

# Graduate Texts in Physics

## Series editors

Kurt H. Becker, Polytechnic School of Engineering, Brooklyn, USA

Jean-Marc Di Meglio, Université Paris Diderot, Paris, France

Sadri Hassani, Illinois State University, Normal, USA

Bill Munro, NTT Basic Research Laboratories, Atsugi, Japan

Richard Needs, University of Cambridge, Cambridge, UK

William T. Rhodes, Florida Atlantic University, Boca Raton, USA

Susan Scott, Australian National University, Acton, Australia

H. Eugene Stanley, Boston University, Boston, USA

Martin Stutzmann, TU München, Garching, Germany

Andreas Wipf, Friedrich-Schiller-Universität Jena, Jena, Germany

## **Graduate Texts in Physics**

Graduate Texts in Physics publishes core learning/teaching material for graduate- and advanced-level undergraduate courses on topics of current and emerging fields within physics, both pure and applied. These textbooks serve students at the MS- or PhD-level and their instructors as comprehensive sources of principles, definitions, derivations, experiments and applications (as relevant) for their mastery and teaching, respectively. International in scope and relevance, the textbooks correspond to course syllabi sufficiently to serve as required reading. Their didactic style, comprehensiveness and coverage of fundamental material also make them suitable as introductions or references for scientists entering, or requiring timely knowledge of, a research field.

More information about this series at <http://www.springer.com/series/8431>

Philipp O.J. Scherer

# Computational Physics

Simulation of Classical and Quantum Systems

Third Edition

 Springer

Philipp O.J. Scherer  
Physikdepartment T38  
Technische Universität München  
Garching  
Germany

ISSN 1868-4513

Graduate Texts in Physics

ISBN 978-3-319-61087-0

DOI 10.1007/978-3-319-61088-7

ISSN 1868-4521 (electronic)

ISBN 978-3-319-61088-7 (eBook)

Library of Congress Control Number: 2017944306

© Springer International Publishing AG 2010, 2013, 2017

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by Springer Nature

The registered company is Springer International Publishing AG

The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

*To Christine*

# Preface to the Third Edition

While the first edition of this textbook was based on a one-year course in computational physics with a rather limited scope, its extent has been increased substantially in the third edition, offering the possibility to select from a broader range of computer experiments and to deepen the understanding of the important numerical methods. The computer experiments have always been a central part of my concepts for this book. Since Java applets, which are very convenient otherwise, have become more or less deprecated and their usage in a browser is no longer recommended for security issues, I decided to use standalone Java programs instead and to rewrite all of the old examples. These can also be edited and compiled with the “netbeans” environment and offer the same possibilities to generate a graphical user interface in short time.

The major changes in the third edition are as follows.

In the first part, a new chapter is devoted to the time-frequency analysis of experimental data. While the classical Fourier transform allows the calculation of the spectrum of a stationary signal, it is not so useful for nonstationary signals with significant variation of the momentaneous frequency distribution. Application of the Fourier transformation to short time windows, a method which is known as short-time Fourier transformation (STFT), allows analyzing the frequency content of a signal as a function of time. Good time resolution, of course, always comes together with a loss in frequency resolution (this is well known as “uncertainty principle”). The STFT method uses the same window for the whole spectrum, therefore the absolute time and frequency resolution is the same for low- and high-frequency components and the time resolution is limited by the period of the lowest frequencies of interest. Analysis of a signal with wavelets, on the other hand, uses shorter windows for the higher frequencies and keeps the relative frequency resolution constant while increasing the time resolution of the high-frequency components. The continuous wavelet transform can be very time consuming since it involves a convolution integral and is highly redundant. The discrete wavelet

transform uses a finite number of orthogonal basis function and can be performed much faster by calculating scalar products. It is closely related to multiresolution analysis which analyzes a signal in terms of a basic approximation and details of increasing resolution. Such methods are very popular in signal processing, especially of audio and image data but also in medical physics and seismology. The principles of the construction of orthogonal wavelet families are explained in detail, but without too many mathematical proofs. Several popular kinds of wavelets are discussed, like those by Haar, Meyer and Daubechies and their application is explored in a series of computer experiments.

