

Index

- Ab initio*, (*see* Molecular orbital theory)
- Acidity, 11, 176, 194, 410–413, 415, 469, 481
- Activated complex, 523–527, 531, 535, 538
- Activation energy, 62, 132, 149–150, 267, 285–288, 300, 349, 378, 390, 422, 440–442, 483–484, 527–539, 543–545
- Active space, (*see* Orbital)
- Adiabatic connection, 264–268, 273, 278–300, 340, 371
- Adiabatic process, 331, 489–490, 497, 505, 519
- Alkane solvation, 388, 407
- Allyl system, 116–119, 234
- Alq3, 513–515
- AM1, 145–156, 193, 281, 287, 313, 319–323, 338, 340, 375, 381–382, 459, 465, 476
- AM1*, 154
- AM1/d, 154
- AM1/OPLS and AM1/TIP3P, (*see* QM/MM)
- AMBER, 51, 59, 99
- AMBER*, 51, 60
- Amine basicity, 91
- Amsterdam Density Functional, 273
- Analytic derivatives, (*see* Gradient)
- Anions, 119, 148, 176, 182, 244–246, 414
- Anomeric effect, 23, 469, 578
- Antisymmetry, 122–126, 190, 265
- AOC, (*see* QM/MM)
- Aqueous solvation, (*see* Water, as solvent)
- Arrhenius equation, 528, 545
- Atom types, 31, 38, 40, 48–49, 310, 356, 404, 408
- Atomic partial charge, (*see also* Population analysis) 31–32, 100, 135, 151–152, 171, 270, 309–324, 402–404, 411, 443, 446, 458, 462, 474–476, 480, 579
- atoms-in-molecules, 309, 315–318
- classes, 310–324
- CM n , ($n = 1–3$), 319–324, 404, 459–461
- conformational dependence, 313, 319
- discretization, 399
- electronegativity equalization, 54, 310–312
- ESP, 318–319, 322–323, 449
- GAPT, 315
- Löwdin, 314–315, 320
- Mulliken, 312–314, 320, 322–323, 404
- NPA, 314–315, 322–323, 578
- SCRF calculations, 404
- Atomic radii, 27, 403
- Atomic units, 15
- Atomization energy, 111, 192, 267, 280–284, 367, 375, 381–382
- Atoms-in-molecules, 315–318
- Autocorrelation function, 86–88
- Avidin, 452–454
- Avogadro's number, 359
- Avoided crossing, 499, 540–541
- B exchange, 263, 266–267, 295
- B1B95, 267–268, 287, 290, 295
- B1LYP, 267, 283, 292, 295, 339
- B1PW91, 267, 283, 292, 295, 339
- B3LYP, 241, 267–268, 271, 278–279, 284–286, 290–292, 294–295, 298–299, 330, 339–340, 347, 350, 381–382, 414, 544–545
- B3LYP*, 268, 295
- B3P86, 284, 290–291, 330

- B3PW91, 266–267, 284, 288, 290–291, 293–295, 330, 339–340
 B86 exchange, 263, 295
 B88 correlation, 263, 295
 B95 correlation, 264, 295
 B97, 285, 287, 295–296, 347
 B98, 264, 285, 287, 295
 BAC, (*see* Bond additivity correction)
 Band structure, 192, 498
 Basis set, (*see also* Orbital; note that individual basis sets below are indexed by name *not distinguishing* between number or type of polarization or diffuse functions),
 114–115, 117, 128–129, 139, 143, 155, 158, 166–180, 220, 227–230, 256, 273–274, 448, 578
 3-21G, 172, 175–176, 192–194, 197, 340
 4-31G, 172
 6-21G, 172
 6-311G, 172, 174, 176–177, 329, 340
 6-31G, 172, 174–177, 192–193, 195, 340
 additivity principle, 177–178
 auxiliary, 261–262, 273
 cc-pCVnZ, ($n = \text{D, T, Q, ...}$), 171, 176, 228–229
 cc-pVnZ, ($n = \text{D, T, Q, ...}$), 171–172, 176–177, 192–193, 197, 228–229, 235, 274, 340
 correlation-consistent, 171, 173, 179, 228
 d functions, 173–174
 density functional, 260–262
 diffuse functions, 176, 180, 194, 279, 331, 412, 414
 effective core potential, 178–179, 192, 224, 345, 447
 EPR-III, 328
 excited-state demands, 494
 f functions, 174–175, 228
 g functions, 174–175
 IGLO-III, 328
 linear dependence, 182
 MAXI- n , ($n = 1, 2, \dots$), 172
 MIDI!, 175–176, 199, 321
 MIDI- n , ($n = 1, 2, \dots$), 172
 MIDIY, 175–176
 MINI- n , ($n = 1, 2, \dots$), 171
 minimal, 170–172, 181–182, 214, 313
 pc- n , ($n = 1, 2, \dots$), 175–176, 274
 plane waves, 273, 448
 polarization functions, 173–175, 197, 228, 514
 Rydberg-state demands, 498
 sp functions, 170–172, 180
 splitting, 170–173, 313
 STO-3G, 155, 169–171, 184–185, 192–193, 214
 STO-MG, 169–170, 172
 superposition error, 195–196, 279, 293
 VB, 478–480
 BB1K, 268, 295
 Becke exchange, (*see* B exchange)
 Benzene, 183, 497, 502
 Benzyne, (*see* Didehydrobenzene)
 Berendsen coupling, 91
 Bergman cyclization, 349
 BH&HLYP, 266, 283, 286, 290, 292, 296, 339
 Biasing potential, (*see* Umbrella potential)
 Biotin, 452–454
 BLYP, 263, 272, 282, 285, 287, 289, 291–294, 330, 339–340, 347, 494–495, 505
 Bm, 285, 296
 Bohr magneton, 15, 327
 Boltzmann distribution, 160, 377, 451, 523, 534–535
 Boltzmann's constant, 71, 358
 Bond additivity correction, 243, 371
 Bond critical point, 316
 Bond dipole moment, 33
 Bond dissociation energy, 20–21, 148, 156, 216, 243, 279, 419
 Bond length, 3, 6–8, 11, 17, 22, 26–28, 34, 42, 44, 145, 160, 183, 197, 235, 243, 291, 293, 453, 479, 483, 542
 equilibrium, 18–19, 40, 337, 342
 Bond order, 38, 320–321
 Bond separation reaction, 373
 Bond stretching, (*see* Potential energy functions)
 Bonding, 5, 28, 34, 38, 49, 112, 118, 153, 171–172, 193–194, 216, 275, 311, 324, 381, 575, 578
 dative, 197, 279
 overemphasis at RHF level, 188, 197
 Born equation, 396–397, 402, 542
 effective radius, 402–403
 generalized, 402–404, 408–409, 415, 420–421, 448

