

Index

Page in *italics* figures and tables.

- Ab initio* methods 15, 19
Absolute Configurations (ACs) 180, 181,
190–2, 202, 213
density function theory (DFT) 213
Absolute free energies of activation 342–3
Absolute shielding scales 127
Acetonitrile 383
Acetylene 134, 139
Adiabatic approximations 97
Adiabatic electronic wave functions 436
Adiabatic magnetic dipole moments 185
Adiabatic reactions 431, 433, 434
Adiabatic states 488
Adiabatic surfaces 446
Alcohols 585
Alkyl halides 359
Amides 504
Aminobiphenyl 408
Anisotropic media 96, 252, 265–79
dielectric continuum (DC) models 266
electrostatic interactions 266
integral equation formalism (IEF) 268–70,
277, 278
Onsager model 266, 276
Antenna chromophores 480
Antenna effect 472
Apolar dimers 505
Apolar solvents 506
Apparent surface charge (ASC) distributions
35, 98, 527
time dependency 121–2
Aprotic solvents 347
Aromatic chromophores 418–19
ASC implicit solvent models 64, 67, 68
ASC model 131, 135
ASC numerical methods 32, 36
ASC–PCM methods 131, 135
optical rotation 211
ASEP/MD method 580–91
density function theory (DFT) 585–6
Hamiltonians 580–1, 588
Atmospheric chemistry 464
Atomic axial tensors (AATs) 185
Atomic polar tensors (APT) 184
Atomic surface tensions 350
Azo chromophores 457
Azobenzene 457, 458
Azomethane 457, 458
Beer's law 180
Bell–Onsager equation 511
Benzo-fused bases 328
Benzocytosine 329
Benzoguanine 329
Betaine dyes 111

- Bichromophoric dendrimers 480
Bifunctional chromophores 425
Birefringence 252–5
 dielectric continuum (DC) models 257, 258
 linear birefringence 252, 255–62
 specific birefringence constants 255, 256
 see also Linear birefringence
BLMOL package 51
Boltzmann's law 240
Bond length alternation (BLA) 441, 558, 564, 566, 568–9, 572
Bond lengths 502–3, 566
Born cavity model 437
Born ions 103
Born radii 511, 514–15
Born–Oppenheimer (BO) approximations 2, 22–3, 82, 84, 86
 adiabatic reactions 433
 magnetic dipole moments 185
 nuclear coordinates 147
 reaction field (RF) models 405
 vibrational transitions 182
Boundary element methods (BEMs) 39, 43, 53
 discretization technique 302
 equations 57–8, 61, 62
 vibrational spectra 172
Brillouin condition 284
Bromination 356
Buckingham effect (BE) 252, 253, 254, 262
Buckingham formula 132, 136, 169
Bulk dielectric constants 309, 349
Bulk dielectric media 349

C=C stretching 231–2, 235
Cage effect 462, 463
Carbon monoxide 292
Carboxylic acids 506
Car–Parrinello method 3, 65
 EPR spectroscopy 160
 extended Lagrangian 69, 160
Catalyst design 360
Cavitation energies 316
Cavities 325–7, 477, 512–13, 526, 527
 Born cavity model 437
 see also Molecular cavities
Cavity fields 259, 270–1
Cavity formation energies 7
Cavity size 136
CC double bonds 441
Charge recombination (CR) processes 392–4, 400
Charge separation (CS) processes 392–4, 400
Charge shift (CSh) processes 392–3, 400, 408–10
Charge transfer (CT) contributions 488
Charging processes 6, 7
Chemical reactions 330, 339, 430–1
Chiral molecules 180, 181, 190, 192, 207
Chloride anion 332, 333
Chromophores 452–3, 480, 481, 486, 490
 antenna chromophores 480
 azo chromophores 457
 bifunctional chromophores 425
 conical intersections (CIs) 440, 442–3
 excited states 415, 416
 hydrogen detachment 425
 polarizable continuum model (PCM) 452–3
 solvation dynamics (SD) 367, 368, 369, 371, 372, 374, 380
Chromophore–solvent clusters 416, 425
Circular dichroism (CD) 180, 206, 209
Claisen rearrangements 357
Classical descriptions 4, 87
Classical–quantum hybrid approaches 602
Clausius–Mosotti relation 478
Clebsch–Gordan coefficients 272
Closed-shell solutes 415
Cluster–continuum model 350, 353
Clusters
 chromophore–solvent clusters 416, 425
 phenol–water clusters 420–3
 photoacid–solvent clusters 424
 photochemistry 462
 Raman optical activity (ROA) 230
 solute–solvent clusters 159, 528, 530
Collocation methods 38–9
Competitive effects 137
Complete active space self-consistent field (CASSCF) method 418, 421, 455
Complex dielectric functions 95
Complex susceptibility functions 96
Computational packages 20, 54
 vibrational circular dichroism (VCD) 187
Computational quantum chemistry 167