In the second part, two new chapters have been added. First I included a discussion of the advection equation. Several methods to solve the one-dimensional problem are discussed from very simple straightforward differencing to quite sophisticated Galerkin-Taylor methods. The properties of these methods are demonstrated in computer experiments, as well by programs in the problems section as by numerous figures in the text. The extension to more dimensions by finite volume methods and dimensional splitting are discussed. A profound understanding of the advection equation and its numerical solution is also the basis for the more complex convection and Navier–Stokes equations.

Another chapter was added to the application of variational methods for quantum systems. The variational principle is very useful to calculate the groundstate energy. Two different types of computer experiments are performed. First we use the variational quantum Monte Carlo method (VQMC) for small atomic and molecular systems like the Helium atom and the Hydrogen molecule. We use trial functions which treat electron correlation explicitly by introducing a Jastrow factor which depends on the electron-electron distances. Such trial functions lead to nonseparable multidimensional integrals which can be efficiently calculated with the VQMC method. A second series of computer experiments studies exciton-phonon coupling in molecular aggregates which are of large interest for energy transfer in artificial and biological systems. The non-Born-Oppenheimer character of the wavefunction makes it necessary to optimize a large number of parameters. Different kinds of trial functions are applied to aggregates of up to 100 molecules to study the localization of the lowest state (so called “self-trapping”).

Apart from these newly added chapters, further improvements have been made throughout the book. The chapter on random numbers now discusses in more detail the principles of modern random number generators, especially the xorshift, multiply with carry (MWC) and complementary multiply with carry (CMWC) methods. Nonstationary iterative Krylov-space methods for systems of linear equations are discussed systematically with a focus on the conjugate gradients (CG) and general minimum residual (GMRES) methods. The QR method for eigenvalue problems is now discussed in much more detail together with its connection to the power iteration method and the Krylov-space methods by Arnoldi and Lanczos.

Finally, I included a computer experiment simulating the transition between two states with wave packet dynamics, which is very helpful to understand the semi-classical approximation, especially the Landau–Zener model, which is the subject of another computer experiment.

Garching, Germany  
March 2017

Philipp O.J. Scherer

# Preface to the Second Edition

This textbook introduces the main principles of computational physics, which include numerical methods and their application to the simulation of physical systems. The first edition was based on a one-year course in computational physics where I presented a selection of only the most important methods and applications. Approximately one-third of this edition is new. I tried to give a larger overview of the numerical methods, traditional ones as well as more recent developments. In many cases it is not possible to pin down the “best” algorithm, since this may depend on subtle features of a certain application, the general opinion changes from time to time with new methods appearing and computer architectures evolving, and each author is convinced that his method is the best one. Therefore I concentrated on a discussion of the prevalent methods and a comparison for selected examples. For a comprehensive description I would like to refer the reader to specialized textbooks like “Numerical Recipes” or elementary books in the field of the engineering sciences.

The major changes are as follows.

A new chapter is dedicated to the discretization of differential equations and the general treatment of boundary value problems. While finite differences are a natural way to discretize differential operators, finite volume methods are more flexible if material properties like the dielectric constant are discontinuous. Both can be seen as special cases of the finite element methods which are omnipresent in the engineering sciences. The method of weighted residuals is a very general way to find the “best” approximation to the solution within a limited space of trial functions. It is relevant for finite element and finite volume methods but also for spectral methods which use global trial functions like polynomials or Fourier series.

Traditionally, polynomials and splines are very often used for interpolation. I included a section on rational interpolation which is useful to interpolate functions with poles but can also be an alternative to spline interpolation due to the recent development of barycentric rational interpolants without poles.

The chapter on numerical integration now discusses Clenshaw-Curtis and Gaussian methods in much more detail, which are important for practical applications due to their high accuracy.

Besides the elementary root finding methods like bisection and Newton–Raphson, also the combined methods by Dekker and Brent and a recent extension by Chandrupatla are discussed in detail. These methods are recommended in most text books. Function minimization is now discussed also with derivative free methods, including Brent’s golden section search method. Quasi-Newton methods for root finding and function minimizing are thoroughly explained.

Eigenvalue problems are ubiquitous in physics. The QL-method, which is very popular for not too large matrices is included as well as analytic expressions for several differentiation matrices.

The discussion of Singular value decomposition was extended and its application to low rank matrix approximation and linear fitting is discussed.

