

## Index

### a

acquisition time 48, 49, 52, 53, 60, 61, 317, 318, 353–354  
 active coupling 248  
 aldehydes 83, 89, 105  
 aliphatics  
   saturated  
     alkanes 85–86  
     functionalized alkanes 86–87  
     structural units 85, 86  
   unsaturated  
     aldehydes 89  
     alkenes 88–89  
     alkynes 87  
 alkanes  
   acyclic  
      $\alpha$ ,  $\beta$ , and  $\gamma$  effects 98–99  
     butane fragment, anti and gauche geometries 101  
     carbon-13 chemical shifts 100, 101  
     methylene carbons 100  
   cyclic 101  
   cyclopropane 85–86  
   functionalized  
     carbon substituent parameters 102, 103  
     chemical shifts 101–102  
     in 1,3-dichloropropane 102, 103  
     methyl groups 86–87  
 alkenes 88–89, 103–104  
 alkynes 87, 104  
 apodization 61, 62  
 APT. *See* attached proton test (APT)  
 aromatics  
   anisole and pyridine 90

nitrobenzene 89  
 nitro group 89–90  
 pyridine and pyrrole 104–105  
 attached proton test (APT)  
   C–H couplings 311  
   double-resonance procedure 201  
   drawbacks 312  
   homonuclear decoupling experiment 202  
   methyl and methine carbons 312  
   proton irradiation 202, 203  
   pulse sequence 311  
   spectral editing experiment 202–203  
   spin vectors 201–202

### b

BB decoupling 43, 57  
 bilinear rotation decoupling (BIRD)  
   sequence 257, 331  
 BIRD. *See* bilinear rotation decoupling (BIRD) sequence  
 BIRD-HMQC  
   delay time (DT) 259  
   pulsed field gradients 257  
   selection of signals from protons 258, 259  
 Bloch equations  
   absorption and dispersion mode 394  
   Cartesian components 391  
   linearly oscillating frequency 393  
   magnetization components 391–392  
   phase relationship 394  
   positive and negative absorption 394, 395

- Bloch equations (*contd.*)  
 positive and negative dispersion 394, 395  
 rotating coordinate system 392  
 Bloch–Siegert shift 191  
 Boltzmann's law 3  
 BURP (Band selective, Uniform Response, Pure phase) 217

## C

- calibrations  
 decoupler field strength 72–73  
 pulse width (flip angle) 70–72  
 CAMELSPIN 266  
 carbon–carbon correlation  
 C,C–COSY 269  
 1D INADEQUATE experiment 268  
 2D INADEQUATE spectrum of menthol 268–270  
 INEPT–INADEQUATE 270  
 carbon–carbon single bond 81  
 carbon chemical shifts and structure  
 carbonyl groups 105  
 electronegativity of groups 97–98  
 empirical calculations 105  
 factors influencing 96–98  
 heavy atom effect 98  
 multiple bonding 98  
 paramagnetic shielding 96–97  
 saturated aliphatics  
 acyclic alkanes 98–101  
 cyclic alkanes 101  
 functionalized alkanes 101–103  
 unsaturated compounds 103–105  
 alkenes 103–104  
 alkynes and nitriles 104  
 aromatics 104–105  
 carbon connectivity  
 INADEQUATE spectrum 212–213  
 one-bond  $^{13}\text{C}$ – $^{13}\text{C}$  coupling 212  
 carboxyl protons 29  
 CASE. *See* computer-assisted structure elucidation (CASE)  
 chemical and magnetic equivalence 435  
 AA'XX' system 128, 130  
 alkenic protons in cyclopropene 127, 128  
 bromochloromethane, protons in 127  
 2-chloroethanol 130  
 deuterium 127  
 diastereotopic protons 131–132  
 1,2-dichlorobenzene 129  
 difluoroethene or difluoromethane, protons in 126–127, 128, 129  
 effect of methyl rotation 131  
 magnetic nonequivalence 129, 130  
 3-methylcyclopropene 127  
 Newman projections 130  
 NMR spectrum, role of symmetry 126  
 chemical shielding anisotropy 31, 418  
 chemical shift  
 alkenes 108–109  
 aromatics 109  
 carbon (*See* carbon chemical shifts and structure)  
 carbonyl compounds 110  
 CW field sweep 9  
 empirical calculations 105  
 isotope effects  
 1,4-dioxane 95–96  
 in undeuterated dioxane 96  
 medium effects  
 aromatic solvent-induced shifts 94, 95  
 electric-field effect 94  
 intermolecular shielding 92  
 methyl chemical shifts 95  
 in *N,N*-dimethylformamide 95  
 solute and solvent 92–93  
 solute methane 94  
 methyl acetate  
 $^1\text{H}$  spectrum and  $^{13}\text{C}$  spectrum 6, 7  
 resonances 7, 8  
 methyl and methylene groups 106–107  
 of nucleus 8–9  
 proton (*See* proton chemical shifts and structure)  
 resonance frequency 6  
 saturated ring systems 107–108  
 shielding 6  
 spectral conventions 9–10  
 tetramethylsilane 8, 9  
 $^{13}\text{C}$  NMR data