- Computer simulations 2–3
 Condensed phase processes 390
 Conductor models 69, 70, 305–6
 Conductor PCM (CPCM)
 extended Lagrangian 77–80
 free energies of solvation 326–7
 free energy functionals 70–1, 76–7
 geometry optimization 76
 Configuration interaction (CI) models 89, 418, 488
 Configuration interaction single-excitation (CIS) method 215, 405, 417, 421
 Configuration state function trial vectors 543
 Conformations 192–6, 206, 505–7
 density function theory (DFT) 195
 Conical intersections (CIs) 430, 433, 440–6, 447, 455
 chromophores 440, 442–3
 excited states 447
 Connolly surfaces 51
 Continuous wave (CW) models 145
 Continuum dielectric theory 367, 371
 Correlated electronic structure wavefunctions 282, 288
 Correlation lengths 100
 COSMO method 29, 36, 42
 electronic circular dichroism (ECD) spectra 215
 optical rotation 212
 reactivity 331
 spin–spin coupling constants 140, 141
 Cotton–Mouton constants 257, 259
 Cotton–Mouton effect (CME) 252, 253, 257, 259, 260, 262
 Coulomb potential 268, 270
 Coumarin 273
 Coupled cluster (CC) methods 91
 Coupled cluster 2 (CC2) method 417
 Coupled oscillator method 181
 Coupled perturbed SCF procedures 319
 Coupling Hamiltonians 347, 348
 CSGTs (continuous sets of gauge transformations) 130
 Cubic response functions 548–9
 Curved surfaces 307
 Cyanochlorobenzene (CCB) 433, 436–7

 DALTON package 212
 DAMP scheme 60
 DCP (dual circular polarization) 222
 Debye model 11
 Decay rates 376, 379
 Decay times, molecules 308
 Decomposition of normal modes 227–8
 DefPol package 51
 Dendrimers 480
 Density function theory (DFT) 88, 417
 absolute configurations 213
 ASEP/MD method 585–6
 conformational analysis 195
 electron transfer (ET) processes 310
 electronic circular dichroism (ECD) spectra 215
 excited states 418
 Kohn–Sham DFT 417, 603
 Kohn–Sham orbitals 120
 multiconfigurational DFT 455
 spin-dependent properties 145
 time-dependent calculations 321, 418
 unrestricted Kohn–Sham approach 152
 vibrational circular dichroism (VCD) spectra 181, 186–7, 197
 vibrational spectra 561, 572, 574–5
 Diabatic free energy model 461
 Diabatic states 395, 405, 442
 Dielectric anisotropy, *see* Anisotropic media
 Dielectric constants 309, 349, 476, 477, 508
 Dielectric continuum (DC) models
 anisotropic media 266
 birefringence 257, 258
 chemical reactions 430–1
 electron transfer (ET) processes 390–2, 397–8, 410–2
 five-zone DC models 402, 406
 inhomogeneous dielectric media 401–2
 nematic media 274
 nonequilibrium solvation (NES) 433, 434
 three-zone DC models 402, 407–8
 two-zone DC models 408
 Dielectric functions 95, 105–6, 107, 508
 distance-dependent dielectric functions 510
 Dielectric PCM (DPCM) method 29, 35, 84
 free energy functional 72–3, 76–7
 geometry optimization 76
 Dielectric permittivity, *see* Permittivity
 Dielectric polarization 171
 Dielectric polarization vectors 239
 Dielectric relaxation 17–18, 380, 381, 383
 Dielectric screening 476, 477, 479, 487, 508
 Dielectric susceptibility 376

- Dielectric theory 10
 Diffuse interfaces 303–4
 Dihedral angles 313, 314, 504
 DIIS scheme 60
 Dimers 482, 505–7, 573–5
 free energies of dimerization 505–6, 507
 Dimethyl formamide (DMF) 438
 Dipolar aprotic solvents 347
 Dipole densities 377
 Dipole moments, *see* Magnetic dipole moments
 Dipole moment operators 476
 Dipole strengths 184
 Discrete models 2–5, 356–7
 transition states (TSs) 357
 Discrete–continuum models 350
 Dispersion energies 8, 303, 306, 316
 Dissociation reaction paths 433
 Distance-dependent dielectric functions 510
 Divide-and-conquer approach 525
 Dividing surfaces (DSs) 25
 DMNO radical 160
 DNA duplexes 406
 Donor–acceptor (D–A) pairs 602
 Donor–bridge–acceptor (D–B–A) systems
 487–8, 494
 Double harmonic approximation 171
 Double-layer potentials 33
 DTBN aqueous solution 161
 Dynamical solute–solvent interactions 25
 Dynamical solvation effects 16, 382
- Eckart–Sayvetz conditions 228
 Effective quadrupolar centres 254
 Ehrenfest equations 283, 284, 286, 545, 547
 Electric dipole–electric dipole tensor 224
 Electric field second harmonic generation
 (EFSHG) 239–40, 242
 Electric saturation effects 12
 Electrodynamic equations, *see* Maxwell's
 equations
 Electron correlation effects 418
 Electron density redistribution 327
 Electron ejection 424
 Electron structure methods 417–18
 Electron transfer (ET) processes 310,
 390–412, 486–9
 density function theory (DFT) 310
 dielectric continuum (DC) models 390–2,
 397–8, 410–2
 excited states 405–6
 integral equation formalism (IEF) 310
 molecular cavities 392, 400
 Onsager model 400
 photoinitiated ET processes 393, 394
 thermal ET rate constants 394
 Electron transitions 590
 Electron–nuclear resonance techniques 145
 Electronic circular dichroism (ECD) spectra
 214–16
 Electronic couplings 486, 488, 489, 491–2,
 493
 Electronic density derivatives 319
 Electronic embedding 524–5
 Electronic energy transfer (EET) 472–83
 Electronic Hamiltonians 128, 243
 Electronic motions 113
 Electronic structure methods 417–18
 Electronically adiabatic reactions 431, 433,
 434
 Electrostatic embedding 577
 Electrostatic equations 94, 97
 Electrostatic interactions 266, 540, 542, 550
 Enantiomers 180, 190–1, 207
 Energy transfer 481, 482
 electronic energy transfer (EET) 472–83
 intramolecular energy transfer 494, 495
 Enzyme catalysis 356
 EPR spectroscopy 145–65
 Car–Parrinello method 160
 computational strategies 159–63
 Hamiltonians 147–8, 150
 Lagrangians 160
 NMR versus EPR spectroscopy 145
 polarizable continuum model (PCM) 146,
 154, 157
 Equilibrium fluxes 340
 Equilibrium free energies of salvation 352,
 434
 Equilibrium geometry 171
 Equilibrium rate constants 340
 Equilibrium solvation (ES) 438–9, 445
 Equilibrium solvation paths (ESPs) 343–4,
 348
 Escaped charges 37–8
 Exchange–correlation functionals 306
 Excitation energies 114, 480, 529, 530,
 532–3
 Excitation energy transfer (EET) 486–96
 Excited state potential energy surfaces 455
 Excited states 110–22

