

Index

a

absorption spectrum 7
 adiabatic rapid passage 4
 alternating linewidths 98
 aminoxyl (nitroxide) radicals 287
 amorphous hydrogenated silicon 17, 56–57
 amplifier, coil driver
 – *see also* scan driver 9
 – heating 22, 28
 – push-pull 25
 amplitude, scan rate dependence 9–11
 anticrossing 86
 AWG (arbitrary waveform generator) 11, 31
 axial Maier–Saupe potential 81

b

B_1 9, 10, 20, 55
 background 28–33
 – removal 37–41
 bandwidth 10, 41
 – *see also* resonator bandwidth 10
 – signal 43, 45
 basis 75
 basis choices in Liouville space 76
 BDPA (α,γ -bis(diphenylene- β -phenylallyl)) 17, 20, 31
 Bloch equations 20, 76
 – Bloch sphere 100
 Bloch magnetization vector propagation 97
 BMPO-OOH 40, 42, 52–54

c

C_{60} 57
 3-carbomyl-2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl (Carbomyl-TEMPYRO) 292
 carbomyl-TEMPYRO 292
 $Ce^{3+}(4f^1)$, SH Parameters 246
 Chebyshev approximation 102

Chebyshev polynomials 86
 chemical exchange 94
 – electron transfer 98
 – general exchange theory 99
 – intermolecular exchange 98
 – intramolecular exchange 98
 – multisite exchange 99
 – mutual exchange 98
 chirp 11
 choke coils 30
 Clebsch–Gordan series 76
 $Co^{2+}(3d^7)$, SH parameters 213–215
 $Co^{3+}(3d^6)$, SH parameters 211
 continuous wave 3
 correlation NMR 4
 coupling between two electron spins 74
 $Cr^+(3d^5)$, SH parameters 189
 $Cr^{2+}(3d^4)$, SH parameters 185
 $Cr^{3+}(3d^3)$, SH parameters 176–183
 $Cr^{3+}(3d^3)$ glasses, SH parameters 183
 $Cr^{4+}(3d^1)$, SH parameters 174
 $Cr^{5+}(3d^1)$, SH parameters 142
 crystal field theory 92
 crystals 80
 CSL 293–294
 CTPO (3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolinyl-1-oxyl) 11

d

DANO 292
 data format
 – BES³T 114
 – ESP 114
 data formats 114
 – JCAMP-DX 114
 deconvolution 6, 17–20
 density matrix 75

density operator 75
 diamond defects 17, 58
 dianisyl-nitroxide (DANO) 292
 direct detection 5, 62
 direction cosines matrix 79
 distance distribution 108
 – MtsslWizard 108
 – PRONOX 108
 double-balanced mixer detection 7
 double-quantum coherence 103
 doubly nitroxide-labeled 96
 down-conversion 15
 DOXYL 293
 3-doxyl-17-hydroxy-5 α -androstane (CSL)
 293–294
 DPPH 4, 20
 DTBN, di-tert-butyl nitroxide 289
D tensor 92
 Dy³⁺(4f⁹), SH parameters 266

e

E 92
E^{prime} defect in quartz 7, 16, 55
 eddy currents 28, 30, 32, 35
 eigenfield 84
eigenframe or *principal-axes frame* 78
 electron spin coupling
 – Heisenberg–Dirac–van Vleck Hamiltonian 74
 – biquadratic exchange 74
 – coupling matrix 74
 – dipole–dipole coupling 74
 – Dzyaloshinskii–Moriya interaction 74
 – isotropic exchange coupling 74
 electron spin relaxation times 7, 17, 20
 electron spin resonance software database (ESDB) 71
 ENDOR
 – ¹H ENDOR 105
 – ⁵⁵Mn ENDOR 105
 – coils 28, 30, 31
 – Davies ENDOR 106
 – detection envelopes 107
 – high-spin pulse ENDOR 107
 – hyperfine enhancement 106
 – inversion pulse 106
 – resonator 32
 – selectivity 106
 ENDOR/transition intensity
 – Boltzmann polarization 106
 energy level crossings 86
 energy level diagram 84
 EPR simulation programs 70
 equations of motion 76