- chemical shifts and number of attached protons 368
- high-resolution mass spectrum 368–369
- spectrum of T-2 toxin 366, 367
- coherence-level diagrams
  - COSY experiment 427–428, 430–431
  - 2D INADEQUATE experiment 432–433
  - double quantum coherence 426
  - DQF-COSY 432
  - in-phase and the antiphase terms 428–430
  - inversion recovery experiment 428
  - NOESY and EXSY experiments 431–432
  - pulse sequences 426–427
  - single quantum coherences 426
  - transformation of antiphase magnetization 426
  - two-spin coherence 425–426, 427
  - zero quantum coherence 426
- COLOC. *See* correlation spectroscopy *via* long-range coupling (COLOC)
- combination line 147
- composite pulses 215
- computer-assisted structure elucidation (CASE) 382–383
  - procedures 383–384
  - T-2 toxin
    - correct and incorrect structures 386
    - NMR data 387
    - one- and two-dimensional NMR raw spectral data 384–385
- continuous-wave (CW) field sweep 9, 39
- correlation spectroscopy (COSY)
  - basic COSY 326–327
  - contour representation of 242
  - COSY 45 experiment 247–248, 327
  - COSY 90 experiment 247
  - DQF COSY 328–329
  - J* coupling, proton-proton correlation 237, 238
  - LR COSY 328
  - molecular fragments 371–372
  - NMR data 370–371
  - for other nuclides 254
  - stacked representation 241–242
  - TOCSY experiment 371
- correlation spectroscopy *via* long-range coupling (COLOC)
  - FLOCK sequence 260
  - of vanillin 260, 261
- COSY. *See* correlation spectroscopy (COSY)
- coupling constants
  - carbon 155–156
  - chemical and magnetic equivalence 126–132
  - in 1-chloro-4-nitrobenzene 16, 17
  - couplings over one bond 134–135
  - diethyl ether 18, 20
  - double resonance 23
  - first-order spectra 16–17, 18–19, 20, 21, 125–126
  - geminal couplings 136–138
  - geminal proton–proton (H–C–H) 153–154
  - 3-hydroxybutyric acid 22, 23
  - indirect spin–spin coupling 17–18
  - isotope satellites 150–151
  - long-range couplings 143–146
  - nitrogen-15 156
  - one-bond 152–153
  - Pascal's triangle 19, 20–21
  - proton decoupling 22, 23
  - second-order spectra 21, 125–126, 147–148
  - shift reagents 150
    - paramagnetic 150
  - signs and mechanisms
    - direct coupling 133
    - Fermi contact mechanism 132, 133
    - Pauli Exclusion Principle 132–133
  - spectral analysis 146–147
  - 1,1,2-trichloroethane 18, 19
  - vicinal couplings 139–142
  - vicinal proton–proton (H–C–C–H) 154–155
  - virtual coupling 149–150
- covariance NMR 358
  - direct 358–359
  - generalized indirect
    - advantages 361
    - HSQC–TOCSY spectra of T-2 toxin 360–361

- CP. *See* cross polarization (CP)
- cross polarization (CP) 32
- cross polarization and magic angle spinning (CP/MAS) 33
- <sup>13</sup>C spectral editing experiments
- APT experiment 311–312
  - DEPT experiment 312–313
- CW field sweep. *See* continuous-wave (CW) field sweep
- d**
- 1D and advanced 2D experiments
- covariance NMR
    - direct 358–359
    - generalized indirect 360–361
  - 1D NOESY and ROESY experiments 347
  - 1D TOCSY experiment
    - comparison spectra 346
    - four-spin system of T-2 toxin 345–346
    - parameters 347
  - H2BC experiment 348–352
  - multiplicity-edited HSQC experiment
    - expansions of 348, 349
    - pulse sequence 347–348
  - nonuniform sampling 352–355
  - pure shift NMR 355–358
- data-acquisition parameters, 2D
- acquisition time 317
  - flip angle 318
  - number of data points 316–317
  - number of scans per time increment 319
  - number of time increments 317
  - receiver gain 318–319
  - relaxation delay 318
  - spectral widths 317
  - transmitter offset 318
- data display, 2D
- phasing and zero referencing 324–325
  - symmetrization 325
  - use of cross sections in analysis 325
- data-processing parameters, 2D
- digital resolution 321–322
  - linear prediction 322–324
  - weighting functions 319–321
  - zero filling 321
- deceptive simplicity 147–148
- decoupler field strength 72–73
- decoupler modulation frequency 73
- decoupling 23
- delayed COSY 248–249, 279
- delays alternating with nutation for tailored excitation (DANTE) experiment 217
- density functional theory (DFT) 92
- DEPT. *See* distortionless enhancement by polarization transfer (DEPT) experiment
- depth gauge 42
- deshielding 78, 79
- deuterium 44
- deuterium lock system 44
- DFT. *See* density functional theory (DFT)
- 2D HMQC spectrum 271
- diamagnetic 75
- diamagnetic anisotropy 78
- diamagnetic shielding 96
- diastereotopic groups
  - chemical shifts 441
  - coupling constant criterion 441
  - diastereotopic ligands 440
- difference decoupling spectrum 190
- diffusion ordered spectroscopy (DOSY)
  - molecular diffusion 277–278
  - three-component system 278–279
  - transformation 278
- digital filtration 56
- digital resolution (DR) 59, 321–322
- digital signal filtration technique 56
- digitization noise 56
- dioctyl phthalate (DOP) 278
- dipolar coupling
  - homonuclear chemical-shift correlation
    - NOESY experiment 342–343
    - ROESY experiment 343–344
- dipole–dipole, dipolar, direct, or D-coupling 30–31
- dipole–dipole relaxation ( $T_1(DD)$ ) 174
- distortionless enhancement by polarization transfer (DEPT) experiment 56, 311, 312–313, 369