- chromophores 415, 416
 conical intersections 447
 density function theory (DFT) 418
 electron transfer (ET) 405–6
 nonequilibrium solvation 445
 photochemistry 461
 polarity effects 111, 113–14
 potential energy surfaces (PESs) 417, 455, 464
 proton transfer 415–26
 state-specific (SS) methods 114–15, 118
 Experimental solvation response function 368
 Extended Lagrangians, *see* Lagrangians

 Fast multipole method (FMM) 42, 61
 Femtochemistry 451
 Fermi Golden Rule expression 475
 Fermi resonance 232, 235, 561
 Finite difference Poisson–Boltzman (FDPB) methods 516–17
 Finite element methods (FEMs) 39
 First-solvation-shell effects 175, 350, 351
 Five–zone dielectric continuum models 402, 406
 Fixed partial charge method 181
 Flexible solutes 500
 Fluorescence resonance energy transfer (FRET) 472, 473
 Fluorescence spectra 368
 Fluorescence-upconversion experiments 372
 Fluorobenzenes 137
 Fock matrices 85–6, 244
 Fock operators 85, 86–7, 245, 596, 597, 598
 FOMO–SCF–CI method 460–1
 Formaldehyde (H₂CO) 75, 76, 77, 78
 Formamide 529–33, 583, 585
 Förster theory 472–5, 479, 482, 487
 Fractional free energies of solvation 510
 Franck–Condon excitation 440–4, 447, 463
 Franck–Condon maxima 399
 Franck–Condon regions 455
 Franck–Condon responses 113
 Franck–Condon transitions 590
 Free energies of activation 332, 354, 356, 395, 437, 589
 absolute free energies 342–3
 transition states (TSSs) 342–3, 395
 Free energies of dimerization 505, 506, 507
 Free energies of hydration 106
 Free energies of reaction 356

 Free energies of solvation 131, 324–5, 349–52, 398, 499, 503, 597, 599
 conductor PCM (CPCM) 326–7
 electrostatic contributions 325–6, 351, 353, 500
 equilibrium free energies 352, 434
 fractional free energies 510
 steric component 509, 511
 Free energy derivatives 315–21
 polarizable continuum model (PCM) 315, 318
 potential energy surfaces (PESs) 318, 319
 second derivatives 319, 321
 Free energy functionals 68–70, 75, 87, 133
 conductor models 69, 70
 conductor–PCM (CPCM) 70–1, 76–7
 dielectric PCM (DPCM) method 72–3, 76–7
 Hessian component 119, 245–6
 polarizable continuum model (PCM) 315
 time-dependent component 245
 Free energy surfaces (FESs) 435–6, 438, 443, 452, 586–8
 Frequency-dependent permittivity 306
 Frequency-dependent polarizability 307
 Frequency shifts 168
 Frozen density function theory (FDFT) method 525
 Frozen-PCM energy 120
 Full multiple spawning (FMS) method 459–60
 Functionals 66–7
 Fundamental excitations 184, 185
 Furan 262

 G-COSMO model 167
g tensors 149, 152, 154, 157–9
 Galerkin methods 38–43
 Gallic acid 175, 176
 Gas-phase geometry optimization 359
 Gas-phase wave functions 501
 Gas-to-liquid shifts 137–8, 139
Gauche alignment 505
 Gauge-invariant atomic orbitals (GIAOs) 150–1, 187, 197, 602
 Gauss quadrature algorithm 279
 Gaussian field model 373
 Gaussian package 181, 212, 528
 Gaussian surfaces 512
 GBSA methods 511, 512–13

