakkingal P. Priyakumari and Eluvathingal D. Jemmis
5.1 Introduction *113*
5.2 Wade's Rule *114*
5.3 Localized Bonding Schemes for Bonding in Polyhedral Boranes *119*
5.4 $4n + 2$ Interstitial Electron Rule and Ring-Cap Orbital Overlap Compatibility *122*
5.5 Capping Principle *125*
5.6 Electronic Requirement of Condensed Polyhedral Boranes – mno Rule *126*
5.7 Factors Affecting the Stability of Condensed Polyhedral Clusters *134*
5.7.1 Exo-polyhedral Interactions *134*
5.7.2 Orbital Compatibility *135*
5.8 Hypoelectronic Metallaboranes *136*
5.9 Electronic Structure of Elemental Boron and Boron-Rich Metal Borides – Application of Electron-Counting Rules *139*
5.9.1 α-Rhombohedral Boron *139*
5.9.2 β-Rhombohedral Boron *140*
5.9.3 Alkali Metal-Indium Clusters *142*
5.9.4 Electronic Structure of $Mg_{\sim 5}B_{44}$ *143*
5.10 Conclusion *144*
References *145*

6 Bound Triplet Pairs in the Highest Spin States of Monovalent Metal Clusters *149*
David Danovich and Sason Shaik
6.1 Introduction *149*
6.2 Can Triplet Pairs Be Bonded? *150*
6.2.1 A Prototypical Bound Triplet Pair in $^3Li_2$ *150*
6.2.2 The NPFM Bonded Series of $^{n+1}Li_n$ ($n = 2$–10) *152*
6.3 Origins of NPFM Bonding in $^{n+1}Li_n$ Clusters *152*
6.3.1 Orbital Cartoons for the NPFM Bonding of the $^3\Sigma_u^+$ State of Li_2 *154*
6.4 Generalization of NPFM Bonding in $^{n+1}Li_n$ Clusters *156*
6.4.1 VB Mixing Diagram Representation of the Bonding in $^3Li_2$ *156*
6.4.2 VB Modeling of $^{n+1}Li_n$ Patterns *158*
6.5 NPFM Bonding in Coinage Metal Clusters *161*
6.5.1 Structures and Bonding of Coinage Metal NPFM Clusters *161*
6.6 Valence Bond Modeling of the Bonding in NPFM Clusters of the Coinage Metals *163*
6.7 NPFM Bonding: Resonating Bound Triplet Pairs *167*
6.8 Concluding Remarks: Bound Triplet Pairs *168*
Appendix *170*
6.A Methods and Some Details of Calculations *170*
6.B Symmetry Assignment of the VB Wave Function *170*

6.C The VB Configuration Count and the Expressions for *De* for NPFM Clusters *171*
References *172*

7 Chemical Bonding in Transition Metal Compounds *175*
Gernot Frenking
7.1 Introduction *175*
7.2 Valence Orbitals and Hybridization in Electron-Sharing Bonds of Transition Metals *177*
7.3 Carbonyl Complexes $TM(CO)_6^q$ ($TM^q = Hf^{2-}$, Ta^-, W, Re^+, Os^{2+}, Ir^{3+}) *181*
7.4 Phosphane Complexes $(CO)_5TM\text{-}PR_3$ and N-Heterocyclic Carbene Complexes $(CO)_5TM\text{-}NHC$ (TM = Cr, Mo, W) *187*
7.5 Ethylene and Acetylene Complexes $(CO)_5TM\text{-}C_2H_n$ and $Cl_4TM\text{-}C_2H_n$ (TM = Cr, Mo, W) *190*
7.6 Group-13 Diyl Complexes $(CO)_4Fe\text{-}ER$ (E = B – Tl; R = Ph, Cp) *195*
7.7 Ferrocene $Fe(\eta^5\text{-}Cp)_2$ and Bis(benzene)chromium $Cr(\eta^6\text{-}Bz)_2$ *199*
7.8 Cluster, Complex, or Electron-Sharing Compound? Chemical Bonding in $Mo(EH)_{12}$ and $Pd(EH)_8$ (E = Zn, Cd, Hg) *203*
7.9 Metal–Metal Multiple Bonding *211*
7.10 Summary *214*
Acknowledgment *214*
References *214*

8 Chemical Bonding in Open-Shell Transition-Metal Complexes *219*
Katharina Boguslawski and Markus Reiher
8.1 Introduction *219*
8.2 Theoretical Foundations *220*
8.2.1 Definition of Open-Shell Electronic Structures *221*
8.2.2 The Configuration Interaction Ansatz *222*
8.2.2.1 The Truncation Procedure *222*
8.2.2.2 Density Matrices *222*
8.2.3 *Ab Initio* Single-Reference Approaches *223*
8.2.4 *Ab Initio* Multireference Approaches *224*
8.2.5 Density Functional Theory for Open-Shell Molecules *229*
8.3 Qualitative Interpretation *230*
8.3.1 Local Spin *230*
8.3.2 Broken Spin Symmetry *233*
8.3.3 Analysis of Bond Orders *235*
8.3.4 Atoms in Molecules *237*
8.3.5 Entanglement Measures for Single- and Multireference Correlation Effects *239*
8.4 Spin Density Distributions—A Case Study *243*
8.4.1 A One-Determinant Picture *243*
8.4.2 A Multiconfigurational Study *245*

