

## Index

- 'ab initio' calculation, 159, 163
- absorption spectrum, 247, 273
- addition reaction, 215, 268
- AH<sub>n</sub> molecules, 140
- alternate hydrocarbon, 226
- angular momentum, 5, 26, 39, 83
  - operator, 26
  - quantization, 47, 50
  - quantum number, 27
- anti-bonding character, 77, 119
- anti-bonding m.o., 75, 116, 141, 249, 261
- antisymmetric wavefunction, 88
- asymmetric stretching, 179
- atomic orbitals for H, 51
- 'aufbau' method, 101
  
- Bader, R.F.W., 169
  - theory, 169, 192, 216
- Balmer–Rydberg equation, 2
- banana bond, 216
- band gap, 261
- band theory of solids, 258
- bent bond, 204
- binding energy, 236
- black-body, 2
- Bohr, N., 4
  - radius, 54
  - model, 5
- Boltzmann, L.W., 3
- bond angle, 140
  - energy, 115, 120, 231
  - length, 115, 120, 241
  - multiplicity, 177
  - order, 125, 175, 227, 241, 282
    - conservation, 242
- bonding character, 77, 119
  - m.o., 75, 116, 141, 249, 261
- Born, M., 11
- Born–Oppenheimer approximation, 71, 114
- boundary condition, 32
- buckminsterfullerenes, 245
- building up method, 101
  
- canonical orbitals, 97, 193, 230
- chemical shifts, 279
- chromophore, 276
- circular distribution of
  - electron probability, 116
- cis–trans isomerism, 270
- closed-shell configuration, 89
- commutator, 23
- commuting operators, 23
- complexes, 248, 281
- complex wavefunction, 11, 19, 63, 64
- Compton, A.H., 6
- Compton effect, 6
  - wavelength, 6, 44
- conduction band, 262
- conductor, 262
- configuration interaction, 95, 114
- conjugation, 222
- conrotatory mode, 271
- conservation of orbitals, 115
  - of symmetry, 270
- constant of motion, 31
- Copenhagen interpretation, 13
- core electrons, 86
- correspondence principle, 36
- Coulomb correlation, 94, 114
  - integral, 79, 122, 142, 159
  - repulsion, 96
- covalent bonding, 70
- crystal field theory, 253
- curvature of wavefunction, 25, 171
- cyclization reactions, 271
- cycloaddition reactions, 273
  
- d-orbitals, 64, 250
- De Broglie, L., 7
- De Broglie equation, 7, 24, 28
  - wavelength, 7, 14
- degenerate eigenfunctions, 20
- delocalization energy, 226
- delocalized m.o.s, 139, 213, 224
- density-functional theory, 23, 95, 111, 138, 164

312

density-matrix, 23  
 density of states, 260  
 diamagnetic term, 280  
 diamagnetism, 120, 256  
 diatomic molecules, 115, 120, 129  
 Diels–Alder reaction, 272  
 diffraction of electrons, 8, 168  
   of X-rays, 8, 168  
 dipole moment, 131, 135, 173  
 Dirac, P., 13  
 Dirac equation  
   theory, 42  
   notation, 20  
 disrotatory mode, 271  
 dissociation energy, 236  
 double-slit experiment, 8, 11

effective atomic number, 100  
   nuclear charge, 99  
 eigenfunction, 19  
 eigenvalue, 19  
 Einstein, A., 3  
 Einstein, coefficient, 278  
 electron charge concentration, 174  
   depletion, 174  
   correlation, 94, 114, 164  
   density, 170, 227, 239  
   diffraction, 8, 168  
   lone pair, 168, 184, 188, 288  
   repulsion, 85, 90, 103  
   spin, 27, 42, 67, 86, 115, 281  
 electronegativity, 129, 136, 172  
 electronic chemical potential, 137  
   configuration, 86, 101  
   energy, 95, 158, 194, 205  
   levels, 105  
   states, 83  
   terms, 105  
   transition, 65, 273  
 electrophile, 268  
 electrophilic substitution, 265  
 elliptical coordinates, 72  
 emission spectra, 2, 106  
 energy diagram for H, 52  
   levels, 52, 68  
   quantization, 1, 4, 30, 51, 66  
 ensemble, 10, 18  
 entropy, 37  
 equivalent bond functions, 197  
 ESCA (electron spectroscopy  
   for chemical analysis), 120  
 exchange energy, 1, 96  
   integral, 96, 159  
   potential, 92  
 exclusion principle, 86  
 expectation value, 21, 90  
 expected value, 10, 21  
 extended Hückel method, 162, 222

