

Contents

1	Introduction to Spectral/Pseudospectral Methods	1
1.1	Introduction	1
1.2	Spectral and Pseudospectral Methods	4
1.2.1	The Spectral Space Representation	5
1.2.2	The Physical Space Representation	8
1.2.3	A Hilbert Space	11
1.2.4	Hermitian and Self-adjoint Operators: The Sturm-Liouville Problem	13
1.2.5	Rayleigh-Ritz Variational Theorem	15
1.3	An Overview of Spectral Methods	16
1.4	The Development of Pseudospectral Methods in Chemistry and Physics: An Overview of the Book	18
	References	22
2	Polynomial Basis Functions and Quadratures	29
2.1	Introduction	29
2.2	Gram-Schmidt Orthogonalization and Three Term Recurrence Relations	33
2.2.1	Legendre and Hermite Polynomials	36
2.2.2	The Rys Polynomials	41
2.3	Numerical Integration Algorithms	44
2.3.1	Polynomial and Lagrange Interpolation	44
2.3.2	Trapezoidal and Simpson's Integration Rules	46
2.3.3	Newton-Cotes Integration Rules; Error Analysis	48
2.3.4	Gaussian Quadrature	51
2.3.5	The Christoffel-Darboux Relation and Quadrature Weights	52
2.3.6	The Gautschi-Stieltjes Procedure, the Jacobi Matrix	54

2.4	The Classical Polynomials; Recurrence Coefficients and Quadratures	55
2.4.1	Legendre Polynomials.	56
2.4.2	Half Range Legendre Polynomials	58
2.4.3	Associated Legendre Polynomials.	59
2.4.4	The Spherical Harmonics	59
2.4.5	Associated Laguerre and Sonine Polynomials.	60
2.4.6	Quantum Mechanics of the Hydrogen Atom	62
2.4.7	Hermite Polynomials	64
2.4.8	Gegenbauer Polynomials	66
2.4.9	Chebyshev Polynomials; Fourier Cosine Basis Functions	67
2.4.10	Fejér Quadratures	69
2.4.11	The Clenshaw-Curtis Quadrature	70
2.4.12	Gauss-Lobatto and Gauss-Radau Quadrature Algorithms	71
2.5	Nonclassical Basis Functions	74
2.5.1	Maxwell Polynomials	74
2.5.2	The Bimodal Polynomials	80
2.5.3	Rys Polynomials; Full-Range and Half-Range	82
2.5.4	Additional Examples of Nonclassical Quadratures	85
2.6	Sinc Interpolation, Cubic B-Splines and Radial Basis Functions	87
2.6.1	Sinc Interpolation.	88
2.6.2	Cubic B-Splines:	89
2.6.3	B-Splines	91
2.6.4	Radial Basis Functions	93
2.7	Moment Methods for Orthogonal Polynomials and the Stieltjes Moment Problem	94
2.8	Two Dimensional Integrals and Cubatures.	97
	References	98
3	Numerical Evaluation of Integrals and Derivatives.	109
3.1	Numerical Evaluation of Integrals.	109
3.2	Some General Principles for the Numerical Evaluation of Integrals	111
3.3	Scaling Quadrature Points and Weights.	112
3.4	Integrals in Density Functional Theory	113
3.4.1	Mapping the Semi-infinite Interval $r \in [0, \infty)$ to $x \in [-1, 1]$	114
3.4.2	Radial Integrals in Density Functional Theory	117

