

## Index

### a

absorption coefficient, for displaced harmonic oscillators 290–294  
 absorption spectrum, of Morse oscillator potential surface 271  
 activation energy 316  
 active system 63  
 adiabatic electron transfer 298  
   donor–acceptor complex 323–336  
   from solid state 355–356  
   transition 347  
 adiabatic exciton 445  
 adiabatic proton transfer 407  
 adiabatic wave function 13  
 Arrhenius rate 316  
 autocorrelation function 96, 106, 292  
 averaged classical limit 279  
 avoided crossing 41

### b

bacteriochlorophyll (BChl) 424  
 Beer's law 183  
 Bixon–Jortner rate 220  
 Bloch model 131, 132, 467, 469  
 Bogoliubov transformation 170  
 Born approximation 107  
 Born–Oppenheimer approximation 14  
 Born–Oppenheimer separation 1, 392, 405  
 Bose–Einstein distribution 113  
 bridge-assisted electron transfer 301  
 Bridge-mediated electron transfer 337  
   arbitrary large bridges 340  
     large intrabridge transfer integrals 341–343  
     small intrabridge transfer integrals 340–341  
   superexchange mechanism 338–340  
 bright state 212, 219

Brownian oscillator model 118, 267, 449  
 Brownian oscillator spectral density 118  
 bulk heterojunction 494

### c

cage effect 223  
 Caldeira–Leggett Hamiltonian 228, 268, 449  
 Caldeira–Leggett model 64, 225, 237  
 canonical density operator 85  
 charge density 10  
 charge transfer exciton 494  
   and charge separation 493–496  
 charge transmission, through single molecules 304, 356  
   elastic 361–365  
   inelastic 359–361  
   vibrational levels 365–367  
 chemical exchange 206, 394  
 chemical potential 348  
*Chlorobaculum tepidum* 424  
 chromophore complex 426  
 chronological time ordering 104  
 classical canonical equations 150  
 coarse graining 93, 110, 130  
 coherences 87  
 coherent dynamics 3  
 coherent dynamics, in coupled two-level system 143–144  
 coherent motion 61  
 coherent superposition 67  
 coherent transfer 451  
 combined density of states 258  
 common vibrational coordinates 462  
 condon approximation 194, 258, 279, 312, 455, 485  
 configurational average 482  
 conical intersection 42, 290

- coordinate
    - active 31
    - reaction 32
    - spectator 31
    - reaction plane 35
    - representation 88
  - correlation
    - dynamic 19
    - static 19
  - Coulomb interaction, classification of 433–435
  - Coulomb matrix elements 432
  - coupled two-level system dynamics
    - coherent dynamics 143–144
    - dissipative dynamics 144–147
      - using zeroth-order states 147–149
  - coupled-channel equations 414
  - coupling modes 290
  - cumulant expansion 194, 195, 245, 264
    - of absorption coefficient 264–266
  - current voltage characteristics 360
  - curve-crossing model 5, 256, 272
  - cyclic invariance property 85
- d**
- damping matrix 126
  - dark state 212, 219
  - Debye frequency 118
  - Debye spectral density 118, 134, 266
  - decoherence 65
  - degree of coherence 86
  - delocalized exciton states 441
  - Density Functional Theory 20
  - density matrix 86, 88
  - density matrix equations for exciton dynamics 466
  - density matrix formulation 63, 284–286
  - density matrix theory 467
  - density of states (DOS) 349, 353, 363
    - of reservoir oscillators 117
  - density operator 84–86
    - equation of motion for 88–90
    - Wigner representation of 90–92
  - dephasing 66, 68
    - rates 129
    - time 260
  - detailed balance 128, 130, 461
  - Dexter transfer 490
  - diabatic representation 38, 406
  - dielectric medium 43
  - dimensionless coupling constant 448
  - dimensionless exciton–vibrational coupling constants 463
  - dipolar coupling Hamiltonian 502
  - dipole–dipole correlation function 185
  - dipole–dipole coupling 432
  - Dirac–Frenkel principle 72, 74
  - dissipation 60
  - dissipative dynamics, in coupled two-level system 144, 147
  - dissipative exciton dynamics 471
  - dissipative superoperator 111
  - donor–acceptor complex 299, 310
    - nonadiabatic electron transfer 323
  - donor-bridge acceptor system 344
  - dynamic(s)
    - coherent 61
    - incoherent 61
  - dynamic coupling 37
  - dynamic disorder 253
  - dynamical classical limit 276
  - Dyson equation 160
- e**
- Ehrenfest method 151
  - elastic charge transmission 361
  - elastic charge transmission through a single molecule 385
  - electric susceptibility 182
  - electron configuration 16
  - electron transfer (ET) 5, 295
    - activationless 327
    - adiabatic 298
    - bimolecular 299
    - bridge-assisted 301, 337
    - charge transmission through single molecules 356
    - classification of 295
    - heterogeneous 302, 347
      - photoinduced 303, 354
    - inner-sphere 301
    - intramolecular 298–299
    - inverted 327
    - Landau-Zener theory 319–322
    - long-range 301
    - nonadiabatic 298, 316
    - nonequilibrium quantum statistical description 343
    - normal 326
    - nuclear tunneling 318
    - outer-sphere 301
    - photoinduced 299, 367
    - regimes of 315–319
    - solvent-controlled 318
    - theoretical models
      - Hamiltonian 305–310