- carbon types,  $\theta$  values 312
- disadvantage 313
- revisited
  - edited spectra 211
  - MQC and HMQC 211
  - one-bond  $^{13}\text{C}$ - $^1\text{H}$  couplings 211
  - protonated carbon resonances 210–211
  - single quantum coherence 211
- sequence
  - carbon substitution patterns 204
  - trisaccharide gentamycin 204, 205
- spectral parameters 312
- subspectra of T-2 toxin 369
- 1D NOESY and ROESY experiments 347
- 3D NOESY/HMQC experiment 271–272, 273
- 2D NOESY spectrum 270–271
- DOSY. *See* diffusion ordered spectroscopy (DOSY)
- double PFG spin echo (DPFGSE)
  - experiment 275
- double-pulse, field-gradient, spin-echo NOE experiment (DPFGSE-NOE) 315–316
- double quantum coherence 426
- double quantum filtered COSY (DQF-COSY) 279
  - phase sensitive experiments 328–329
  - T-2 toxin 329
- double resonance or double irradiation 23, 188
- doublet of doublets 24
- DQF-COSY. *See* double quantum filtered COSY (DQF-COSY)
- 1D TOCSY experiment 345–347
- dwelt time 49
- dynamic effects
  - cyclohexane 29, 30
  - of methanol 28
- e**
- enantiotopic groups
  - chemical shifts 439
  - coupling constants 439–440
  - enantiotopic ligands 438–439
  - methylene protons 438
- equation, NMR 389–390
- exchange spectroscopy (EXSY) 188, 264, 280
- excitation
  - absorption of energy 11
  - collection of nuclei 10
  - linearly and circularly oscillating fields 11–12
  - magnetization (M) 10–11
  - rotating coordinate system 12
- excitation sculpting 275, 276, 277
- exponential weighting
  - free-induction decay 59, 61
  - resolution enhancement 59, 60
  - sensitivity enhancement 59, 60
- EXSY. *See* exchange spectroscopy (EXSY)
- f**
- Fermi contact mechanism 132, 133
- FID. *See* free induction decay (FID)
- filter bandwidth 52
- first-order spectra
  - characteristics 125
  - correction 65
  - left-phase 64
  - paramagnetic effect 96
  - phase correction 64
  - spin-spin splitting patterns 20, 21
  - three-spin system ( $A_2X$ ) 18–19
  - two-spin system (AX) 16–17, 125, 126
  - $A_2X_3$  spectrum 18, 20
- flip angle 52–54, 318
- flip-flop mechanism 13
- FLOCK experiment 260, 325
  - BIRD pulses 338–339
  - COLOC sequence 338
  - fixed delay times 339
  - resolution enhancement 339–340
  - WALTZ decoupling 339
- Fourier transformation (FT) 15
- free induction decay (FID) 14, 15–16, 237, 238, 239
  - acquisition times 60–61
  - apodization 61, 62

free induction decay (FID) (*contd.*)  
 lock signal 45  
 truncation artifacts 61–62  
 full width at half maximum (FWHM) 63

**g**

GARP or WURST sequences 331  
 geminal couplings  
 for alkanes 136  
 effect of  $\pi$  withdrawal 137  
 H—C—F couplings 138  
 $\sigma$  effects (induction) 136  
 two-bond couplings 138  
 vicinal H—C—C—H coupling constant 139  
 gHMBC. *See* gradient HMBC (gHMBC) pulse sequence  
 gradient echo 274  
 gradient HMBC (gHMBC) pulse sequence 336, 337, 338  
 gradient pulse. *See* pulsed field gradients (PFG)  
 gradient shimming 48  
 gyromagnetic or the magnetogyric ratio 2, 5

