

Subject Index

A

A_n spin system 32
 A_2B_2 spin system 123
 A_2X_2 spin system 123
AA'BB' ($[AB]_2$) spin system 70, 124
AA'XX' ($[AX]_2$) spin system 124
AB spin system 74, 77, 118, 307, 312
 AB_2 spin system 120
ABC spin system 125
ABX spin system 121
 AK_2 spin system 120
AMX spin system 31, 121
AX spin system 27, 116
 AX_2 spin system 29, 120
 AX_n spin system 30
Absolute value 15, 256, 257
– see also Magnitude spectrum
Absorption 7
– signal 15
Abundance, isotopic 3
Accumulation 16, 35
Acetylacetone 68
– keto-enol Tautomerism 326
Acetylation 146, 154
Acetylene, magnetic anisotropy 48, 42, 66
Acid anhydrides 68
Acids 59, 68
Acquisition time 17
Activation energy (Arrhenius, E_A) 312
Activation enthalpy (ΔH^\ddagger) 313
Activation enthalpy, free (ΔG^\ddagger) 313
Activation entropy (ΔS^\ddagger) 313
Activation parameters, limits of error 314
Additivity (of substituent effects)
– see Substituent increments 141 ff.
Alcohols 59, 327, 340
Aldehydes 48, 58, 67, 95, 319
Alkali metals 40, 81
Alkali earth metals 40, 81
Alkanes 54, 59, 141, 148, 170
Alkenes 49, 56, 63, 142, 151, 340
Alkynes 49, 57, 66, 96
Allenes 66, 96
Allowed transitions 7, 118, 291
 α -effect 62

Amides, hindered rotation in 319
Amidines, hindered rotation in 320
Amines 59, 340
Amino acids 69
Aminoboranes, hindered rotation in 320
Amplification factor (NOE) 204, 208, 213
– see also Enhancement factors 293
Amplifier 21
– see Pulsed NMR Spectrometer 18
Angular momentum (of nucleus) 2
Anisotropy effects (on δ) 47, 145
Annulene, [18]- 50, 324, 326
APT – see Attached proton test 200
Arenes 49, 56, 64, 95, 99, 143, 153
Aromaticity 50
Arrhenius equation 312
Assignment of 1H and ^{13}C signals 139–159
Asymmetrical atom 75, 321
Atropisomerism 76
Attached proton test (APT) 181, 200, 286
– see also Spin-echo, J-modulated
Average excitation energy (ΔE) 45

B

Back-folding 21
Base pairs 361
Benzene 49, 52, 100
– disubstituted 70
– isotope effect (deuterium) 51
– ring current 49
– solvent anisotropic 51
 β -effect 62
Biopolymers 355–365
Biosynthesis studies 369–380
BIRD sequence 217
Bloch equation 13, 172
Boltzmann constant 6, 313
Boltzmann distribution 6
Bond angle and $J(H,H)$ 87, 87
Boron (^{10}B , ^{11}B) NMR 38, 79
Broad-band decoupling
– see Decoupling, 1H broad band 133
Brownian motion 46
Bullvalene, valence tautomerism 325

C

Calcium NMR (^{43}Ca) 81
Carbohydrates 146
Carbon, isotopes of 3
Carbonyl group, magnetic anisotropy of 49
Carr-Purcell pulse sequence 173
Carr-Purcell-Meiboom-Gill pulse sequence 387, 389
C,H-COSY 247 – see also HETCOR
Chair conformation, cyclohexane 91, 315
Charge density 44
Chemical equivalence 114
Chemical exchange – see Dynamic NMR Spectroscopy 305
Chemical shift 22, 43–84
– anisotropy (CSA) 254
– averaging of 46, 51, 60, 305 ff.
– definition 24
– δ -scale 24
– dependence on
– – anisotropic neighbors 47
– – charge density 44
– – electric field 47, 51
– – hydrogen bonding 51, 145
– – pH 378
– – magnetic field strength 4
– – ring current effects 49, 323
– – solvent 47, 51, 69, 145, 154
– – substituents 47, 53 ff.
– – temperature 145, 154
– empirical correlations for predicting 141, 148
– heavy atom effect on 62, 65, 65, 66
– reference 24, 26
– typical values for
– – ^{13}C 45
– – ^1H 44
Chiral molecules 72, 340
Chiral shift reagents 340
Chiral solvents 342
Coalescence temperature 306
Cobalt NMR (^{59}Co) 40
Complex formation 336
Complex pulse sequences 181–229
Composite pulses 134
Computer 21, 125
– programs for
– – DNMR spectroscopy 310
– – spectrum analysis 125, 156
Conformational analysis 90
Connectivities 225, 257
Contact interaction 336
– see also Fermi contact term
Continuous-wave (CW) method 8
Contour plot 236

