

Contents

Preface XIII

List of Contributors XXIII

1	The Physical Origin of Covalent Bonding	1
	<i>Michael W. Schmidt, Joseph Ivanic, and Klaus Ruedenberg</i>	
1.1	The Quest for a Physical Model of Covalent Bonding	1
1.2	Rigorous Basis for Conceptual Reasoning	3
1.2.1	Physical Origin of the Ground State	3
1.2.2	Physical Origin of Ground State Energy Differences	5
1.2.3	Relation between Kinetic and Potential Energies	8
1.3	Atoms in Molecules	10
1.3.1	Quantitative Bonding Analyses Require Quasi-Atoms in a Molecule	10
1.3.2	Primary and Secondary Energy Contributions	10
1.3.3	Identification of Quasi-Atoms in a Molecule	11
1.4	The One-Electron Basis of Covalent Binding: H_2^+	13
1.4.1	Molecular Wave Function as a Superposition of Quasi-Atomic Orbitals	13
1.4.2	Molecular Electron Density and Gradient Density as Sums of Intra-atomic and Interatomic Contributions	16
1.4.2.1	Resolution of the Molecular Density	16
1.4.2.2	Resolution of the Molecular Gradient Density	17
1.4.3	Dependence of Delocalization and Interference on the Size of the Quasi-Atomic Orbitals	18
1.4.3.1	Charge Accumulation at the Bond Midpoint	19
1.4.3.2	Total Charge Accumulation in the Bond	19
1.4.3.3	Origin of the Relation between Interference and Quasi-Atomic Orbital Contraction/Expansion	20
1.4.4	Binding Energy as a Sum of Two Intra-atomic and Three Interatomic Contributions	22
1.4.5	Quantitative Characteristics of the Five Energy Contributions	24
1.4.5.1	Intra-atomic Deformation Energy: $E_{\text{intra}} = T_{\text{intra}} + V_{\text{intra}}$	24

1.4.5.2	Quasi-Classical Interaction between the Atoms: V_{qc}	24
1.4.5.3	Potential Interference Energy: V_I	25
1.4.5.4	Kinetic Interference Energy: T_I	25
1.4.5.5	Interference Energies and Quasi-Atomic Orbital Contraction and Expansion	25
1.4.6	Synergism of the Binding Energy Contributions along the Dissociation Curve	27
1.4.6.1	First Column: Zeroth Order Approximation to ψ_A, ψ_B by the $1s_A, 1s_B$ Hydrogen Atom Orbitals	27
1.4.6.2	Second Column: Optimal Spherical Approximation to ψ_A, ψ_B by the Scaled Orbitals $1s_A^*, 1s_B^*$	29
1.4.6.3	Third Column: Exact Quasi-Atomic Orbitals ψ_A, ψ_B	30
1.4.6.4	Conclusion	30
1.4.7	Origin of Bonding at the Equilibrium Distance	30
1.4.7.1	Contributions to the Binding Energy	30
1.4.7.2	Energy Lowering By Electron Sharing	31
1.4.7.3	Energy Lowering by Quasi-Atomic Orbital Deformation	32
1.4.7.4	Variational Perspective	32
1.4.7.5	General Implications	33
1.5	The Effect of Electronic Interaction in the Covalent Electron Pair Bond: H_2	34
1.5.1	Quasi-Atomic Orbitals of the FORS Wave Function	35
1.5.2	FORS Wave Function and Density in Terms of Quasi-Atomic Orbitals	38
1.5.3	Binding Energy as a Sum of Two Intra-atomic and Five Interatomic Contributions	39
1.5.3.1	Overall Resolution	39
1.5.3.2	Interatomic Coulombic Contributions	40
1.5.3.3	Interatomic Interference Contributions	41
1.5.3.4	Binding Energy as a Sum of Two Intra-atomic and Five Interatomic Contributions	42
1.5.4	Quantitative Synergism of the Contributions to the Binding Energy	42
1.5.4.1	Quantitative Characteristics	42
1.5.4.2	Synergism along the Dissociation Curve	43
1.5.5	Origin of Bonding at the Equilibrium Distance	45
1.5.5.1	The Primary Mechanism as Exhibited by Choosing the Free-Atom Orbitals as Quasi-Atomic Orbitals	46
1.5.5.2	Effect of Quasi-Atomic Orbital Contraction	46
1.5.5.3	Effect of Polarization	47
1.5.5.4	Binding in the Electron Pair Bond of H_2	47
1.5.6	Electron Correlation Contribution to Bonding in H_2	48
1.6	Covalent Bonding in Molecules with More than Two Electrons: $B_2, C_2, N_2, O_2,$ and F_2	51
1.6.1	Basis of Binding Energy Analysis	52