- Born-Oppenheimer approximation, 110–111, 331, 489–490, 540
- Boundary-element method, 400, 404
- BP86, 277, 282, 285–289, 291–292, 340, 347–348
- BPW91, 233, 257, 266, 282, 285, 288–289, 291–292, 294, 321, 339, 422–423, 495, 502
- BR exchange, 264, 296
- Brillouin's theorem, 213–214, 221, 496, 507, 573
- Broken symmetry, (*see* Density functional theory)
- Bromide/methyl bromide, 440
- Brownian dynamics, 80
- Brueckner orbital, 226, 231–234
- 1,3-Butadiene, 207–208, 293
- t*-Butylvinylidene, 494
- BVWN, 282, 330
- BVWN5, 494
- Cage critical point, 316
- CAM exchange, 263, 296
- Canonical ensemble, 357–358
- Car-Parrinello, 447–448
- Carbon monoxide, 244, 294, 299–300, 347–348
- Carbon tetrachloride solution, 409, 446, 460
- Carbonic anhydrase, 481
- CASPT2, (*see* Perturbation theory, multireference)
- CASSCF, (*see* Self-consistent field, multiconfiguration)
- Cavitation, 387–388, 406–407, 417
- Cavity, 388, 394–406, 410–411, 415, 419–421
- charge penetration, 415
- general solute, 395, 398, 410
- spherical radius, 395–398, 406
- CBS, (*see* Multilevel methods)
- Centrifugal distortion, 334
- CFF, 50, 53
- Charge transfer, 196, 269, 279, 293, 415, 422, 448, 503
- Charge-charge interaction, (*see also* Electrostatic and Nonbonded interactions), 48, 90, 157, 307, 309, 400, 404, 445
- Charge-dipole interaction, 307, 446
- CHARMM, 52, 60, 99, 408, 476, 482–483
- CHELPG, (*see* Atomic partial charge, ESP)
- Chem-3D, 50, 55
- Chem-X, 53, 60
- Chemical shift, 344–349, 451, 472
- scaled, 345–346
- Chloride/allyl chloride, 198, 293
- Chloride/methyl chloride, 185–186, 390
- Chloroform solution, 387, 409, 411, 416, 446, 465
- Circular dichroism, 504
- CIS, 140, 187, 214, 496–499, 502, 514–515
- CISD, (*see* Configuration interaction)
- Claisen rearrangement, 392, 448–449, 463–464
- CM n , ($n = 1–3$; *see* Atomic partial charge)
- CNDO, 136–139
- Coarse-grained models, 35, 98
- Code, (*see* Software)
- Collective coordinates, 35, 98
- Collision theory, 528, 542
- Comparative molecular field analysis, 308–310
- Complete basis set, (*see* Multilevel methods)
- Compressibility, 418, 446
- Condensed-phase effects, (*see also* Solvation and Solvatochromism), 379, 385–393, 538–539
- Condon-Slater rules, 212–213, 221, 510
- Configuration interaction, (*see also* CIS), 211–216, 224–227, 244–246, 328, 336, 401, 496–502
- full, 211, 224, 278
- matrix elements, 212–213
- multireference, 216, 495, 501, 505
- quadratic, 226–227, 281, 286–287, 292, 336, 340
- single-reference, 211–216, 496–497
- spin-flip, 215–216, 234, 496
- VB, 477–481
- Configuration state function, 206–212, 220, 499
- Conformational analysis, 19, 97, 150, 313, 459
- Conformational averaging, 64–66, 97, 193, 288, 377–378, 563
- Conical intersection, 499–500
- Continuum solvation, (*see* Solvation)
- Contraction, (*see* Orbital)
- Convergence
- binding energy, 196
- correlation energy, 228–229, 236
- DFT with respect to basis set size, 274, 288

- Convergence (*continued*)
 finite-field calculation, 327
 geometry optimization, 40–50, 141, 183, 191
 HF SCF, 121, 128–129, 166, 181–182, 207, 262, 491
 induced dipole moment, 446
 KS SCF, 274, 491, 495
 multipole-multipole interactions, 307
 quadratic, 181
 SCRF, 396–397
 simulation, 93–96, 444
 solvation free energy, 401
Core electrons, 134, 178–179, 195, 228, 240, 345, 474
Core potential, (*see* Basis set)
Correlation, (*see also* Electron correlation), 110
Correlation energy density, 259, 263
COSMO, (*see* Solvation)
Coulomb integral, (*see* Two-electron integral)
Coulomb radius, 403–404
Coulomb's law, 2, 14, 37, 402
Counterpoise correction, 195
Coupled-cluster theory, 224–227, 229–237, 242, 244–246, 336, 401, 465, 574
 predictions from, 244–246, 281, 292, 339, 375, 381–382, 422–423, 495, 544–546
 scaled, 229–230
 spin-flip, 227
Coupling parameter, 265, 433–437, 443–444, 449, 458, 464, 481
Cross terms, 34–36
CS correlation, 296
Curtin-Hammett principle, 300
Cutoff distance, 47, 88–90
CVFF, 53, 60
Cyclobutene, 207–208

d orbitals, 153–155, 167, 285, 291
Darwin relativistic correction, 223–224
Davidson correction, 215
Debye-Hückel parameter, 395, 403
Decay time, 87, 95
Degeneracy, 204–206, 231, 244, 324, 333, 350, 359–364, 498, 563
 structural, 364, 563
Degrees of freedom, 6, 20, 34, 42–43, 69, 75, 78–80, 88, 92, 183–186, 338, 342, 394, 429, 442, 523, 525–526, 531–532, 535, 538, 563

Delta SCF, 194–195, 288, 330–331, 494–496, 503
Density functional theory, 249–300, 371
 broken symmetry, 275–276, 545
 multideterminantal, 276
 overdelocalization, 279–280, 294, 330–331
 predictions from, (*see* individual functional names)
 projected, 494, 506–507
 SCI and MRCI, 498, 501
 tight-binding, 268–271, 321–322, 404
 time-dependent, 497, 501–504, 514–515
Density matrix, 127–128, 181, 188–189, 196, 261–262, 308, 328, 396, 404, 476
 spin, 189, 328, 330
 spin-difference, 328
Deprotonation, (*see* Acidity)
Diazene, 505–507
1,2-Dichloroethane, 398, 459–460
Didehydrobenzene
 1,3-, 197
 1,4-, 231–234, 254, 275, 277, 349–350, 374–375
2,5-Didehydropyridinium cation, 231–234, 275
Dielectric constant, 2, 32–33, 98, 101, 394–397, 403, 405, 417, 421, 452, 460, 512, 542
Diels-Alder reaction, 285, 460
Diffusion, 88, 543
Dipole moment, 32–33, 37, 82–84, 143, 152, 198, 294, 306–307, 310, 315, 320–326, 332, 342, 387–388, 397, 411, 445, 463–464
 induced, 33, 325, 387–388, 446, 463–464
Dipole-dipole interaction, (*see also* Electrostatic and Nonbonded interactions), 23–28, 32, 47, 90, 307, 445
Dirac δ , 84–85, 224, 439
Direct dynamics, 532
Direct methods, 13, 191
Dispersion, (*see also* Nonbonded interaction), 28–29, 149, 155, 192, 195, 198, 271, 293, 371, 388, 406–408, 447, 513
Divide-and-conquer formalism, 274
DNA, (*see* Nucleic acids)
Docking, 62–64, 404, 420, 454
Double-wide sampling, 434
DREIDING, 38, 53
Drug design, 62, 152–153, 309–310
Dry cleaning, 422