Contrast agent (Gd^{3+}) 390
Coordinate system, rotating 10
Cope rearrangement 325
Copolymers 352
Correlation peaks 256 – see also Cross peaks
Correlation time 163, 290
COSY (correlated spectroscopy) 246–278
– see also C,H-, H,C-, H,H-COSY
– reverse 263
Coupling – see Spin-spin coupling 26, 85–109
Coupling constant, indirect or scalar 26, 85–109
– absolute value 86
– averaged 90–92
– correlation between $J(\text{C,H})$ and $J(\text{H,H})$ 101
– direct 27, 354
– residual 136
– sign 33, 86, 88, 103, 117, 122
– – definition 117
Cross peaks 256
Cross-polarization, -relaxation 278, 280
Cryomagnet 9
CW (Continuous wave) method 8
Cycloalkanes 55, 62, 88, 91, 97
Cycloalkenes 97
Cyclohexane (d_{11})
– coupling constants 91, 96
– ring inversion 315, 322
Cyclopropane 55, 62, 87, 88, 91, 93, 97

D

2D NMR spectroscopy – see Two-dimensional NMR spectroscopy 231–288
Data
– accumulation 16
– acquisition 17
– banks 156
– points 35
– storage 17
Decay curve 14 – see also FID
Deceptively simple spectra 126
Decoupling 129, 145, 154
– gated 135
– ^1H broad-band 133
– ^1H off-resonance 136, 286
– ^1H selective 137, 145, 154
– heteronuclear 133
– heteronuclear selective 137
– homonuclear 130
– inverse gated 135
– with composite pulses (CPG) 134
Degassing 167, 178, 297
Delay time 164, 187
 δ -scale 24, 377
DEPT 218–222, 286

Detection 21
 Detector, phase-sensitive 20
 Deuteration 52, 60, 74, 146, 154, 168, 315
 Deuterium NMR (^2H) 17, 40, 52, 78
 Deuterium isotope effects 52
 Diads 350
 Diagonal peaks 256
 Diamagnetic shielding term 44
 Diastereomers 72
 Diastereotopic groups (or protons) 74
 Difference spectroscopy (NOE) 296
 Digitization 21
 Dihedral angle 89, 99
 Dimethylformamide
 – NOE 289, 298
 – DNMR 305, 311, 313
 Dipolar coupling 26, 231, 276, 293
 Dipolar relaxation 162, 291
 Dipol, nuclear 2
 Directional quantization 4
 Dispersion signal 15, 256
 DNA (deoxyribonucleic acid) 360
 Double cone for
 – precession 4, 6, 12
 – magnetic anisotropy effects 48
 Double helix 361
 Double quantum coherence 226, 281
 Double quantum transition 8, 226, 291
 Double resonance experiments 129–138
 Dynamic NMR Spectroscopy (DNMR)
 305–333

E

Echo 173, 191, 200 – see also Spin-echo
 Effective magnetic field 22
 Electric field effects (on δ) 47, 51
 Electric quadrupole moment (Q) 3, 40, 105, 354
 – see also Relaxation 163; Line-width 177
 Electromagnet 9
 Electron-nuclear coupling 102, 337
 Electronegativity effects 54, 89, 93
 Emission 7, 204
 Enamines, hindered rotation in 320
 Enantiomers 72 – see also Chiral molecules
 Enantiotopic groups 74
 Energy
 – activation (E_A) 312
 – levels 6, 116, 290
 – of magnetic dipoles 5
 Enhancement factors 293
 Enrichment, ^{13}C 155, 370 ff.
 – see also Isotopic labeling
 Enthalpy of activation (ΔH^\ddagger) 313
 – free (ΔG^\ddagger) 313

