

Contents

1	Introduction	1
1.1	Molecular Modeling and Molecular Mechanics	1
1.2	Historical Background	3
1.3	The Molecular Mechanics Method in Brief	5
	References	7
	Part I: Theory	9
2	Parameterization, Approximations and Limitations	10
2.1	Concepts	10
2.2	Potential Energy Functions	14
2.2.1	Bond Length Deformation	16
2.2.2	Valence Angle Deformation	18
2.2.3	Torsion Angle Deformation	22
2.2.4	Cross-terms	24
2.2.5	Van der Waals Interactions	24
2.2.6	Electrostatic Interactions	26
2.2.7	Hydrogen Bonding Interactions	27
2.2.8	Out-of-plane Deformation	28
2.3	Force Field Parameters	28
2.4	Spectroscopic Force Fields	31
2.5	Model and Reality	32
2.6	Electronic Effects	34
2.7	The Environment	36
2.8	Entropic Effects	37
2.9	Summary	38
3	Computation	40
3.1	Input and Output	40
3.2	Energy Minimization	42
3.2.1	The Simplex Method	44

VIII *Contents*

3.2.2	Gradient Methods	44
3.2.3	Conjugate Gradient Methods	45
3.2.4	The Newton–Raphson Method	45
3.2.5	Least-squares Methods	47
3.3	Constraints and Restraints	47
4	The Multiple Minima Problem	48
4.1	Deterministic Methods	49
4.2	Stochastic Methods	49
4.3	Molecular Dynamics	50
4.4	Practical Considerations	51
4.5	Making Use of Experimental Data	52
5	Conclusions	53
	References for Part I	55
	Part II: Applications	59
6	Structural Aspects	60
6.1	Accuracy of Structure Predictions	60
6.2	Molecular Visualization	61
6.3	Isomeric Analyses	63
6.4	Analysis of Structural Trends	64
6.5	Unraveling Crystallographic Disorder	65
6.6	Comparison with Solution Properties	66
7	Stereoselectivities	67
7.1	Conformational Analysis	67
7.2	Enantioselectivities	70
7.2.1	Racemate Separation	70
7.2.2	Stereoselective Synthesis	73
7.3	Structure Evaluation	74
7.4	Mechanistic Information	78
8	Metal Ion Selectivity	80
8.1	Chelate Ring Size	81
8.2	Macrocycle Hole Size	85
8.3	Preorganization	88
8.4	Conclusions	89
9	Spectroscopy	91
9.1	Vibrational Spectroscopy	92
9.2	Electronic Spectroscopy	94
9.3	EPR Spectroscopy	100

9.4	NMR Spectroscopy	106
10	Electron Transfer	108
10.1	Redox Potentials	108
10.2	Electron Transfer Rates	112
11	Electronic Effects	114
11.1	d-Orbital Directionality	115
11.2	The <i>trans</i> Influence	117
11.3	Jahn–Teller Distortions	118
12	Bioinorganic Chemistry	123
12.1	Complexes of Amino Acids and Peptides	123
12.2	Metalloproteins	124
12.3	Metalloporphyrins	125
12.4	Metal–Nucleotide and Metal–DNA Interactions	127
12.5	Other Systems	129
12.6	Conclusions	130
13	Organometallics	131
13.1	Metallocenes	132
13.2	Transition Metal–Allyl Systems	135
13.3	Transition Metal–Phosphine Compounds	136
13.4	Metal–Metal Bonding	137
13.5	Carbonyl Cluster Compounds	139
14	Compounds with s, p and f Block Elements	141
14.1	Alkali and Alkaline Earth Metals	141
14.1.1	Crown Ethers	141
14.1.2	Cryptands	142
14.1.3	Spherands	143
14.1.4	Biologically Relevant Ligands	143
14.2	Main Group Elements	144
14.3	Lanthanides and Actinides	145
14.4	Conclusions	147
	References for Part II	148
	Part III: The Practice of Molecular Mechanics	155
15	Developing a Force Field	156
15.1	Introduction	156
15.2	Bond Length Deformation	157
15.3	Valence Angle Deformation	159
15.4	Torsion Angle Deformation	161

X	<i>Contents</i>	
15.5	Out-of-plane Deformation	163
15.6	Van der Waals Interactions	163
15.7	Electrostatic Interactions	164
15.8	Hydrogen Bonding Interactions	166
15.9	Summary	166
16.	Carrying Out the Calculations	168
16.1	Setting up a Starting Model	168
16.2	Energy Minimization Procedures	169
16.3	Scanning Potential Energy Surfaces	171
16.4	Mapping Potential Energy Surfaces	171
17	Interpreting and Using the Results	173
17.1	Structural Outcomes	173
17.2	Energy Outcomes	174
	References for Part III	176
	Appendices	179
	Glossary	180
	Fundamental Constants, Units and Conversion Factors	186
	Software and Force Fields	188
	Subject Index	193