Er³⁺(4f¹¹), SH parameters 266
 Ernst equation 58
 error analysis 109
 ESEEM
 – rf-driven 103
 Eu²⁺(4f⁷), SH parameters 251–254
 Euler angles 79
 exchange
 – Heisenberg exchange 94
 exchange interactions 21

f

fast-motion limit 94
 fast-motion regime 94
 Fe²⁺(3d⁶), SH parameters 211, 212
 Fe³⁺(3d⁵), SH parameters 189–197
 Fe⁵⁺(3d³), SH parameters 184
 Fermi contact 73
 field modulation 78
 field-swept echo detection 57–58
 filter
 – Butterworth 20
 – comb 15
 – low-pass 20
 filtering 114
 – analog 114
 – Savitzky–Golay 114
 finite-element methods 104
 Floquet theory 103
 Fourier transform 41
 Fourier transformation 93
 frames 78
 Frank–Condon factor 88
 free induction decay 3
 Fremy's salt 20
 frequency, 250 MHz 12, 13, 19, 35
 frequency scans, microwave 5, 11, 64
 frequency-sweep 93
 frequency-to-field conversion factor 84, 88
 frozen solution 79, 81
 FT-EPR 57–58

g

Gd³⁺(4f⁷), SH parameters 254–264
 glasses 81
 global dynamics 97
g-matrix 73
g-matrix/*g*-factor
 – nuclear *g*-factor 73
 gradient smoothing 93

h

Hall probe 21
 Hellmann–Feynman theorem 91

high-field limit 98
 high-spin systems 102
 Hilbert space 75
 hindered rotation 99
 $\text{Ho}^{3+}(4f^{10})$, SH parameters 266
 homogeneous 90
 homogeneous broadening 20, 21
 hybrid models 88
 17 β -hydroxy-4,4-dimethylspiro
 (5 α -androstane-3,2'-oxazolidin)-3'-yloxy
 293
 4-hydroxy-TEMPOL 290
 hyperfine (hf) interaction 73
 hyperfine coupling matrix *A* 73
 HYSORE 101

i

image reconstruction
 – filtered back projection 60
 – maximum entropy method 61
 – regularized optimization 61
 inhomogeneous 90
 inhomogeneous broadening 6
 interpolation schemes 83
 ions, detected by EPR 139, 140
 irradiated tooth 5

j

Jacobi diagonalization 86
 Jahn–Teller pseudorotation 99

k

Kramers-Kronig relation 42

l

Lanczos methods 104
 Larmor precession 76
 least-squares fitting 108
 – bacterial foraging 111
 – error function 110
 – fitting algorithms 110
 – Gauss–Newton 110
 – genetic (evolutionary) algorithm 111
 – Hooke and Jeeves pattern search 111
 – Levenberg-Marquardt 111
 – metropolis algorithm 111
 – Nelder–Mead 111
 – neural network models 111
 – nonlinear least-squares methods 112
 – parameter values 110
 – particle-swarm optimization 111
 – Powell's conjugate gradient method 111
 – principal component analysis 112
 – systematic grid searches 112

line broadening
 – dipolar broadening 91
 – Pake broadening 91
 – strain
 – – strain broadenings 91
 line broadenings 90
 linear response regime 18
 lineshape
 – Voigt function 92
 – pseudo-Voigt profile 92
 – convolution 92
 – Gaussian function 92
 – Holtzmark 92
 – lineshapes 92
 – Stoneham 92
 – Tsallis distribution 92
 Liouville basis
 – basis of irreducible spherical tensor
 operators 76
 – Cartesian Zeeman product operator basis
 76
 Liouville space 75
 Liouville–von Neumann (LvN) equation 77
 LiPc (lithium phthalocyanine) 8, 9, 18, 20,
 60, 61
 Litz wire 22, 23, 28
 looping transitions 86
 Lorentzian function 92
 Lorentzian lineshape 44

m

magic angle spinning 103
 magnet
 – air-core 23
 – four-coil 21
 – Helmholtz 21
 – iron-core 23
 magnetic dipole–dipole coupling 73
 magnetic field
 – gradients 60
 – homogeneity 21
 – modulation 3
 magnetic isotopes 77
 – structural and kinetic isotope effects 78
 magnetically concentrated 20
 matrix diagonalization 85
 – extrapolation 85
 – Hermite cubic spline interpolation 85
 – homotopy 85
 – least-squares fitting 85
 – root-finding algorithms 85
 mechanical vibrations 30, 33

