

Index

a

- active orbitals 192
- Al₂Cu 374
- aliphatic nucleophilic substitution 366
- antibonding 24
- aromaticity, Jahn–Teller distortions, resonance structures, and 3c/2e bonding 111–114
- asphericity shifts and breakdown of standard X-ray model 311–313
- atomic graph 293, 330
- atomic shells and cores 358
- atoms in molecules (AIM) 170, 173, 176
- primary and secondary energy contributions 10–11
- quantitative bonding analyses and quasi-atoms in molecule 10
- quasi-atomic molecules 11–13
- atom transfer reactivity 188–189

b

- basins 351, 352–353
- basis set superposition error (BSSE) 207
- Bent's rule 103
- benzene 209–214
- Berkowitz–Parr relationship 258
- bifurcation diagrams 350–351
- binding energy as sum of two intra-atomic and five interatomic contributions 42
- interatomic Coulombic contributions 40–41
- interatomic interference contributions 41–42
- overall resolution 39–40
- binding energy contributions synergism along dissociation curve 27
- exact quasi-atomic orbitals 30

- optimal spherical approximation by scaled orbitals 29
- zeroth order approximation by hydrogen atom orbitals 27, 29
- block-localized wavefunction (BLW) 79–80, 199–201
- exemplary applications
- – benzene 209–214
- – butadiene 214–216
- – ethane 217–221
- – H₃B–NH₃ 221–223
- methodology evolutions
- – BLW method at DFT level 204–205
- – decomposing intermolecular interaction energies with BLW method 205–207
- – electron transfer probing with BLW-based two-state models 207–208
- – simplifying *ab initio* VB theory to BLW method 202–204
- bond critical point (BCP) 170, 284–295
- bond-distorted orbitals (BDOs) 211
- bonding origin at equilibrium distance 30
- contributions to binding energy 30, 31
- energy lowering
- – by electron sharing 31–32
- – by quasi-atomic-orbital deformation 32
- – general implications 33–34
- – variational perspective 32–33
- bond path 284–295
- bond polarity 163, 164
- bonds 360–361
- butadiene 214–216

c

- carbon cusp density in diamond derived by EHC model 324–325
- carbon–element bonding in CH₃–X 146–148

- CASVB method 87, 88
 - charge density distributions precision in experimental and theoretical studies 313–322
 - charge-shift (CS) bonding
 - additional factors 183–184
 - covalent bond and possibility of becoming CS bonds by substitution 184–187
 - experimental manifestations 187
 - – atom transfer reactivity 188–189
 - – electron density measurements 187–188
 - – silicon ionic chemistry in condensed phases 189–190
 - physical origins 178
 - – atomic size role 178–179
 - – Pauli repulsion pressure role 179–181
 - resonance energy 162, 163
 - scope and territory 190–192
 - chemical unicorns 124
 - closed-shell interactions 170, 292
 - complete active space self-consistent field (CASSCF) 82, 83, 88, 204
 - conceptual density functional theory 233–235
 - basics 235–238
 - perturbative approach to chemical reactivity and bond formation process 238–240
 - – Berlin's approach in conceptual DFT context 261, 262–264
 - – electronegativity equalization principle 252–256
 - – global response functions 240–242
 - – hard and soft acids and bases principle 256–261
 - – local response functions 242, 245–249
 - – nonlocal response functions 249–252
 - constrained DFT (CDFT) 201, 204–205, 208
 - core density deformations induced by chemical bonding 322–325
 - Coulomb interaction energy 296
 - Coulson–Fischer wave function 80
 - coupling force constant 302
 - covalent bonding
 - atoms in molecules
 - – primary and secondary energy contributions 10–11
 - – quantitative bonding analyses and quasi-atoms in molecule 10
 - – quasi-atomic molecules 11–13
 - conceptual reasoning 3
 - – ground state energy differences physical origin 5–8
 - – ground state physical origin 3–5
 - – kinetic and potential energies 8–10
 - electronic interaction effect in covalent electron pair bond 34–35
 - – binding energy as sum of two intra-atomic and five interatomic contributions 39–42
 - – bonding origin at equilibrium distance 45–48
 - – electron correlation contribution to H₂ bonding 48–51
 - – FORS wave function and density in terms of quasi-atomic orbitals 38–39
 - – quantitative characteristics 42–43
 - – quasi-atomic orbitals of FORS wave function 35–38
 - – synergism along dissociation curve 43–45
 - in molecules with more than two electrons 51–52
 - – binding energy analysis basis 52–53
 - – binding origin at equilibrium geometry 53, 54–57
 - – dynamic correlation effect on covalent bonding 61–62
 - – synergism along dissociation curve 57–61
 - one-electron basis 13
 - – binding energy 22–24, 27–30
 - – bonding origin at equilibrium distance 30–34
 - – delocalization and interference dependence on quasi-atomic orbitals size 18–22
 - – energy contributions quantitative characteristics 24–27
 - – molecular density resolution 16–17
 - – molecular gradient density resolution 17–18
 - – molecular wave function as quasi-atomic orbitals superposition 13–16
 - physical model quest 1–3
 - cylindrical symmetry effects 362, 363
- d**
- deformation density 279
 - modeling 316–317
 - delocalization 363–364
 - delocalization and interference dependence on quasi-atomic orbitals size 18
 - charge accumulation at bond midpoint 19
 - origin of relation between interference and quasi-atomic orbital contraction and expansion 20–22
 - total charge accumulation in bond 19–20