- Dual topology, 443
- Dynamics,
 molecular, 72–80, 91–96, 273–274, 399,
 420–421, 431–434, 438–440, 444,
 447–454, 463, 474–477, 482–484,
 513, 538
 non-adiabatic, 539–544
 reaction, 357, 423, 482–484, 519–546
- ECEPP, 54
- Eckart potential, 536
- EDF1, 268, 282, 296
- Effective core potential, (*see* Basis set)
- Effective fragment potential, 447, 465
- Eigenfunction, 106, 111, 120–122, 126, 166,
 173, 182, 188, 190, 212, 216–218, 220,
 255–256, 324–325, 328, 332, 336,
 507–509, 565–570
- Eigenvalue, 95, 106–107, 110–111, 121–122,
 149, 190, 206, 214, 216, 219–220, 250,
 253, 255, 272, 325, 330–333, 335–337,
 362, 479, 496, 502, 507, 540, 565–570
- Electric multipole moment, (*see* Multipole
 moment, electric)
- Electrochemistry, 410, 413–415, 422–424,
 541–544
- Electron affinity, 137, 176, 195, 270, 285,
 288–290, 311, 330–331, 414, 423
- Electron correlation, 111, 128–129, 132–133,
 149, 165, 173, 178, 192–195, 203–246,
 251, 280, 330, 388, 493, 574
 angular, 228
 core, 228, 242–243
 core-valence, 228, 240–241
 dynamical, 203–205, 211, 216, 223, 233,
 497, 501
 effect on geometries, 197–198, 235
 effect on solvation free energy, 401, 406
 effect on vibrational intensities, 341
 energy, 129, 132–133, 149, 165, 178, 214,
 224, 242, 370–372
 exchange, 128, 189, 251, 265–267, 274, 278
 non-dynamical, 182, 203–205, 209, 212,
 216, 223, 246, 275–277, 285, 291, 351,
 495, 501
 radial, 228
 scaled energies, 238–239
- Electron density, (*see also* Density functional
 theory and Gradient), 61, 112, 249–280,
 314–318, 421, 475–476, 577
- Electron spin resonance, 189, 305, 327–330
- Electron transfer, 422–424, 541–544
- Electronegativity, 23, 31, 152, 171, 270, 307,
 310, 313, 318, 474
- Electronic energy, 110–111, 121, 148, 154,
 203, 206, 220, 238, 332–333, 366, 375,
 412, 525
- Electronic excited state, 140–141, 176,
 186–187, 254, 273, 360–361, 487–513
- Electronic *g* value, 327, 330
- Electrostatic interaction, (*see also*
 Charge-charge, Dipole-dipole, and
 Nonbonded interactions), 30–34, 88, 90,
 100, 195, 198, 387–388, 393–406, 444,
 447, 461–462, 467, 474, 478
- Electrostatic potential, (*see also* Atomic partial
 charge), 199, 308–309, 318–319,
 394–395, 399–400, 405
- Electrostriction, 452
- Elementary reaction, 519–523, 531
- Empirical valence bond, 477–482
- Enantiomeric excess, 160
- Enediyne, 349–350
- Enolase, 482–484
- Ensemble, 69, 82, 91–93, 99, 355–366,
 432–434, 440, 463
- Ensemble average, (*see also* Expectation
 value), 70, 83–88, 429, 431–437, 441,
 443, 452–454, 463
- Enthalpy, (*see also* Heat of formation), 10, 92,
 355–356, 358, 366–378, 381–383, 412,
 430, 444, 527–528, 537, 545
- Entropy, 355, 358–366, 376–378, 386, 430,
 445, 452–453, 527–528, 545
 bottleneck, 523, 533
- Enzyme-substrate binding, 62–63, 400,
 438–439, 442, 452–454, 457–458,
 482–484
- Equation-of-motion method, (*see* Propagator
 method)
- Equilibration, 92–93, 96, 311
- Equilibrium constant, 11, 41, 62, 132,
 379–380, 386, 389, 416, 432, 520,
 524–525
- Equilibrium fraction, 377
- Ergodicity, 72, 93, 431
- ESFF, 54, 60
- Essential dynamics, (*see* Principal components
 analysis)

- Euler's approximation, 75, 77
Even function, 342–343
Ewald sum, 47, 89–90, 101
Exchange, (*see* Electron correlation)
Exchange energy density, 258–259
Exchange functional, 257, 263–264
Exchange integral, (*see* Two-electron integral)
Exchange repulsion, 24, 28, 407, 447, 467
Exchange-correlation energy, 256, 260, 262, 265–266, 271, 338
Excited state, (*see* Electronic excited state)
Expectation value, (*see also* Ensemble average), 61, 71, 83, 94, 142, 190, 203, 209, 218, 220, 223, 244, 253–256, 262, 265–266, 271–275, 324–327, 342, 387, 397, 432, 452, 461–463, 466, 495, 505–510, 567–573
Extended Hückel theory, (*see* Hückel theory)
Extrapolation, 176–177, 230, 239–244, 528

Fast multipole methods, 48, 191, 274
Fenske-Hall theory, 135
Fermi contact integral, 327–328
Fermi hole, 125, 189, 251
Fermi resonance, 341
Ferromagnetism, 136
Finite-field calculation, 327
First derivative, (*see* Gradient)
Fluorine scanning, 452–454
Fluoromethane, 333, 347–348
Fluoromethyl radical, 343–344
Fluorovinylidene, 493–494
Fock operator, 126–129, 189, 203, 219, 462, 562, 577, 578
Force constant, 18–21, 35, 37, 39, 192, 338–339, 341, 443, 473, 522, 529 scaled, 341
Force field, 17–66, 75, 98–99, 156, 312, 318–319, 404, 411, 452–454, 459, 465
Force-biased Monte Carlo, 82
Four-index integral, (*see* Two-electron integral)
Fourier decomposition, 23–24
Fourier transform, 88, 101, 448
Franck-Condon overlap, 490, 511
Free energy, 355, 389, 429–444
 activation, (*see* Activation energy)
 cycle, 391–393, 412, 418, 437–439, 452–454
Gibbs, 358, 368–369, 376–380, 430, 437–443, 452–454, 531, 542–543
Helmholtz, 430–436, 443
 perturbation, 432–444, 449, 453, 458, 463–464, 481
 solvation, (*see* Solvation, free energy)
 transfer, 386–389
Free rotor, 376–377
Frequency, (*see also* Vibrational spectroscopy),
 absorption, 333, 335, 341, 489, 507–511
 imaginary, 338, 523, 526, 535
 intensity, 341, 507–511
 isotopic dependence, 357, 530
 reaction coordinate, 526, 535
 scale factor, 339–341, 345, 349–350, 356, 545
 vibrational, 228, 245, 305, 315, 334–342, 345, 349–351, 356–357, 365–366, 370, 375–376, 429, 452, 472, 526, 528–529, 545
Friction, 73, 80, 334, 420, 421, 538
FT97 exchange, 263, 296
Functional derivative, 256
2-Furfural, 459–460

 G_n , ($n = 1, 2, \dots$; *see* Multilevel methods)
G96, 296
Gas constant, (*see* Universal gas constant)
Gauge origin, 344–345
Gaussian function, 168–169
Gaussian-type orbital, (*see* Orbital)
GB/SA, (*see* Solvation)
Gear predictor-corrector algorithms, 78
Generalized Born equation, (*see* Born equation)
Generalized gradient approximation, 263–264, 266–268, 278–279, 285, 291
Geometry
 comparing theory to experiment, 61, 69
 effect on SCF convergence, 181
 optimization, 40–50, 182–187, 190–192, 196–198, 238, 334, 472–473, 490, 497, 499–500, 505, 514
 quality of predicted, 150–151, 196–198, 235–236, 291–294, 329–330, 573
 relaxation, 489, 542
 rotational spectroscopy dependence, 332, 364
 UV/VIS spectroscopy dependence, 140, 489–490
 vibrational spectroscopy dependence, 338
GHO, (*see* Orbital, generalized hybrid)
GIAO, 345

