

VALENCY AND BONDING

A Natural Bond Orbital Donor–Acceptor Perspective

FRANK WEINHOLD AND CLARK R. LANDIS

Department of Chemistry, University of Wisconsin-Madison, Wisconsin 53706



Contents

<i>Preface</i>	<i>page</i> vii
1 Introduction and theoretical background 1	
1.1 The Schrödinger equation and models of chemistry	1
1.2 Hydrogen-atom orbitals	8
1.3 Many-electron systems: Hartree–Fock and correlated treatments	13
1.4 Perturbation theory for orbitals in the Hartree–Fock framework: the donor–acceptor paradigm	16
1.5 Density matrices, natural localized and delocalized orbitals, and the Lewis-structure picture	21
1.6 Natural resonance structures and weightings	32
1.7 Pauli-exchange antisymmetry and steric repulsions	36
1.8 Summary	40
Notes for Chapter 1	41
2 Electrostatic and ionic bonding 45	
2.1 Introduction	45
2.2 Atomic and ionic orbitals	47
2.3 Charge transfer and hybridization in ionic bonding	49
2.4 Donor–acceptor theory of hybridization in ionic bonding	55
2.5 Ionic–covalent transitions	60
2.6 Ion–dipole and dipole–dipole bonding	64
2.7 Bent ionic compounds of heavy alkaline earths	73
2.8 Ionic bonding in d-block elements	76
2.9 Summary	86
Notes for Chapter 2	87

3	Molecular bonding in s/p-block elements	89
3.1	Introduction	89
3.2	Covalent and polar covalent bonding	90
3.3	Conjugation and aromaticity	182
3.4	Hyperconjugation	215
3.5	Hypervalency: 3c/4e “ ω bonds”	275
3.6	Hypovalency: 3c/2e bridge bonds	306
3.7	Summary	351
	Notes for Chapter 3	353
4	Molecular bonding in the d-block elements	363
4.1	Introduction	363
4.2	Lewis-like structures for the d-block elements	365
4.3	Hybridization and molecular shape	372
4.4	Covalent and polar-covalent bonding	387
4.5	Coordinative metal–ligand bonding	434
4.6	Beyond sigma bonding: transition-metal hyperbonding and pi back/frontbonding	447
4.7	Hypovalency, agostic interactions, and related aspects of catalytic activation at metal centers	479
4.8	Hyperconjugative effects	519
4.9	Multielectron coordination	522
4.10	Vertical trends in transition-metal bonding	545
4.11	Localized versus delocalized descriptions of transition-metal bonding and hyperbonding	563
4.12	Summary	573
	Notes for Chapter 4	575
5	Supramolecular bonding	579
5.1	An introductory overview of intermolecular forces	579
5.2	Hydrogen bonding	593
5.3	Charge-transfer complexes	661
5.4	Transition-state species	678
5.5	Coupling of intramolecular and intermolecular interactions	693
5.6	Summary	702
	Notes for Chapter 5	704
	Appendix A. Methods and basis sets	710
	Appendix B. Chemical periodicity	715
	Appendix C. Units	723
	<i>Chemical-species index</i>	727
	<i>Author index</i>	732
	<i>Subject index</i>	740