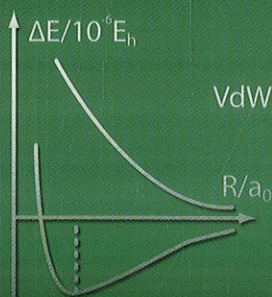


Valerio Magnasco

Models for Bonding in Chemistry

 WILEY



Contents

Preface	xi
1 Mathematical Foundations	1
1.1 Matrices and Systems of Linear Equations	1
1.2 Properties of Eigenvalues and Eigenvectors	6
1.3 Variational Approximations	10
1.4 Atomic Units	15
1.5 The Electron Distribution in Molecules	17
1.6 Exchange-overlap Densities and the Chemical Bond	19
Part 1: Short-range Interactions	27
2 The Chemical Bond	29
2.1 An Elementary Molecular Orbital Model	30
2.2 Bond Energies and Pauli Repulsions in Homonuclear Diatomics	34
2.2.1 The Hydrogen Molecular Ion H_2^+ ($N=1$)	35
2.2.2 The Hydrogen Molecule H_2 ($N=2$)	35
2.2.3 The Helium Molecular Ion He_2^+ ($N=3$)	35
2.2.4 The Helium Molecule He_2 ($N=4$)	36
2.3 Multiple Bonds	37
2.3.1 $\sigma^2\pi^2$ Description of the Double Bond	38
2.3.2 B_1^2B_2^2 Bent (or Banana) Description of the Double Bond	40
2.3.3 Hybridization Effects	42
2.3.4 Triple Bonds	46
2.4 The Three-centre Double Bond in Diborane	47
2.5 The Heteropolar Bond	49
2.6 Stereochemistry of Polyatomic Molecules	55

2.6.1	The Molecular Orbital Model of Directed Valency	55
2.6.2	Analysis of the MO Bond Energy	58
2.7	<i>sp</i> -Hybridization Effects in First-row Hydrides	60
2.7.1	The Methane Molecule	61
2.7.2	The Hydrogen Fluoride Molecule	64
2.7.3	The Water Molecule	75
2.7.4	The Ammonia Molecule	87
2.8	Delocalized Bonds	96
2.8.1	The Ethylene Molecule	98
2.8.2	The Allyl Radical	98
2.8.3	The Butadiene Molecule	100
2.8.4	The Cyclobutadiene Molecule	102
2.8.5	The Benzene Molecule	104
2.9	Appendices	108
2.9.1	The Second Derivative of the Hückel Energy	108
2.9.2	The Set of Three Coulson Orthogonal Hybrids	109
2.9.3	Calculation of Coefficients of Real MOs for Benzene	110
3	An Introduction to Bonding in Solids	119
3.1	The Linear Polyene Chain	120
3.1.1	Butadiene $N = 4$	122
3.2	The Closed Polyene Chain	123
3.2.1	Benzene $N = 6$	126
3.3	A Model for the One-dimensional Crystal	131
3.4	Electronic Bands in Crystals	133
3.5	Insulators, Conductors, Semiconductors and Superconductors	138
3.6	Appendix: The Trigonometric Identity	143
Part 2: Long-Range Interactions		145
4	The van der Waals Bond	147
4.1	Introduction	147
4.2	Elements of Rayleigh–Schrödinger (RS) Perturbation Theory	149
4.3	Molecular Interactions	151
4.3.1	Non-expanded Energy Corrections up to Second Order	152
4.3.2	Expanded Energy Corrections up to Second Order	153
4.4	The Two-state Model of Long-range Interactions	157

4.5	The van der Waals Interactions	159
4.5.1	Atom–Atom Dispersion	161
4.5.2	Atom–Linear Molecule Dispersion	162
4.5.3	Atom–Linear Dipolar Molecule ¹⁰ Induction	163
4.6	The C_6 Dispersion Coefficient for the H–H Interaction	165
4.7	The van der Waals Bond	167
4.8	The Keesom Interaction	169
5	The Hydrogen Bond	177
5.1	A Molecular Orbital Model of the Hydrogen Bond	178
5.2	Electrostatic Interactions and the Hydrogen Bond	179
5.2.1	The Hydrogen Fluoride Dimer (HF) ₂	182
5.2.2	The Water Dimer (H ₂ O) ₂	185
5.3	The Electrostatic Model of the Hydrogen Bond	186
5.4	The Rg–HF Heterodimers	197
	References	201
	Author Index	209
	Subject Index	213