**h**

Hartmann–Hahn condition 32  
 H2BC. *See* heteronuclear two-bond correlation (H2BC) experiment  
 heavy atom effect 98  
 HETCOR. *See* heteronuclear chemical-shift correlation (HETCOR)  
 heteronuclear chemical-shift correlation (HETCOR) 317  
 adamantane derivative 256  
 advantages 256–257  
 COSY spectra 257  
 decoupling 255–256  
 delay times 335  
 WALTZ decoupling 335  
 X-nucleus-detected experiment 334–335  
 heteronuclear double resonance experiment 191  
 heteronuclear multiple bond correlation (HMBC) experiment 325, 372

gHMBC pulse sequence 336, 337, 338  
 H—C couplings 260–261  
 mixed-mode processing 336  
 pulse sequence 261–263  
 spectrum of heterocycle 262–263  
 heteronuclear multiple quantum coherence (HMQC) experiment 211  
 for camphor 257, 258  
 carbon decoupling 331  
 gradient-selected HMQC (absolute-value) experiments 332  
 inverse detection 257  
 LP and NUS methods 332  
 pulse sequence 257  
 heteronuclear relay coherence transfer dimethyl acetal of acrolein 263–264  
 H—H—C RCT 264  
 heteronuclear shift correlation (HSC) 256  
 heteronuclear single quantum correlation (HSQC) experiment 260, 370  
 double-INEPT pulse sequence 332, 333  
 expansion spectra 332, 333  
 GARP or WURST sequences 333  
 gradient-selected 334  
 LP and NUS 333  
 heteronuclear two-bond correlation (H2BC) experiment  
 comparison spectra 349, 350  
 HMBC experiment 348–349  
 longer-range C—H couplings 352  
 parameters 352  
 pulse sequence 349–350  
 HMBC. *See* heteronuclear multiple bond correlation (HMBC) experiment  
 HMQC. *See* heteronuclear multiple quantum coherence (HMQC) experiment  
 homonuclear double resonance experiments 190  
 HOmonuclear HArtmann-HAhn or HOHAHA, experiment 252  
 homotopics groups  
 chemical shifts 436, 437  
 gauche couplings 438  
 homotopic ligands 436, 437

- methyl protons 436, 437–438
  - Newman projections 436
  - HSQC. *See* heteronuclear single quantum correlation (HSQC) experiment
  - HSQC–TOCSY experiment
    - comparison 341–342
    - pulse sequence 341
    - spectral dispersion 340–341
  - Hückel rule for aromaticity 80
- i**
- indirect coupling 18
  - INEPT. *See* insensitive nuclei enhanced by polarization transfer (INEPT) sequence
  - INEPT–INADEQUATE 270, 280
  - insensitive nuclei enhanced by polarization transfer (INEPT) sequence 206
    - antiphase 206
    - carbon transitions 207
    - of pyridine 207–208
    - refocused (*See* refocused INEPT)
    - spin vectors 206
    - two-spin system 206–207
  - integrals 68
  - integration 68
  - interferograms 319
  - inversion-recovery experiment 175, 310–311
  - inversion-recovery-Fourier transformation (IR-FT) method 309–310
  - isochronous nuclei or groups 435
  - isotopes 2, 95–96
    - satellites 150–151
- j**
- J* coupling, proton-proton correlation
    - for annulene 242–243
    - axial peaks 246
    - AX spin system 240
    - Fourier transformation 239, 240
    - free-induction decay (FID) 237, 238, 239
    - J*-resolved spectroscopy 252–254
    - LRCOSY or delayed COSY 248–249
    - magnetization or population transfer 240–241
    - multiple quantum filtration 250–252
    - phase-sensitive COSY ( $\phi$ -COSY) 249–250
    - Pro–Leu–Gly 245, 246
    - relayed COSY 252
    - symmetrization 246
    - TOCSY 252
    - tripeptide Pro–Leu–Gly in DMSO 244–245
  - J*-filter 336
  - J* modulation. *See* attached proton test (APT)
  - J*-resolved spectroscopy
    - glucose derivative 253
    - proton–proton decoupled proton spectrum 253, 254
    - spin echo experiment 252–254
- k**
- Karplus equation 139
- l**
- Larmor frequency 3, 4, 390
  - linear prediction (LP) 317
    - coefficients 322
    - data-processing method 323–324
    - 2D experiments 322
    - expanded HSQC spectra 324
    - FIDs 322–323
  - line broadening functions 59
  - lock phase 44
  - lone-pair anisotropy 83
  - long-range COSY (LR-COSY) 248–249, 279, 328
  - long-range couplings
    - lone-pair-mediated, through-space couplings 145–146
    - $\sigma$ – $\pi$  overlap
      - alkynic and allenic systems 144
      - benzylic couplings 144
      - five-bond doubly allylic coupling (homoallylic) 143
      - four-bond allylic coupling 143
    - zigzag pathways
      - aromatic meta couplings 145
      - percaudal interaction 145
  - LP. *See* linear prediction (LP)

