

Index

a

- ab initio molecular dynamics (AIMD) 110, 111
 abpy and bpip bridged diruthenium complexes 140
 absorption intensity 28, 253, 440
 acetyl-CoA synthase activity 329
 A-cluster 329, 330
 alkene 366, 375
 anharmonic regime 52, 53, 57, 63, 69, 74, 75, 79, 82
 anion-responsive compounds 378–380
 azobenzene 366, 375, 376, 480

b

- basic FeS clusters 325–326
 benzimidazole 381, 382
 bidirectional redox active 128
 2,2'-bis(2-pyridyl)bibenzimidazole 381
 bis-bidentate 2,5-pyrazine-dicarboxylate (BL_1^{2-}) 124
 2,2'-bis(benzimidazol-2-yl)-4,4'-bipyridine (bbbpypH₂) 382
 bis(ferrocenyl)bis(mesityl)porphyrin 384
 bis(pentaammineruthenium) complex 366
 bis(trianisylamine)s 312
 bistriarylamine compounds 378
 bistriarylamine radical cations 94
 BLYP35-based pragmatic protocol 104
 B3LYP hybrid functional 302
 BNB molecule 75
 BO approximation 48, 49, 51, 58, 64–65, 72, 75, 76, 81
 bridge band 302
 bridged M₂ dimers 231
 bridged MV compounds 9
 bridging units 121, 185, 270, 297–299, 302, 304–309

c

- carbon monoxide dehydrogenase (CODH) 323, 329–331
 carbon neutrality 432, 453
 catalysis in uncoupled mixed-valence systems 414
 C₄ butadiynediyl bridge 98
 C-clusters 330
 [Cd(BPPTzTz)(tdc)] · 2DMF 399
 charge-delocalized excited state 181
 charge-transfer-induced spin transitions (CTIST) 463–465
 Chisholm 233
 chloroperoxidase 331
 chromium triazolate framework 413
cis/trans-configuration 280
 Class I ribonucleotide reductases (RNPs) 339
 CNS model 32–34, 242
 cobalt 412
 cobalt-based catalysts 416–417
 comproportionation constant 13, 122, 133, 168, 231, 350, 351
 conducting polymers of metal complexes 447–452
 copper 408
 copper-based catalysts 417
 coupled harmonic-oscillator model 48–54
 coupling integral 2, 3, 15, 16, 24, 26
 coupling regimes 49–53, 57–59, 61, 63, 65, 68–70, 73, 74, 76, 81
 covalently-bonded diruthenium complexes 9
 covalent-organic frameworks (COFs) 407–408, 442–443
 Cp'(L₂)Ru-based termini 158–163
 Creutz-Taube complexes 5, 297
 Creutz-Taube ion (CT ion) 121, 182, 272, 432
 Cross conjugation and quantum destructive effect 257
 cubane-type [4Fe-4S] clusters 325