- Global minimum, 23, 46, 97, 146, 383
Glucose, 60, 150–151, 193, 235, 240, 385
Gradient,
 corrected density functionals, (*see*
 Generalized gradient approximation)
 electron density, 263–264
 potential energy surface, 43–45, 133, 144,
 196–198, 221, 234–235, 238, 243, 260,
 291, 319, 401, 472, 477, 497, 505, 522,
 532, 573
Green's function, (*see* Propagator method)
Grid, 62–64, 260, 308, 318, 338, 399–401,
 466–467
 docking, 62–64
 for ESP charge, 318
 integration over, 260, 338, 399–400
GROMOS, 54, 60, 99
Ground state, 109, 115, 360, 487–504,
 507–508, 511, 513–515
Group theory, (*see* Point group and Symmetry)
GVB, 209

H&H, 266, 296
Half-electron method, (*see* Hartree-Fock
 theory)
Half-life, 521
Hamiltonian, 72, 106–111, 119–122, 154, 157,
 166, 179, 203, 212, 215, 219–220, 223,
 249–250, 252–255, 262, 321, 325–327,
 387, 396–397, 434, 436, 457, 459, 461,
 478, 496, 508, 562, 572–575
 determination from electron density,
 249–250, 252–254, 475
 EVB, 477–482
 including radiation field, 508
 non-interacting, 122, 219–220, 255–256,
 265
 QM/MM, 457, 459–462, 467–469
Hardness, 270
Harmonic oscillator, 61, 72–74, 336–342, 356,
 364–365, 376, 484, 527, 531, 539
Harris functional, 269
Hartree product, 120–122
Hartree-Fock theory, 126–129
 ab initio, 126–129, 165–199, 203–205, 327
 and DFT, 258, 267
 half-electron, 148
 instability, 234
 limit, 128–129, 165–166, 173, 176–178,
 228, 230
 periodic, 192
 predictions from, 192–199, 281, 287–289,
 292–294, 322–323, 330–331,
 338–340, 346–348
 projected, 506, 571–574
 QM/MM modifications, 462
 restricted, 126–128, 190, 197, 205, 234, 487
 restricted open-shell, 188–190, 206, 325,
 328–329
 semiempirical, 128, 131–147
 TS structures, 197–198
 unrestricted, 148, 188–190, 234, 244, 272,
 324–325, 328, 506, 545, 571–574
Hartree-Fock-Slater method, 252
HCTH, 264, 274, 283, 285, 287, 289, 292, 296
Heat capacity, 366, 445–446
Heat of formation, 37, 40–41, 142, 147–148,
 155, 192, 240–244, 356, 366–375, 378,
 381–383
Heaviside function, 534
Heisenberg spin ladder, 505
Hellmann-Feynman theorem, 264, 326
Hessian, 44–46, 185, 191, 221, 260, 336–338,
 365–366
Hexachloroethane, 422–424
HF/3–21G/OPLS, (*see* QM/MM)
Hindered rotor, 376–377
Histogram, 83–86, 439, 541
Hohenberg-Kohn theorems, 252–254, 273, 494
Hole function, 251, 257, 278
Hooke's law, 18
Hückel theory, 115–119, 269
 extended, 134–136, 181
Hund's rule, 204
Hybrid DFT, (*see* Adiabatic connection)
Hydrazine, 138–139, 151
Hydrogen bonding, 33, 50, 112, 145, 149–151,
 156, 158, 193, 195, 198, 279, 293, 309,
 386, 407, 433, 449, 460, 463, 513
Hydrogen cyanide, 316, 322, 347, 430–435
Hydrogen electrode, 410, 414, 423
Hydrogen fluoride, 176, 236, 294, 347–349
Hydrogen-atom transfer, 267, 286, 537–538
Hydrophobicity, 152, 388, 407–408, 449, 452
Hydroxylamine, 381–383
8-Hydroxyquinoline, 513–515
Hyperconjugation, 24–25, 313, 578–579
Hyperfine coupling, 10, 189, 305, 327–330,
 343–344

- Hyperpolarizability, 325–327
Hypervalency, 143, 148, 153–155, 174–175, 197
Hysteresis, 434
- Ideal gas assumption, 358–359, 361–362, 379, 527
IGLO, 345
IMOMM, (*see* QM/MM)
Implicit solvation, (*see* Solvation)
Improper torsions, 27
Index of refraction, 409, 512, 542
INDO, 139–143, 153, 181
INDO/S, 139–141, 153, 497, 502, 514–515
Infrared spectroscopy, (*see* Vibrational spectroscopy)
Intensity, (*see* Frequency)
Internal coordinates, 6–7, 29, 34, 36, 46–48, 82, 336, 459, 522, 539, 541
Internal energy, 92, 356, 358–366, 376–377, 430–432, 444, 453, 525
Intrinsic reaction coordinate, (*see* Reaction coordinate)
Ion convention, 378
Ionic strength, 394–395
Ionization potential, 116, 135, 137, 194–195, 270, 272, 285, 311, 330–331, 414, 502
 predicted values, 141, 143, 149, 194–195, 288–290, 423
 valence-shell, 135
IPCM, (*see* Solvation)
IRC, (*see* Minimum-energy path)
Irreversible reaction, 520, 522, 524
ISM, 264, 296
Isodesmic equation, 166, 372–375, 381–382, 413
Isogyric, 373–374
Isotope effect, 357, 528–531
 kinetic, 482–484, 528–531, 533, 537–538
- Jahn-Teller distortion, 206
Jellium, 250
- KCIS, 264, 296
Kinetic-energy density, 264
Kinetic-energy functional, 250, 255–258, 262, 264, 274–275
Kinetic-energy operator, 107, 266, 269, 274, 332, 344
- Kinetic isotope effect, (*see* Isotope effect)
Kinetics, 199, 267, 334, 344, 390, 393, 421, 482–483, 519, 523, 537
Kirkwood-Onsager equation, 396–397
KMLYP, 286–288, 296
Kohn-Sham theory, (*see also* Self-consistent field), 255–257, 274–278, 397, 448, 578
 QM/MM modifications, 461–462
Koopmans' theorem, 149, 194–195, 272, 330–331
Kramers-Grote-Hynes theory, 539
Kronecker δ , 107, 224
- Landau-Zener model, 541
Langevin dipole, 466–467
Langevin dynamics, 80, 539
Lap correlation, 264, 297
Laplacian operator, 107, 127, 562
LCAO approach, 111–113
Leapfrog algorithm, 77–78, 101
Lennard-Jones potential, 29–30, 33, 47, 155, 271, 461–463, 478
Lewis structure, 209, 578–579
LG exchange, 263, 297
Line search, 44
Linear response theory, 387
Linear scaling, (*see* Scaling behavior)
Link atom, 473–477
Liquid crystal, 417
Local density approximation, 258–263, 266
Local minimum, 6, 41–46, 61, 69, 183, 185–186, 235, 291, 337–338, 377–378, 419, 522–523
Local spin density approximation, 259–267, 278, 282, 285–286, 288–289, 291–292, 294, 345–348
Locally enhanced sampling, 98
London forces, (*see* Dispersion)
LT2A, 297
LYP correlation, 263, 266, 291, 297
- MACROMODEL, 50–51
Magnetic multipole moment, (*see* Multipole moment, magnetic)
Marcus theory, 541–544
Markov chain, 82
Mass-velocity relativistic correction, 223
Mataga-Nishimoto integral, 137