- density functional theory (DFT) 80, 83–87, 204–205. *See also* conceptual density functional theory
- Diels Alder addition 367–368
- different Lewis structures for different spins (DLDS) 96, 104–106, 112
- different orbitals for different spins (DODS) 96
- dihalogens bonding 144–146
- Dirac–Coulomb–Breit equation 384
- Dirac–Coulomb equation 384
- Dirac picture 384, 385
- donor–acceptor paradigm 106–110
- 3c/4e hypervalency 114–117
 - aromaticity, Jahn–Teller distortions, resonance structures, and 3c/2e bonding 111–114
 - hyperconjugative effects in bond bending 110–111
- e**
- Ehrenfest force 262
- electron counting 356
- electron delocalization energy 80
- electron density 233–239, 242, 245, 247, 249, 252, 257, 261, 262, 264
- measurements 187–188
 - multipolar expansion 315–316
- electronegativity 163, 164, 181–183, 394–396
- equalization principle 252–256
- electronic chemical potential 240
- electronic interaction effect in covalent electron pair bond 34–35
- binding energy as sum of two intra-atomic and five interatomic contributions 39–42
 - bonding origin at equilibrium distance 45–48
 - electron correlation contribution to H₂ bonding 48–51
 - FORS wave function and density in terms of quasi-atomic orbitals 38–39
 - quantitative characteristics 42–43
 - quasi-atomic orbitals of FORS wave function 35–38
 - synergism along dissociation curve 43–45
- electron localization function (ELF)
- 169–170, 173–176, 272, 273
 - calculated basin properties mathematical expressions 376
 - – basin electrostatic moments 378
 - – basin populations 376–377
 - – ELF and AIM approaches combination 378–379
 - – potential energy contributions 379
 - – probability distributions 378
 - chemical structure given by electronic structure 345
 - choices 346–347
 - definitions 347–348
 - – basins 351
 - – bifurcation diagrams 350–351
 - – ELF from experimental data 353
 - – ELF maxima 348
 - – *f*-localization domains 349–350
 - – interpretation hints 354–356
 - – quantities obtained from ELF basins 352–353
 - – sensitivity to technical details 356–357
 - – simplified forms 354
 - – terminology 351, 352
 - examples
 - – atomic shells and cores 358
 - – bonds 360–361
 - – cylindrical symmetry effects 362, 363
 - – delocalization 363–364
 - – ions 359
 - – lone pairs 361, 362
 - – molecular reactions 364–368
 - – multicenter bonds 362
 - – multiple bonds 361
 - – squeezing effects 359, 360
 - – structured cores 359
 - molecules and crystals as objects in three dimensions 345
 - perspectives 375
 - solids 369
 - – elemental metals 370–372
 - – intermetallic compounds 372–375
 - – ionic compounds 369
 - – molecular compounds 370
- electron-pair bonds global behavior 181–183
- electrostatic attraction 129–131, 134, 141, 143, 144, 146, 155
- elemental metals 370–372
- ellipticity 295
- energy decomposition analysis (EDA)
- 121–125, 301
 - basic principles 125–126
 - bonding comparison in isoelectronic N₂, CO and BF 133–135
 - bonding in diatomic molecules E₂ of first octal row E= Li–F 135–144
 - carbon–element bonding in CH₃–X 146–148
 - dihalogens bonding 144–146

- energy decomposition analysis (EDA) (*contd.*)
 - H_2 and N_2 chemical bonding 127–133
 - -NOCV
 - – analysis of chemical bonding in transition state 148–155
 - – method 126–127
- energy partitioning 295–302
- ethane 217–221
- exchange correlation energy 296, 298
- experimental density 309–311
 - asphericity shifts and breakdown of standard X-ray model 311–313
 - charge density distributions precision in experimental and theoretical studies 313–322
 - core density deformations induced by chemical bonding 322–325
 - elusive charge density 333–339
 - Laplacian topology and MO picture 330–333
 - relativistic effects on electron density topology 326–330
 - static electron density distribution bias by thermal motion 325–326
- external potential 236