For the integration of equations of motion (i.e. of initial value problems) many methods are available, often specialized for certain applications. For completeness, I included the predictor-corrector methods by Nordsieck and Gear which have been often used for molecular dynamics and the backward differentiation methods for stiff problems.

A new chapter is devoted to molecular mechanics, since this is a very important branch of current computational physics. Typical force field terms are discussed as well as the calculation of gradients which are necessary for molecular dynamics simulations.

The simulation of waves now includes three additional two-variable methods which are often used in the literature and are based on generally applicable schemes (leapfrog, Lax–Wendroff, Crank–Nicolson).

The chapter on simple quantum systems was rewritten. Wave packet simulation has become very important in theoretical physics and theoretical chemistry. Several methods are compared for spatial discretization and time integration of the one-dimensional Schroedinger equation. The dissipative two-level system is used to discuss elementary operations on a Qubit.

The book is accompanied by many computer experiments. For those readers who are unable to try them out, the essential results are shown by numerous figures.

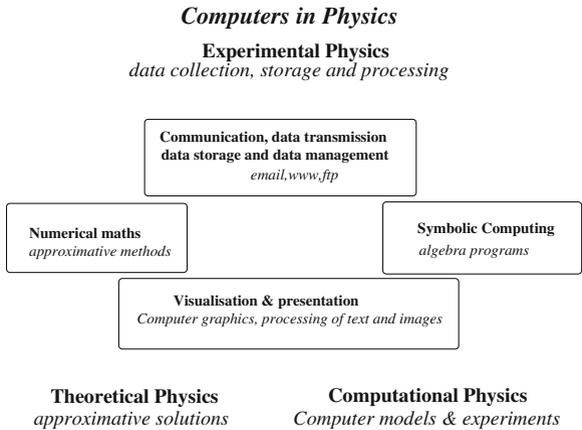
This book is intended to give the reader a good overview over the fundamental numerical methods and their application to a wide range of physical phenomena. Each chapter now starts with a small abstract, sometimes followed by necessary physical background information. Many references, original work as well as specialized text books, are helpful for more deepened studies.

Garching, Germany  
February 2013

Philipp O.J. Scherer

# Preface to the First Edition

Computers have become an integral part of modern physics. They help to acquire, store and process enormous amounts of experimental data. Algebra programs have become very powerful and give the physician the knowledge of many mathematicians at hand. Traditionally physics has been divided into experimental physics which observes phenomena occurring in the real world and theoretical physics which uses mathematical methods and simplified models to explain the experimental findings and to make predictions for future experiments. But there is also a new part of physics which has an ever growing importance. Computational physics combines the methods of the experimentalist and the theoretician. Computer simulation of physical systems helps to develop models and to investigate their properties.



This book is a compilation of the contents of a two-part course on computational physics which I have given at the TUM (Technische Universität München) for several years on a regular basis. It attempts to give the undergraduate physics students a profound background in numerical methods and in computer simulation

methods but is also very welcome by students of mathematics and computational science who want to learn about applications of numerical methods in physics. This book may also support lecturers of computational physics and bio-computing. It tries to bridge between simple examples which can be solved analytically and more complicated but instructive applications which provide insight into the underlying physics by doing computer experiments.

The first part gives an introduction into the essential methods of numerical mathematics which are needed for applications in physics. Basic algorithms are explained in detail together with limitations due to numerical inaccuracies. Mathematical explanations are supplemented by numerous numerical experiments.

The second part of the book shows the application of computer simulation methods for a variety of physical systems with a certain focus on molecular biophysics. The main object is the time evolution of a physical system. Starting from a simple rigid rotor or a mass point in a central field, important concepts of classical molecular dynamics are discussed. Further chapters deal with partial differential equations, especially the Poisson–Boltzmann equation, the diffusion equation, nonlinear dynamic systems and the simulation of waves on a 1-dimensional string. In the last chapters simple quantum systems are studied to understand e.g. exponential decay processes or electronic transitions during an atomic collision. A two-state quantum system is studied in large detail, including relaxation processes and excitation by an external field. Elementary operations on a quantum bit (Qubit) are simulated.

Basic equations are derived in detail and efficient implications are discussed together with numerical accuracy and stability of the algorithms. Analytical results are given for simple test cases which serve as a benchmark for the numerical methods. Many computer experiments are provided realized as Java applets which can be run in the web browser. For a deeper insight the source code can be studied and modified with the free “netbeans”<sup>1</sup> environment.