LR-COSY. *See* long-range COSY (LR-COSY)

## m

magic angle spinning (MAS) 31–32  
 magnetic equivalence 435  
 magnetic field homogeneity 63  
 magnetic resonance imaging (MRI) 273  
 magnetization (M) 10  
 medium effects 92–95  
 methyl acetate, resonances 7, 8  
 MLEV-16 (Malcolm LEVitt) 194  
 modern spectrometers 40  
 molecular assembly procedure  
   allylic and W-type couplings 376  
   C–H couplings 376  
   chemical shifts 379  
   COSY and HMBC correlations 375–376  
   cyclohexene fragment 375  
   four- and five-bond, C–H couplings 372  
   HMBC 374–375  
   three-bond correlation 377, 378  
   two- and three-bond C–H couplings 373–374  
   two-bond correlations 378  
   vicinal coupling 375  
 MQC. *See* multiple quantum coherence (MQC)  
 multinuclear spectrometers 40  
 multiple irradiation. *See* multiple resonance  
 multiple quantum coherence (MQC) 211  
 multiple quantum filtration  
   DQF-COSY experiment 250–251  
   TOCSY spectra of lysine 251  
   TQF-COSY experiment 252  
 multiple resonance  
   difference decoupling 190  
   experiments, classes of 190–191  
   off-resonance decoupling 191–194  
   spin decoupling 188–190

## n

nitrides 104  
 NOE. *See* nuclear Overhauser effect (NOE)

NOE spectroscopy (NOESY) experiment 264–265, 280  
 AB-ring systems 380–381  
 delay (DT) times 339–340  
 Dreiding model 381  
 EXSY experiments 342, 343  
 NMR data 379–380  
 phase-sensitive experiments, parameters 343  
 three-dimensional representation of T-2 toxin 381–382  
 noise decoupling 191  
 non-selective irradiation or broadband decoupling 191  
 nonuniform sampling  
   conventional uniform sampling 353–354  
   heteronuclear 2D experiments 352  
   NUS 352–353, 354–355  
 nonuniform sampling (NUS) method 332  
 nuclear Overhauser effect (NOE)  
   applications  
     heteronuclear examples 199  
     on internuclear distances 199–200  
     spin–lattice relaxation 199  
   difference experiment 314–315  
     of progesterone 198  
     three-spin effect 199  
   double-pulse, field-gradient, spin-echo NOE experiment 315–316  
   enhancements 313  
   limitations 200  
   observation  
     dipolar mechanism 196–197  
     double irradiation 195–196, 197  
     nondipolar relaxation mechanisms 196  
   structural determination 313  
   two-spin (AX) system 194–195  
 nuclei, magnetic properties  
   benzene 4, 5  
   classes of 1, 2  
   energy between spin states 3–6  
   external magnetic field 2–3  
   gyromagnetic ratio 5  
   magnetic moment 1, 2  
   NMR properties of 26



- nonmagnetic (nonspinning) nuclei 1–2
- precessional motions 3
- resonance frequency 4
- spinning nucleus 1, 2
- spin quantum number 1–2
- Zeeman effect 2
- nuclides 2, 26
  - natural abundance 27
  - natural sensitivity 27
  - receptivity 27
  - spin 26–27
- number of scans (ns) 55
- NUS. *See* nonuniform sampling (NUS)
  - method
- O**
- off-resonance decoupling procedure 72
  - composite pulses and phase cycling 194
  - heteronuclear decoupling 193
  - irradiation frequency 192–193
  - spectral editing 201
  - of vinyl acetate 192
- one bond couplings
  - carbon-13 and protons 134
  - CH couplings 134
  - INADEQUATE technique 135
  - nitrogen and hydrogen 135
- one-dimensional NMR spectroscopy
  - carbon connectivity 212–213
  - composite pulses 215
  - <sup>13</sup>C spectral editing experiments 311–313
  - multiple resonance 188–194
  - NOE experiments 194–200, 313–316
  - phase cycling 213–215
  - sensitivity enhancement 205–211
  - shaped pulses 215–217
  - spectral editing 200–205
  - spin–lattice and spin–spin relaxation 173–180
  - time scale, reactions on 180–188
  - T*<sub>1</sub> measurements 309–311
- oversampling 56
- P**
- PANACEA 280
- parallel transition 240
- paramagnetic shielding 96
- parameters, NMR
  - acquisition parameters 69
  - chemical shifts and coupling constants 66–68
  - peak-picking programs 66, 67–68
  - processing parameters 69
  - spectral display 69
- Pascal's triangle 19, 21
- Pauli exclusion principle 132–133
- peak-picking programs 66–68
- peak suppression or solvent suppression 177
- PFG. *See* pulsed field gradients (PFG)
- phase cycling
  - broadband heteronuclear decoupling 214
  - inversion recovery experiment 213–214
  - quadrature detection 215
  - reference frequency 214–215
  - selection of coherence pathways 215
- phase-sensitive COSY ( $\phi$ -COSY)
  - dispersion-mode and absorption-mode spectra 249
  - 2D phase quadrants 250
  - magnitude, or absolute-value, spectrum 249–250
- phasing and zero referencing 324–325
- planar W. *See* zigzag pathways
- Planck's constant 390
- polar or inductive effects 75
- polymer polyvinyl chloride (PVC) 278
- precession 3
- prochiral groups 435
- product-operator formalism
  - chemical shifts 422–423
  - out-of-phase (or antiphase) component 424
  - pulses 421–422
  - scalar coupling 421–422
  - second (antiphase) term 424–425
  - spin-spin coupling 421
- progressive transition 240
- proton chemical shifts and structure
  - aromatics 89–90
  - empirical calculations 91–92
  - carbon, hybridization of 77