- Generalized Born (GB) model 64, 65, 327, 511–15
- Generalized Brillouin condition 546
- Generalized Langevin equations (GLEs) 26, 348
- Generalized Mulliken–Hush (GMH) approach 487, 488–9, 496
- Generalized spherical polygons 55
- Geometry optimization 43–4, 74–7, 501
- conductor–PCM (CPCM) 76
 - dielectric PCM (DPCM) method 76
 - gas-phase optimization 359
 - GEPOL package 55
 - liquid-phase optimization 355
 - MPE method 135
 - ONIOM method 524, 530
 - polarizable continuum model (PCM) 76
 - transition states 353–4, 355
- Geometry relaxation 110, 159, 213, 500–2
- polarizable continuum model (PCM) 500
- GEPOL package 52–3, 55–6
- geometry optimization 55
- Gibbs free energies 331–2
- Gibbsian ensembles 2
- Glucose 213
- Grote–Hynes theory 439–40
- Group coupling matrices 229, 231, 234
- Halogenation 355–6
- Halomethanes 313
- Hamiltonians 2, 3, 5, 82–4, 87, 539
- ASEP/MD method 580–1, 588
 - coupling Hamiltonians 347, 348
 - Ehrenfest equations 545
 - electronic Hamiltonians 128, 243
 - electrostatic component 83
 - EPR spectroscopy 147–8, 150
 - FOMO–SCF–CI method 461
 - heterogeneous dielectrics 288–9
 - magnetic Hamiltonians 163
 - NMR spectroscopy 126, 128, 141
 - nonelectrostatic component 316, 369
 - nonlinear Hamiltonians 84, 86, 87, 89, 115
 - reaction field (RF) models 402–4, 406
 - state specific (SS) methods 118
 - time-dependent Hamiltonians 16, 118
 - zeroth-order regular approximation (ZORA) Hamiltonians 141
- Hammond postulate 437
- Harcourt model 488, 490–3, 495, 496
- Harmonic force fields (HFFs) 186
- Hartree–Fock (HF) equation 85, 87
- time-dependent HF equation 244–5
- Hartree–Fock (HF) method 119–20, 598
- united atom HF (UAHF) method 354
 - unrestricted HF method 417
 - vibrational circular dichroism (VCD) spectra 181
- Helmholtz-type free energies 597
- Hessian matrices 27, 321, 588
- Heteroatoms 112
- Heterogeneous catalysis 305
- Heterogeneous dielectrics 282, 288–90, 384
- Hamiltonians 288–9
 - time-dependent electromagnetic properties 290
 - two-photon absorption (TPA) 292
- Heterotransfer 480
- Homogeneous dielectrics 285, 290
- dispersion energies 303
 - polarizable continuum model (PCM) 293–5, 296
 - two-photon absorption (TPA) 293–5, 296
- Homotransfer 480
- Hybrid functionals 188, 190
- Hybrid methods 524
- Hydration effects 140
- Hydration shell models 510
- Hydrogen-bonded liquids 258
- Hydrogen-bonded networks 530, 531
- Hydrogen bonding 14, 112, 330–1, 348
- Hydrogen detachment 416–17, 419–20, 422, 425
- chromophores 425
- Hydrogen transfer 420–4, 425
- Hydrophobic effect 505
- Hyperfine coupling constants (HCCs) 151, 152, 153, 160
- Hyperfine coupling tensors 151
- Hypernetted-chain (HNC) approximation 595, 598
- Hyperpolarizability tensor 554
- Hypersusceptibilities 254
- IC processes 456
- ICP (incident circular polarization) 221, 222

- IEF-PCM method 36, 42, 90, 481, 483, 487, 526–7
 electronic circular dichroism (ECD) spectra 214–15
 optical rotation 211, 212–14
 spin–spin coupling constants 140
 surfaces 302
- Ill-defined tesserae 56
- Image charges method 289
- Implicit solvent models 64–5
 ASC implicit solvent models 64, 67, 68
- Indirect solvent effects 313–15
- Infinite planar surfaces 301, 310
- Infinitely dilute solutions 9
- Infrared (IR) frequencies 174
- Infrared (IR) intensities 168, 169, 174
- Infrared (IR) spectra 175, 176, 213, 320, 561, 567, 568, 570, 576
- Inhomogeneous broadening 163
- Inhomogeneous dielectric media 401, 407
- Integral equation formalism (IEF) 12, 29, 35, 36, 42, 268
 anisotropic media 268–70, 277, 278
 electron transfer (ET) reactions 310
 interfaces 301
- Integral equation theory (IET) 105, 596, 603, 604
- Integral equations 29–46
- Integral susceptibility kernel 102
- Interaction energies 540–1
- Interaction operators 539, 549
- Interfaces 300–4, 325
 integral equation formalism (IEF) 301
 nonelectrostatic interactions 302–3, 304
 polarizable continuum model (PCM) 303
see also Surfaces
- Interlocking spheres 50, 52
- Intermolecular charge transfer 64
- Intersecting spheres 54
- Intramolecular correlation function 595
- Intramolecular energy transfer 494, 495
- Intramolecular force constants 570
- Ion–dipole complexes 600
- Ionic compounds 326
- Ionic reactions 353–4
- Ionic species 351
- Isodensity surfaces 50
- Isoguanine 329
- Isotropic media 46, 479
- Isotropic shielding constants 127
- Jacobi iterative algorithm 59–61
- k*-dependence effects 96, 101
- Karplus scheme 57, 72
- KAT parameters 132
- KDP electro-optic modulators 180
- Kerr constants 261
- Kerr effect (KE) 252, 253
- Kerr susceptibility 239, 249
- Kerr virial coefficients 256
- Kinetic isotope effects 343, 358
- Kohn–Sham density function theory (DFT) 417, 603
- Kohn–Sham orbitals 120, 151
- Krames–Kronig relation 96
- Lagrangians 65–80
 conductor PCM (CPCM) 69, 77–80
 coupled-cluster methods 91
 EPR spectroscopy 160
 polarizable continuum model (PCM) 66, 70, 77–80
- Landau–Teller formula 447
- Langevin equations 26, 348
- Layered models 11
- Length-gauge formulation 210
- Lennard-Jones parameters 589, 595
- Light harvesting complexes 480, 481
- Lindhard–Mermin dielectric function 308–9
- Linear birefringence 252, 255–62
- Linear isotropic dielectrics 46
- Linear response approximations (LRAs) 94, 97, 352, 370
- Linear response equations 550
- Linear response functions 548
- Linear response (LR) method 114–15, 118, 120–1
- Liouville equations 147–9
- Liquid crystals 267
- Liquid-phase geometry optimization 355
- Living organisms 22
- Local fields 168, 172, 256, 477
- London atomic orbitals (LAOs) 129–30, 209, 210
see also Gauge-invariant atomic orbitals (GIAOs)
- Lorentz approximation 211, 244
- Lorentz model 478
- Lorentzian fitting 188–9, 191