- Matrix diagonalization, (*see also* Scaling behavior), 14, 212–214, 262, 274, 462, 480, 496, 522
- Matrix elements, (*see also* Configuration interaction), 114, 116, 119, 127–128, 138, 184–185, 213, 222, 257, 269, 272, 345, 462, 496–497, 502, 510, 562, 573
- Matrix isolation, 349–351
- Mayer bond order, 320–321
- MBPT n , (*see* Perturbation theory)
- MCG3, (*see* Multilevel methods, multicoefficient models)
- MCSCF, (*see* Self-consistent field, multiconfiguration)
- Membrane, 418, 421
- Memory, 13, 191
- Menschutkin reaction, 393
- meta-Generalized gradient approximation, 264, 268, 278, 285
- Metal, (*see also* Solid and Transition metal), 26, 38, 61, 141, 179, 275, 286, 291, 299, 328, 452, 542
- Metastability, 96
- Methanol, 100, 156, 208, 211, 299–300, 319, 347, 437–438
- Methyl radical, 116, 188–189, 330, 343–344, 374
- Methyldiazonium cation, 317
- Metropolis sampling, 81–82, 451, 459
- Microcanonical ensemble, 91
- MINDO/3, 141–145
- Minimum, (*see* Global and Local minima)
- Minimum-energy path, (*see also* Reaction coordinate), 7, 449, 522–523, 531–532, 538, 545
- Missing parameters, 39–41
- MM2, 38, 40, 50, 55, 59–60
- MM2*, 50–51
- MM3, 14, 20–21, 38, 50, 55, 59–60, 64–65, 341, 469–471
- MM3*, 50–51
- MM4, 55
- MMFF, 38, 50, 56, 60, 341, 459
- MMX, 56
- MNDO, 143–156, 158, 193, 281, 287, 346–347
- MNDO/d, 145, 153–155
- MNDOC, 145
- Model, (definition), 2
- Model chemistry, 180, 240
- Mole, 355
- Molecular dynamics, (*see* Dynamics)
- Molecular electrostatic potential, (*see* Electrostatic potential)
- Molecular mechanics, 17–66, 150, 264, 341, 445, 457–484, 532
- Molecular orbital, (*see* Orbital)
- Molecular orbital theory, 105–129, 203–244, 271–280, 285, 575–579
- ab initio*, 129, 131, 133, 143, 165–246
- semiempirical, 128, 131–162, 237, 260, 375
- Molecular rotational constant, 333
- Molecular weight, 100, 152, 362, 380, 450
- Molecularity, 519
- MOMEC, 56
- Moment of inertia, 6, 94, 332–334, 362–364, 377
- Monte Carlo, 64, 80–82, 90, 92–93, 259, 431–434, 438–440, 444, 447, 449, 451, 459, 463, 513
- Morse potential, 20–21, 30, 311, 478
- m*PBE exchange, 263, 279, 297
- MP n , ($n = 2, 3, 4, \dots$; *see* Perturbation theory)
- m*PW exchange, 263, 297
- MPW1K, 267–268, 279, 283, 285–288, 297
- m*PW1N, 268, 297
- MPW1S, 268, 297
- m*PW1PW91, 268, 283, 287, 290, 292, 297, 339
- m*PW3PW91, 284, 293, 339
- m*PWPW91, 283, 285, 287, 290, 292, 339, 503
- MST, (*see* Solvation, PCM)
- Mulliken, (*see* Population analysis)
- Multiconfigurational molecular mechanics, 50, 532
- Multilevel methods, 239–244, 260
- CBS, 239, 242, 281, 286–289, 371, 382
- G n , ($n = 1–3$), 240–243, 281, 284, 289, 291, 371, 382
- multicoefficient models, 242–243, 281, 287
- W n , ($n = 1–4$), 242, 282, 289
- Multiple-minima problem, 96–98, 451
- Multipole expansion, 154, 307–308, 397–398, 401, 416

- Multipole moment,
 electric, 30–33, 144, 154, 305–308,
 317–318, 387–388, 397–398
 magnetic, 326, 344
- NBO, (*see* Orbital, natural)
- NDDO, 143–158, 371, 476
- Newton's equations of motion, 74
- Newton's second law, 74
- Newton's third law, 79
- Newton-Raphson minimization, 44–46
- NHE, (*see* Hydrogen electrode)
- Non-classical reflection, 534–535
- Non-crossing rule, 499
- Non-local DFT, (*see* Generalized gradient approximation and Gradient, electron density)
- Nonbonded interaction, (*see also* Charge-charge, Dipole-dipole, and Steric interactions and Dispersion), 19, 27, 30, 33–35, 40, 47, 62–64, 88, 100, 149, 151, 157, 195, 271, 278–279, 293, 311, 371, 432–434, 443, 459, 461, 467, 480
- Normal mode, 46, 337, 341–342, 356, 364–366, 376, 391, 452, 514–515, 523, 530–531, 535
- Normalization, 71, 84–87, 107, 124, 168, 203, 206, 218, 321, 361, 418, 439, 462, 504, 572
- Nosé-Hoover coupling, 92
- Nuclear magnetic resonance, 10, 36, 64–66, 305, 344–349, 411
- Nuclear motion spectroscopy, (*see also* Rotational and Vibrational spectroscopies), 331–344
- Nuclear Overhauser effect, 35–36, 99
- Nuclear repulsion energy, 106, 110–111, 145, 158
- Nucleic acids, 35, 38, 47, 57, 99, 156, 279, 387, 408, 411, 416–417, 421, 462, 469, 472
- O exchange, 263, 267, 297
- O3LYP, 267, 284, 287–288, 290, 297
- Occupation number, 206, 210, 489
- Octanol solution, 409, 446
- Octanol-water partitioning, 152, 416, 438
- Odd function, 342
- OM n , ($n = 1, 2$), 158
- One-electron integral, 127, 137–138, 153, 184, 262
 external potential, 262
 symmetry, 184
- Open-shell singlet, 136, 190, 208, 276–277, 505, 570
- Operator, 4, 106, 216–221, 249, 271, 396, 463, 565–566
 cluster, 224–226
 Coulomb and exchange, 127, 220, 265, 273–274
 Fock, (*see* Hartree-Fock theory and Reaction field)
 Hamiltonian, (*see* Hamiltonian)
 Kirkwood-Onsager, 396
 Kohn-Sham, (*see* Kohn-Sham theory)
 one-electron, 120–122, 126–129, 203, 223, 253, 255–256, 462, 466, 475, 510
 permutation, 123–124
 S^2 , 188, 324–325, 328, 506, 565–572
 spin-annihilation, 506, 571–573
 S_z , 122, 272, 324–325, 327, 565–571
- OPLS, 38, 56, 60, 98–99, 438, 446, 449, 459–460
- OPLSA*, 51
- Optical rotatory dispersion, 504
- Orbital, (*see also* Basis set)
 active space, 207–210, 233–234, 239, 499–501
 banana-bond, 576
 complex, 234
 contracted, 168–173, 180
 core, 134, 171–172, 209, 215, 224, 328, 345
 energy, 111, 115–119, 128, 195, 219, 230–231, 269, 498, 502, 577
 floating, 173
 frozen, 215, 475–476
 gauge-including, 345
 Gaussian-type, 155, 167–180, 273–274, 328
 generalized hybrid, 476–477, 483
 hydrogenic, 112, 128, 134, 167–168
 Kohn-Sham, 256–257, 264, 272, 306, 448, 502
 localized, 209, 221, 345, 475–476, 575–579
 molecular, 39, 100, 105–129, 149, 158, 165–199, 203–244, 306, 324, 328, 343, 475, 487–500, 506, 559–562, 571, 573, 575–577
 natural, 578