3.5	Chemical and Nuclear Reaction Rate Coefficients	122
3.5.1	Equilibrium Rate Coefficient for Chemical Reactions	122
3.5.2	Rate Coefficients for Fusion Reactions; Non-resonant Cross Sections	125
3.6	Integrals in Collision Theory and Kinetic Theory	129
3.6.1	The Reactive and Elastic Collision Frequencies	130
3.6.2	Integration Over a Cusp; the Boltzmann Equation	134
3.6.3	Viscosity of a Simple Gas	140
3.6.4	Eigenvalues of the Boltzmann Collision Operator for Maxwell Molecules	142
3.6.5	The JWKB Phase Shifts and Quantum Elastic Cross Sections	144
3.7	The Calculation of Matrix Elements of Multiplicative Operators	150
3.7.1	Matrix Representation of the Collision Frequency in Laguerre and Maxwell Polynomials	154
3.7.2	Matrix Representation of the Harmonic Oscillator Potential in Hermite Polynomials	158
3.8	Challenging Integrals	161
3.8.1	Molecular and Atomic Electronic Structure; Electron Pair Repulsion Integrals	161
3.8.2	Relaxation Times for ^3He - ^3He Spin Exchange Collisions—Oscillatory Integrands	165
3.8.3	The SIAM 100-Digit Challenge; a “Twisted Tail” Integral	166
3.9	Numerical Evaluation of Derivatives	167
3.9.1	Finite Difference Formulas for Derivatives	168
3.9.2	Interpolation and Differentiation	169
3.9.3	Sturm-Liouville Eigenvalues Problems	174
3.9.4	Discrete Singular Convolution; Whittaker’s Sinc Interpolation	176
	References	177
4	Representation of Functions in Basis Sets	187
4.1	Introduction	187
4.2	Approximation of Functions in a Basis Set; The Least Squares Error	189
4.3	Expansions in Hermite Polynomials; Spectral Convergence	191
4.3.1	An Asymmetric Hermite Expansion	192
4.3.2	A Symmetric Hermite Expansion; Spectral Convergence	196
4.3.3	Expansion of $\sin(x)$ in Hermite Polynomials	199

4.4	Expansion of a Maxwellian with Chebyshev Polynomials	201
4.5	Expansion in Laguerre Polynomials	202
4.5.1	Asymmetric Laguerre	202
4.5.2	Expansion of a Kappa Distribution in Laguerre Polynomials.	205
4.6	Representation of Functions in Periodic Fourier Series	208
4.6.1	Fourier Series	209
4.6.2	Fourier Series in Complex Basis Functions	212
4.6.3	Fourier Interpolation and Discrete Fourier Transforms	213
4.6.4	Fourier Transforms	215
4.6.5	The Solution of the Diffusion Equation with Fourier Transforms	217
4.6.6	Construction of a Quantum Wave Packet	219
4.6.7	Fourier Transform Analysis of Time Series and Fourier Transform Spectroscopy.	222
4.7	Gibbs Phenomenon.	223
4.7.1	The Direct Method	225
4.7.2	The Inverse Method; Odd Functions $f(-x) = -f(x)$. . .	227
4.7.3	The Inverse Method Is Exact for Polynomials	229
4.7.4	Numerical Comparisons	231
4.7.5	Minimizing the Inverse Method Round-Off Errors . . .	235
4.7.6	Local Reconstruction and Image Resolution.	238
4.8	The Runge Phenomenon	239
	References	240
5	Integral Equations in the Kinetic Theory of Gases and Related Topics.	247
5.1	Introduction	247
5.2	Classes of Integral Equations and the Use of Quadratures	249
5.3	Radiative Transfer and Neutron Transport Theory	252
5.4	The Boltzmann Equation and Transport Theory	257
5.4.1	The Chapman-Enskog Method of Solution of the Boltzmann Equation for Transport Coefficients	258
5.4.2	The Linearized Collision Operator, J , in the Boltzmann Equation	263
5.4.3	Matrix Representation of the Spherical Component ($\ell = 0$) of J in Sonine-Laguerre Basis Functions	265
5.4.4	Spectral Solution of the Boltzmann Equation for the Departure from Maxwellian for an Elementary Reaction in a Spatially Uniform System	268