- Spin-Boson Model 312
  - vibrational coordinates 313–314
  - vibrational Hamiltonian of
    - donor–acceptor complex 310–314
  - vibrational state representation
    - Hamiltonian 314
  - through–bond 301
  - through–space 301
  - unimolecular 298
  - emission spectrum 280, 281
  - encounter complex 300
  - energy gap law 288, 289
  - energy relaxation rates 128
  - energy representation 87
  - environment 2
  - equation of motion
    - for density operator 88, 90
    - for reduced density operator 97, 98
  - equilibrium distribution function 79, 113
  - excitation electron transfer (EET) 6
  - excitation energy donor 421
  - excitation energy transfer among different
    - aggregates 471–472
  - excitation energy transfer via two–electron
    - exchange 490–493
  - exciton
    - charge transfer 425
    - Frenkel 422
    - Wannier–Mott 425
  - exciton–exciton annihilation 421, 496–497
  - exciton expansion coefficients 444
  - exciton Hamiltonian 442, 449
  - excitonic coupling 435, 453
  - exciton state 442
  - exciton transfer
    - coherent 427, 451
    - hopping 471
    - incoherent 427, 451
    - partly coherent 451
    - strong exciton–vibrational coupling 472
  - exciton–vibrational coupling 448
    - inclusion of 484
    - matrix 448–449
  - exclusive coupling to intramolecular
    - vibrations 445
- f**
- Förster radius 456
  - Fenna–Matthews–Olson (FMO) proteins 424
  - Fermi distribution 348
  - Fermi level 303
  - Fermi resonance 216
  - Fermi’s Golden Rule 75
  - fewest switches surface hopping (FSSH) 154
  - Feynman diagrams 192
  - Feynman–Vernon influence functional 139
  - finite molecular chain and the molecular
    - ring 443
  - flip operator 86
  - fluctuation–dissipation theorem 122, 230
  - fluorescence resonance energy transfer (FRET) 422
  - Fokker–Planck equation 135
  - force autocorrelation function 233
  - fourth–order donor–acceptor transition rate 382
  - Franck–Condon
    - blockade 361
    - factor 30, 51, 252, 258, 284, 314
    - overlap integrals 455
    - progression 254, 261
    - principle 251
    - transition energies 441
  - Frenkel exciton model 421–422, 441
- g**
- gated proton transfer 400
  - Gaussian disorder 482
  - generalized linear susceptibilities 121
  - generalized master equation 94, 157
  - generalized Mulliken–Hush method 310, 376
  - generalized rate equations 157, 158
  - Golden rule 3, 75, 78, 219, 454
  - Grätzel cell 303
  - green fluorescent protein 425
  - Green’s function approach 81
  - Green’s operator 81, 352, 362, 366
  - Grotthuss mechanism 392
  - Ground and excited state PES, of diatomic
    - molecule vs. bond distance 251
- h**
- H–aggregate 480
  - Haken–Strobl–Reineker model 425
  - Hamiltonian proton transfer
    - condensed phase 404–405
    - adiabatic representation 405–406
    - diabatic representation 406–407
    - hydrogen bonds 395–399
    - intramolecular proton transfer 399–400
  - Harmonic oscillator reservoir 114, 116
  - Hartree approximation 98
  - Hartree product 17, 413, 428, 429