- primitive, 168–173
- Slater-type, 134, 136–138, 141, 148, 155, 158, 167–172, 181–182, 270, 273, 328, 347–348
- spin, 124–126, 188–190, 234, 324, 575
- valence, 134, 140, 145, 155, 171–173, 328, 345, 498
- virtual, 195, 205–212, 216, 221, 228–229, 272, 487–496
- Orthogonality, 107, 126, 158, 177, 182, 206, 221, 314, 475–476, 491–492, 495–496, 501, 509
- Orthonormality, 107, 218, 312, 314, 540, 565, 567, 569
- Oscillator strength, 141
- Overlap integral, 114, 134–138, 262, 312–314, 321, 325, 328, 571
- Overtone, 341
- Oxygen atom, 227–228
- P exchange, 263, 297
- P86 correlation, 263, 290, 297
- Pairlist, 47, 90
- Pairwise descreening, 404, 420
- Parameterization, 36–39, 140–142, 145–147, 154, 172, 237–244, 266–271, 341–342, 410–411, 418, 445–447, 459–463, 477–482, 497, 514
- Parameterized correlation methods, 237–244, 370–371
- Pariser-Parr approximation, 137
- Pariser-Parr-Pople model, 138, 502
- Partial charge, (*see* Atomic partial charge)
- Particle in a box, 361
- Particle-mesh Ewald, (*see* Ewald sum)
- Partition coefficient, 411, 416–419
- Partition function, 71, 357–366, 429–432, 525–531, 562–563
 - activated complex, 525–532, 535
 - electronic, 359–361
 - molecular, 359–366
 - rotational, 359, 362–364, 528–529, 563
 - translational, 359, 361–362, 526–529
 - vibrational, 359, 364–366, 484, 528–529
- Pauli exclusion principle, 123–124, 179, 251
- PBE, 263, 283, 285, 287, 289, 292, 297
- PBE1PBE, 267, 283, 285, 287, 290, 292, 298, 330, 347, 503–504
- PCI-80, 238, 286, 370
- PCM, (*see* Solvation)
- PDDG, 158
- PEF95SAC, 54
- Penalty function, 36–37, 41, 146, 154
- Perchloroethylene, 423–424, 460
- Periodic boundary conditions, 86–89, 101, 273, 431, 448, 452, 459
- Permutation operator, 123–124
- Perturbation theory, 216–224, 226, 228–243, 336, 401, 469, 498, 573–574
 - convergence, 228–229
 - localized MP2, 222
 - multireference, 223, 233–234, 375, 495, 501
 - predictions from, 281, 287–289, 291–292, 294, 321–323, 327–330, 338–340, 343, 346–347, 366
 - spin-component-scaled, 239
 - spin-projected, 574
 - time-dependent, 507
- Phase angle, 23, 25–26, 35, 40
- Phase point, 70–72, 80–83, 448
- Phase space, 70–82, 92–98, 420, 429–430, 439, 443–444, 448, 450–451, 538
- Phenylnitrene, 276, 490–492, 494–496, 500–501, 504–505
- Phenylnitrenium cation, 272
- Pierotti's formula, 406
- pK_a , (*see* Acidity)
- PKZB, 264, 283, 285, 289, 292, 298
- Planck's constant, 15, 107, 356, 489, 507
- PM3, 146–156, 158, 160–162, 193, 281, 320–323, 338, 340, 469
- PM3_{BP}, 156
- PM3(tm), 154
- PM4 and PM5, 151, 155
- Point group, 183–186, 232, 234, 254, 362–363, 490–492, 494, 514, 559–563, 577
- Poisson equation, 394–402
- Poisson-Boltzmann equation, 394–395, 399–400, 453
- Polarizability, 33–34, 90–91, 155, 294, 325–327, 387, 407, 446–447, 451, 464, 466–467, 513
 - frequency-dependent, 502
- Polarization, 90–91, 156, 173–175, 387, 411, 459, 462, 466–467, 512
- free energy, 394–405, 449

- Population analysis, (*see also* Atomic partial charge), 315, 476, 578
bond order, 320
Löwdin, 314–315, 320
Mulliken, 199, 270, 312–315, 319–323
natural, 314–315, 321–323, 578
- Potential energy functions
bond stretching, 18–21, 473
torsions, 22–27, 377, 474
valence angle bending, 21–22, 26, 473
van der Waals, 27–30, 46
- Potential energy surface, 6–10, 17, 99, 111, 183–187, 216, 221, 238, 244–246, 331, 334–338, 356, 469, 511–512, 522–523, 535–536
electron-transfer, 542–543
EVB, 478–481
excited-state, 490, 500, 511–512, 539–544
solvated, 389–393, 409, 415, 380, 423, 511–512, 538–539
- Potential of mean force, 146, 419–420, 439–442, 463–464
- PPP, (*see* Pariser-Parr-Pople)
- Pressure, 92–93, 358–359, 380, 385, 430, 443
standard-state, 361–362
- Principal components analysis, 95, 421
- Probability, (*see also* Transition probability), 4, 12, 69, 81, 83, 85, 92–93, 98, 106, 112, 121, 125, 166, 262, 377, 430–432, 439–441, 541
- Projection, (*see* Spin, projection)
- Prolate top, 333, 362
- Propagation, 74–79
- Propagator method, 497, 501–504
- Propylene oxide, 544–546–497
- Protein, (*see also* Enzyme-substrate binding), 31, 35, 38, 54, 56–59, 77, 96–97, 99, 157, 408, 421, 444, 452, 473, 475–476, 481–484, 538
- Proton affinity, 148, 194, 291
- Proton transfer, 442, 477–481
- Pseudobond/pseudoangle, 35–36
- Pseudohalogen, 474, 477
- PW exchange, 263, 267, 298, 330
- PW91 correlation, 263, 266, 291, 298
- PWPW91, 283, 285, 287, 289, 339
- QCISD, (*see* Configuration interaction, quadratic)
- QM/MM, 61, 157, 447, 457–484, 513, 532
AM1/OPLS, 465
AM1/TIP3P, 463–465
AOC, 459–460, 463
boundary, 458, 467–468, 473–476
HF/3–21G/OPLS, 465
IMOMM, 472
ONIOM, 473
XSOL, 465
- QSAR and QSPR, (*see* Structure-activity relationship)
- Quadrature, 260, 338
- Quadrupole, 31, 144, 154, 307, 398
- Quantization, 105
- Quantum mechanics, 1, 4–5, 28, 105–129, 309, 326, 357, 457–484, 575
- Quantum numbers, 122–123, 134, 167, 229, 324, 333, 336, 361
- R12 method, 229–230, 249
- Radial distribution function, 84–86, 449, 465
- Radical, 105, 117, 119, 148, 179, 185–190, 194–195, 199–200, 234, 244, 279, 329, 331, 349
- Radical polymerization, 199–200
- Radius, (*see* Born equation, Cavity, and van der Waals)
- Raman spectroscopy, 341
- Random number, 82
- Rare event, 440, 442
- RASSCF, (*see* Self-consistent field, multiconfiguration)
- Rate constant, 12, 519–522, 532–538, 541–546
- Rate-determining step, 481–482, 537
- Reaction coordinate, 48–49, 207, 211, 241, 277, 391–392, 409, 419, 439–442, 449, 451, 457–458, 463–464, 479–484, 511, 522–526, 536–538, 542–546
intrinsic, (*see* Minimum-energy path)
- Reaction dynamics, (*see* Dynamics)
- Reaction field, (*see also* Solvation), 387, 394, 396, 400–401, 404, 513, 542
charge transfer, 415, 448
self-consistent, 393–406, 410–424, 449–450, 513
- Reaction quotient, 379
- Redox potential, (*see* Electrochemistry)
- Reduced mass, 17, 332, 336–337, 357, 535