- cyanide bridged mixed-valence (Fe–CN–Co) chromophore 464
- cyanide-bridged MMCT complexes electric dipole 474–478 molecular nanomagnet behavior 472–483 thermal expansion (TE) 478–480
- cyanide-bridged MV complex advantage 270 dinuclear 272 electron transfer and electron coupling 271 tetranuclear and higher nuclear 284–290 trinuclear 276–284
- cyanide–isocyanide configuration 274
- cynoacetylide bridging ligand (CCCN) 101
- cyclometalated diruthenium complex 452
- cyclometalated MV systems 366
- cyclopenta-ring-fused rylene π -bridged bis(dianisylamine) radical cations 304
- cytochrome c oxidase 121, 332, 333
- cytochrome c peroxidase 331, 332
- d**
- D-B-A experimental models 231
- D-B-A model 270
- D-COSMO-RS 97, 110
- degenerate MV systems 299
- density-functional theory (DFT) 48
- deprotonated 2-thiouracil 133
- dianionic 124, 126, 133
- dianionic 2,5-bis (2-oxidophenyl)pyrazine (BL_3^{2-}) bridging ligand 126
- dianionicoxamidot (2^-) bridged diruthenium(III) complex 136
- 2,5-diboryl-1,4-phenylene bridge 379
- dicarboxylates 232, 233
- 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone 401
- diethynylated diacetoxanthracene unit 385
- diethynylethene-linked di-ferrocene 376
- dihydropyrenes (DHP) derivatives 376
- dimanganese complexes 273
- 2,5-dimercapto-1,3,4-thiadiazolate (DMcT) ligand 383
- dimer of dimers 9, 141, 231, 235, 243
- dimetal tetracarboxylate 231, 233
- dimethylidihydropyrene 366, 376, 377
- dimolybdenum dimers of dimers 234
- dinitroaryl radical anions 96
- 1,3-dinitrobenzene 96, 110, 111
- dinuclear complex 100, 122, 157, 162, 163, 170, 381, 382
- dinuclear cyanide-bridged mixed-valence complex 272
- dinuclear iron-ethynyl complexes with butadiyndiyyl bridge 153–154 with non-conjugated C_4 -bridge core 156–157
- dinuclear pentaammineruthenium complex 380
- dinuclear Ru(dppe)₂ complex 385
- dinuclear ruthenium-ethynyl complexes with alternating polyyndiyil and capped Ru–Ru units 165–166
- Cp'(L₂)Ru-based termini 158–163
- ruthenium-ethynyl termini and core units 166–168 with Ru(dppe)₂X-based termini 163–165
- diprotic bridging ligand 233
- diruthenium(II) complexes 130
- dithienylethene (DTE) 366
- dithienyl perhydro/perfluorocyclopentene units 372
- divinylphylene diruthenium complex 352
- donor-bridge-acceptor molecule 378
- double exchange mechanism 315
- d(δ)(M₂)-p(π)(ligand) conjugation 235
- DTE-bridged diruthenium complex 368
- e**
- electric dipole 474–478
- electrochemical methods 13–14
- electrochromic martials (ECMs) 431
- electrochromism, defined 431
- electronic coupling 151 and electron transfer conformational effects of 252–255 distance-dependence of 247–252 hydrogen bonds 258–260 [M₂–BL–M₂]⁺ systems 247 modulation via host-guest or through-space interaction 356–361
- through hydrogen bonds between MV organic fragments 353–356 between transition metal centers 350–353
- electron paramagnetic resonance (EPR) spectroscopy 12–13
- electron transfer 269, 365 pathways 122 process 121 reactions 50
- electron-transfer-coupled spin transitions (ETCST) 463
- electron transporters 323
- energy conversion processes 4
- environmental effects 109
- enzymes' biocatalystas 323
- ethynylene 376
- exact-exchange (EXX) admixture 95