Garching, Germany  
April 2010

Philipp O.J. Scherer

---

<sup>1</sup>[www.netbeans.org](http://www.netbeans.org).

# Contents

## Part I Numerical Methods

<b>1</b>	<b>Error Analysis</b> . . . . .	3
1.1	Machine Numbers and Rounding Errors . . . . .	3
1.2	Numerical Errors of Elementary Floating Point Operations . . . . .	7
1.2.1	Numerical Extinction . . . . .	7
1.2.2	Addition . . . . .	8
1.2.3	Multiplication . . . . .	9
1.3	Error Propagation . . . . .	10
1.4	Stability of Iterative Algorithms . . . . .	12
1.5	Example: Rotation . . . . .	13
1.6	Truncation Error . . . . .	14
	Problems . . . . .	15
<b>2</b>	<b>Interpolation</b> . . . . .	17
2.1	Interpolating Functions . . . . .	17
2.2	Polynomial Interpolation . . . . .	19
2.2.1	Lagrange Polynomials . . . . .	19
2.2.2	Barycentric Lagrange Interpolation . . . . .	19
2.2.3	Newton's Divided Differences . . . . .	21
2.2.4	Neville Method . . . . .	22
2.2.5	Error of Polynomial Interpolation . . . . .	23
2.3	Spline Interpolation . . . . .	24
2.4	Rational Interpolation . . . . .	28
2.4.1	Pade Approximant . . . . .	29
2.4.2	Barycentric Rational Interpolation . . . . .	30
2.5	Multivariate Interpolation . . . . .	35
	Problems . . . . .	37
<b>3</b>	<b>Numerical Differentiation</b> . . . . .	39
3.1	One-Sided Difference Quotient . . . . .	39
3.2	Central Difference Quotient . . . . .	41

- 3.3 Extrapolation Methods . . . . . 41
- 3.4 Higher Derivatives . . . . . 44
- 3.5 Partial Derivatives of Multivariate Functions . . . . . 45
- Problems . . . . . 46
- 4 Numerical Integration . . . . . 47**
  - 4.1 Equidistant Sample Points. . . . . 48
    - 4.1.1 Closed Newton–Cotes Formulae . . . . . 49
    - 4.1.2 Open Newton–Cotes Formulae . . . . . 50
    - 4.1.3 Composite Newton–Cotes Rules . . . . . 50
    - 4.1.4 Extrapolation Method (Romberg Integration). . . . . 51
  - 4.2 Optimized Sample Points . . . . . 53
    - 4.2.1 Clenshaw–Curtis Expressions . . . . . 53
    - 4.2.2 Gaussian Integration . . . . . 56
  - Problems . . . . . 61
- 5 Systems of Inhomogeneous Linear Equations . . . . . 63**
  - 5.1 Gaussian Elimination Method . . . . . 64
    - 5.1.1 Pivoting . . . . . 68
    - 5.1.2 Direct LU Decomposition . . . . . 68
  - 5.2 QR Decomposition . . . . . 69
    - 5.2.1 QR Decomposition by Orthogonalization . . . . . 69
    - 5.2.2 QR Decomposition by Householder Reflections . . . . . 71
  - 5.3 Linear Equations with Tridiagonal Matrix . . . . . 74
  - 5.4 Cyclic Tridiagonal Systems. . . . . 77
  - 5.5 Linear Stationary Iteration. . . . . 78
    - 5.5.1 Richardson-Iteration. . . . . 79
    - 5.5.2 Matrix Splitting Methods. . . . . 80
    - 5.5.3 Jacobi Method . . . . . 80
    - 5.5.4 Gauss-Seidel Method. . . . . 81
    - 5.5.5 Damping and Successive Over-relaxation . . . . . 81
  - 5.6 Non Stationary Iterative Methods . . . . . 83
    - 5.6.1 Krylov Space Methods . . . . . 83
    - 5.6.2 Minimization Principle for Symmetric Positive Definite Systems . . . . . 84
    - 5.6.3 Gradient Method . . . . . 85
    - 5.6.4 Conjugate Gradients Method . . . . . 86
    - 5.6.5 Non Symmetric Systems . . . . . 89
  - 5.7 Matrix Inversion . . . . . 92
  - Problem. . . . . 93
- 6 Roots and Extremal Points . . . . . 97**
  - 6.1 Root Finding. . . . . 98
    - 6.1.1 Bisection . . . . . 98
    - 6.1.2 Regula Falsi (False Position) Method . . . . . 99
    - 6.1.3 Newton–Raphson Method . . . . . 100