proton chemical shifts and structure  
(*contd.*)

- electron density 76
- methyl resonances 75–76
- polar or inductive effects 75
- unshielded nucleus 76
- nonlocal fields
  - benzene ring, shielding geometry 79
  - carbon–carbon single bond 81
  - in 1-chloro-2-fluorobenzene 84–85
  - diamagnetic anisotropic properties 78, 82–83, 84
  - electron withdrawal or donation 83–84
  - <sup>19</sup>F spectroscopy 84, 85
  - Hückel rule for aromaticity 80
  - methano[10]annulene 79
  - methyl protons 81–82
  - in *N*-methylpiperidine 82
  - nonspherical substituents 84
  - oblate ellipsoid, shielding 78
  - in perfluorocyclohexane 85
  - polar bonds 84
  - prolate ellipsoid 80–81
  - spherical (isotropic) group, shielding 77–78
  - van der Waals effect 84, 85
  - on oxygen and nitrogen 90–91
  - saturated aliphatics 85–87
  - unsaturated aliphatics 87–89
- proton decoupling 23
- proton–heteronucleus correlation
  - BIRD-HMQC 257–260
  - carbon-13 254
  - COLOC 260
  - HETCOR 255–257
  - heteronuclear relay coherence transfer 263–264
  - HMBC 260–263
  - HMQC 257
  - HSQC 260
- pulsed experiments
  - FID 14, 15–16
  - magnetization vector *M* 13–14
  - y*-axis, induced magnetization 14–15
- pulsed field gradients (PFG)
  - for brucine 274–275
  - DPFGSE experiment 275–276
  - excitation sculpting 275, 276, 277
  - INADEQUATE 274
  - NOE experiment 275
  - phase cycling 274
  - rephasing process 274
  - transverse magnetization 273
  - WATERGATE 274
- pulse Fourier transform 39
- pulse width (flip angle) 57
- <sup>13</sup>C spectra 72
  - magnetization vectors 70
  - one-scan spectrum 71
- pure shift-covariance NMR 362
- pure shift NMR
  - broadband proton decoupling 355, 357–358
  - multiplicity-edited HSQC spectra of menthol 356, 357
  - PSYCHE 355
  - Zangger–Sterk refocusing element 355–356
- pure shift yielded by chirp excitation (PSYCHE) 355

**q**

- quadrupolar nuclei 2
- quantitation and complex splitting
  - of ethyl *trans*-crotonate 23–24
  - resonance, overlapping peaks 24–25
- quantization process 3
- quantum mechanical treatment, two-spin system
  - energy-level diagram 399, 400, 403, 404, 405, 406
  - first-order wave functions 399
  - Hamiltonian matrix 400, 401, 404, 405
  - NMR, Hamiltonian operator for 397–398
  - Schrödinger's wave equation 397
  - second-order (AB) with coupling 405, 407
  - spin wave functions 398
  - stationary-state wave function 406
  - three-spin systems 407
  - transition probabilities 402