- extended mixed-valence materials
covalent-organic frameworks (COFs)
407–408
introduction to 397
naphthalenediimide-based compounds
405–406
phenalenyl-based compounds 406
tetraoxolene-based compounds 400–405
tetrathiafulvalene (TTF)-based compounds
399–400
thiazolo[5,4-*d*]thiazole (TzTz)-based
compounds 397–399
- f**
faster vibrational spectroscopic techniques
123
[FeFe]-hydrogenase 323, 326–328
Fe(II,III) MV tetranuclear cage complexes
356
ferredoxin [2Fe-2S] cofactors 349
ferridoxin 328
ferrocene-terminated azobenzene derivative
375
ferrocenyl-functionalized heterocycles 181
ferrocenyl-functionalized 5-membered
heterocycles
with group-13 elements 183
with group-14 elements 183–184
with group-15 elements 185–201
with group-16 elements 201–213
with transition metal elements 213–217
ferrocenyl-functionalized 6-membered
heterocycles 217–218
ferrocenyl methylhydantoin 5-ferrocenyl-
5-methylimidazolidine-2,4-dione 351
FeS clusters 325–326
field-free absorption spectrum 57
finite-field difference spectrum 57
first-derivative correction 59
first row transition metals 408–414
flavanthoxins 328
formamidinate ancillary ligands 233
fragile entanglement 63
fragment molecular orbitals (FMO) 304
Franck-Condon
principle 3, 395
progressions 57
transition 2, 17
free energy surfaces (FESS) 299
functionalized dinuclear iron-ethynyl
complexes 157–158
- g**
gauge problem of LHS 105
generalized Mulliken–Hush theory (GMH)
27–28
- generalized Mulliken–Hush three-state
analysis 302–303
ground-state delocalisation, Creutz-Taube ion
68–69
GS adiabatic 77
- h**
Hartree–Fock exchange 95
Hartree–Fock theory 94, 95
hemocyanins 333
hexa(dianisylamine)-substituted
hexaarylbenzene 311
5,5'(4H,4H')-spirobi[cyclopenta[*c*]
pyrrole]2,2,6,6'-tetrahydro cation
109
hole transport in a molecular conducting
material 68
homodinuclear metal-ethynyl complexes
152
horseradish peroxidase 331
Hush formula 123, 127, 128, 134
Hush model 3, 5, 14, 245, 276
HXH bond angle 47, 76, 78
hybrid functionals 95, 100, 105, 112, 302
hydrogen bond (HB) 353
BLs 11
bridged MV systems 350
hydrogen-bond acceptor (HBA) 472
- i**
inorganic MV compounds (MVCs) 396
inorganic NIR electrochromic materials
433–434
intermediate-coupling regime 51–53, 61, 63,
73, 74
intermolecular mixed-valence 298
intervalence charge-transfer (IVCT) 97, 123,
151, 298, 393
intramolecular charge transfer (CT) reaction
299
intramolecular electron transfer 2, 121, 124,
127, 232, 244, 269, 273
inverted region 20, 52, 66
iron 409
iron-based catalysts 415–416
iron-ethynyl complexes
dinuclear iron-ethynyl complexes
with butadiynediyl bridge 153–154
with non-conjugated C₄-bridge core
156–157
functionalized dinuclear iron-ethynyl
complexes 157–158
iron (Fe) nitrogenase 328
IVCT absorption 256

k

Kubelka-Munk analysis 399

l

Landau-Zener model 31, 249, 252
lanthanoids 414
Levich-Dogonadze–Marcus expression 31,
252
ligand bridged mixed valent diruthenium
complex 122
Liptay equation 57
local hybrid functionals (LHs) 100, 104
localization/delocalization 95
local mixing function (LMF) 104

m

macrocyclic tetranuclear platinum(II) complex
356
magnetic protein biocompass 323, 326
Marcus-Hush theory 25, 26, 212, 242, 248,
252, 254, 259, 262, 298, 352, 395, 398
M-BL-M 34
M₂-BL-M₂ systems 239, 240, 247, 256
McConnell's theory 6
McConnell superexchange expression 32–34
metal-based mixed valency
catalysis 414–418
first row transition metals 408–414
metal complexes 444–447
metal-metal charge transfer (MMCT) 272
metal(M₂)-metal(M₂) coupling 239
metal-metal quadruple bonds 230, 262
metal to ligand charge transfer (MLCT) 192,
195, 239, 368, 464
metal-to-metal charge transfer (MMCT)
cyanide-bridged MMCT complexes
472–483
switchable cyanide bridged MMCT systems
465–472
meta-para paradigm 310
mixed-valence (MV) chemistry
analysis of IVCT band shape 28
attraction of 2
BO approximation 64–65
compounds 1
coupled harmonic-oscillator model 48–54
definition 1
diversity of 6–12
electric fields on MV optical band shapes
56–58
electrochemical methods 13–14
electronic coupling matrix element and the
transition moments 26–27
electron paramagnetic resonance
spectroscopy 12–13