1.6.2	Origin of Binding at the Equilibrium Geometry	53
1.6.3	Synergism along the Dissociation Curve	57
1.6.4	Effect of Dynamic Correlation on Covalent Binding	61
1.7	Conclusions	62
	Acknowledgments	65
	References	65
2	Bridging Cultures	69
	<i>Philippe C. Hiberty and Sason Shaik</i>	
2.1	Introduction	69
2.2	A Short History of the MO/VB Rivalry	69
2.3	Mapping MO-Based Wave Functions to VB Wave Functions	74
2.4	Localized Bond Orbitals – A Pictorial Bridge between MO and VB Wave Functions	78
2.5	Block-Localized Wave Function Method	79
2.6	Generalized Valence Bond Theory: a Simple Bridge from VB to MOs	80
2.7	VB Reading of CASSCF Wave Functions	82
2.8	Natural Bonding Orbitals and Natural Resonance Theory – a Direct Bridge between MO and VB	83
2.8.1	Natural Bonding Orbitals	83
2.8.2	Natural Resonance Theory	84
2.9	The Mythical Conflict of Hybrid Orbitals with Photoelectron Spectroscopy	85
2.10	Conclusion	87
	Appendix	88
	References	88
3	The NBO View of Chemical Bonding	91
	<i>Clark R. Landis and Frank Weinhold</i>	
3.1	Introduction	91
3.2	Natural Bond Orbital Methods	92
3.2.1	NBO Analysis of Free Atoms and Atoms in Molecular Environments	97
3.2.2	NBO Analysis of Simple Chemical Bonds: LiOH and H ₂ O	99
3.2.3	Lewis-Like Structures of the P- and D-Block Elements	101
3.2.4	Unrestricted Calculations and Different Lewis Structures for Different Spins (DLDS)	104
3.3	Beyond Lewis-Like Bonding: The Donor–Acceptor Paradigm	106
3.3.1	Hyperconjugative Effects in Bond Bending	110
3.3.2	C ₃ H ₃ Cation, Anion, and Radical: Aromaticity, Jahn–Teller Distortions, Resonance Structures, and 3c/2e Bonding	111
3.3.3	3c/4e Hypervalency	114
3.4	Conclusion	117
	References	118

4	The EDA Perspective of Chemical Bonding	121
	<i>Gernot Frenking and F. Matthias Bickelhaupt</i>	
4.1	Introduction	121
4.2	Basic Principles of the EDA Method	125
4.3	The EDA-NOCV Method	126
4.4	Chemical Bonding in H_2 and N_2	127
4.5	Comparison of Bonding in Isoelectronic N_2 , CO and BF	133
4.6	Bonding in the Diatomic Molecules E_2 of the First Octal Row $E = Li-F$	135
4.7	Bonding in the Dihalogens $F_2 - I_2$	144
4.8	Carbon-Element Bonding in CH_3-X	146
4.9	EDA-NOCV Analysis of Chemical Bonding in the Transition State	148
4.10	Summary and Conclusion	155
	Acknowledgements	156
	References	156
 5	 The Valence Bond Perspective of the Chemical Bond	 159
	<i>Sason Shaik, David Danovich, Wei Wu, and Philippe C. Hiberty</i>	
5.1	Introduction	159
5.2	A Brief Historical Recounting of the Development of the Chemical Bond Notion	160
5.3	The Pauling-Lewis VB Perspective of the Electron-Pair Bond	162
5.4	A Preamble to the Modern VB Perspective of the Electron-Pair Bond	165
5.5	Theoretical Characterization of Bond Types by VB and Other Methods	168
5.5.1	VB Characterization of Bond Types	168
5.5.2	ELF and AIM Characterization of Bond Types	169
5.5.2.1	ELF Characterization of Bond Types	169
5.5.2.2	AIM Characterization of Bond Types	170
5.6	Trends of Bond Types Revealed by VB, AIM and ELF	170
5.6.1	VB and AIM Converge	170
5.6.2	VB and ELF Converge	173
5.6.3	Convergence of VB, ELF and AIM	176
5.6.4	The Three Bonding Families	176
5.7	Physical Origins of CS Bonding	178
5.7.1	The Role of Atomic Size	178
5.7.2	The Role of Pauli Repulsion Pressure	179
5.8	Global Behavior of Electron-Pair Bonds	181
5.9	Additional Factors of CS Bonding	183
5.10	Can a Covalent Bond Become CS Bonds by Substitution?	184
5.11	Experimental Manifestations of CS Bonding	187
5.11.1	Marks of CS Bonding from Electron Density Measurements	187
5.11.2	Marks of CS Bonding in Atom Transfer Reactivity	188

