

Contents

Part I Collision Theory

1 Potential Scattering	3
1.1 Scattering by a Short-Range Potential	4
1.2 Scattering by a Coulomb Potential	10
1.3 Analytic Properties of the S -Matrix	16
1.4 Effective Range Theory	23
1.4.1 Short-Range Potentials	23
1.4.2 Long-Range Potentials	29
1.4.3 Coulomb Potential	35
1.5 Variational Principles	41
1.6 Relativistic Scattering: The Dirac Equation	45
2 Multichannel Collision Theory	57
2.1 Wave Equation and Cross Section	58
2.2 Target Eigenstates and Pseudostates	60
2.2.1 Target Eigenstates	60
2.2.2 Target Pseudostates	64
2.3 Close Coupling Equations	69
2.3.1 Foundations of the Method	69
2.3.2 Derivation of the Close Coupling Equations	74
2.4 K -Matrix and Kohn Variational Principle	84
2.5 S -Matrix, T -Matrix and Cross Sections	91
3 Resonances and Threshold Behaviour	101
3.1 Analytic Properties of the S -Matrix	102
3.2 Bound States and Resonances	109
3.2.1 Bound-State and Resonance Poles in the S -Matrix	110
3.2.2 Behaviour of the S -Matrix Near a Resonance	112
3.2.3 Behaviour of Eigenphases Near a Resonance	117
3.2.4 Time-Delay Matrix	121

3.2.5	Feshbach Projection Operator Theory	125
3.2.6	Hyperspherical Coordinates	129
3.3	Threshold Behaviour of Cross Sections	135
3.3.1	Excitation: Short-Range Potentials	135
3.3.2	Excitation: Dipole Potentials	139
3.3.3	Excitation: Coulomb Potential	145
3.3.4	Multichannel Quantum Defect Theory	151
3.3.5	Threshold Behaviour of Ionization	159

Part II R-Matrix Theory and Applications

4	Introduction to R-Matrix Theory: Potential Scattering	167
4.1	Wigner–Eisenbud Theory	170
4.2	Generalized R-Matrix Theory	175
4.3	Variational Principles for the R-Matrix	179
4.4	R-Matrix Approximation Methods	181
4.4.1	Homogeneous Boundary Condition Method	181
4.4.2	Buttle Corrections to the R-Matrix and Wave Function	184
4.4.3	Arbitrary Boundary Condition Methods	187
4.4.4	Linear Equations Method	191
4.4.5	Eigenchannel Methods	192
4.4.6	Lagrange Mesh Methods	197
4.4.7	B-Spline Methods	201
4.4.8	Direct Calculation of Siegert State Parameters	207
4.5	Propagator Methods	209
4.5.1	Light–Walker Propagator	210
4.5.2	BBM Propagator	213
4.6	Dirac R-Matrix Theory	215
5	Electron Collisions with Atoms and Ions	227
5.1	Multichannel R-Matrix Theory	228
5.1.1	Introduction and Computer Programs	229
5.1.2	Internal Region Solution	232
5.1.3	External Region Solution	238
5.1.4	Asymptotic Region Solution	240
5.2	Variational Principle for the R-Matrix	242
5.3	Continuum Basis Orbitals and Correction Methods	247
5.3.1	Homogeneous Boundary Condition Method	248
5.3.2	Buttle Correction to the R-Matrix and Wave Function	250
5.3.3	Arbitrary Boundary Condition Methods	254
5.3.4	Partitioned R-Matrix Method	256
5.4	Inclusion of Relativistic Effects	260
5.4.1	Transformation of the K- and S-Matrices	261
5.4.2	Breit–Pauli Hamiltonian	265
5.4.3	Frame-Transformation Theory	272