electron transfer in 3
Generalized Mulliken–Hush theory (GMH)
27–28
history 4–6
from localized to delocalized 16–17
McConnell superexchange mechanism and
the CNS model 32–34
molecules and iconic model systems
ground-state delocalisation,
Creutz–Taube ion 68–69
hole transport in a molecular conducting
material 68
MV excited states in a bis-metal complex
66–68
photochemical charge separation 66
photochemical charge separation during
bacterial photosynthesis 70–73
MV complexes as potential quantum qubits
60–63
non-adiabatic effects 58–60
optical analysis 14–15
origins within chemical bonding theory
47–48
potential energy surfaces from classical
two-state model 18–20
prominent feature of 6
quantum description of the potential energy
surfaces 20–24
reorganization energies 24–26
solvent control of electron transfer 17–18
stereoisomerism
ammonia 75–79
aromaticity in benzene 80–81
BNB molecule 75
proton-transfer reactions 79
pyridine 74–75
mixed-valence complex 34, 231, 232, 254,
272–275
mixed-valence (MV) compounds 365
mixed valence diruthenium dimers 260–262
mixed-valence iron-sulfur clusters in biological
and bio-mimic systems
basic FeS clusters 325–326
carbon monoxide dehydrogenase 329–331
[FeFe]-hydrogenase 326–328
nitrogenases 328–329
mixed-valence metal complexes 323
mixed-valence multi-copper cofactors 332
mixed-valence multi-manganese cofactors
339
mixed-valence phenomena 4
mixed valence systems
diversity of 6
Multiiron-contained biological systems
331–332
mixed-valence (MV) systems 93, 349

- mixed valency
 classifications of 395–396
 fundamental aspects of 393–394
 Marcus-Hush theory 395
 organic 396
 quantum mechanical considerations 394–395
- $\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CC}_6\text{H}_5)$ 242
 $\text{Mo}_2(\text{DAniF})_3(\text{S}_2\text{CC}_6\text{H}_5)$ 242
 $\text{Mo}_2(\text{DArF})_4$ 230
 $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ 230
 MOF nanozymes 417–418
 molecular nanomagnets 472–474
 molecule-based materials 463
 molecules and iconic model systems
 ground-state delocalisation, Creutz-Taube ion 68–69
 hole transport in a molecular conducting material 68
 MV excited states in a bis-metal complex 66–68
 photochemical charge separation 66
 photochemical charge separation during bacterial photosynthesis 70–73
 molybdenum (Mo) 414
 nitrogenase 328–329
 monolayer and multilayer assembled films 452–453
 monoruthenium complex 373
 Mulliken charge transfer theory 5
 Mulliken–Hush expression 5, 13, 15, 26, 27, 34, 241, 262, 352
 Mulliken–Hush formalism 16
 Mulliken–Hush treatment 93
 Mulliken–Hush two-mode analysis 301–302
 multi-configuration self-consistent-field (MCSCF) approaches 94
 multicopper oxidase (MCO) 333, 334
 multidimensional organic MV systems 315
 MV copper(I/II) systems 408
 MV excited states in a bis-metal complex 66–68
 MV tetraoxolene frameworks 403
- n**
 naphthalenediimide-based compounds 405–406
 near-infrared electrochromic materials
 applications
 military camouflage 454
 molecular logic gates and optical storage 453
 optical communication 453–454
 smart windows 453
 inorganic NIR electrochromic materials 433–434
- organic-inorganic hybrid NIR
 electrochromic materials 444–453
 organic NIR electrochromic materials 435–443
 near-infrared (NIR) electrochromism 431
 neutral in cation geometry (NCG) method 240
 nitrogenases 323, 328
 nitrous oxide reductase 333
 N,N' -dimethyl-4,4'-bipyridinium 359
 N,N' -dimethylpiperidine (DMP^+) 108
 non-adiabatic corrections 59
 non-adiabatic effects 58–60
 non-adiabatic weak-coupling limit 60
 norbornadiene 366, 367
- o**
 octacyanometallates 466
 oligo(*p*-phenylene)(OPP) 306, 308
 oligoacene-bridged MV systems 308
 one-electron oxidation 133, 232
 one-electron reduction of $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$ 127
 organic conducting polymers 439–441
 organic-inorganic hybrid NIR electrochromic materials
 conducting polymers of metal complexes 447–452
 metal complexes 444–447
 monolayer and multilayer assembled films 452–453
 organic mixed-valence systems
 bridging units and electronic coupling 304–309
 charge and/or spin localization 315
 delocalization 315
 electronic coupling 299
 generalized Mulliken–Hush three-state analysis 302–303
 history of 297–298
 intramolecular charge transfe 299
 IVCT band 303
 Mulliken–Hush two-mode analysis 301–302
 redox centers 310–311
 through-bond or through-space 311–313
 organic mixed valency 396
 organic NIR electrochromic materials
 covalent organic framework 442–443
 organic conducting polymers 439–441
 triphenylamine derivatives 437–439
 viologen derivatives 435–437
 organoboron systems 378
 organometallic mixed-valence (MV) complexes 151
 organometallic MV systems 103
 organometallic Ru (II/III) building blocks 6