- f**
 - Feynman force 262
 - f*-localization domains 349–350
 - Frank-Condon principle 208
 - free-atom orbitals choosing, as quasi-atomic orbitals 46
 - Fukui function 242, 245, 246–249, 259, 379

- g**
 - GAMESS software 201
 - Gaussian-type orbitals (GTOs) 213
 - geminal two-electron function 81
 - generalized valence bond theory 80–82
 - gradient interference density 18
 - gradient path (GP) 272, 273, 283–284, 290
 - and natural coordinates 284–286
 - ground state
 - energy differences physical origin 5–8
 - physical origin 3–5

- h**
 - H_2 and N_2 chemical bonding 127–133
 - H_2 electron pair bond binding 47–48
 - $\text{H}_3\text{B-NH}_3$ 221–223
 - hard and soft acids and bases (HSAB)
 - principle 241, 256–261
 - hardness kernel 258
 - Hartree–Fock function 77–80, 82, 83, 85, 86, 87, 91
 - Heitler–London–Slater–Pauling (HLSP) 200
 - Heitler–London energy 206, 223
 - Heitler–London Valence Bond (HLVB)
 - approach 70, 72, 73, 75
 - Hellmann–Feynman theorem 261
 - hidden bonding 355
 - HL-wave function 70
 - Hohenberg–Kohn functional 237
 - homeomorphism 300
 - Hückel rule 72
 - hybridization 70, 71, 73, 82, 83, 85, 42. *See also* natural bond orbital (NBO) view of chemical bonding
 - hyperconjugation effect 218
 - hyperhardness 242
 - hypervalency 114–117
 - hypovalency 114

- i**
 - interacting quantum atoms (IQA) 296, 301, 302
 - interaction energy 123–126, 128, 130, 141, 143, 146, 149, 155
 - intra-atomic deformation energy 24
 - interatomic surfaces 281
 - interference energies and quasi-atomic orbital contraction and expansion 25–27
 - intermetallic compounds 372–375
 - ionic bonding 159, 162, 164, 165, 168–171, 173–175, 176, 199
 - ionic compounds 369
 - ions 359

- j**
 - Jahn–Teller distortions 399

- k**
 - Kekulé structures 209, 210, 211, 214
 - kinetic and potential energies 8–10
 - kinetic interference energy 25
 - Kohn–Sham orbitals 238, 353

- l**
 - Laplacian of electron density 292–294
 - Laplacian topology and MO picture 330–333
 - Lewis-like structures of p-block and d-block elements 101, 102–104
 - Lewis structures 79, 83, 84
 - LiOH and H_2O analysis 99–101
 - localized bond orbitals 78–79
 - local-virial theorem expression 170

lone-pair bond-weakening effect (LPBWE)
180, 194

lone pairs 361, 362

m

Marcus-Hush two-state model 207–208

maximum, importance of 354–355

minimalism principle 283

molecular compounds 370

molecular fragment, with well-defined kinetic
energy 277–278

molecular orbital (MO) 69. *See also* valence
bond (VB)

– -based wave functions mapping to VB wave
functions 74–77

– block-localized wave function method
79–80

– history of rivalry with VB 69–74

– hybrid orbitals mythical conflict with
photoelectron spectroscopy 85–86

– localized bond orbitals 78–79

– natural bonding orbitals 83

– natural resonance theory 84–85

molecular reactions 364

– aliphatic nucleophilic substitution 366

– Diels Alder addition 367–368

– proton transfer in malonaldehyde 364–366

monosynaptic basin 169

multicenter bonds 362

multiconfigurational self-consistent field
(MCSCF) 82. *See also* covalent bonding

multiple bonds 361

n

natural bonding orbitals 83

natural bond orbital (NBO) view of chemical
bonding 91–92

– donor–acceptor paradigm 106–110

– – 3c/4e hypervalency 114–117

– – aromaticity, Jahn–Teller distortions,
resonance structures, and 3c/2e
bonding 111–114

– – hyperconjugative effects in bond bending
110–111

– methods 92–96

– – free atoms analysis and atoms in
molecular environments 97–99

– – Lewis-like structures of p-block and
d-block elements 101, 102–104

– – LiOH and H₂O analysis 99–101

– – unrestricted calculations and DLSDS
104–106

natural electron configuration (NEC) 93–95

natural hybrid orbitals (NHOs) 101

natural Lewis structure (NLS) 95–96

natural localized molecular orbitals (NLMOs)
95, 96

natural minimal basis (NMB) 95

natural population analysis 95

natural resonance theory 84–85, 108, 111,
113

nonnuclear attractors 333–339

nuclear Fukui function 261, 262–264

o

one-electron basis 13

– binding energy 22–24

– – contributions synergism along
dissociation curve 27–30

– bonding origin at equilibrium distance
30–34

– delocalization and interference dependence
on quasi-atomic orbitals size 18–22

– energy contributions quantitative
characteristics 24–27

– molecular density resolution 16–17

– molecular gradient density resolution
17–18

– molecular wave function as quasi-atomic
orbitals superposition 13–16

orbital amplitude 18

orbital delocalization 18

orbital interactions 122, 125–127, 131, 134,
135, 137–141, 143, 145, 147, 149, 151–155