- Hartree–Fock equation 18
- heat bath 60–63  
coupled multilevel system dynamics 93–96
- Heisenberg picture 68
- Hellmann–Feynman force 409
- Hessian matrix 22
- heterodyne detection 199, 202
- heterogeneous electron transfer (HET) 302, 347  
nonadiabatic charge injection, single–electron model 348, 351–352  
nonadiabatic electron transfer 355–356  
ultrafast photoinduced 354–355
- Hierarchy equations of motion 140–142, 147
- Hole transfer 300
- Holstein Hamiltonian 447
- HOMO–LUMO scheme 422
- homogeneous broadening 62, 253, 267
- Huang–Rhys factor 261, 446
- Hückel model 55
- hydrogen bond 42, 396–398
- i**
- impulsive excitation limit 284
- impulsive pulse limit 200
- incoherent motion 3, 61
- incoherent rate equation approach 425
- inelastic charge transmission 359
- influence functional 139, 172  
stochastic unraveling 173
- inhomogeneous broadening 62, 253, 267, 482
- initial correlations 102, 152
- instantaneous adiabatic states 409
- instantaneous normal modes 114, 227
- interaction representation 70–71  
reduced density operator 99
- interaggregate coupling 472
- intermolecular Coulomb interactions 427, 430
- internal conversion (IC) process 4, 250, 255, 498
- intersystem crossing 250
- intramolecular electronic transitions 249  
density matrix formulation 284–286  
emission spectrum 280–281  
internal conversion dynamics 286–290  
internal conversion rate 287–288  
ultrafast internal conversion 288–290  
internal conversion process 5, 255  
optical absorption coefficient 255, 258, 260, 263, 264, 266, 268, 269, 273, 275  
optical preparation, of excited electronic state 281–286  
optical transitions 250–255  
intramolecular proton transfer 399  
intramolecular vibrational redistribution 4, 212  
intramolecular vs. reservoir normal mode vibrations 449  
IVR threshold 221
- j**
- J-aggregate 480
- k**
- Kasha rule 250, 286
- kinetic isotope effect 390
- Kohn–Sham equations 20
- Koopmans theorem 348
- l**
- Landau–Zener 319  
length 322  
rate 321  
transition amplitude 378
- lattice phonons 225
- Lennard–Jones potential 49
- light–matter interaction 180
- Lindblad form 109, 132
- linear absorption coefficient  
for curve crossing system 273  
for MBO model 277
- linear dielectric susceptibility 183
- linear response functions 120–122
- linear vibronic coupling Hamiltonian 290
- lineshape  
function 258, 259, 290
- Lorentzian 192
- Liouville equation 92
- Liouville space approach 89, 155–156  
fourth–order rate expressions 164–165  
three level system with sequential coupling 165–168  
generalized rate equations 157–158  
memory kernels 159–162  
projection operator technique 156  
rate equations 159  
second–order rate expressions 161–165
- Liouville space pathways 162
- Liouville superoperator 89, 111
- Liouville–von Neumann equation 89, 97
- local field approximation 181

long wavelength approximation 179  
 long-range ET 301  
 longitudinal relaxation time 129

## **m**

Marcus formula 326  
 Markov approximation 109–112  
 Massey parameter 321–322  
 master equation 61  
 Matsubara frequency 119  
 mean-field approximation 19, 73, 98, 99,  
 149, 151, 152, 414, 415  
 mean-field Hamiltonian 73  
 membrane-bound protein complexes 1  
 memory effect 107, 109, 124, 139  
 memory kernel 94, 159, 162  
 memory matrix 124  
 microenvironment 62  
 minimal coupling Hamiltonian 178  
 minimum energy path 31  
 mixed quantum classical approach 150  
 mixing angle 41, 55  
 modified Redfield theory 484  
 molecular aggregate 424, 426  
 molecular dimer 429  
 molecular electronics 304  
 molecular mechanics force fields 49  
 molecular ring 57  
 molecule solid coupling function 350, 363  
 monomer cyanine unit 423  
 monomer Hamiltonians 438  
 motional line narrowing 267  
 multi-mode Marcus formula 379  
 multiconfiguration time-dependent Hartree  
 (MCTDH) approach 72, 415  
 multidimensional wave packet dynamics  
 71, 74, 413  
 multiexciton states 436  
 multilayer MCTDH 74  
 multilevel Redfield equations 126, 127  
 coherence dephasing 129  
 population transfer 127–128  
 remaining elements 129–130