8.5 Summary *246*
Acknowledgments *247*
References *247*

9 Modeling Metal–Metal Multiple Bonds with Multireference Quantum Chemical Methods *253*
Laura Gagliardi
9.1 Introduction *253*
9.2 Multireference Methods and Effective Bond Orders *253*
9.3 The Multiple Bond in $Re_2Cl_8^{2-}$ *254*
9.4 Homonuclear Diatomic Molecules: Cr_2, Mo_2, and W_2 *255*
9.5 Cr_2, Mo_2, and W_2 Containing Complexes *259*
9.6 Fe_2 Complexes *264*
9.7 Concluding Remarks *265*
Acknowledgment *266*
References *266*

10 The Quantum Chemistry of Transition Metal Surface Bonding and Reactivity *269*
Rutger A. van Santen and Ivo A. W. Filot
10.1 Introduction *269*
10.2 The Elementary Quantum-Chemical Model of the Surface Chemical Bond *272*
10.3 Quantum Chemistry of the Surface Chemical Bond *276*
10.3.1 Adatom Adsorption Energy Dependence on Coordinative Unsaturation of Surface Atoms *276*
10.3.2 Adatom Adsorption Energy as a Function of Metal Position in the Periodic System *284*
10.3.3 Molecular Adsorption; Adsorption of CO *286*
10.3.4 Surface Group Orbitals *296*
10.3.5 Adsorbate Coordination in Relation to Adsorbate Valence *301*
10.4 Metal Particle Composition and Size Dependence *303*
10.4.1 Alloying: Coordinative Unsaturation versus Increased Overlap Energies *303*
10.4.2 Particle Size Dependence *305*
10.5 Lateral Interactions; Reconstruction *310*
10.6 Adsorbate Bond Activation and Formation *317*
10.6.1 The Reactivity of Different Metal Surfaces *317*
10.6.2 The Quantum-Chemical View of Bond Activation *321*
10.6.2.1 Activation of the Molecular π Bond (Particle Shape Dependence) *321*
10.6.2.2 The Uniqueness of the (100) Surface *323*
10.6.2.3 Activation of the Molecular σ Bond; CH_4 and NH_3 *325*
10.7 Transition State Analysis: A Summary *328*
References *333*

11 Chemical Bonding of Lanthanides and Actinides *337*
Nikolas Kaltsoyannis and Andrew Kerridge
11.1 Introduction *337*
11.2 Technical Issues *338*
11.3 The Energy Decomposition Approach to the Bonding in f Block Compounds *338*
11.3.1 A Comparison of U–N and U–O Bonding in Uranyl(VI) Complexes *339*
11.3.2 Toward a 32-Electron Rule *340*
11.4 f Block Applications of the Electron Localization Function *341*
11.5 Does Covalency Increase or Decrease across the Actinide Series? *342*
11.6 Multi-configurational Descriptions of Bonding in f Element Complexes *347*
11.6.1 U_2: A Quintuply Bonded Actinide Dimer *347*
11.6.2 Bonding in the Actinyls *349*
11.6.3 Oxidation State Ambiguity in the f Block Metallocenes *350*
11.7 Concluding Remarks *353*
References *354*

12 Direct Estimate of Conjugation, Hyperconjugation, and Aromaticity with the Energy Decomposition Analysis Method *357*
Israel Fernández
12.1 Introduction *357*
12.2 The EDA Method *359*
12.3 Conjugation *361*
12.3.1 Conjugation in 1,3-Butadienes, 1,3-Butadiyne, Polyenes, and Enones *361*
12.3.2 Correlation with Experimental Data *363*
12.4 Hyperconjugation *370*
12.4.1 Hyperconjugation in Ethane and Ethane-Like Compounds *370*
12.4.2 Group 14 β-Effect *371*
12.5 Aromaticity *372*
12.5.1 Aromaticity in Neutral Exocyclic Substituted Cyclopropenes $(HC)_2C=X$ *374*
12.5.2 Aromaticity in Group 14 Homologs of the Cyclopropenylium Cation *375*
12.5.3 Aromaticity in Metallabenzenes *376*
12.6 Concluding Remarks *378*
References *379*

13 Magnetic Properties of Aromatic Compounds and Aromatic Transition States *383*
Rainer Herges
13.1 Introduction *383*
13.2 A Short Historical Review of Aromaticity *384*

13.3 Magnetic Properties of Molecules *386*
13.3.1 Exaltation and Anisotropy of Magnetic Susceptibility *387*
13.3.2 Chemical Shifts in NMR *391*
13.3.3 Quantum Theoretical Treatment *392*
13.4 Examples *397*
13.4.1 Benzene and Borazine *397*
13.4.2 Pyridine, Phosphabenzene, and Silabenzene *398*
13.4.3 Fullerenes *400*
13.4.4 Hückel and Möbius Structures *401*
13.4.5 Homoaromatic Molecules *403*
13.4.6 Organometallic Compounds *404*
13.4.7 Aromatic Transition States *406*
13.4.8 Coarctate Transition States *411*
13.5 Concluding Remarks *415*
References *415*