5.4.5	Pseudospectral Solution of the Boltzmann Equation for Shear Viscosity with the Maxwell Quadrature.	274
5.5	Spectral Theory for the Linearized Boltzmann Collision Operator	277
5.5.1	Spectral Calculation of the Eigenvalue Spectrum of J	278
5.5.2	Pseudospectral Calculation of the Eigenvalue Spectrum of J	280
5.6	Relaxation to Equilibrium in Binary Gas Mixtures	284
5.6.1	Spectral Calculation of the Eigenvalue Spectrum of the Linear Collision Operator, L , for a Binary Gas	285
5.6.2	Pseudospectral Calculation of Eigenvalue Spectrum of the Linear Collision Operator, L , for a Binary Gas	286
5.6.3	Spectral Method of Solution of the Linear Boltzmann Equation with Quantum Cross Sections; Relaxation to Equilibrium and the Kullback-Leibler Entropy.	290
5.7	Two Dimensional Anisotropic Distributions.	296
5.7.1	Pseudospectral/Spectral Solution of the Boltzmann Equation; Relaxation of Anisotropic Distributions in a Binary Gas	296
5.7.2	A Spectral Method of Solution of the Milne Problem	301
5.7.3	A Mixed Spectral/Pseudospectral Solution of the Boltzmann Equation for the Escape of Light Atoms from a Planetary Atmosphere	308
5.7.4	Electric Field Induced Ion Drift in Buffer Gases; Applications to Ionospheric and Space Physics	312
5.8	The Nonlinear Isotropic Boltzmann Equation.	315
5.8.1	Finite Difference Method of Solution of the Nonlinear Boltzmann Equation; Approach to Equilibrium	316
5.8.2	Finite Difference Discretization of the Nonlinear Boltzmann Equation	317
5.8.3	Time Dependent Solutions.	319
	References	321

6	Spectral and Pseudospectral Methods of Solution of the Fokker-Planck and Schrödinger Equations	331
6.1	The Fokker-Planck Equation in Chemistry, Physics, Astrophysics and Other Fields	331
6.1.1	From the Langevin Equation to the Fokker-Planck Equation; Brownian Motion.	333
6.1.2	Spectral Solution of the Ornstein-Uhlenbeck Fokker-Planck Equation	335
6.1.3	Rayleigh and Lorentz Fokker-Planck Equations from the Boltzmann Equation; The Kramers-Moyal Expansion	337
6.1.4	Spectral Solution of the Rayleigh Fokker-Planck Equation	338
6.2	Numerical Methods for the Solution of the Fokker-Planck Equation	340
6.2.1	Spectral Methods with Nonclassical Basis Functions. . .	340
6.2.2	Pseudospectral Methods with Nonclassical Quadratures	342
6.2.3	The Chang-Cooper Finite Difference Method of Solution of the Fokker-Planck Equation.	344
6.3	Electron Thermalization; The Lorentz Fokker-Planck Equation Revisited	346
6.3.1	Hard Sphere Cross Section and Zero Electric Field, $E = 0$	349
6.3.2	Transformation of the Fokker-Planck Eigenvalue Problem to a Schrödinger Equation; Supersymmetric Quantum Mechanics	351
6.3.3	Pseudospectral Representation of the Schrödinger Equation; Supersymmetric Quantum Mechanics	354
6.4	Relaxation and Wave-Particle Heating in Space Plasmas	355
6.4.1	Pseudospectral Solution of the Coulomb Fokker-Planck and Associated Schrödinger Equations; The Approach to Equilibrium and the Continuous Spectrum	356
6.4.2	Fokker-Planck Equation for Wave Particle Heating of Ions; Kappa Distributions, and Tsallis Nonextensive Entropy.	361
6.5	Fokker-Planck or Smoluchowski Equation for Bistable Potentials	365
6.6	Kramers Equation and Nonequilibrium Chemical Kinetics; A Spectral Solution	373
6.7	Sturm-Liouville Problems and the Schrödinger Equation	381
6.7.1	Classical Polynomials as Eigenfunctions of the Sturm-Liouville and Schrödinger Equations	382

6.7.2	Legendre Polynomials; Quantized Rotational States of a Rigid Rotor.	382
6.7.3	Hermite Polynomials; Quantum Harmonic Oscillator	384
6.7.4	The Schrödinger Equation for the Electron Relaxation Problem	388
6.7.5	Quantum Mechanics for the Vibrational States of a Diatomic Molecule; Morse Potential.	390
6.7.6	Pseudospectral Solution of the Two Dimensional Schrödinger Equation for the Henon-Heles Potential; Nonclassical Basis Sets	397
	References	401
	Index	411

Spectral Methods in Chemistry and Physics
Applications to Kinetic Theory and Quantum Mechanics
Shizgal, B.
2015, XVII, 415 p. 102 illus., 2 illus. in color., Hardcover
ISBN: 978-94-017-9453-4