## **n**

Nakajima-Zwanzig equation 101–104  
 non-Markovian dynamics 108, 140  
 non-Markovian regime 140  
 nonadiabatic coupling 152, 287  
 nonadiabatic electron transfer 298, 316,  
 317  
 donor-acceptor complex 323  
 high-temperature case 323–327

two independent sets of vibrational  
 coordinates 327–330  
 low-temperature case, nuclear tunneling  
 330–333  
 mixed quantum-classical case 333–355  
 nonadiabatic proton transfer 410  
 noncrossing rule 42  
 nonequilibrium quantum statistical  
 description  
 adiabatic electron transfer transition  
 347–351  
 donor-bridge acceptor system 344–346  
 of Forster transfer 458–462  
 nonlinear response function 190  
 nonperturbative and non-Markovian  
 exciton dynamics 475  
 normal modes 24  
 nuclear tunneling 318

## **o**

Ohmic dissipation limit 118  
 Ohmic spectral density 117–119  
 open molecular system 2  
 operator  
 annihilation 27  
 Coulomb 18  
 creation 27  
 displacement 29, 179  
 exchange 18  
 Fock 18  
 nonadiabaticity 12  
 squeezing 51  
 optical absorption coefficient  
 absorption lineshape and spectral density  
 263–264  
 cumulant expansion 264–266  
 density of states 258–260  
 and dipole-dipole correlation function  
 269  
 Golden Rule formulation 255–258  
 harmonic potential energy surfaces  
 260–263  
 mixed quantum-classical computation of  
 275  
 for model spectral densities 266–268  
 and reduced density operator propagation  
 273–275  
 and wave packet propagation 269–273  
 optical preparation, of excited electronic  
 state 281  
 wave function formulation 281–283  
 long pulse duration 284  
 short pulse duration 284

optical properties of aggregates 477  
 optical transitions 250, 255  
 orientation factor 456  
 oscillator strength 480  
 overcoherence error 154

**p**

partially coherent motion 3  
 partition function 85  
 path integral representation, of density matrix 135–140  
 Pauli master equation 61, 80, 81, 458  
 Pauli principle 10, 16  
 permutation operator 17  
 perylene diimide (PDI) donor 434  
 phase space 89  
 photocatalytic reactions 295  
 photoinduced electron transfer 299  
 photoinduced ultrafast electron transfer 367  
   rate expressions 377  
   quantum master equation for electron transfer reactions 372–376  
 photon correlation functions 505–506  
 photon-mediated long-range excitation energy transfer 501  
 photosynthesis 296, 391, 423  
 pigment-protein complex 423  
 polarization energy 325  
 polarization field 45  
 potential energy surface 1, 13  
   excitonic 450  
 projection operator technique 156  
 proton pump 296, 391  
 proton transfer (PT) 389  
   adiabatic 407–410  
   classical hybrid methods 412  
   Hamiltonian  
     adiabatic representation 405–406  
     condensed phase 404–405  
     diabatic representation 406–407  
     hydrogen bonds 395–399  
     intramolecular proton transfer 399–401  
   intermolecular 396  
   multidimensional wave packet dynamics 413–415  
   nonadiabatic proton transfer 410–412  
   proton-coupled electron transfer 417–419  
     quantum tunneling 400  
     surface hopping 415–417  
 proton transfer coordinate 396

proton-coupled electron transfer (PCET) 392, 417  
 pseudopotential 306  
 pump-probe spectroscopy 253  
   of wave packet dynamics 254  
 pure dephasing 112, 129, 197, 243  
 pure state 84

**q**

QM/MM method 50  
 quantum beats 68, 201  
 quantum-classical hybrid method 150  
 quantum-classical dynamics 333, 408  
 quantum Liouville equation 89  
 quantum master equation (QME) 107–109, 260  
   in energy representation 123  
   Markov approximation 109–112  
 quantum mechanics, Golden Rule of 75, 83  
 quantum of resistance 364  
 quantum statistical approaches, to excitation energy transfer 452–453  
 quantum transitions, from single state 75, 78  
 quantum tunneling 400

**r**

radiationless transition 286  
 rate equations for exciton dynamics 465  
 rate of exciton-exciton annihilation 499  
 rate of photon-mediated excitation energy transfer 506  
 reaction center 296  
 reaction coordinate 298  
 recurrence 60  
 Redfield tensor 127, 371  
 Redfield theory 127  
   modified 473  
 reduced density matrix (RDM) 65  
   coordinate and Wigner representation 133–135  
   in energy representation 123–133  
   path integral representation 135–140  
 reduced density operator (RDO) 96–97  
   equation of motion for 97–98  
   interaction representation 99–101  
   Nakajima-Zwanzig equation 101–104  
   second-order equation of motion 105–107  
 regimes of excitation energy transfer 451  
 relaxation 60  
 relaxation matrix 127  
 relaxation superoperator 111