14 Chemical Bonding in Inorganic Aromatic Compounds *421*
Ivan A. Popov and Alexander I. Boldyrev
14.1 Introduction *421*
14.2 How to Recognize Aromaticity and Antiaromaticity? *422*
14.3 "Conventional" Aromatic/Antiaromatic Inorganic Molecules *426*
14.3.1 Inorganic $B_3N_3H_6$ Borazine and 1,3,2,4-Diazadiboretiidine $B_2N_2H_4$ *427*
14.3.2 Aromatic P_4^{2-}, P_5^-, P_6 and Their Analogs *428*
14.4 "Unconventional" Aromatic/Antiaromatic Inorganic Molecules *430*
14.4.1 σ-Aromatic and σ-Antiaromatic Species *431*
14.4.2 σ-/π-Aromatic, σ-/π-Antiaromatic, and Species with σ-/π-Conflicting Aromaticity *432*
14.4.3 σ-/π-/δ-Aromatic, σ-/π-/δ-Antiaromatic, and Species with σ-/π-/δ-Conflicting Aromaticity *436*
14.5 Summary and Perspectives *440*
Acknowledgments *441*
References *441*

15 Chemical Bonding in Solids *445*
Pere Alemany and Enric Canadell
15.1 Introduction *445*
15.2 Electronic Structure of Solids: Basic Notions *447*
15.2.1 Bloch Orbitals, Crystal Orbitals, and Band Structure *447*
15.2.2 Fermi Level and Electron Counting *449*
15.2.3 Peierls Distortions *451*
15.2.4 Density of States and its Analysis *453*
15.2.5 Electronic Localization *456*
15.3 Bonding in Solids: Some Illustrative Cases *458*

15.3.1 Covalent Bonds in Polar Metallic Solids: A_3Bi_2 and A_4Bi_5 (A = K, Rb, Cs) *459*
15.3.2 Electronic Localization: Magnetic versus Metallic Behavior in K_4P_3 *462*
15.3.3 Crystal versus Electronic Structure: Are There Really Polyacetylene-Like Gallium Chains in Li_2Ga? *466*
15.3.4 $Ba_7Ga_4Sb_9$: Do the Different Cations in Metallic Zintl Phases Play the Same Role? *470*
15.4 Concluding Remarks *473*
Acknowledgments *474*
References *474*

16 Dispersion Interaction and Chemical Bonding *477*
Stefan Grimme
16.1 Introduction *477*
16.2 A Short Survey of the Theory of the London Dispersion Energy *480*
16.3 Theoretical Methods to Compute the Dispersion Energy *485*
16.3.1 General *486*
16.3.2 Supermolecular Wave Function Theory (WFT) *486*
16.3.3 Supermolecular Density Functional Theory (DFT) *488*
16.3.4 Symmetry-Adapted Perturbation Theory (SAPT) *490*
16.4 Selected Examples *492*
16.4.1 Substituted Ethenes *492*
16.4.2 Steric Crowding Can Stabilize a Labile Molecule: Hexamethylethane Derivatives *493*
16.4.3 Overcoming Coulomb Repulsion in a Transition Metal Complex *494*
16.5 Conclusion *495*
16.6 Computational Details *496*
References *496*

17 Hydrogen Bonding *501*
Hajime Hirao and Xiaoqing Wang
17.1 Introduction *501*
17.2 Fundamental Properties of Hydrogen Bonds *502*
17.3 Hydrogen Bonds with Varying Strengths *504*
17.4 Hydrogen Bonds in Biological Molecules *506*
17.5 Theoretical Description of Hydrogen Bonding *508*
17.5.1 Valence Bond Description of the Hydrogen Bond *508*
17.5.2 Electrostatic and Orbital Interactions in H Bonds *509*
17.5.3 Ab Initio and Density Functional Theory Calculations of Water Dimer *510*
17.5.4 Energy Decomposition Analysis *511*
17.5.5 Electron Density Distribution Analysis *513*
17.5.6 Topological Analysis of the Electron Density and the Electron Localization Function *514*

17.5.7 Resonance-Assisted Hydrogen Bonding *515*
17.5.8 Improper, Blueshifting Hydrogen Bonds *516*
17.6 Summary *517*
Acknowledgment *517*
References *517*

18 Directional Electrostatic Bonding *523*
Timothy Clark
18.1 Introduction *523*
18.2 Anisotropic Molecular Electrostatic Potential Distribution Around Atoms *524*
18.3 Electrostatic Anisotropy, Donor–Acceptor Interactions and Polarization *528*
18.4 Purely Electrostatic Models *530*
18.5 Difference-Density Techniques *531*
18.6 Directional Noncovalent Interactions *533*
18.7 Conclusions *534*
Acknowledgments *534*
References *534*

Index *537*