5.11.3	Marks of CS Bonding in the Ionic Chemistry of Silicon in Condensed Phases	189
5.12	Scope and Territory of CS Bonding	190
5.12.1	Concluding Remarks	191
	Appendix	192
5.A	Modern VB Methods	192
5.B	The Virial Theorem	193
5.C	Resonance Interaction and Kinetic Energy	195
	References	195
6	The Block-Localized Wavefunction (BLW) Perspective of Chemical Bonding	199
	<i>Yirong Mo</i>	
6.1	Introduction	199
6.2	Methodology Evolutions	202
6.2.1	Simplifying <i>Ab Initio</i> VB Theory to the BLW Method	202
6.2.2	BLW Method at the DFT Level	204
6.2.3	Decomposing Intermolecular Interaction Energies with the BLW Method	205
6.2.4	Probing Electron Transfer with BLW-Based Two-State Models	207
6.3	Exemplary Applications	209
6.3.1	Benzene: Evaluating the Geometrical and Energetic Impacts from π Conjugation	209
6.3.2	Butadiene: The Rotation Barrier Versus the Conjugation Magnitude	214
6.3.3	Ethane: What Force(s) Governs the Conformational Preference?	217
6.3.4	H ₃ B-NH ₃ : Quantifying the Electron Transfer Effect in Donor-Acceptor Complexes	221
6.4	Conclusion	223
6.5	Outlook	225
	Acknowledgements	225
	References	225
7	The Conceptual Density Functional Theory Perspective of Bonding	233
	<i>Frank De Proft, Paul W. Ayers, and Paul Geerlings</i>	
7.1	Introduction	233
7.2	Basics of DFT: The Density as a Fundamental Carrier of Information and How to Obtain It	235
7.3	Conceptual DFT: A Perturbative Approach to Chemical Reactivity and the Process of Bond Formation	238
7.3.1	Basics: Global and Local Response Functions	238
7.3.1.1	Global Response Functions	240
7.3.1.2	Local Response Functions	242
7.3.1.3	Nonlocal Response Functions: the Linear Response Kernel	249

7.3.2	Combined use of DFT-Based Reactivity Indices and Principles in the Study of Chemical Bonding	252
7.3.2.1	Principle of Electronegativity Equalization	252
7.3.2.2	Hard and Soft Acids and Bases Principle	256
7.3.2.3	Berlin's Approach in a Conceptual DFT Context: the Nuclear Fukui Function	261
7.4	Conclusions	264
	Acknowledgments	264
	References	265
8	The QTAIM Perspective of Chemical Bonding	271
	<i>Paul Lode Albert Popelier</i>	
8.1	Introduction	271
8.2	Birth of QTAIM: the Quantum Atom	274
8.3	The Topological Atom: is it also a Quantum Atom?	278
8.4	The Bond Critical Point and the Bond Path	284
8.5	Energy Partitioning Revisited	295
8.6	Conclusion	302
	Acknowledgment	303
	References	303
9	The Experimental Density Perspective of Chemical Bonding	309
	<i>Wolfgang Scherer, Andreas Fischer, and Georg Eickerling</i>	
9.1	Introduction	309
9.2	Asphericity Shifts and the Breakdown of the Standard X-ray Model	311
9.3	Precision of Charge Density Distributions in Experimental and Theoretical Studies	313
9.4	Core Density Deformations Induced by Chemical Bonding	322
9.5	How Strongly Is the Static Electron Density Distribution Biased by Thermal Motion?	325
9.6	Relativistic Effects on the Topology of Electron Density	326
9.7	The Topology of the Laplacian and the MO Picture – Two Sides of the Same Coin?	330
9.8	Elusive Charge Density Phenomena: Nonnuclear Attractors	333
	References	339
10	The ELF Perspective of chemical bonding	345
	<i>Yuri Grin, Andreas Savin, and Bernard Silvi</i>	
10.1	Introduction	345
10.1.1	Context	345
10.1.1.1	Chemical structure given by the electronic structure	345
10.1.1.2	Molecules and crystals are objects in three dimensions	345
10.1.2	Choices	346
10.1.2.1	Fix the nuclei	346