6.1.4	Secant Method . . . . .	101
6.1.5	Interpolation . . . . .	101
6.1.6	Inverse Interpolation . . . . .	102
6.1.7	Combined Methods . . . . .	105
6.1.8	Multidimensional Root Finding . . . . .	111
6.1.9	Quasi-Newton Methods . . . . .	113
6.2	Function Minimization . . . . .	114
6.2.1	The Ternary Search Method . . . . .	115
6.2.2	The Golden Section Search Method (Brent’s Method) . . . . .	116
6.2.3	Minimization in Multidimensions . . . . .	121
6.2.4	Steepest Descent Method. . . . .	122
6.2.5	Conjugate Gradient Method. . . . .	124
6.2.6	Newton–Raphson Method . . . . .	124
6.2.7	Quasi-Newton Methods . . . . .	125
	Problems . . . . .	126
<b>7</b>	<b>Fourier Transformation . . . . .</b>	<b>129</b>
7.1	Fourier Integral and Fourier Series . . . . .	129
7.2	Discrete Fourier Transformation . . . . .	130
7.2.1	Trigonometric Interpolation . . . . .	132
7.2.2	Real Valued Functions. . . . .	134
7.2.3	Approximate Continuous Fourier Transformation . . . . .	135
7.3	Fourier Transform Algorithms . . . . .	136
7.3.1	Goertzel’s Algorithm. . . . .	136
7.3.2	Fast Fourier Transformation. . . . .	138
	Problems . . . . .	141
<b>8</b>	<b>Time-Frequency Analysis . . . . .</b>	<b>145</b>
8.1	Short Time Fourier Transform (STFT) . . . . .	145
8.2	Discrete Short Time Fourier Transform . . . . .	152
8.3	Gabor Expansion . . . . .	156
8.4	Wavelet Analysis . . . . .	158
8.5	Wavelet Synthesis. . . . .	160
8.6	Discrete Wavelet Transform and Multiresolution Analysis . . . . .	164
8.6.1	Scaling Function and Multiresolution Approximation. . . . .	164
8.6.2	Construction of an Orthonormal Wavelet Basis . . . . .	171
8.7	Discrete Data and Fast Wavelet Transform. . . . .	178
8.7.1	Recursive Wavelet Transformation . . . . .	178
8.7.2	Example: Haar Wavelet. . . . .	180
8.7.3	Signal Reconstruction . . . . .	181
8.7.4	Example: Analysis with Compactly Supported Wavelets . . . . .	182
	Problems . . . . .	184