- oxido/carboxylato and oxido/pyrazolato bridged diastereomeric 138
- oxygen (O) centered triruthenium cluster 10
- oxygen evolution complex (OEC) 323, 336
- oxygen evolving center (OEC) 12, 3336
- p**
- peroxidases 331, 332
- phenalenyl-based compounds 406
- phenothiazine (PTZ) electron donor 374
- phenylene bridged Mo₂-Mo₂ series 247
- photochemical charge separation 66
during bacterial photosynthesis 70–73
- photoinduced multielectron charge transfer process 284
- photoswitchable MV compounds 365
- polycyanometallates 465, 466, 470–472, 481, 483
- polynuclear complexes 121
- polyoxometalate-based catalysts 416
- polyoxometalates (POMs) 412
- polyoxovanadates (POVs) 412
- porphyrins 384
- potential-energy surfaces 50
- proton-coupled electron transfer (PCET) 12, 328, 351
- proton-responsive compounds 380–385
- proton-transfer reactions 79, 328
- prussian blue analogues (PBAs) 465
- putative magnetic receptor 326
- pyrazine (pz) bridged mixed-valent Ru^{II}Ru^{III} state 124–130
- pyridine 74–75
- q**
- quadruply-bonded dimolybdenum compounds 350
- quadruply-bonded M₂ complexes 229
- quadruply-bonded M₂ unit 229, 230
- quantitative analysis 51, 53, 73, 79, 82
- quantum-chemical approaches 94
- quantum conductance 355
- quantum entanglement 46, 51, 60, 81
- quantum information systems 60
- r**
- redox-active centers 297–299, 302, 314, 418
- redox-inactive alkylammonium-based counterions 404
- reorganization energy 24–26, 299
- Resonant valency 4
- respiratory complex IV 332
- Rieske proteins 325
- rigid wire-like metal diynediyl complexes 152
- Robin-Day classes 17, 93, 98, 240–247
- Robin-Day's classification 5, 16, 30, 69, 94, 232, 464
- of MV compounds 16
- Ru(dppe)₂Cl]⁺ (dppe = 1,2-bis(diphenylphosphino)ethane) moieties 371
- Ru^{III}Ru^{IV} mixed valent systems 135–139
- Ru^{II}Ru^I and Ru^{II}Ru⁰ mixed valent systems 139–141
- Ru^{II}Ru^{III} mixed valent systems
deprotonated 2-thiouracil 133
diruthenium(II) complexes 130
oxido bridged diruthenium complex 134
pyrazine derived bridges 124–130
- Ru(dppe)₂X-based termini 163–165
- Rydberg orbitals 47
- s**
- scanning tunneling microscopy break junction (STMBJ) technique 355
- single-chain magnets 473, 476
- single-molecule magnets 473, 474
- spin-density distributions 107, 127, 138, 159
- spiro cation 109
- star-shaped tri-Ru complex 453
- state-interaction pair-density functional theory (SI-PDFT) 109
- stereoisomerism
ammonia 75–79
aromaticity in benzene 80–81
BNB molecule 75
proton-transfer reactions 79
pyridine 74–75
- strong-coupling regime 51
- superexchange model 2
- superexchange pathway 122
- switchable cyanide bridged MMCT systems 465–472
- symmetric diruthenium complex 383
- t**
- TDDFT 97, 102, 105, 107, 108
- terephthalaldehyde (PDA) 407
- tetracyanoquinodimethane (TCNQ) 297, 298
- N,N',N',N'-tetrakis(4-aminophenyl)-1,4-benzenediamine (TPDA) 407
- tetrakis(4-methoxyphenyl)benzidine (MeO-TPD) 379
- tetrakis(dianisylamine)-substituted tetraazacyclopahne 314
- tetranuclear and higher nuclear cyanide-bridged mixed-valence complex 284–290
- tetraoxolene-based compounds 400–405
- tetraruthenium metallacycle 352