Fermi hole, 97  
   contact mechanism, 283  
   level, 262

## Index

fermion, 43, 86  
 forbidden transition, 67  
 free particle in a ‘box’, 31, 37, 40  
   in a parabolic potential, 39  
   on a ring, 38, 47  
   on a spherical surface, 39, 49, 247  
 frontier orbitals, 266  
 Fukui, K., 266  
 Fukui, contour map, 269

gaussian function, 162  
 generalized Pauli principle, 88

hamiltonian, 26  
 harmonic oscillator, 39  
 Hartree–Fock method, 91, 162  
   orbitals, 92  
 Heisenberg, W., 13  
 Heisenberg principle, 2, 14  
 Heitler, W.H., 180  
 hermitian operator, 20  
 heterodiatom molecules, 129  
 Hoffmann, R. 162  
 HOMO (highest energy occupied m.o.),  
   175, 266, 275  
 homonuclear diatomic molecule,  
   70, 115, 120  
 Hückel, E., 222  
 Hückel, theory, 219, 246, 273  
 Hund, F., 108  
 Hund’s rules, 108  
 hybrid orbitals, 64, 83, 182, 187, 201, 286  
 hyperconjugation, 269, 288

incompatible observables, 13  
 independent bonds, 175  
 independent electron approximation,  
   87, 162, 205, 219  
 indeterminacy, 10  
 indeterminacy principle, 2, 14  
 indistinguishability of electrons, 1, 88, 181  
 insulator, 262  
 interatomic surface, 171  
 interference, 8, 12, 16, 75  
 internal rotation, 157, 166, 215  
 ionic bonding, 264  
 ionization energy, 4, 85, 100, 102  
   potential, 85, 98  
 isodensity contour plots, 54, 77, 123, 126,  
   133, 135, 136, 146, 151, 170,  
   172, 210

Jahn–Teller theorem, 257  
 jj-coupling, 111

Karplus equation, 284  
 kinetic energy, 30, 78  
   operator, 25  
 Kohn, W., 112  
 Kohn–Sham orbitals, 112

- Koopmans theorem, 98, 195  
Kronecker symbol, 21
- laplacian, 25  
laplacian of electron density, 171  
Lewis, G.N., 4  
Lewis acid, 254  
  base, 254  
  model, 168, 174  
ligand field theory, 253  
  splitting, 253  
linear combination of a.o.s., 74, 139  
linear momentum, 7, 14  
  operator, 24  
  probability distribution, 34  
linear operator, 19  
Linnett's model, 188  
localized functions, 182, 193  
  molecular 'orbitals', 199, 230, 249  
London, F.W., 180  
LUMO (lowest energy unoccupied m.o.),  
  175, 266, 275
- magnetic quantum number, 49  
magnetism, 120  
matrix diagonalization, 21  
mean value, 10  
molecular geometry, 165, 185, 201, 238  
mechanics, 186  
orbital, 70  
  energy diagram, 118, 122, 128, 132,  
  134, 147, 149, 152, 154, 156, 209,  
  252, 257  
  theory, 70, 115, 139, 156  
  strain, 203  
 $\pi$  molecular orbital, 80, 148, 205  
 $\sigma$  molecular orbital, 75, 205  
moment of inertia, 38  
  distribution, 60  
Mulliken, R.S., 136  
mutual polarizability, 282
- neglect of overlap, 163  
nodal plane, 60  
  surface, 54  
node, 25, 36, 75, 141, 218  
non-bonding m.o.s., 131, 148, 175, 249  
non-independent bonds, 175  
non-localizable molecular orbitals, 213, 224  
normalized function, 19  
normalization factor, 19, 54, 74  
nuclear spin-spin coupling, 282  
  magnetic shielding, 279  
  resonance, 279  
nucleophile, 268  
nucleophilic substitution, 267
- observable, 10, 13, 18  
octahedral complexes, 248, 281  
octet rule, 236  
open shell configuration, 89
- operator, 13, 18  
orbital angular momentum, 26, 39, 48  
  quantum number, 48  
  conservation, 115  
  contraction, 78, 281  
  definition, 1, 12  
  energy, 51, 86, 95, 97, 103  
  expansion, 281  
  penetration, 99  
  symmetry, 53, 75, 250  
  conservation, 270  
orthogonal functions, 20  
orthonormal function, 20  
overlap integral, 20, 74, 141
- p-orbitals, 60  
paramagnetic complexes, 256, 281  
paramagnetic term, 280  
paramagnetism, 120, 256  
parity, 75, 250  
particle in a box, *see* free particle in a box  
Pauli, W., 42  
Pauli, correlation, 94  
  matrix, 43  
  principle, 86  
Pauling, L., 136  
perfect pairing, 183  
phase factor, 12, 29  
  difference, 12  
photochemically controlled cyclization  
  reactions, 270  
photoelectric effect, 4  
photoelectron spectra, 127, 150, 178, 195  
photon, 4  
Planck, M., 2  
Planck constant, 3  
  theory, 3  
Planck-Einstein equation, 3  
Pople, J.A., 163  
  theory of nuclear spin-spin  
  coupling, 282  
potential energy, 25, 40, 45, 78  
  curve, 71, 119, 166  
principal quantum number, 50  
probability, 1, 9, 28, 87  
  density, 19, 23, 31, 38, 44  
  distribution, 1, 12, 18, 28, 117  
  of electronic transition, 67, 277
- quantization of energy, 1, 4, 30, 51, 66  
quantum of energy, 3  
  numbers, 5, 27, 33, 37, 42, 43, 50, 68
- radial distribution of probability, 58, 93  
redox reactions, 266  
relativistic corrections, 112  
  particle in a box, 44  
  wavefunctions, 69  
relativity theory, 42  
residual interaction, 163, 183, 198, 201, 211