Entropy of activation (ΔS^\ddagger) 313
 Entropy process 172
 Equilibration processes 329
 Equilibrium 6, 161
 – constant 314
 Equivalence 70
 – chemical 114
 – magnetic 114
 Ethane, derivatives
 – chemical shifts 54, 62
 – hindered rotation 314
 – vicinal coupling 89
 Europium(III) chelate complex 335 ff.
 Ethanol, proton exchange 327
 Evolution phase 232
 Exchange 60, 276 – see Dynamic
 NMR Spectroscopy 305
 – intermolecular 308, 316, 327
 – intramolecular 305 ff.
 Excitation energy, average (ΔE) 45, 49, 66
 EXSY 276, 327
 External standard 25
 Eyring equation 313

F

Fermi contact term 102
 FID (Free induction decay) 14
 Field
 – frequency stability 17
 – gradients, linear 187
 – homogeneity 17, 20
 – inhomogeneities 17, 172, 177
 – sweep 8
 First-order process 162, 306
 First-order spectrum 33
 Fluorine (^{19}F) 39, 80
 Flux density, magnetic 4, 9
 Folding 21, 39
 Forbidden transitions 8, 226, 291
 Fourier transformation 14, 382 ff.
 – two-dimensional 235
 Four-spin systems
 (A_2B_2 , A_2X_2 , $AA'BB'$, $AA'XX'$) 124
 Free induction decay (FID) 14
 Frequency
 – domain spectrum 15
 – sweep 8
 FT – see Fourier transformation 14

G

γ -effect 62
 Gated decoupling 135
 Geminal coupling 87, 87

Glucose 92, 329
Gradient
– phase 383
– read 383
– slice selecting 383
Gradient-echo experiment 191
Gradient, pulsed field 187–191, 381
Gradient-selected (gs-)HMBC 269
Gradient-selected (gs-)HMQC 269
Gradient-selected (gs-)TOCSY 274
Gyromagnetic ratio 2, 104, 203, 293
– negative 40

H

Half-height width 35, 177
Hammett constants 65, 148
H,C-COSY 263
H,D coupling 104
Heavy atom effect 62, 65, 66
Heisenberg's uncertainty principle 177
Heteronuclear couplings 106 ff.
Heteronuclides
– see "Other" Nuclides 38, 78, 106
HETCOR (C,H-COSY) 247–255
Heterotactic triads 350
H,H-COSY 255–261, 284
– long-range 261
High-resolution NMR 1
– of solids 46
Hindered rotation 76, 305, 317 ff.
HOHAHA 223 – see also Selective TOCSY
Homogeneity, field 17, 20
Homonuclear decoupling 130
Homotopic groups 74
Hückel rules 50
Hund's rule 103
Hybridization and coupling constants 86, 87, 97
Hydrogen bonding 60, 69, 326
Hydroxyl proton/group 60, 145, 170, 326, 327
HMBC (gs-) 269, 358
HMQC 263
HSQC 263

I

Imaginary part of signal 16
INADEQUATE
– one-dimensional 225–228, 286
– two-dimensional 281–285, 286
Incremental relationships 54, 140 ff.
– see also Substituent increments
Inductive effects 43, 54, 98
INEPT 205–218
– refocussed 209

– reverse 213–218
Inhomogeneity, field 172, 177
Insensitive nuclides 2, 9, 16, 203, 293
Integral, Integration 34
Intensities in multiplets 31
Intensity 34
– of ^{13}C signals 35
– of ^1H signals 34
– enhancement through NOE 36, 293
Interferogram (FID) 14
Internal standard 24, 78
Inversion
– of ring compounds 315, 322
– at N and P atoms 321
Inversion recovery method 164, 367
In vitro experiments 370–374
In vivo experiments 375–380
Iron NMR (^{57}Fe) 38, 82
Isochronous nuclei 75, 115
Isotactic polymers, diads, triads 349
Isotope effects 51, 155
Isotope-selective pulse 215
Isotopic abundances 3
Isotopic labeling 40, 100, 155, 362, 370 ff.
– double (^{13}C) 373
Iteration 125