**9 Random Numbers and Monte-Carlo Methods** . . . . . 187

  9.1 Some Basic Statistics . . . . . 187

    9.1.1 Probability Density and Cumulative Probability  
          Distribution . . . . . 187

    9.1.2 Histogram . . . . . 188

    9.1.3 Expectation Values and Moments . . . . . 189

    9.1.4 Example: Fair Die . . . . . 190

    9.1.5 Normal Distribution . . . . . 191

    9.1.6 Multivariate Distributions . . . . . 192

    9.1.7 Central Limit Theorem . . . . . 193

    9.1.8 Example: Binomial Distribution . . . . . 194

    9.1.9 Average of Repeated Measurements . . . . . 195

  9.2 Random Numbers . . . . . 196

    9.2.1 Linear Congruent Mapping (LC) . . . . . 197

    9.2.2 Xorshift . . . . . 197

    9.2.3 Multiply with Carry (MWC) . . . . . 198

    9.2.4 Complementary Multiply with Carry (CMWC) . . . . . 199

    9.2.5 Random Numbers with Given Distribution . . . . . 199

    9.2.6 Examples . . . . . 200

  9.3 Monte-Carlo Integration . . . . . 202

    9.3.1 Numerical Calculation of  $\pi$  . . . . . 202

    9.3.2 Calculation of an Integral . . . . . 202

    9.3.3 More General Random Numbers . . . . . 204

    9.3.4 Configuration Integrals . . . . . 204

    9.3.5 Simple Sampling . . . . . 206

    9.3.6 Importance Sampling . . . . . 207

    9.3.7 Metropolis Algorithm . . . . . 207

  Problems . . . . . 210

**10 Eigenvalue Problems** . . . . . 213

  10.1 Direct Solution . . . . . 214

  10.2 Jacobi Method . . . . . 214

  10.3 Tridiagonal Matrices . . . . . 217

    10.3.1 Characteristic Polynomial of a Tridiagonal  
          Matrix . . . . . 217

    10.3.2 Special Tridiagonal Matrices . . . . . 218

  10.4 Reduction to a Tridiagonal Matrix . . . . . 223

  10.5 The Power Iteration Method . . . . . 225

  10.6 The QR Algorithm . . . . . 228

  10.7 Hermitian Matrices . . . . . 230

  10.8 Large Matrices . . . . . 231

  10.9 Non-symmetric Matrices . . . . . 234

  Problems . . . . . 234

- 11 Data Fitting** . . . . . 235
  - 11.1 Least Square Fit . . . . . 236
    - 11.1.1 Linear Least Square Fit . . . . . 237
    - 11.1.2 Linear Least Square Fit with Orthogonalization. . . . . 239
  - 11.2 Singular Value Decomposition . . . . . 242
    - 11.2.1 Full Singular Value Decomposition. . . . . 243
    - 11.2.2 Reduced Singular Value Decomposition . . . . . 243
    - 11.2.3 Low Rank Matrix Approximation . . . . . 245
    - 11.2.4 Linear Least Square Fit with Singular Value Decomposition. . . . . 248
    - 11.2.5 Singular and Underdetermined Linear Systems of Equations . . . . . 251
- Problems. . . . . 253
- 12 Discretization of Differential Equations** . . . . . 255
  - 12.1 Classification of Differential Equations . . . . . 256
  - 12.2 Finite Differences . . . . . 259
    - 12.2.1 Finite Differences in Time . . . . . 259
    - 12.2.2 Stability Analysis. . . . . 260
    - 12.2.3 Method of Lines . . . . . 261
    - 12.2.4 Eigenvector Expansion . . . . . 262
  - 12.3 Finite Volumes . . . . . 265
    - 12.3.1 Discretization of fluxes . . . . . 268
  - 12.4 Weighted Residual Based Methods. . . . . 270
    - 12.4.1 Point Collocation Method . . . . . 271
    - 12.4.2 Sub-domain Method . . . . . 271
    - 12.4.3 Least Squares Method . . . . . 272
    - 12.4.4 Galerkin Method . . . . . 273
  - 12.5 Spectral and Pseudo-Spectral Methods . . . . . 273
    - 12.5.1 Fourier Pseudo-Spectral Methods. . . . . 273
    - 12.5.2 Example: Polynomial Approximation . . . . . 274
  - 12.6 Finite Elements . . . . . 277
    - 12.6.1 One-Dimensional Elements . . . . . 277
    - 12.6.2 Two-and Three-Dimensional Elements . . . . . 278
    - 12.6.3 One-Dimensional Galerkin FEM . . . . . 282
  - 12.7 Boundary Element Method . . . . . 286
- 13 Equations of Motion** . . . . . 289
  - 13.1 The State Vector. . . . . 290
  - 13.2 Time Evolution of the State Vector . . . . . 291
  - 13.3 Explicit Forward Euler Method. . . . . 292
  - 13.4 Implicit Backward Euler Method . . . . . 295
  - 13.5 Improved Euler Methods . . . . . 296
  - 13.6 Taylor Series Methods . . . . . 298
    - 13.6.1 Nordsieck Predictor-Corrector Method. . . . . 298
    - 13.6.2 Gear Predictor-Corrector Methods . . . . . 300