5.5	Dirac R-Matrix Theory	275
5.5.1	Introduction and Computer Programs	276
5.5.2	Internal Region Solution	277
5.5.3	External Region Solution	284
5.5.4	Asymptotic Region Solution	287
5.5.5	Continuum Basis Orbitals	289
5.5.6	Buttle Correction	291
5.6	Low-Energy Electron Collision Calculations	292
5.6.1	Electron Collisions with H	292
5.6.2	Electron Collisions with He	294
5.6.3	Electron Collisions with Ne	298
5.6.4	Electron Collisions with Si III	299
5.6.5	Electron Collisions with Fe II	301
5.6.6	Electron Collisions with Fe XV	307
5.6.7	Electron Collisions with Xe XXVII	309
6	Intermediate-Energy Collisions	311
6.1	Overview of Intermediate-Energy Methods	312
6.2	R-Matrix with Pseudostates Method	316
6.3	Intermediate-Energy R-Matrix Method	322
6.3.1	General Procedure	323
6.3.2	Two-Electron Example	327
6.4	T-Matrix Energy Averaging	337
6.5	Distorted Wave and Second-Born Methods	343
6.6	Intermediate-Energy Electron Collision Calculations	348
6.6.1	Electron Collisions with H	348
6.6.2	Electron Collisions with C IV	351
6.6.3	Electron Impact Excitation–Ionization of He	352
7	Positron Collisions with Atoms and Ions	355
7.1	Multichannel R-Matrix Theory	356
7.1.1	Introduction	356
7.1.2	Internal Region Solution	360
7.1.3	External Region Solution	367
7.1.4	Asymptotic Region Solution	370
7.2	Positron and Positronium Collision Calculations	373
7.2.1	Positron Collisions with H	373
7.2.2	Positronium Collisions with He	375
7.2.3	Target Polarization in Positronium Collisions	377
8	Photoionization, Photorecombination and Atoms in Fields	379
8.1	Atomic Photoionization	380
8.1.1	Introduction and General Theory	380
8.1.2	R-Matrix Theory	390

8.2	Photorecombination and Radiation Damping	404
8.2.1	Introduction	404
8.2.2	<i>R</i> -Matrix Theory	406
8.3	The Opacity Project	414
8.4	Spectra of Atoms in Fields	416
8.5	Illustrative Examples	422
8.5.1	Photoionization of Li	423
8.5.2	Photoionization of Fe VII	424
8.5.3	Photorecombination in Electron Collisions with O VIII	426
8.5.4	Radiation Damping in Electron Collisions with Fe XXVI	428
8.5.5	Radiation Damping in Electron Collisions with W XLVII	428
8.5.6	Photoionization Spectrum of Li in a Magnetic Field	431
9	Multiphoton Processes: Floquet Theory	433
9.1	<i>R</i> -Matrix–Floquet Theory	434
9.1.1	Introduction	434
9.1.2	Internal Region Solution	436
9.1.3	External Region Solution	441
9.1.4	Asymptotic Region Solution in the Velocity Gauge	451
9.1.5	Asymptotic Region Solution in the Acceleration Frame	456
9.1.6	Asymptotic Region Solution: Simplified Analysis	466
9.1.7	Harmonic Generation	473
9.1.8	Non-hermitian Floquet Dynamics	477
9.2	Illustrative Examples	480
9.2.1	Resonances in Multiphoton Ionization	480
9.2.2	Harmonic Generation	484
9.2.3	Laser-Induced Degenerate States	487
9.2.4	Laser-Assisted Electron–Atom Collisions	489
10	Multiphoton Processes: Time-Dependent Theory	493
10.1	Time-Dependent <i>R</i> -Matrix Theory	494
10.1.1	Introduction	494
10.1.2	Internal Region Solution	499
10.1.3	External Region Solution	506
10.1.4	Computational Methods	511
10.1.5	Analysis of Applications	516
10.2	Illustrative Examples	523
10.2.1	Multiphoton Ionization of Ne	524
10.2.2	Multiphoton Ionization of Ar	528