methoxy-TEMPO 291
 4-methoxy-2,2,6,6-tetramethylpiperidine-
N-oxyl 291
 mHCTPO 13, 47–50
 250 MHz 3, 12, 13, 19, 35
 microphonics 33
 microwave power 50
 Mims matrix 101
 $\text{Mn}^{2+}(3d^5)$, SH parameters 198–209
 $\text{Mn}^{2+}(3d^5)$ glasses, SH parameters 210
 $\text{Mn}^{3+}(3d^4)$, SH parameters 186–188
 $\text{Mn}^{4+}(3d^3)$, SH parameters 184
 $\text{Mn}^{5+}(3d^2)$, SH parameters 174
 $\text{Mo}^{3+}(4d^3)$, SH parameters 245
 $\text{Mo}^{5+}(4d^1)$, SH parameters 244
 modulation broadening 7
 modulation coils, Bruker 22, 46
 molecular dynamics 95
 MOMD 96
 Monte Carlo 99
mosaic misorientation linewidth model 83
 MTSSL/MTSL 291

n

N@C_{60} 57
 NARS (nonadiabatic rapid sweep) 5, 62
 $\text{Nd}^{3+}(4f^3)$, SH parameters 247–250
 Newton–Raphson method 90
 $\text{Ni}^+(3d^9)$, SH parameters 244
 $\text{Ni}^{2+}(3d^8)$, SH parameters 215–217
 nitroxide (aminoxyl) radicals 287
 NMR 103
 noise 17
 – reduction 15
n-SASL, oxazolidine-*N*-oxyl stearic acid 294
 nuclear electric quadrupole moment 73

o

objective function 109
 organic radicals 109
 oscillations (see also wiggles) 6, 22
 oxazolidine spin label
 N-oxyl-4',4-methyloxazolidine 293
 oxazolidine-*N*-oxyl stearic acid 294
 (1-Oxyl-2,2,5,5-tetramethyl- Δ^3 -pyrroline-3-
 methyl) methanethiosulfonate
 (MTSSL/MTSL) 291

p

Padé approximation 102
 parallelization 103
 parameter space 91
 passage effects 4
 path integrals 82

$\text{Pd}^+(4d^9)$, SH parameters 246
 periodic signal 15, 16
 perturbation theory 87
 – Scalar perturbational expressions 87
 powder sample 79
 power saturation 9, 16
 projection techniques 93
 propagator matrices 102
 pseudomodulation 20
 pulse EPR 81
 – integration window 103
 – multifrequency 103
 – product rules 103
 – pulse DEER 108
 pulsed EPR 3, 45, 54–58

q

quadrature detection 41
 – mixer 41
 – nonorthogonality 40
 quantitative EPR 13
 quaternions 79

r

rapid scan 3–64
 – acquisition parameters 42–45
 – background 28, 32, 37–42
 – bridge 41
 – coil driver 24–29
 – coils 22, 24, 28, 46–50
 – deconvolution 18–20, 64
 – digital 11, 13
 – driving function 18
 – Fourier transform NMR spectroscopy 3
 – imaging 59–62
 – multifrequency 46
 – post-acquisition treatment 17–20
 – scan rate selection 45
 – signal bandwidth 43, 45, 46
 – signal-to-noise advantage 14, 15, 17,
 53–58, 64
 – simulation 8–10, 20
 – sinusoidal 11, 19, 24, 28, 29, 34, 40–41, 64
 – T_2 measurement 51, 52
 – trapezoidal 21
 – triangular 11, 17–18, 25–28, 37–38, 64
 Redfield–Wangsness–Bloch relaxation theory
 95
 reduced spin system 106
 reference frame
 – lab frame 79
 – *molecular frame* 79
 references (chapter 4) 270–286
 relaxation times 45, 54, 58

- resistance, AC 23
- T_1 46
- T_2 6, 21, 44, 46, 50, 52
- T_2^* 3, 6, 43–45

resonator

- 250 MHz 35, 36
- bandwidth 10, 43
- cross-loop 33, 42
- design 32–41
- dielectric 33–35, 46, 47
- isolation 33
- Q 11, 33, 35, 43–46
- rectangular 33, 34
- shield 30
- split-ring 33, 34
- $\text{Rh}^+(4d^8)$, SH parameters 245
- $\text{Rh}^{2+}(4d^7)$, SH parameters 245
- rigid limit* 80
- rigidly attached labels 97
- rotational dynamics 79, 94
- correlation time τ_c 94

