

Contents

Preface XV

List of Contributors XIX

1	Chemical Bonding of Main-Group Elements	1
	<i>Martin Kaupp</i>	
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 <i>Outer</i> 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
	<i>Gernot Frenking</i>	
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 <i>David E. Woon and Thom H. Dunning Jr.</i>
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 ¹ A ₁) 58
3.4.2	SF ₂ (a ³ B ₁) 59
3.4.3	SF ₂ (b ³ A ₂) 61
3.4.4	OF ₂ (X ¹ A 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 <i>Gernot Frenking and Ralf Tonner</i>
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 ₂ L ₂ 94
4.3.1	Two-Center Group 14 Complexes Si ₂ L ₂ – Pb ₂ L ₂ (L = NHC) 95
4.3.2	Two-Center Group 13 and Group 15 Complexes B ₂ L ₂ and N ₂ L 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
	<i>Chakkingal P. Priyakumari and Eluvathingal D. Jemmis</i>	
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 $\text{Mg}_{\sim 5}\text{B}_{44}$	143
5.10	Conclusion	144
	References	145
 6	 Bound Triplet Pairs in the Highest Spin States of Monovalent Metal Clusters	 149
	<i>David Danovich and Sason Shaik</i>	
6.1	Introduction	149
6.2	Can Triplet Pairs Be Bonded?	150
6.2.1	A Prototypical Bound Triplet Pair in $^3\text{Li}_2$	150
6.2.2	The NPFM Bonded Series of $^{n+1}\text{Li}_n$ ($n = 2-10$)	152
6.3	Origins of NPFM Bonding in $^{n+1}\text{Li}_n$ 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 $^{n+1}\text{Li}_n$ Clusters	156
6.4.1	VB Mixing Diagram Representation of the Bonding in $^3\text{Li}_2$	156
6.4.2	VB Modeling of $^{n+1}\text{Li}_n$ 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 D_e for NPFM Clusters 171
	References 172
7	Chemical Bonding in Transition Metal Compounds 175
	<i>Gernot Frenking</i>
7.1	Introduction 175
7.2	Valence Orbitals and Hybridization in Electron-Sharing Bonds of Transition Metals 177
7.3	Carbonyl Complexes $\text{TM}(\text{CO})_6^q$ ($\text{TM}^q = \text{Hf}^{2-}, \text{Ta}^-, \text{W}, \text{Re}^+, \text{Os}^{2+}, \text{Ir}^{3+}$) 181
7.4	Phosphane Complexes $(\text{CO})_5\text{TM-PR}_3$ and N-Heterocyclic Carbene Complexes $(\text{CO})_5\text{TM-NHC}$ ($\text{TM} = \text{Cr}, \text{Mo}, \text{W}$) 187
7.5	Ethylene and Acetylene Complexes $(\text{CO})_5\text{TM-C}_2\text{H}_n$ and $\text{Cl}_4\text{TM-C}_2\text{H}_n$ ($\text{TM} = \text{Cr}, \text{Mo}, \text{W}$) 190
7.6	Group-13 Diyl Complexes $(\text{CO})_4\text{Fe-ER}$ ($\text{E} = \text{B} - \text{Tl}; \text{R} = \text{Ph}, \text{Cp}$) 195
7.7	Ferrocene $\text{Fe}(\eta^5\text{-Cp})_2$ and Bis(benzene)chromium $\text{Cr}(\eta^6\text{-Bz})_2$ 199
7.8	Cluster, Complex, or Electron-Sharing Compound? Chemical Bonding in $\text{Mo}(\text{EH})_{12}$ and $\text{Pd}(\text{EH})_8$ ($\text{E} = \text{Zn}, \text{Cd}, \text{Hg}$) 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
	<i>Katharina Boguslawski and Markus Reiher</i>
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	<i>Ab Initio</i> Single-Reference Approaches 223
8.2.4	<i>Ab Initio</i> 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
	<i>Laura Gagliardi</i>	
9.1	Introduction	253
9.2	Multireference Methods and Effective Bond Orders	253
9.3	The Multiple Bond in $\text{Re}_2\text{Cl}_8^{2-}$	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
	<i>Rutger A. van Santen and Ivo A. W. Filot</i>	
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
	<i>Nikolas Kaltsoyannis and Andrew Kerridge</i>	
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
	<i>Israel Fernández</i>	
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) ₂ C = X	374
12.5.2	Aromaticity in Group 14 Homologs of the Cyclopropenylum 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
	<i>Rainer Herges</i>	
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
	<i>Ivan A. Popov and Alexander I. Boldyrev</i>	
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
	<i>Pere Alemany and Enric Canadell</i>	
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
	<i>Stefan Grimme</i>	
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
	<i>Hajime Hirao and Xiaoqing Wang</i>	
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
	<i>Timothy Clark</i>	
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