orbital shrinkage mechanism 194

overlap-enhanced orbitals (OEOs) 211

oxidation numbers and formal charges 356

p

Pauling–Lewis VB perspective of electron-pair
bond 162–165

Pauli repulsion 122, 123, 125, 129, 130, 131,
133, 134, 137, 139, 140, 141, 142, 143, 144,
145, 146, 147, 148, 155

– pressure role 179–181

perturbative approach to chemical reactivity
and bond formation process 238–240

– Berlin's approach in conceptual DFT context
261, 262–264

– electronegativity equalization principle
252–256

– global response functions 240–242

– hard and soft acids and bases principle
256–261

– local response functions 242, 245–249

– nonlocal response functions 249–252

photoelectron spectroscopy 85–86

- polarization 206
 - effect 47
 - energy 206–207
- potential energy surfaces (PES) 3,
- potential interference energy 25
- proton transfer in malonaldehyde 364–366

- q**
- quantum atom 274–278
- quantum chemical topology (QCT) 272, 273–274
- quantum electrodynamics (QED) 384
- Quantum Theory of Atoms in Molecules (QTAIM) 233, 271–274, 319
 - bond critical point and bond path 284–295
 - energy partitioning 295–302
 - quantum atom 274–278
 - topological atom 278–284
- quantum topological molecular similarity (QTMS) 295
- quasi-atomic orbital contraction effect 46–47
- quasi-atoms in molecule 11–13
 - and quantitative bonding analysis 10
- quasi-classical interaction between atoms 24

- r**
- relativistic effects on electron density topology 326–330
- relativity and chemical bonding 383–387, 393–399
 - direct and indirect relativistic effects and spin–orbit coupling
 - – scalar-relativistic effects 387–391
 - – spin–orbit effects 391–393
- resonance interaction and kinetic energy 195
- resonance phenomenon 122
- reverse configuration interaction 208
- ring critical point (RCP) 289

- s**
- scalar-relativistic effects 387–391
- Schrödinger equation 107
- silicon ionic chemistry in condensed phases 189–190
- singular value decomposition (SVD) 12, 14
- Slater-type orbitals (STOs) 213, 314, 317
- softness kernel 258
- spherical atom Kappa formalism 314
- spin–orbit effects 391–393
- static electron density distribution bias by thermal motion 325–326
- steric repulsion 217
- strong orthogonality constraint 81

- structured cores 359
- synaptic order 352

- t**
- topological atom 278–284
- transition metals penultimate shells and ELF 373–374

- u**
- unitary transformation 78
- unrestricted calculations and DLSDS 104–106

- v**
- valence bond 69, 159. *See also* molecular orbital (MO)
 - bond types theoretical characterization 168
 - – AIM characterization of bond types 170
 - – ELF characterization of bond types 169–170
 - CASSCF wave functions 82–83
 - convergence with AIM 170–173
 - convergence with ELF 173–176
 - – and AIM 176
 - covalent bond and possibility of becoming CS bonds by substitution 184–187
 - CS bonding additional factors 183–184
 - CS bonding experimental manifestations 187
 - – atom transfer reactivity 188–189
 - – electron density measurements 187–188
 - – silicon ionic chemistry in condensed phases 189–190
 - CS bonding physical origins 178
 - – atomic size role 178–179
 - – Pauli repulsion pressure role 179–181
 - CS bonding scope and territory 190–192
 - electron-pair bonds global behavior 181–183
 - generalized valence bond theory 80–82
 - historical counting of chemical bond notion development 160–162
 - modern methods 192–193
 - Pauling–Lewis VB perspective of electron-pair bond 162–165
 - preamble to modern VB perspective of electron-pair bond 165–167
 - resonance interaction and kinetic energy 195
 - three bonding families 176, 177
 - virial theorem 193–195
- valence bond configuration interaction (VBCI) method 193

- valence bond self-consistent field (VBSCF) 192
- valence shell electron pair repulsion (VSEPR) model 293
- variational competition 3, 5–7, 9, 33, 34, 63
- variational process 5
- vertical resonance energy (VRE) 211–213
- virial theorem 9–10, 193–195
- w**
- Woodward–Hoffmann rules 247, 248
- x**
- XMVB program 201
- z**
- Zintl–Klemm concept and ELF 372–373