S

- saturation-transfer EPR 4, 89
- $\text{Sb}^{2+}(5s_25p_1)$, SH parameters 269
- scan coils 21–24, 46–49
- scan driver
 - sinusoidal 6, 27–29
 - triangular 6, 25–28
- Schrödinger equation 76
- second-harmonic out-of-phase detection 5
- segmental acquisition of spectra 4, 63
- semiquinones 13
- signal-to-noise advantage 3
 - *see also* rapid scan 3
- simulation noise 93
- simulations software
 - DDPOW 71
 - DIPFIT 71
 - E-SpiReS 71
 - EasySpin 70
 - EPRNMR 71
 - EPRSIM-C 71
 - EPRsim32 71
 - EWVoigt 71
 - GENDOR 71
 - HYSORE 71
 - MAGRES 71
 - Molecular Sophe 71
 - OPTESIM 71
 - QPOW 71
 - Sim 71
 - SimBud 71
 - SimFonia 71
 - SIMPOW6 71
 - SIMPSON 72
 - Sophe 71
 - SPIN 71
 - Spinach 72
 - SpinCount 71
 - SPINEVOLUTION 72
 - WinMOMD 71
 - WinSIM 71
 - Xemr 71
 - XSophe 71
- slow and intermediate motion
 - regime 94
- slow-scan spectrum 6, 18
- $\text{Sm}^{3+}(4f^5)$, SH parameters 250
- smoothing 114
- sodium in liquid ammonia 4
- solid-state cw EPR 75
- Sparse matrix methods 104
- spherical grid 81
 - igloo grid 82
 - analytical 82
 - Delaunay triangles 82
 - Fibonacci grid 83
 - icosahedral 83
 - iteratively generated grid 83
 - Lebedev grids 83
 - numerically optimized 82
 - octahedral 83
 - randomly generated 82
 - Voronoi cells 82
 - Zaremba–Conroy–Wolfsberg scheme 83
- spin basis
 - coupled basis 75
 - eigenbasis 75
 - uncoupled Zeeman 75
- spin echo 100
- spin Hamiltonian 72
 - isotropic 89
- spin Hamiltonian, non-zero coefficients of
 - spin operators for various symmetries 139
- spin quantitation 113
- spin relaxation 76
- spin system 72
- spin trapping 40, 52–54
- spin–orbit coupling 72
- spin-relaxation 94
- SRLS 96
- stochastic dynamics 95
 - Brownian rotational diffusion 95
 - jump diffusion 95
- strain
 - A strains 92
 - D strain 92

- strain (*contd.*)
 - *g* strain 91
 - spin–strain tensor 92
- strains 91
- sum of squared deviations 109
- superhyperfine (shf) interactions 90
- superoperator 75
 - *Liouville superoperator* 77
 - chemical exchange superoperator 77
 - stochastic relaxation superoperator 77
 - super-Hamiltonian 84
 - Zeeman superoperator 84
 - zero-field superoperator 84
- symmetry 80
 - Laue classes 80
 - molecular symmetry group 80
 - space group 80
- t**
 - TANOL 290
 - TCNQ 5, 62
 - TEMPO 291
 - TEMPOL 290
 - TEMPONE 290
 - tempone- d_{16} 19, 50, 51
 - 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (TEMPOL) 290
 - 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) 291
 - 2,2,6,6-tetramethylpiperidinone 1-oxyl (TEMPONE) 290
 - $Ti^{2+}(3d^2)$, SH parameters 175
 - $Ti^{3+}(3d^1)$, SH parameters 142, 143
 - Tikhonov regularization 108
 - time domain 94
 - $Tm^{3+}(4f^3)$, SH parameters 268
 - transition field 84
 - transition frequencies 105
 - transition intensity
 - Fermi’s Golden Rule 88
 - nuclear overlap matrix 88
 - spin transition moment 88
 - thermal polarization 89
 - transition probability 88
 - transition preselection 86
 - transition metal complexes 92
 - transition probability 81
 - triangle projection 83
 - triplet spectra 82
 - trityl radical 13, 44, 60
 - tunneling 99
- u**
 - uncertainty analysis 14
- v**
 - $V^{2+}(3d^3)$, SH parameters 184
 - $V^{3+}(3d^2)$, SH parameters 175, 176
 - $V^{4+}(3d^1)$ glasses and solutions, SH parameters 143–146
 - $V^{4+}(3d^1)$, SH parameters 146–148
 - vanadyl porphyrin 7
 - $VO^{2+}(3d^1)$, SH parameters 148–160
 - $VO^{2+}(3d^1)$ glasses, SH parameters 161–173
- w**
 - W-band 11
 - wiggles 4, 6
 - Wigner functions 96
 - Wigner rotation matrices 79
- y**
 - $Yb^{3+}(4f^{13})$, SH parameters 269
- z**
 - Zeeman interaction 72
 - electron 72
 - higher order electron Zeeman terms 73
 - nuclear Zeeman interaction 73
 - zero-field spin-Hamiltonian parameters(ZFSHP), common notations 140, 141
 - zero-field splitting 74
 - B_{kq} 74
 - O_{kq} 74
 - zero-field tensor D 74