- relevant system 63
  - reorganization energy 34, 36, 117, 325
  - rephasing 66
  - representation
    - coordinate 88
    - energy 87
    - state 87
  - reservoir correlation function 106
    - classical description 122–123
    - general properties of 112–114
    - harmonic oscillator reservoir 114–116
    - linear response theory 120–122
    - spectral density 116–120
  - response function
    - nonrephasing 200
    - rephasing 200
  - Rhodobacter Sphaeroides 297
  - rigid bond method 233
  - rotating wave approximation 130, 192, 197, 240, 257
- S**
- scattering matrix 70
  - Schwarz inequality 87
  - second quantization notation of the
    - aggregate Hamiltonian 500
  - second-order electron transfer rate 380
  - secular approximation 130–131
  - self-energy 77, 83
  - self-assembled double-walled nanotube 423
  - self-consistent field 18
  - semiclassical molecule–field interaction 180
  - shift operator 91
  - signal
    - excited state absorption 201
    - ground state bleaching 201
    - stimulated emission 201
  - single and double excitations of the
    - aggregate 436
  - single excited state matrix elements 438
  - single-particle functions 72
  - site energy 441
  - Slater determinant 17
  - solvation energy 49
  - solvation shell 47
  - solvent-controlled ET 318
  - S-operator 70, 71
  - spectral density 116, 120, 235, 263, 466
    - Brownian oscillator 118, 267
    - Debye 118, 134, 266
    - electron transfer 331
    - Ohmic 117–119
  - spectral overlap 456
  - spin orbitals 16
  - spin states 11
  - spin–boson Hamiltonian 313
  - spin–boson model 312–313
  - spontaneous emission 206
  - state expansion, of system–reservoir
    - coupling 131, 132
  - state representation 87
  - state vector 70
  - static approximation 278
  - static classical limit (SCL) 278
  - static coupling 39
  - static disorder 62, 253
  - statistical operator 85
  - Stokes shift 256, 261, 263, 265, 278, 460
  - strong exciton–vibrational coupling 488
  - superexchange 42, 302, 509
  - superoperator 89, 101
  - surface hopping method 152, 154, 415
  - surface hopping simulations 290
  - survival probability 68, 69
  - system–reservoir coupling model 64
    - state expansion of 131–132
  - system–reservoir Hamiltonian 35, 63, 237
- t**
- terrylene diimide (TDI) acceptor 434
  - thermal ensemble, transition rate for 78
  - three-level description of the molecules in the aggregate 498
  - through-bond electron transfer 301
  - through-space electron transfer 301
  - tier model 220
  - tight-binding Hamiltonian 308
  - time-dependent Hartree method 72
  - time-dependent Schrödinger equation
    - 60–61
    - interaction representation 69–71
    - multidimensional wave packet dynamics 71–74
    - wave packets 66–69
  - time-dependent self-consistent field 413
  - time-evolution operator 66, 504
  - time-ordering operator 71
  - trace formula 85
  - trajectory-based methods
    - mean-field approach 149–152
    - surface hopping method 152–155
  - transfer dynamics, in strong excitonic
    - coupling 465
  - transfer integral 308

transfer processes 1  
transistor 305  
transition amplitude 76  
transition charge density 431  
transition frequencies 466  
transition rate, for thermal ensemble  
78  
transverse relaxation time 129  
tuning modes 290  
two-exciton state 427, 442

**U**

ultrafast internal conversion 288--290  
ultrafast photoinduced HET 303

**V**

vibrational energy relaxation 4, 214  
vibrational Hamiltonian of donor-acceptor  
complex 310  
vibrational modulation of the excitonic  
coupling 464

vibrational progression 254, 261  
vibrational spectroscopy map 244  
vibrational state representation Hamiltonian  
314  
vibrational state space model 221  
virtual photon exchange 507

**W**

wave mixing 187  
wave packet 66-67, 69  
excitonic 466  
weak exciton-vibrational coupling 487  
wide-band limit 351, 353, 367  
Wigner representation 88-90  
of density operator 92  
Wigner transformation, partial 276

**Z**

zero-phonon transition 260  
zeroth-order state 212, 216, 219  
Zundel cation 391