13.7	Runge–Kutta Methods . . . . .	301
13.7.1	Second Order Runge–Kutta Method . . . . .	302
13.7.2	Third Order Runge–Kutta Method . . . . .	302
13.7.3	Fourth Order Runge–Kutta Method . . . . .	303
13.8	Quality Control and Adaptive Step Size Control . . . . .	304
13.9	Extrapolation Methods . . . . .	305
13.10	Linear Multistep Methods . . . . .	306
13.10.1	Adams-Bashforth Methods . . . . .	306
13.10.2	Adams-Moulton Methods . . . . .	307
13.10.3	Backward Differentiation (Gear) Methods . . . . .	308
13.10.4	Predictor-Corrector Methods . . . . .	309
13.11	Verlet Methods . . . . .	310
13.11.1	Liouville Equation . . . . .	310
13.11.2	Split Operator Approximation . . . . .	311
13.11.3	Position Verlet Method . . . . .	312
13.11.4	Velocity Verlet Method . . . . .	313
13.11.5	Stoermer-Verlet Method . . . . .	313
13.11.6	Error Accumulation for the Stoermer-Verlet Method . . . . .	315
13.11.7	Beeman’s Method . . . . .	315
13.11.8	The Leapfrog Method . . . . .	317
	Problems . . . . .	318

## Part II Simulation of Classical and Quantum Systems

<b>14</b>	<b>Rotational Motion . . . . .</b>	<b>325</b>
14.1	Transformation to a Body Fixed Coordinate System . . . . .	325
14.2	Properties of the Rotation Matrix . . . . .	326
14.3	Properties of $W$ , Connection with the Vector of Angular Velocity . . . . .	328
14.4	Transformation Properties of the Angular Velocity . . . . .	330
14.5	Momentum and Angular Momentum . . . . .	332
14.6	Equations of Motion of a Rigid Body . . . . .	333
14.7	Moments of Inertia . . . . .	334
14.8	Equations of Motion for a Rotor . . . . .	334
14.9	Explicit Methods . . . . .	335
14.10	Loss of Orthogonality . . . . .	337
14.11	Implicit Method . . . . .	338
14.12	Example: Free Symmetric Rotor . . . . .	341
14.13	Kinetic Energy of a Rotor . . . . .	342
14.14	Parametrization by Euler Angles . . . . .	342
14.15	Cayley–Klein-Parameters, Quaternions, Euler Parameters . . . . .	343
14.16	Solving the Equations of Motion with Quaternions . . . . .	346
	Problems . . . . .	347

<b>15</b>	<b>Molecular Mechanics</b>	351
15.1	Atomic Coordinates	352
15.2	Force Fields	355
15.2.1	Intramolecular Forces	355
15.2.2	Intermolecular Interactions	357
15.3	Gradients	358
15.4	Normal Mode Analysis	364
15.4.1	Harmonic Approximation	364
	Problems	367
<b>16</b>	<b>Thermodynamic Systems</b>	369
16.1	Simulation of a Lennard–Jones Fluid	370
16.1.1	Integration of the Equations of Motion	370
16.1.2	Boundary Conditions and Average Pressure	371
16.1.3	Initial Conditions and Average Temperature	372
16.1.4	Analysis of the Results	373
16.2	Monte-Carlo Simulation	378
16.2.1	One-Dimensional Ising Model	378
16.2.2	Two-Dimensional Ising Model	380
	Problems	381
<b>17</b>	<b>Random Walk and Brownian Motion</b>	385
17.1	Markovian Discrete Time Models	385
17.2	Random Walk in One Dimension	386
17.2.1	Random Walk with Constant Step Size	387
17.3	The Freely Jointed Chain	389
17.3.1	Basic Statistic Properties	389
17.3.2	Gyration Tensor	392
17.3.3	Hookean Spring Model	393
17.4	Langevin Dynamics	395
	Problems	397
<b>18</b>	<b>Electrostatics</b>	399
18.1	Poisson Equation	400
18.1.1	Homogeneous Dielectric Medium	400
18.1.2	Numerical Methods for the Poisson Equation	402
18.1.3	Charged Sphere	403
18.1.4	Variable $\epsilon$	406
18.1.5	Discontinuous $\epsilon$	407
18.1.6	Solvation Energy of a Charged Sphere	408
18.1.7	The Shifted Grid Method	409
18.2	Poisson–Boltzmann Equation	411
18.2.1	Linearization of the Poisson–Boltzmann Equation	412
18.2.2	Discretization of the Linearized Poisson Boltzmann Equation	413