J

J-modulated spin-echo 192–200, 286
J-values 85–109 – see Spin-spin coupling

K

Karplus relationship 90, 360
Keto-enol tautomerism 68, 326
Ketones 67
Kinetic measurements – see Dynamic NMR spectroscopy 305–333

L

Labeling – see Isotopic labeling 155, 359, 370 ff.
Lamb formula 44
Lanthanide shift reagents 335–345
Laocoon III program 310
Larmor precession frequency 4, 7
Lifetime
– in dynamic processes 309
– of spin state 105, 130, 177
Line broadening 105, 164, 358 – see also Line-width
Line shape 15, 35
– analysis, complete 309
– Lorentzian 177
Line-width 35, 172, 177

Lock unit 17
Long-range coupling 85, 96, 99
Long-range COSY 261
Longitudinal relaxation 13
LSR (Lanthanide shift reagents) 335–342

M

Macromolecules 169, 347–368
Magic angle 355
Magic angle spinning (MAS) 355
Magnesium NMR (^{25}Mg) 81
Magnet 9, 18, 348
– large bore 357
Magnetic equivalence 114
Magnetic flux density 4, 9
Magnetic field
– alternating 10
– effective 22
– gradients 187, 381 ff.
– homogeneity/inhomogeneity 17, 172, 378
– static 4
Magnetic moment 2
– induced 47
Magnetic quantum number 4
Magnetic resonance microscopy 384
Magnetic resonance spectroscopy, ^1H MRS
390–392
Magnetic resonance tomography, imaging (MRI)
380–392
Magnetization
– macroscopic 6, 10, 162
– transfer 204, 249
– transverse 11, 184
Magnitudes spectrum 15, 256
MAS, magic angle spinning 355
McCConnell equation 48
Mesomeric effects 46, 63
Mesomeric limiting structures/
canonical forms 56, 65, 305
Metabolites 376
Mixing phase, time 233, 236, 253
Molecular motions 46, 163, 298
– anisotropic 170
Molecular size, effect on T_1 169
Multiplets 26 ff. – see also Spin-spin coupling
Multiplicity rules 30
Multislice procedure 386
Mutarotation 329

N

Natural abundance 3, 225
Negative signal 12, 256
Newman projection formulas 75

Nitrogen NMR (^{14}N , ^{15}N) 38, 79
NMR
– discovery of 1
– dynamic (DNMR) 305–333
– high-resolution 1
– microscopy 384
– pulsed 9
– in solids 1, 27, 46, 353
– tomography, imaging 380–392
– two-dimensional 231–288
NOE (Nuclear Overhauser Enhancement/Effect)
36, 163, 276, 289–303, 358 ff.
– dependence on
– – gyromagnetic ratios 293
– – internuclear distance 293
– difference spectroscopy 296, 298
– indirect 294
– suppression of 37
NOESY 276–280, 286, 302
Noise 16
– decoupling – see Decoupling, ^1H broad-band 133
Non-equivalent nuclei 114
Nuclear magnetic resonance – see NMR
Nuclear Overhauser effect/enhancement
– see NOE 289–303
Nuclear spin 2
Nuclei
– chemically equivalent 114
– equivalent 32, 70, 104
– isochronous 75, 115
– magnetically equivalent 114
Nucleus
– angular momentum of 2
– magnetic moment of 2
– spin of 2
Nuclides
– insensitive 2, 9, 203, 208, 293
– properties of (table) 3
– sensitive 2, 8, 203, 208, 293
Nyquist frequency 21

O

Off-resonance decoupling 136
Oligosaccharides 362–365
Optical purity 342, 343
Order of a spectrum 33
“Other” Nuclides 36, 78, 106
Overhauser effect (NOE)
– electron-nuclear 290
– nuclear 289–303 – see also NOE
Oxygen
– dissolved 167, 178, 298
– nuclear properties 3
Oxygen NMR (^{17}O) 36, 80