- Lorentzian functions 100, 107
 Lorentzian peaks 106
 LR–SS differences 115
- Magnetic dipole moments 184–5
 transition dipole moments 477
 Magnetic Hamiltonians 163
 Magnetic tensors 146, 148, 277
 Magnetizabilities 257, 259
 Maier–Meier theory 277
 Maxwell's equations 94, 95
 Mean field approximations (MFAs) 580, 584,
 585, 587–8, 591
 Mechanical embedding 524
 Medium polarization 65
 Mehler model 514
 Menshutkin reactions 589
 Metals 305–10
 Methyl acetate 331
 Methyl formate 354–5
 Microsolvation 526, 529
 Mid-IR vibrational circular dichroism (VCD)
 spectra 189
 Minimization protocols 507
 Minimum energy paths (MEPs) 344–5, 348,
 416, 443–4, 456
 Mixed electric dipole–magnetic dipole
 polarizability 207–9
 Molar extinction coefficients 209
 Molecular cavities 49–50, 172, 513
 electron transfer (ET) 392, 400
 see also Cavities
 Molecular dynamics (MD) models 64–5, 66,
 68, 105, 368, 508, 519
 Molecular electronics 128, 310
 Molecular mechanics force fields (MMFFs)
 195
 Molecular mechanics (MM) methods 523
 Molecular motions 113
 Molecular orbit (MO) theory 596, 597, 601,
 602, 603
 Molecular Orenstein–Zernike (MOZ) theory
 603
 Molecular polarizability 269–70
 Molecular surfaces 49
 Moller–Plesset (MP) methods 90–1
 Moller–Plesset, second-order (MP2) theory
 321, 417
 Monte Carlo (MC) methods 508, 513, 518,
 519
- MPE method 134–5, 139
 MSDOT package 51
 Multichromophore molecules 480
 Multiconfigurational density function theory
 (DFT) 455
 Multiconfigurational self-consistent field
 (MCSCF) model 138–9, 283, 285, 310,
 321, 418, 538–55
 Multiconfigurational self-consistent field
 (MCSCF) wave functions 88–9, 539,
 542, 546
 Multiconfigurational time-dependent Hartree
 (MC–TDH) method 458–9
 Mutual polarization 84–5
- Nanoparticles 307, 309
 Nematic distribution functions 276
 Nematic media 158, 265, 273–4
 dielectric continuum (DC) models 274
 Nitro-amino-trans-stilbene (NATSB) 293,
 294–5, 296
 Nitrogen shielding constants 137
 Nitroxide radicals 149
 NMR spectroscopy 125–41
 chemical shifts 602
 computational models 133
 EPR versus NMR spectroscopy 145
 Hamiltonians 126, 128, 141
 Nonadiabatic dynamics 460, 461
 Nonclassical reflection 346
 Noncovalent complexes 505
 Noncovalent interactions 21
 Nonelectrostatic interactions 302–3, 304
 Nonequilibrium solvation (NES) 64, 339,
 347–8, 430–47
 dielectric continuum (DC) models 433,
 434
 excited states 445
 state-specific methods 118
 transition states (TSs) 431, 438–9
 vibration spectra 173–4
 Nonlinear dielectric media 10–11, 66
 Nonlinear Hamiltonians 84, 86, 87, 89, 115
 Nonlinear optical (NLO) properties 238–50,
 282, 290
 Onsager model 238
 Nonlinear optical molecular coefficients 588
 Nonlinear Poisson–Boltzmann equation 45
 Nonlocal dielectric theory 12–13, 370–2
 Nonlocal metal response 308