- Reductive dechlorination, 422–424
Reference interaction site model, 465–467
Relativistic effects, 107, 140, 179, 223–224, 345, 368, 565
Relativity, 123, 129, 565
Renner-Teller, 244
Reorganization energy, 454, 542–543
Resolution of the identity, 573
Resonance energy, 118–119
Resonance integral, 114, 134, 144
Rice-Ramsperger-Kassel-Marcus theory, 536
Rigid-rotor approximation, 332–334, 362, 527, 531
Ring critical point, 316
RNA, (*see* Nucleic acids)
Root switching, 499–500
Roothaan, 126–128
Root-mean-square deviation, 94
Rotation, 23, 97, 119, 150, 194, 280, 332–335, 363, 370, 439, 557–558
 barriers about bonds, 150, 158, 194
 spectroscopy, 332–334
RPA, (*see* Propagator method)
RRKM theory, (*see* Rice-Ramsperger-Kassel-Marcus theory)
Runge-Kutta integration, 78
Rydberg states, 113, 141, 498

Saddle point, (*see also* Transition state), 6, 9, 522–523, 531, 533–534, 539
SAM1, 154–155
Sampling, (*see also* Metropolis sampling), 72, 75, 82, 93, 95, 98, 415, 420, 432–445, 448, 450–451, 463
Scaling behavior, 46–48, 128, 190
 CCSD, 225, 237
 CCSD(T), 237
 CCSDT, 225, 237
 CISD, 214, 237
 DFT, 262, 273–274
 Ewald summation, 47
 fast multipole methods, 48
 Hartree-Fock theory, 128, 178, 190, 237, 262
 linear, 14, 48, 157, 191, 222, 237, 274
 matrix inversion/diagonalization, 14, 45, 185, 262, 274
 molecular mechanics, 29, 47–48
 MP2, 221, 237
 MP4, 222, 237
 QCISD, 237
Schrödinger equation, 106, 539
 electronic, 110, 120, 122, 128–129, 134, 165, 167, 170, 211, 225, 228, 237, 246, 250, 254–255, 278, 332–333, 507
 non-linear, 225, 396–397, 400
 nuclear, 331, 540
 one-dimensional, 334–335, 536
 rigid-rotor, 332–333, 362–363
 time-dependent, 507, 532, 536
SCIPCM, (*see* Solvation)
Second derivatives, (*see* Hessian)
Secular equation, 113–115, 134–136, 212, 256
Selection rules, 332–333, 336, 341, 510
Self-consistent field, (*see also* Density functional, Hartree-Fock, and Kohn-Sham theories), 121–122, 126–129, 448, 475, 482, 493–496, 505, 514, 577
 localized, 475–477
 multiconfiguration, 205–211, 233–235, 246, 336, 349–350, 495, 499–501, 574
 reaction field, (*see* Reaction field, self-consistent)
Self-interaction error, 251, 263, 278, 280
Semiempirical, (*see* Molecular orbital theory)
SHAKE, 79
SHAPES, 26, 58
Shear viscosity, 88
Simulated annealing, 97
Simulation, 38, 69–99, 319–320, 357, 429–454, 459, 462–465, 475–477, 513
SINDO1, 141–143, 153
Single-point calculation, 129, 192, 345, 473
Single topology, 443
Singlet-triplet splitting, 138, 216, 232–234, 275–277, 350, 493–495
Size-consistency, 215, 221, 225–226, 241, 257
Slater determinant, 124–126, 166, 203, 255–256, 265, 272, 274, 328, 396, 400, 461, 487–488, 493, 504, 573
Slater exchange, 252, 258, 260
Slater-type orbitals, (*see* Orbital)
Slow growth, 435–437, 443
SM x model, (*see* Solvation)
 S_N2 reaction, 185–186, 198, 293, 390, 440
Software, 12–15

- Soil, 418
- Solid, (*see also* Metal), 9, 49, 89, 99–101, 136, 186, 192, 252, 269, 273, 366, 418, 470, 498, 559
- Solubility, 418
- Solvation, (*see also* Condensed-phase effects and Reaction Field),
continuum, 385–386, 393–424, 448–454, 460, 462, 467, 469, 473, 513, 538
convergence, 401
COSMO and COSMO-RS, 404–406
effect on UV/Vis spectroscopy, (*see* Solvatochromism)
effective coordinate, 539, 542–544
electrostatic component, 397–410, 449
explicit modeling, 91, 429–454, 459–460, 462
explicit/implicit hybrid models, 421, 451–452
free energy, 386–424, 429, 437–439, 458, 463–466
generalized Born, (*see* Born equation)
GB/SA, 408–409
IEF-PCM, 401
ions, 90, 447
IPCM, 401
MST-ST, 408–410, 416–417
non-electrostatic component, (*see also* Cavitation and Dispersion), 406–410, 421
non-equilibrium, 421–422, 450–451, 538, 542–543
non-isotropic, 418
PCM, 400–401, 405, 417, 473
proton, 410, 412
SCIPCM, 401
separable equilibrium, 538
shell, 86, 385–386, 410, 420, 449–452, 512–513
SMx, 387–388, 404, 409, 411, 416–418, 422–424, 438, 448, 460, 462
supermolecule, 415–416, 450–451
time scale, 421–422
- Solvatochromism, 393, 511–5133
- Solvent-accessible surface area, (*see* Surface area)
- Solvent model, 400–403
- Solvent-separated pair, 419–420
- Solvent-solvent interaction, 432, 436
- Space group, 559
- SPC, (*see* Water)
- Spherical harmonics, 134, 332–333
- Spin, 122–124, 136, 258, 324–325, 360, 487–488, 492, 565–574
contamination, 190, 234, 272–273, 275–276, 324–325, 328–330, 494–495, 506–507, 571–574
degeneracy, 360
density, 189, 199, 330
polarization, 188–190, 199, 258–259, 328
projection, 234, 325, 328–329, 506–507, 571–574
- Spin-orbit coupling, 107, 129, 242, 361, 368–369
- Spin-orbital, (*see* Orbital)
- Spin-spin coupling constant, 305, 345–349
- SRP, 155–156
- Standard state, 361–362, 366–375, 386, 526
conversion, 378–379, 386, 423
elemental, 366–372
- State-averaging, 500
- Stationary point, 24–25, 45–46, 133, 135, 183, 185, 192, 262, 300, 338, 356, 389–393, 423, 511, 523, 527, 529, 531, 545
- Statistical mechanics, 357–366, 377, 386
- Steepest descent minimization, 44
- Steric interaction, 19, 24, 27–30, 452–454, 467, 579
- Stirling's approximation, 359, 362
- STO-3G, (*see* Basis set)
- Stochastic dynamics, 79–80
- Stokes shift, 489, 515
- Strain energy, 21, 40–41, 355–356
- Structure-activity relationship, 152–153, 418
- Structure prediction, 19, 61
- Sublimation, 418
- Sucrose, 469–472
- Sum method, 494–495, 504–507, 570
- Supercritical fluid, 417
- Surface area, 47, 152, 386, 400, 407
solvent-accessible, 407–409
- Surface hopping, 540–541
- Surface tension, 407–410, 452, 467
- SVWN, 260, 282, 286, 289, 291, 294, 339
- Switching function, 47, 100, 394
- Switching parameter, (*see* Coupling parameter)