10.1.2.2	Compute, then analyze	346
10.1.2.3	Choose regions of space	346
10.2	Definitions	347
10.2.1	Definition of the Electron Localization Function (ELF)	347
10.2.2	Definition of auxiliary quantities	348
10.2.2.1	ELF maxima	348
10.2.2.2	Spatial regions: f -localization domains	349
10.2.2.3	Bifurcation diagrams	350
10.2.2.4	Spatial regions: Basins	351
10.2.2.5	ELF terminology	351
10.2.2.6	Quantities obtained for ELF basins	352
10.2.2.7	ELF from experimental data	353
10.2.2.8	Simplified forms of ELF	354
10.2.3	Hints for interpretation	354
10.2.3.1	ELF and mesomerism	354
10.2.3.2	How important is a maximum?	354
10.2.3.3	When several maxima merge into a single one	355
10.2.3.4	Hidden bonding	355
10.2.3.5	Electron counting: oxidation numbers and formal charges	356
10.2.4	Sensitivity of ELF to technical details	356
10.3	Simple examples	358
10.3.1	Atoms and ions	358
10.3.1.1	Atomic shells and cores	358
10.3.1.2	Structured cores: TiH_4 , CrH_6	359
10.3.1.3	Ions	359
10.3.1.4	Squeezing effects	359
10.3.2	Bonds and lone pairs	360
10.3.2.1	Bonds: C_2H_6 , diamond	360
10.3.2.2	Multiple bonds: Allene	361
10.3.2.3	Lone pairs: NH_3 , H_2O , ice	361
10.3.2.4	Multicenter bonds: B_2H_6	362
10.3.2.5	Cylindrical symmetry effects: C_2H_2 , HF	362
10.3.2.6	Delocalization: Butadiene, benzene	363
10.3.3	Molecular reactions	364
10.3.3.1	Proton transfer in malonaldehyde	364
10.3.3.2	Aliphatic nucleophilic substitution $\text{S}_{\text{N}}2$	366
10.3.3.3	Diels Alder addition	367
10.4	Solids	369
10.4.1	Ionic compounds	369
10.4.2	Molecular compounds	370
10.4.3	Elemental metals	370
10.4.4	Intermetallic compounds	372
10.4.4.1	Zintl–Klemm concept and ELF	372
10.4.4.2	ELF for penultimate shells of transition metals	373
10.4.4.3	Case of Al_2Cu	374

10.4.4.4	Surprises	374
10.5	Perspectives	375
	Appendix	376
10.A	Mathematical expressions of calculated basin properties	376
10.A.1	Basin populations	376
10.A.2	Variance and covariance of basin populations	377
10.A.3	Probability distributions	378
10.A.4	Basin electrostatic moments	378
10.A.5	Combining ELF and AIM approaches	378
10.A.6	Potential energy contributions	379
10.A.7	Miscellaneous	379
	References	380
11	Relativity and Chemical Bonding	383
	<i>Peter Schwerdtfeger</i>	
11.1	Introduction	383
11.2	Direct and Indirect Relativistic Effects and Spin–Orbit Coupling	387
11.2.1	Scalar-Relativistic Effects	387
11.2.2	Spin–Orbit Effects	391
11.3	Chemical Bonding and Relativistic Effects	393
11.4	Conclusions	400
	Acknowledgments	400
	References	400
	Index	405