P

Paramagnetic species 37, 163, 167, 298, 335
– see also Lanthanide shift reagents;
Oxygen, dissolved
Paramagnetic shielding term 45, 66
Parts per million, ppm 25
Pascal's triangle 31
Pascual-Meier-Simon rule 142
Pauli exclusion principle 103
Pentads 346
Peptides 356–360
Permanent magnet 9
PFG 18, 188 – see Pulsed field gradient 187
pH within the cells 378
Phase coherence 12, 172
Phase correction 16
Phase cycle 216
Phase-sensitive detector/detection 20, 256
Phenols 60
Phosphorus NMR (^{31}P) 38, 81
– *in vivo* 376
Planck constant 2
Platinum NMR (^{195}Pt) 82
Point dipole model 48
Polarization transfer 202–218
Polymers 343–350
Polynucleotides 360–362
Populations (of Energy levels) 6, 12, 174,
202 ff., 290
Potassium NMR (^{39}K) 81
Precession 4
– classical picture of 4, 6
– frequency 4
Preparation phase 232
Presaturation 217
PRESS (point resolved Spectroscopy) 391
Probe-Head 19
Prochiral center 77, 321
Progressively connected transitions 118
Projection, filtered back 381, 383
Proteins 356–360
Protein structures
– sequence, primary 357
– three-dimensional, secondary 358 ff.
Protonation 51
Proton exchange 327
– alcohols 327
– ammonium ions 329
Pseudo-asymmetric carbon atom (in polymers) 348
Pseudocontact interaction 336
Pulse 9
– angle 10
– duration (length, width) 9
– generator 9

– “hard” 10
– power 36
– repetition rate or time 37
– “soft” 224, 382
Pulsed field gradients (PFG) 18, 187, 217, 375, 381
Pulsed gradient Spin Echo Experiment 200–202
Pulsed NMR-spectrometer 18
Pulsed NMR Method 9

Q

Quadrature detection 21
Quadrupolar broadening 105, 178
Quadrupolar relaxation 163
Quadrupole moment, electric 3, 40, 105
Quantitative analysis 35
Quantum number
– angular momentum 2
– magnetic or directional 4
Quarternary carbon atoms/nuclei 136

R

Radio-frequency (r.f.) field 7
Rate constant 276, 307, 309
Reaction pathways in biochemistry 370–374
Real part of signal 15
Receiver 20
– see The Pulsed NMR Spectrometer 18
Reduced coupling constant 136
Reference compound 24
Reference spectra 156
Regressively connected transitions 118
Relaxation 13, 161–179, 290, 385
– agents 37
– by chemical shift anisotropy 162
– by paramagnetic species 37, 163, 335
– by quadrupolar nuclei 163
– by scalar coupling 162
– by spin rotation 162, 169
– dipolar 162, 168, 291, 293
– longitudinal (Spin lattice) 13
– mechanisms 162
– transverse (Spin-spin) 13
Relaxation time
– longitudinal or spin-lattice T_1 36, 154,
162–171, 385
– – measurements 150
– transverse or spin-spin T_2 171–178, 385
– – measurements 173
Repetition rate/time (pulse) 35
Resolution 177, 244, 375
– digital 36
Resonance 7
Resonance condition 7, 23, 381

Reverse H,C-COSY 263
– HMBC (gs-) 269
– HMQC 263
– HSQC 263
Reverse INEPT 213
Ring current effects 49, 323
Ring inversion 315, 322
Ring size effects 94, 97, 169
ROESY 276–280, 358, 365
Roof effect 28, 118, 118
Rotating coordinate system 10
Rotation 168, 317
– hindered 76, 305, 318
– rapid 90, 318
Rotation barriers 318
Rotational isomers 75, 90

S

Sample changer 19
Sample tubes, coaxial 19
Satellites in
– ¹³C spectra 225, 281
– ¹H spectra 33, 126, 137
Saturation 7, 133
– transfer 130
Scalar coupling 28 – see also Spin-spin coupling
Segmental mobility 170
Selection rules 8
Selective decoupling 137
Selective population inversion (SPI) 202–205
Selective TOCSY 223
Sensitive nuclides 2, 9, 203, 208, 293
Sensitivity 3, 181, 203, 375
Shielding anisotropy 46
Shielding constant 22 – see also Chemical shift
Shielding term
– diamagnetic 44
– paramagnetic 45
Shift reagents 335–345
Shim coils 20
Shoolery's rule 54, 141
Signal broadening 105, 177, 305, 335
– see also Line-width 177
Signal-to-noise ratio (S:N) 16
Silicon NMR (²⁹Si) 82
Single quantum transition 8
Slice selection 363
Sodium NMR (²³Na) 40, 81
Solid state NMR 353–355
Solvents
– chiral 338–340
– deuterated 132, 295
– effects on δ 47, 51, 145, 154
– suppression of signals 132, 171