- two equivalent spin, parameters for 403–404
- wave functions 401–402, 403
- quartet 24
- r**
- radio frequency (RF) coils 43
- RCT. *See* relayed coherence transfer (RCT)
- recovered magnetization 310
- refocused INEPT 208
- <sup>13</sup>C spectrum of chloroform 208, 209
- spectral editing
  - carbon resonances 209, 210
  - for methylene and methyl groups 208–209
  - signal intensities 209, 210
- spin echo 208
- regressive transition 240
- relaxation
  - correlation time 417
  - dipolar interaction 416–417
  - extreme narrowing condition 416
  - I nucleus 415
  - Larmor frequency 416
  - nuclear Overhauser effect (NOE) 419–420
  - spin–lattice or longitudinal 12–13, 415
    - chemical shielding anisotropy 418
    - quadrupole 419
    - scalar coupling 419
    - spin rotation 418–419
    - unpaired electrons 419
  - spin–lock relaxation 417–418
  - spin–spin or transverse 12, 13, 418
  - tumbling frequency 415–416
- relayed coherence transfer (RCT) 252
- relayed COSY
  - COSY and RCT 252, 253
  - three-spin systems (AMX and A'M'X') 252, 253
- resolution enhancement function 59
- resonance 4
- resonance frequency 6
- ROESY. *See* rotating-frame NOESY experiment (ROESY) experiment
- rotating coordinate system 12
- rotating-frame NOESY experiment (ROESY) experiment 266–267, 280
  - enhancement factors 343
  - NOESY experiments 344
  - TOCSY artifacts 343–344
- s**
- sample tube placement 42–43
- saturation or magnetization transfer 187–188
- scalar coupling
  - direct heteronuclear chemical-shift correlation
    - HMQC experiment 331–332
    - HSQC experiment 332–335
    - X-nucleus-detected experiments 331
  - homonuclear chemical-shift correlation experiments
    - COSY family 326–329
    - TOCSY experiment 330–331
  - indirect heteronuclear chemical-shift correlation
    - FLOCK experiment 338–340
    - HMBC experiment 336–338
    - HSQC–TOCSY experiment 340–342
- second-order spectra
  - AX<sub>2</sub> system 409–410
  - paramagnetic effect 96
  - three- and four-spin systems
    - AA'XX' spectrum, four spin systems 412–413
    - ABC spectrum 141, 411–412
    - AB<sub>2</sub> spectrum 147, 409–410
    - ABX spectrum 134, 148, 149, 410–411
- selective irradiation or selective decoupling 191
- sensitivity enhancement
  - DEPT revisited 210–211
  - INEPT sequence 206–208
  - refocused INEPT 208
    - spectral editing with 208–210
- shaped pulses
  - DANTE pulses 217
  - Gaussian shape 216–217
  - hard pulses 215–216
  - soft pulses 216

- shielding 6, 75, 78, 79
- shimming process 45
  - gradient shimming 48
  - homogeneity requirement 44–45
  - maximum lock signal level 45
  - misadjusted shim settings, effects of 46–47
  - superconducting magnets 46
- sine bell function
  - pseudo-echo 320
  - shifted 320, 321
  - squared 320, 321
- single quantum coherences 426
- space or chemical exchange, proton-proton correlation
  - COSY signals 264, 265
  - 1D NOE experiment 265–266
  - EXSY experiment 267–268
  - NOE and chemical exchange 264
  - NOESY experiment 264–265, 266
  - ROESY experiment 266–267
  - spin diffusion 266
- spectral-acquisition parameters
  - acquisition time 52
  - dwelt time 49
  - experiments 57–58
  - filter bandwidth 52
  - flip angle 52–54
  - number of data points 50
  - number of scans 55
  - oversampling and digital filtration 56
  - pulse sequence 58
  - receiver gain 54
  - sinusoidal signals 48–49
  - spectral resolution 48
  - spectral width 50–51, 52
  - steady-state scans 55–56
  - transmitter offset 52
  - X nuclei, decoupling 56–57
- spectral analysis
  - <sup>13</sup>C NMR data 366–369
  - COSY experiment 370–371
  - DEPT experiment 369
  - HMBC experiment 372
  - <sup>1</sup>H NMR data 365–366, 367
  - HSQC experiment 370
  - molecular assembly strategy
    - general 372–374
    - specific 374–379
  - NOESY experiment 379–382
  - second-order, two-spin (AB) system 146, 147
  - three-spin systems 147
  - trial-and-error procedure 147
- spectral editing
  - attached proton test 201–204
  - DEPT sequence 204–205
  - off-resonance decoupling procedure 200–201
  - spin-echo experiment 201
- spectral-processing parameters
  - exponential weighting 59
  - FID truncation and spectral artifacts 60–62
  - resolution 62–63
  - zero filling 59–60
- spectral resolution (SR) 48
- spectral width (sw) 50–51, 317
- spectra of solids
  - chemical shielding anisotropy 31
  - CP/MAS 32–33
  - dipole–dipole, dipolar, direct, or D-coupling 30–31
  - J-coupling 31
  - MAS 31–32
  - polycrystalline  $\beta$ -quinol methanol clathrate 32
  - relaxation times 32
- spectra: spectral presentation
  - baseline correction 65–66
  - NMR parameters 66–69
  - signal phasing
    - absorption and dispersion signal 64
    - first-order or left-phase control 64–65
    - zero-order and first-order phase correction 64
    - zero-order or right-phase control 64
  - signal-truncation effects 65
  - zero referencing 66, 67
- spectrometer
  - components of 39–41
  - field/frequency locking 43–44
  - NMR instrumentation 39–40