- Nonlocal Poisson equation 103
 Nonlocal theories 94–108
 polarizable continuum model (PCM) 101
 Nonpolar solvents 19
 Nonprotic solvents 136, 380
 Nuclear motions 113
 Nuclear relaxation 246
 Nuclear repulsion energies 86
 Nuclear shielding 127, 133, 134, 528
 Nucleobase dimers 506
 Numerical methods 29, 38
 computational efficiency 42
 polarizable continuum model (PCM) 41

 Octant rule 180
 Oligothiophene 572
 One-atom cage effect 462
 One-electron operators 85, 544, 549
 ONIOM method 453–5, 523–34
 geometry optimization 524, 530
 Onsager model 110, 172, 478
 anisotropic media 266, 276
 electron transfer (ET) processes 400
 frequency shifts 168
 nonlinear optical (NLO) properties 238
 PCM versus Onsager model 172
 Raman spectra 170
 Onsager–Lorentz theory 171
 Onsager–Wortmann–Bishop (OWB) model 247–9
 Optical rotation (OR) 206, 207–14, 216
 computational techniques 211–12
 COSMO method 212
 IEF–PCM method 211, 212–14
 rotary strengths 206, 210
 solvent effects 211, 212
 Orbital operators 128
 Orbital trail vectors 543
 Orbital Zeeman (OZ) operator 150
 Organic free radicals 145
 Organometallic systems 291
 Orientational distribution function 271, 273
 Orientational order parameters 272, 273, 274, 275
 Ornstein–Zernike (OZ) equation 594, 595
 Overscreening 105–6, 107

 Pair correlation functions (PCFs) 593–5, 596, 597, 600
 Para-nitroaniline (PNA) 559–63

 Parallel pathways 359
 Parameterized models 349–52, 503
 Partial closure method 61
 PCM–LR model 487–8, 489–90, 493, 494, 495, 496
 Pekar factors 398, 400
 Peptides 313–14
 Perfect caging 463
 Permittivity 275–7, 476
 frequency-dependent permittivity 306
 Permittivity tensors 158, 265
 wave vector-dependent dielectric tensors 376–8, 382, 383
 Perturbation theory 90–1, 490
 time-dependent perturbations 243
 Phase space 339, 434
 see also Transition states (TSs)
 Phenol 418–19, 420, 422, 424, 425
 Phenol–water clusters 420–3
 Phenomenological solvent model 132
 Phenoxide 75, 76, 79, 80
 Photoacids 415, 418
 Photoacid–solvent clusters 424
 Photobases 415
 Photochemistry 415, 430, 451–66
 excited states 461
 potential energy surfaces (PESs) 463, 465, 466
 supramolecular photochemistry 465–6
 Photodissociation 462–5
 Photoelastic modulators (PEMs) 181
 Photofragments 465
 Photoinitiated electron transfer (PIET) processes 393, 394
 Photoisomerization 461
 Photosynthesis 472, 486
 Picosecond dynamics 147
 Placzek polarization theory 223, 227
 Planar infinite surfaces 301, 310
 Plane-polarized light 207–8
 Pockels susceptibility 239
 Point dipoles 309
 Point-multipolar models 392
 Poisson–Boltzman (PB) model 508–9, 515–17
 finite difference methods 516–17
 Polar solvents 328, 500, 503, 505, 568
 Polarity effects 111, 113–14

- Polarizability 241–2, 247, 260
 frequency-dependent polarizability 307
 mixed electric dipole–magnetic dipole
 polarizability 207–9
 solute polarizability 248–9
 vibrational component 246
- Polarizable continuum model (PCM) 6–9, 11,
 64, 374–5, 526
 chromophores 452–3
 complex-valued realization 99
 dispersion energies 316
 EPR spectroscopy 146, 154, 157
 free energy derivatives 315, 318
 free energy functionals 315
 geometry optimization 76
 geometry relaxation 500
 homogeneous dielectrics 293–5, 296
 indirect solvent effects 314–15
 interfaces 303
 ionic reactions 353
 Lagrangians 66, 70, 77–80
 nonlocal extension 101
 numerical methods 41
 Onsager model versus PCM 172
 post-HF procedures 321
 potential energy surfaces (PESs) 76, 452
 repulsion energies 316
 solvation dynamics 375
 solvent effects 492
 surfaces 301, 309
 vibrational spectra 574–6
- Polarizable point dipoles 309
- Polarization energies 288
- Polarization fields 476
- Polarization functions 16, 113, 561
- Polarization interactions 540
- Polarized light 180
- Polyconjugated systems 571
- Polyhedral approximations 39–40
- Polypeptides 313–14
- Population operators 596
- Position-dependent effects 12
- Post-HF procedures 321
- Potential energy surfaces (PESs) 22, 416,
 435, 456
 excited states 417, 455, 464
 free energy derivatives 318, 319
 indirect solvent effects 313
 nonadiabatic dynamics 460, 461
 photochemistry 463, 465, 466
 polarizable continuum model (PCM) 76,
 452
 vibrational circular dichroism (VCD) 183
- Potentials of mean force (PMFs) 341, 342,
 345, 346, 347
- Proline 75, 76
- Protic solvents 112, 353
- Proton transfer 415–26
- Protonated Schiff bases (PSBs) 440–1, 442
- PROXYL radical 162
- Pulsed laser spectrometers 371
- Push–pull molecules 558, 564–5
- Pyridine 137, 559
- Quadratic configuration interaction single and
 double (QCISD) theory 153
- Quadratic response equations 552–3
- Quadratic response functions 548
- Quadrupolar solvents 384
- Quantum mechanical (QM) descriptions 4–5,
 82–92
- Quantum mechanical/molecular mechanics
 (QM/MM) methods 593, 596, 597, 603,
 604
- Quantum mechanical self-consistent reaction
 field (QM–SCRf) models 325, 326,
 327, 329, 330–3
- Quantum wave packets methods 467
- Quasi-chemical theory 350
- Quasi-stacked conformations 506–7
- Radial distribution functions 4
- Radical anions 432–3, 440, 441, 442, 444,
 447
- Radical reactions 357–8
- Ramachandran maps 314, 505, 507
- Raman bands 232, 234, 571
- Raman intensities 170, 174, 224, 229, 232
- Raman optical activity (ROA) 220–35
 clusters 230
- Raman scattering 174, 220, 221, 224, 226,
 227, 231
- Raman spectra 170, 221, 222, 227, 232, 233,
 235, 558–63, 567, 568, 569, 572–4, 576
 Onsager model 170
 para-nitroaniline (PNA) 560–3
 thiophene oligomers 572
- Raman spectroscopy 220, 221, 225
- Reaction barriers 434
- Reaction coordinates 340