Spectral width 10, 36, 40, 80
Spectrometer
– CW 8
– pulsed 18
Spectrum
– accumulation 16
– first-order 33
– higher-order 33, 112, 126
– simulation 123, 124, 125
– zero-order 33
Spectrum analysis 111–127
– computer-aided 125, 156–158
SPI (Selective population inversion) 202–205
Spin (of nucleus) 2
Spin decoupling 129 – see Decoupling
Spin density (of unpaired electron) 336
Spin-echo 173, 192, 385
– J-modulated 192–200
Spin functions 5
Spin-lattice relaxation 13 – see also Relaxation
Spin-lock 224, 273, 279
Spin-orbit coupling 62
Spin-rotation relaxation 162
Spin-spin coupling
– H,H; C,H 26, 85–109
– – dipolar/direct 27, 276
– – equivalent nuclei 104
– – geminal (H,H) 87, 98
– – indirect 26, 28, 85–109
– – long-range 96, 99
– – mechanisms 102
– – π -electron effects on 78
– – reduced 136
– – s-fraction effect on 97, 102
– – sign of, definition 86, 103, 117, 122
– – substituent effects on 93, 97
– – temperature dependence of 91
– – through space 106
– – vicinal
– – (C,H) 97
– – (H,H) 89–95, 101
– C,C 225, 370–374
– H,D 104
– heteronuclear 106
– P,P 377
Spin-spin relaxation 13 – see also Relaxation
Spin systems, nomenclature 113
Spin-tickling 132
Stacked plot 236
Standard, Reference compound 24, 26
– external 25
– internal 24
Stereoregularity (of polymers)
– see Tacticity 348–351
Steric effects 62, 149

Sub-spectra
– ABX 122
– DEPT 218
Substituent increments 54, 141, 148
Sugars 92
Suppression of the water signal 132, 171,
331, 391
Surface coils 375
Susceptibilities 48
Sweep (CW) 8
Symmetry 70, 111, 123
Syndiotactic polymers, diads, triads 349

T

T₁ 13, 162 – see Relaxation time,
longitudinal or spin-lattice
T₂ 13, 171 – see Relaxation time,
transverse or spin-spin
Tacticity 348–351
Taft constants 65, 148
Temperature effects on
– δ 145, 154
– J 91
– populations of energy levels 6
Tetrads 351
Tetramethylsilane 24
Thioamids, hindered rotation in 319
Three-spin systems
(A₃; AB₂; AK₂; AX₂; ABX; AMX) 29, 31
Time-averaged spectra 46, 60
– see Dynamic NMR Spectroscopy 305
Time domain spectrum 15
Tin NMR (¹¹⁹Sn) 82
TOCSY 273–275, 364
– selective 223
Tomography, magnetic resonance 380–392
Torsion angle 86 –
see also Dihedral angle 89–93
Transition metals 82

Transitions
– allowed 8, 118, 291
– double quantum 8, 226, 291
– forbidden 8, 226, 291
– progressively/regressively connected 118
– single quantum 8, 291
– zero quantum 7, 226, 291
Transmitter frequency 8, 20
Transverse relaxation T₂ 13
Triads 350
Triple resonance experiments 131
Tritium NMR (³H) 78
TROSY 359
Two-spin systems (A₂; AB; AX) 27, 116–119
Two-dimensional (2D) NMR spectroscopy 231–288
– J-resolved 241

U

Unpaired electrons 163, 336

V

Valence tautomerism 325
Vicinal coupling
– (C,H) 97
– (H,H) 87–93
Volume selection, selectivity 375, 379, 381
Voxel 384

W

Walden inversion 321, 329
WIN-DAISY (program) 310

Z

Zeeman levels 5
Zero-crossing point 167, 171
Zero quantum transition 8, 226, 291