- SYBYL, 58
Symmetry, 182–188, 209, 215, 275–276, 279,
335, 490–491, 498–500, 510, 557–562
number, 362–364, 377
 τ_1 correlation, 264, 298
 τ HCTH, 264, 285, 298
 T_1 diagnostic, 226
TDDFT, (*see* Density Functional Theory)
Temperature, 28, 61, 69–71, 75, 77–78, 82,
91–92, 97, 336, 356–357, 360, 362–363,
369–370, 372, 377, 380, 438, 442, 444,
447, 519, 523, 527–528, 531–533,
535–538, 542, 544, 546
Tetramethylsilane, 346
Theory, (definition), 1
Thermal electron convention, 378
Thermodynamic integration, 435–437, 443,
454
Thermodynamics, 11, 39–40, 355–380,
429–445
Thomas-Fermi functional, 251
Thomas-Fermi-Dirac functional, 252
TIPnP, ($n = 3, 4$; *see* Water)
Torsions, (*see also* Potential Energy Functions),
22, 27, 356, 376–377, 469, 578–579
TPSS, 264, 279, 283, 290, 292, 298
TPSSH, 283, 290, 292, 298
Trajectory, (*see also* Propagation), 70–80,
482–484, 522, 541
Transition dipole moment, 501–502, 510, 563
Transition metal, (*see also* Metal), 58,
140–141, 154, 179, 268, 275, 285–286,
291, 299, 345, 504
Transition probability, 272, 305, 507–511
Transition state, (*see also* Geometry), 7, 9, 11,
46, 48–50, 62, 133, 159–162, 185–186,
208, 235, 279, 293, 300, 338, 378,
390–93, 421–422, 440, 450–452,
463–464, 468, 482–484, 507, 522–533,
536, 538–539, 544–546
Transition-state theory, 160, 524–537
microcanonical, 536
variational, 531–533, 536, 538
Translation, 6, 327, 361–362, 378, 386
Transmission coefficient, 535–537
Trichloroacetic acid, 422–424
Trimethylenemethane, 204–209, 277, 504
Tunneling, 482, 530, 533–538, 544
Turning point, 511
Two-electron integral, 127–129, 132,
136–140, 143–144, 154, 158, 166, 169,
191, 221, 251, 257, 273, 462, 475
Coulomb, 122, 125–127, 138, 189–191,
273–274, 402
exchange, 125–127, 189, 191, 214, 261
symmetry, 186
UFF, 38, 58, 60, 469
Umbrella potential, 99, 440–441, 451, 481
Uncertainty principle, 334
Uniform electron gas, 250–252, 259–260, 262
United-atom model, 38, 51, 446
Universal gas constant, 359, 542
Urey-Bradley term, 26, 100
UV-Vis spectroscopy, 135–136, 139–141, 393,
411, 507–508, 511–515
effect of solvation, (*see* Solvatochromism)
VALBOND, 38, 58
Valence angle bending, (*see* Potential Energy
Functions)
Valence bond, (*see also* Empirical valence
bond), 49
van der Waals,
interaction, (*see* Potential Energy Functions)
radius, 311, 399, 401, 408
surface, 308, 318, 400, 408
van't Hoff plot, 444
Vapor pressure, 152, 405
Variational principle, 108–110, 172, 203, 212,
215, 222, 251, 253–254, 257, 490–491,
499
Verlet algorithm, 77–79
Vertical process, 331, 423, 489–490, 505–506,
511–513
Vibrational averaging, 61, 342–344
Vibrational frequency, (*see* Frequency)
Vibrational motion, 76, 334–336, 356
Vibrational spectroscopy, 17, 21, 35, 88, 101,
332, 334–342, 349–351, 411, 514
Voronoi cell, 318
VSXC, 264, 283, 285, 287, 290, 292, 298, 340
VTST, (*see* Transition-state theory)
VWN, 259–260, 298
VX, 177–178

- Wn , ($n = 1-4$; *see* Multilevel methods)
- Water, 2, 82–83, 85, 91, 151, 172–173, 184,
230, 236, 291, 294, 306–307, 309, 315,
347–348, 559
acidity, 477–481
as solvent, 385–387, 390, 392, 407–408,
422–424, 429–433, 437–438, 445,
449, 452, 460, 462–464, 480–481
density anomaly, 447
polarizable models, 90, 446–447
SPC, 446
TIPnP, ($n = 3, 4$), 446, 449, 462
- Water dimer, 149–151
- Wave function, 4, 105–129, 166, 181,
186–190, 230, 244, 249, 312, 324, 326,
411, 459–466, 561–562, 575–577
adiabatic, 478, 539–540
CIS, 214, 496–498
determination from electron density,
253–254
excited-state, 487–494, 497–501, 504–507
harmonic oscillator, 335–337, 510–511
Kohn-Sham, 271–273, 448, 506
mixed-spin state, 504–507, 566–570
multideterminantal, 190, 203–216, 230–235,
274–277, 324, 487–488, 562
nuclear, 111, 331–333, 335–337, 342–343,
539–541
rigid-rotor, 332–333, 510
single-determinantal, 203–205, 222, 226,
230–232, 271–273, 487–488, 493
stability, 187, 192, 234, 275, 475, 498
VB, 477–479
vibrational, 61, 334–337, 342–343,
510–511
- Weighted histogram analysis method, 441–442
- Wigner correction, 535
- X exchange, 263, 298
- $X\alpha$ method, 252, 259
- X-ray crystallography, 3, 61–62, 84, 315,
470–471
- X3LYP, 267, 279, 284, 290, 298
- XLYP, 283, 290
- XSOL, (*see* QM/MM)
- Zeolite, 99–101, 312
- Zero-flux surface, 316–317
- Zero-point vibrational energy, 62, 69,
356–357, 364–365, 368–369, 375, 484,
490, 495, 511, 525, 529–532, 545
- Zwitterion, 392, 465