

Contents

1	Introduction	1
1.1	Quantum Theory and the Chemical Bond	1
1.2	Analyzing Scalar Fields	3
1.3	Topological Analyses	6
	References	7
2	Topological Spaces	9
2.1	Topological Spaces	9
2.2	Dynamical Systems (DS)	13
2.2.1	Critical Points of a Scalar Field	14
2.2.2	Basins, Separatrices and Induced Topologies	19
2.3	Topological Invariants (Advanced)	21
	References	28
Part I Descriptors		
3	The Electron Density	31
3.1	Introduction	31
3.2	Topological Analysis of ρ	35
3.3	Properties at Critical Points	42
3.3.1	The Density at a Bond Critical Point	43
3.3.2	Ellipticity	44
3.3.3	Bond Radii	45
3.4	The Quantum Theory of Atoms in Molecules	46
3.4.1	Surface Terms	47
3.4.2	Hermiticity	49
3.4.3	Time Evolution of Open Systems	54
3.4.4	Equations of Motion in Open Subsystems	62
3.4.5	One-Electron Atomic Observables	66
3.4.6	Atomic Properties	70
3.4.7	Transferability of Atomic Properties	75
3.5	Reduced Density Matrices and Multielectron Descriptors	77

3.5.1	The Pair Density	78
3.5.2	Energy: Interacting Quantum Atoms	82
3.5.3	Pair Density and Electron Localization	88
3.5.4	Domain-Averaged Fermi Holes and Natural Adaptive Orbitals	92
3.5.5	Other Density and Reduced Density-Based Descriptors	95
	References	98
4	Electron Pairing Descriptors	103
4.1	Introduction	103
4.2	The Pauli Principle	105
4.3	The Electron Localization Function (ELF)	107
4.3.1	Definition	107
4.3.2	Prototype Bond Types	123
4.3.3	Analyzing ELF Results	125
4.3.4	IQA for ELF	139
4.3.5	ELF, Orbitals and Others	143
4.4	Other Localization Descriptors	150
4.4.1	The Laplacian of the Electron Density	151
4.4.2	The Pair Density	162
4.4.3	ELI	166
4.4.4	LOL	168
4.4.5	Electron Pair Localization Function (EPLF)	170
	References	171
5	Weak Interactions	175
5.1	Introduction	175
5.2	Insight from Previous Tools	176
5.2.1	QTAIM	176
5.2.2	ELF	178
5.3	The Non-covalent Interactions Index (NCI)	181
5.3.1	Definition	181
5.3.2	General Shape of s	183
5.3.3	When to Use NCI	190
5.3.4	Analysis of NCI Results	198
5.4	Other Descriptors	212
5.4.1	LED	212
5.4.2	DORI	213
5.4.3	Comparison	213
	References	215

Part II Applications

6	Molecules	221
6.1	Structure	221
6.1.1	QTAIM	221
6.1.2	ELF	226
6.1.3	NCI	228
6.2	Reactivity	231
6.2.1	Catastrophe Theory	231
6.2.2	QTAIM	233
6.2.3	QTAIM+ELF	236
6.3	Trying to Go Predictive	241
6.3.1	QTAIM	242
6.3.2	ELF	244
6.3.3	NCI	246
	References	249
7	Solid State	253
7.1	Periodicity and Topology	253
7.1.1	Topological Features	254
7.1.2	Crystal Properties	258
7.2	Structure	260
7.2.1	QTAIM	260
7.2.2	ELF	269
7.2.3	NCI	277
7.3	Phase Transitions	279
7.3.1	QTAIM	280
7.3.2	ELF	283
7.3.3	NCI	286
7.4	Experimental Densities	288
7.4.1	QTAIM	288
7.4.2	NCI	290
7.4.3	ELF	292
	References	294

Part III Exercises

8	Algorithms and Software	301
8.1	Algorithms	301
8.1.1	CP Location	301
8.1.2	Basin Integration	303
8.2	Available Software	309
8.2.1	AIMAll	310
8.2.2	ToPMoD	311
8.2.3	NCIPLOT	311
8.2.4	CRITIC2	313

8.2.5	NCIMilano	313
References	314
9	Exercises	317
9.1	Topology	317
9.1.1	Exercises	317
9.2	Before Starting: Obtaining the Electronic Structure Files	317
9.2.1	Molecular Calculations: The wfn File	317
9.2.2	Solid-State Files	318
9.3	AIMAll	320
9.3.1	Basic Instructions	320
9.3.2	Running AIMQB	321
9.3.3	Visualizing Results	321
9.3.4	Exercises	324
9.4	TopMod	328
9.4.1	Basic Instructions	328
9.4.2	Exercises	334
9.5	NCIPLLOT	337
9.5.1	Basic Instructions	337
9.5.2	Exercises	342
9.6	CRITIC2	350
9.6.1	Basic Instructions	350
9.6.2	Exercises	354
References	356
10	Solutions	359
Epilogue	397
Index	401