- Reaction field (RF) models 402–5
 Hamiltonians 402–4, 406
 Reaction fields 29, 270–1, 490, 500, 528
 Reaction paths (RPs) 22–3, 416, 417, 418, 431, 438–9
 dissociation reaction paths 433
 Reaction potentials 30, 34, 83, 84, 130
 Reaction rate constants 439–40
 Reactivity 327, 330
 COSMO method 331
 Redox couples 403
 Reference interaction site model (RISM) 595, 596–603
 Refractive indexes 476–7, 479, 480, 481, 483
 Relaxation times 20
 Relaxation, molecules 110, 159, 213, 500–2
 Relaxed densities 89, 121
 Reorganization energies 310
 Repulsion energies 8, 303, 316
 Response functions 84, 547–9
 experimental solvation response function 368
 Response matrices 119
 Response theory 210, 282
 Retardation effects 97, 307–8
 Rigid solutes 499
 RISM–SCF descriptions 4
 ROA bands 232, 234
 ROA couplets 232–4
 ROA intensities 224, 229, 232
 ROA scattering 222, 226, 227, 231
 ROA spectra 222, 226, 232, 233, 235
 ROA spectroscopy 225
 Rosenfeld tensor 207
 Rotary strengths 206, 210
 Rotational strengths 185, 191–6, 198, 200, 201

 Saddle point geometry 344
 Salt effects 514
 Saupe matrices 272–3
 Scalar nonlinearity (Hamiltonians) 87
 Scale functions (tessellations) 56
 Scaled particle theory (SPT) 7
 Scanning near-field optical microscopy (SNOM) 307
 Scattered circular polarization (SCP) 222
 Schrödinger equation 82–3, 84, 581, 588
 time-dependent equation 244
 Screening, dielectric 476, 477, 479, 487, 508

 Second harmonic generation (SHG) 239, 300
 Self-consistent field (SCF) cycles 60
 Self-consistent field (SCF) energies 317
 Self-consistent reaction field (SCRf) models 167, 349–50
 quantum mechanical SCRf models 325, 326, 327, 329, 330–3
 Semiclassical descriptions 3–4
 Semicontinuum models 257, 258
 Separable equilibrium solvation (SES) 343–4, 346–7, 348
 Sharp dielectric surfaces 301
 Sharp interfaces 303
 Shielding constants 127, 128, 129, 131–2, 134–5, 137
 isotropic shielding 127
 nitrogen shielding 137
 nuclear shielding 127, 133, 134
 Sigmoidal functions 11–12
 Single-histogram method (SHM) 518
 Single-layer potentials 33, 35
 Solute cavities, *see* Cavities
 Solute charge densities/distributions 97, 500
 Solute polarizability 248–9
 Solute–solvent clusters 159, 528, 530
 Solute–solvent interactions 13, 16, 499, 526, 599, 602
 dynamical interactions 25
 Solvation dynamics (SD) 367–84
 chromophores 367, 368, 369, 371, 372, 374, 380
 polarizable continuum model (PCM) 375
 Solvation energies 2, 14, 103
 Solvatochromic shifts 384
 Solvatochromism 110, 111, 113
 Solvent-accessible surfaces (SASs) 50, 51, 401, 505, 514
 Solvent effects 16, 382, 481, 492, 494, 590
 indirect solvent effects 313–15
 optical rotation (OR) 211, 212
 polarizable continuum model (PCM) 314–15, 492
 vibrational circular dichroism (VCD) 198, 201
 Solvent-excluded surfaces (SESs) 50, 51
 Solvent-excluded volumes 50, 62, 101
 Solvent-induced electronic polarization 327
 Solvent permanent potentials 84
 Solvent polarization 173, 328, 431, 590
 Solvent reorganization energies 107