- tetrathiafulvalene (TTF) 297
 based compounds 399–400
- thermal expansion (TE) 478–480
- thiazolo[5,4-*d*]thiazole (TzTz)-based
 compounds 397–399
- thieno[3,2-*b*]thiophene-2,5-
 dicarbaldehyde (TTDA) 407
- thienylene bridging ligand 244
- thioacetyl-terminated diruthenium alkynyl
 complex 372
- three-redox-centered MV system 314
- through-bond IVCT 394
- tppz bridged diruthenium complexes 128
- transition-metal complexes 100
- transition metal-ethynyl complexes
- dinuclear Group-8 (Os) and Group-9 (Co)
 metal-polyyndiyi complexes 170–171
 - dinuclear group-6 (Cr, Mo) metal-ethynyl
 complexes 168–169
 - dinuclear group-7 (Mn, Re)
 metal-polyyndiyi complexes
 169–170
- transition-metal MV systems 97
- transition state theoretic model (TST) 30
- triarylamine-based (TAA) MV systems 99
- triarylamine derivatives 353, 368, 385
- triarylamine-dithienylethene-acetylide ligands
 373
- triarylamine-terminated dithienylethene
 derivatives 369
- 2,5,8-tri(4-pyridyl)-1,3-diazaphenalenone
 (TPDAP) 406
- trinuclear cyanide-bridged MV complexes
 276–284
- triphenylamine derivatives 437–439
- triphenylamine dimer 372
- tris(4-aminophenyl)amine (TAPA) 407
- TTF-based ligand tetrathiafulvalene
 tetrabenzoate (TTFTB) 399
- two coupled diabatic potential-energy surfaces
 46
- 2D honeycomb chloranilate frameworks 403
- 2D tetraoxolene honeycomb frameworks 401
- U**
- unimolecular mixed-valence D-B-A systems 8
- urea-bridged cyclometalated diruthenium
 complex 378
- ureido pyrimidinedione (UPy) derivatives 355
- V**
- valence tautomerism (VT) 463, 464
- valency oscillation 4
- vanadium (V) nitrogenase 328–329
- variable optical attenuator (VOA) 453
- vertical reorganization energy 395
- vertical transition energy (IVCT) 53, 240
- vinyl-functionalized ruthenium-amine
 complex 450
- viologen derivatives 435–437
- Vivianite 4
- W**
- wild-type (WT) 71, 72
- Wurster-type redox system 298
- X**
- XE cyanide-bridged MMCT complexes
 photochromis 480
- XE photochromis 480
- Z**
- Zimmerman's system 355