11	Collisions with Molecules	533
11.1	Electron Collisions with Molecules	535
11.1.1	Introduction	535
11.1.2	Fixed-Nuclei <i>R</i> -Matrix Theory	536
11.1.3	Inclusion of Nuclear Motion	544
11.1.4	Non-adiabatic <i>R</i> -Matrix Theory	548
11.1.5	Resonant <i>R</i> -Matrix Theory	560
11.1.6	Scattering Amplitudes and Cross Sections	561
11.1.7	Illustrative Examples: N ₂ , O ₂ , N ₂ O, H ₃ ⁺	566
11.2	Positron Collisions with Molecules	573
11.2.1	<i>R</i> -Matrix Theory and Calculations	573
11.2.2	Illustrative Examples: H ₂ O, CO ₂	575
11.3	Molecular Multiphoton Processes	579
11.3.1	Molecular <i>R</i> -Matrix–Floquet Theory	579
11.3.2	Illustrative Example: H ₂	588
12	Electron Interactions in Solids	591
12.1	Electron Collisions with Transition Metal Oxides	592
12.1.1	Introduction	592
12.1.2	<i>R</i> -Matrix Theory	592
12.1.3	Illustrative Example	594
12.2	Electron Transport in Semiconductor Devices	596
12.2.1	Introduction	596
12.2.2	<i>R</i> -Matrix Theory	597
12.2.3	Illustrative Example	602
Part III Appendices		
Appendix A Clebsch–Gordan and Racah Coefficients		607
A.1	Clebsch–Gordan Coefficients	607
A.2	Racah Coefficients	612
A.3	6- <i>j</i> Symbols	615
A.4	9- <i>j</i> Symbols	615
A.5	Higher Order 3 <i>n</i> - <i>j</i> Symbols	617
Appendix B Legendre Polynomials and Related Functions		619
B.1	Legendre Polynomials	619
B.2	Associated Legendre Functions	621
B.3	Spherical Harmonics	623
B.4	Phase of Spherical Harmonics	628
B.5	Transformation Under Rotations	632

Appendix C Bessel Functions and Related Functions	639
C.1 Bessel Functions	639
C.2 Spherical Bessel Functions	642
Appendix D Applications of Angular Momentum Algebra	647
D.1 Long-Range Electron–Atom Potential Coefficients	647
D.1.1 Non-relativistic Collisions	647
D.1.2 Inclusion of Relativistic Effects	652
D.2 <i>R</i> -Matrix–Floquet Multiphoton Potential	654
D.3 Time-Dependent Multiphoton Potential	657
D.4 Atomic Photoionization Cross Section	662
Appendix E Propagator Methods	665
E.1 Light–Walker Propagator Method	666
E.2 Log-Derivative Propagator Method	671
E.3 BBM Propagator Method	675
E.4 Propagation of Driven Equations	678
E.5 Propagator Method with First-Order Derivative	681
E.6 Propagation of Sets of Uncoupled Channels	684
Appendix F Asymptotic Expansions	693
F.1 Electron and Positron Collisions	693
F.2 Multiphoton Processes	700
References	707
Index	731

Units

Atomic units (a.u.) will be used throughout this monograph. They are such that $\hbar = m = e = 1$, where \hbar is Planck's constant h divided by 2π , m is the mass of the electron and $-e$ is the charge of the electron. Thus the atomic unit of length $a_0 = \hbar^2/me^2 \approx 5.292 \times 10^{-9}$ cm, which is the radius of the first Bohr orbit of the hydrogen atom with infinite nuclear mass. Using this unit of length, collision cross sections, which have the dimension of an area, are then expressed, either in units of $a_0^2 \approx 2.800 \times 10^{-17}$ cm² or in units of $\pi a_0^2 \approx 8.797 \times 10^{-17}$ cm². The atomic unit of time is given by $\hbar^3/me^4 = 2.419 \times 10^{-17}$ s, while the unit of velocity is $e^2/\hbar = 2.188 \times 10^8$ cm s⁻¹. The atomic unit of energy is $e^2/a_0 \approx 27.21$ eV, which is twice the ionization energy of the hydrogen atom in its ground state and twice the Rydberg unit of energy. The fine-structure constant $\alpha = e^2/\hbar c \approx 1/137$ is dimensionless, where c is the velocity of light in a vacuum.