314

resonance, 183, 213  
   energy, 226  
   hybrid, 183, 213, 237  
   integral, 79, 122, 142, 284  
 $4n + 2$  rule, 227  
 Russell–Saunders coupling, 111  
 Rutherford, E., 4  
 Rydberg constant, 2

s-character, 286  
 s-orbitals, 54  
 SCF orbitals, 92, 162  
 Schrödinger, E., 13  
 Schrödinger equation, 27, 45  
 Screening constant, 99  
 secular determinant, 161  
   equations, 161  
 selection rule, 67, 279  
 semi-conductor, 264  
 semi-empirical methods, 163, 222  
 $\sigma$ - $\pi$  separation, 205  
 singlet state, 108, 110  
 Slater, J., 98  
   Slater determinant, 89, 116, 139  
   orbitals, 101, 162  
   rules, 100  
 spectrochemical series, 277  
 spherical symmetry, 54  
   of a set of p orbitals, 63  
   harmonics, 39  
   polar coordinates, 46, 57  
 spin, 27, 67  
   angular momentum, 27, 42  
   correlation, 94  
   multiplicity, 106, 108, 254  
   quantum number, 42, 67  
   transfer, 281  
 spin-coupled valence-bond theory, 183  
 spin-orbit coupling constant, 106  
   interaction, 68  
 spin-orbital, 88  
 spinor, 142  
 state function, 11, 175  
   preparation, 10, 14  
 stationary state, 5, 29  
 statistical ensemble, 10, 18  
 Stern–Gerlach experiment, 67

*Index*

strong field complex, 254  
 superposition of wavefunctions, 12  
   of waves, 12  
   principle, 22  
 symmetric stretching, 179  
   wavefunction, 88  
 symmetry adapted orbitals, 150, 206, 250  
   conservation, 270  
   group, 250, 252

thermally controlled reactions, 270  
 time-dependent wave equation, 29  
 triatomic molecules, 140  
 triplet state, 108, 110  
 total angular momentum, 68  
   operator, 68  
   quantum number, 68  
 transition dipole moment, 279  
 tunnelling, 40

unitary transformation, 89, 196  
 unrestricted HF calculations, 94

valence band, 263  
   bond theory, 70, 180  
   electrons, 86  
   orbitals, 86  
 valence shell electron pair  
   repulsion (VSEPR) model, 185  
 variational principle, 92, 157  
 virial theorem, 58, 71, 78, 169

Walden inversion, 267  
 Walsh diagram, 148  
 wave equation, 18, 25  
 wavefunction, 11, 18  
 wave-particle duality, 6  
 weak field complex, 254  
 well-behaved function, 49  
 Woodward–Hoffmann rules, 270

X-ray diffraction, 8, 168

zero-flux surface, 171  
 zero-point energy, 33