- probe tuning 43
  - sample preparation 41–42
  - sample tube placement 42–43
  - shimming (*See* shimming process)
  - spectroscopy 4, 5
  - spin decoupling 188–190
  - spin diffusion 420
  - spin diffusion limit 420
  - spin–echo experiment 201
  - spin–lattice and spin–spin relaxation 12, 13, 309
    - anisotropic motion 177–178
    - causes of relaxation
      - carbon relaxation 174
      - dipole–dipole relaxation 174
      - fluctuating magnetic fields 174–175
    - measurement of relaxation time
      - inversion recovery experiment 175–176
    - partially relaxed spectra 178
    - quadrupolar relaxation
      - <sup>14</sup>N decoupling 180
      - nitromethane 179
      - spin states for nucleus 178–179
    - segmental motion 178
    - structural ramifications 177
    - transverse relaxation
      - mechanisms of *xy* relaxation 176–177
      - spin diffusion 176–177
  - spin locking 32, 188
  - spinner turbine 42
  - spin–orbit coupling 98
  - spin–spin splitting, indirect coupling, or *J*-coupling 17
  - steady-state, or dummy, scans 55–56
  - stereochemical considerations
    - diastereotopic groups 440–441
    - enantiotopic groups 438–440
    - homotopic groups 436–438
  - subtraction artifacts 275
  - symmetrization 325
- t**
- tetrahydrofuran (THF) 278
  - tetramethylsilane (TMS) 8, 9, 66
  - thermal noise 56
  - THF. *See* tetrahydrofuran (THF)
  - time scale, reactions
    - atomic inversion 183–184
    - fast and slow exchange 181
    - hindered rotation 181–182
    - laboratory time scale 180
    - magnetization transfer and spin locking 187–188
    - quantification 187
    - ring reversal 183
    - valence tautomerizations and bond shifts 185–187
  - T*<sub>1</sub> measurements
    - inversion-recovery experiment 310–311
    - IR-FT method 309–310
    - recovered magnetization 310
  - TMS. *See* tetramethylsilane (TMS)
  - TOCSY. *See* total correlation spectroscopy (TOCSY) experiment
  - TOCSY–HMQC 272
  - topicity 435
  - total correlation spectroscopy (TOCSY)
    - experiment 252, 326
    - HOHAHA experiment 252
    - pulse sequence 330
    - spectra of lysine 251, 252
    - and Z-TOCSY (phase-sensitive)
      - experiments, parameters 330–331
  - TQF-COSY. *See* triple quantum filtered COSY (TQF-COSY) experiment
  - triple quantum filtered COSY (TQF-COSY)
    - experiment 252
  - triple-resonance experiment 188
  - triplet–quartet pattern 18
  - T-2 toxin 327, 384–387
  - two-bond couplings 138
  - two-dimensional NMR spectroscopy
    - carbon–carbon correlation 268–270
    - diffusion-ordered spectroscopy 277–279
    - higher dimensions 270–273
    - proton–heteronucleus correlation 254–264
    - proton–proton correlation
      - through *J* coupling 237–246

two-dimensional NMR spectroscopy  
(*contd.*)

through space or chemical exchange  
264–268

pulsed field gradients 273–277

two-dimensional techniques

data-acquisition parameters 316–319

data display 324–325

data-processing parameters 319–324

dipolar coupling 342–344

experiments 345–361

pure shift-covariance NMR 362

scalar coupling constants (*See* scalar  
coupling)

## V

valence tautomerizations

and bond shifts 185–186

cyclooctatetraene, fluxional behavior  
185

fluxional organometallic species  
186

3,4-homotropilidene, Cope  
rearrangement 185

1,5-sigmatropic shifts 186–187

van derWaals effect 84

vicinal couplings

acrylonitrile 141, 142

in alkenes 141

benzene derivatives 142

cyclohexanes 139–140

substituent electronegativity 141–142

vicinal H—C—C—H coupling constant  
139

virtual coupling

$\beta$ -methylglutaric acid 149–150

dimethylbenzoquinones 150

## W

WALTZ-16 194

WALTZ decoupling 331  
scheme 57, 70

WATER suppression by gradient-tailored  
excitation (WATERGATE) 274

weighting functions

absolute-value data 319–320

interferograms 319

modern spectrometers 320–321

phase-sensitive data 321

## X

X nuclei, decoupling for 56–57

## Z

Zangger–Sterk refocusing element  
355–356

Zeeman effect 2, 390

zero filling 59–60, 321

zero-order or right-phase control 64

zero quantum coherence 426

zero referencing

chemical shift data 66, 67

tetramethylsilane 66

zigzag pathways 144–145