- Space-fixed axes 241
- Spatial dispersion effects 99
- Specific birefringence constants 255, 256
- Specific interactions 111
- Spectral bands 110, 111
- Spherical cavities 134
- Spherically symmetrical Born case 102
- Spin-dependent properties 145
- Spin Hamiltonians 126
- Spin-orbit coupling constants 155
- Spin-spin coupling constants 127, 129, 131–3, 138–41
 - COSMO method 140, 141
 - diamagnetic spin-orbital (DSO) contribution 129
 - IEF-PCM method 140
- Standard-state free energies 340, 341, 352, 353
- Stark energies 585
- State specific (SS) methods 114–15, 118
- State transfer operator 546
- Static dielectric responses 306
- Static dielectric screen effects 97
- Static susceptibility 100
- Statistical mechanics 2, 240, 593
- Stephens theory 181, 196
- Steric components 509, 511
- Steric retardation 332
- Stochastic coordinates 148
- Stokes shifts 106, 368–9
- Supercritical fluids 384
- Supermolecular models 137–8, 175, 257, 258, 577, 593
- Supramolecular photochemistry 465–6
- Surface hopping (SH) method 459
- Surface second harmonic generation (SSHG) 300
- Surface tensor model 274
- Surfaces 300–2
 - metals 305–10
 - polarizable continuum model (PCM) 301, 309
 - see also* Interfaces
- Susceptibility functions 96
- System-bath decomposition 154

- Tautomerism 328–9
- TCFs 380
- TD variational wave 119
- TEMPO 151, 155, 156, 158

- Tessellationless (TsLess) approach 57
- Tessellations 53–7
 - scale functions 56
- Thermal averages 6
- Thermal ET (electron transfer) rate constants 394
- Thiophene oligomers 572
- Three-zone dielectric continuum models 402, 407–8
- Through-bond (TB) contributions 487, 494, 496
- Through-space (TS) contributions 494, 496
- Time-dependent charges 98
- Time-dependent Hamiltonians 16, 118
- Time-dependent Hartree-Fock (HF) equation 244–5
- Time-dependent perturbations 243
- Time-dependent polarization functions 16
- Time-dependent Schrödinger equation 244
- Time-dependent Stokes shifts 106
- Torsional profiles 504–5
- Trace operators 86
- Trans-stilbene (TSB) 293
- Transition amplitude tensors 291–2
- Transition dipole moments 477
- Transition states (TSs) 22–6, 339–45, 438
 - discrete models 357
 - equilibrium solvation paths (ESPs) 343–4, 348
 - free energies of activation 342–3, 395
 - geometry optimization 353–4, 355
 - nonequilibrium solvation 431, 438–9
 - reaction rate constants 439–40
 - separable equilibrium solvation (SES) 343–4
 - variational TST (VTST) 25–6, 342, 344, 358
- Transmission coefficients 345
- Transparency regions 96–7
- Triazene 586
- TsAre option 56
- TSH method 463
- Tunneling 346, 358
- Two-component relativistic density functional approach 141
- Two-photon absorption (TPA) 291–5, 296, 554
 - heterogeneous dielectrics 292
 - homogeneous dielectrics 293–5, 296
- Two-photon transition matrices 548

- Two-sphere models 400
- Two-state models 564
- Two-zone dielectric continuum models 408

- Uniaxial media 276
- Uniform space 103–4
- United atom Hartree–Fock (UAHF) method 354
- Unrestricted Hartree–Fock method 417
- Unrestricted Kohn–Sham approach 152

- Vacuum potentials 101
- Valence bond (VB) methods 89–90, 432
- Valence bond (VB) states 434, 440, 441
- Van der Waals complexes 462
- Van der Waals energies 573
- Van der Waals forces 572
- Van der Waals interactions 540
- Van der Waals surfaces (VWSs) 41, 50, 51
- Variable occupation numbers 456
- Variational transition states (VTSs) 25–6, 342, 344, 358
- Velocity gauge formulation 208–9
- Vertical transitions 113–14, 117
- Vibrational absorption spectra 186
- Vibrational circular dichroism (VCD) 177, 181–202
 - computational packages 187
 - density function theory (DFT) 181, 186–7, 197
 - errors 198
 - mid-IR VCD spectra 189
 - potential energy surfaces (PESs) 183
 - solvent effects 198, 201
- Vibrational energy redistribution 456
- Vibrational Raman scattering 223
- Vibrational spectra 167–78, 558–77
 - absorption spectra 186
 - boundary element methods (BEMs) 182
 - density function theory (DFT) 561, 572, 574–5
 - frequencies 171, 174
 - Hartree–Fock (HF) method 181
 - intensities 171, 174
 - nonequilibrium solvation (NES) 173–4
 - polarizable continuum model (PCM) 574–6
- Vibrational transitions 182
- Virial coefficients 256

- Wave vector-dependent dielectric permittivity tensors 376–8, 382, 383
- Weak ionic solutions 45
- Wigner matrices 272

- Z-vectors 121
- Zeeman interactions 147
- Zeeman operator 150
- Zeroth-order regular approximation (ZORA) Hamiltonians 141
- Zwitterion 357, 564, 566