18.3	Boundary Element Method for the Poisson Equation . . . . .	413
18.3.1	Integral Equations for the Potential . . . . .	414
18.3.2	Calculation of the Boundary Potential . . . . .	416
18.4	Boundary Element Method for the Linearized Poisson–Boltzmann Equation . . . . .	420
18.5	Electrostatic Interaction Energy (Onsager Model). . . . .	421
18.5.1	Example: Point Charge in a Spherical Cavity . . . . .	422
	Problems. . . . .	423
<b>19</b>	<b>Advection</b> . . . . .	427
19.1	The Advection Equation . . . . .	427
19.2	Advection in One Dimension . . . . .	428
19.2.1	Spatial Discretization with Finite Differences. . . . .	430
19.2.2	Explicit Methods . . . . .	433
19.2.3	Implicit Methods . . . . .	443
19.2.4	Finite Volume Methods . . . . .	445
19.2.5	Taylor–Galerkin Methods . . . . .	449
19.3	Advection in More Dimensions . . . . .	451
19.3.1	Lax–Wendroff Type Methods . . . . .	452
19.3.2	Finite Volume Methods . . . . .	452
19.3.3	Dimensional Splitting . . . . .	454
	Problems. . . . .	454
<b>20</b>	<b>Waves</b> . . . . .	455
20.1	Classical Waves . . . . .	455
20.2	Spatial Discretization in One Dimension. . . . .	458
20.3	Solution by an Eigenvector Expansion . . . . .	461
20.4	Discretization of Space and Time . . . . .	463
20.5	Numerical Integration with a Two-Step Method . . . . .	464
20.6	Reduction to a First Order Differential Equation. . . . .	467
20.7	Two Variable Method. . . . .	470
20.7.1	Leapfrog Scheme . . . . .	471
20.7.2	Lax–Wendroff Scheme. . . . .	472
20.7.3	Crank–Nicolson Scheme . . . . .	474
	Problems. . . . .	477
<b>21</b>	<b>Diffusion</b> . . . . .	479
21.1	Particle Flux and Concentration Changes . . . . .	479
21.2	Diffusion in One Dimension. . . . .	481
21.2.1	Explicit Euler (Forward Time Centered Space) Scheme . . . . .	483
21.2.2	Implicit Euler (Backward Time Centered Space) Scheme . . . . .	485
21.2.3	Crank–Nicolson Method . . . . .	486
21.2.4	Error Order Analysis . . . . .	488
21.2.5	Finite Element Discretization. . . . .	489

21.3	Split-Operator Method for Multidimensions . . . . .	490
	Problems . . . . .	491
<b>22</b>	<b>Nonlinear Systems</b> . . . . .	<b>493</b>
22.1	Iterated Functions . . . . .	494
22.1.1	Fixed Points and Stability . . . . .	494
22.1.2	The Ljapunov-Exponent . . . . .	496
22.1.3	The Logistic Map . . . . .	497
22.1.4	Fixed Points of the Logistic Map . . . . .	498
22.1.5	Bifurcation Diagram . . . . .	500
22.2	Population Dynamics . . . . .	501
22.2.1	Equilibria and Stability . . . . .	501
22.2.2	The Continuous Logistic Model . . . . .	502
22.3	Lotka–Volterra Model. . . . .	503
22.3.1	Stability Analysis. . . . .	504
22.4	Functional Response . . . . .	505
22.4.1	Holling–Tanner Model . . . . .	506
22.5	Reaction-Diffusion Systems . . . . .	509
22.5.1	General Properties of Reaction-Diffusion Systems . . . . .	509
22.5.2	Chemical Reactions . . . . .	509
22.5.3	Diffusive Population Dynamics . . . . .	511
22.5.4	Stability Analysis. . . . .	511
22.5.5	Lotka Volterra Model with Diffusion. . . . .	513
	Problems . . . . .	514
<b>23</b>	<b>Simple Quantum Systems</b> . . . . .	<b>517</b>
23.1	Pure and Mixed Quantum States. . . . .	518
23.1.1	Wavefunctions . . . . .	519
23.1.2	Density Matrix for an Ensemble of Systems . . . . .	520
23.1.3	Time Evolution of the Density Matrix . . . . .	520
23.2	Wave Packet Motion in One Dimension. . . . .	522
23.2.1	Discretization of the Kinetic Energy . . . . .	523
23.2.2	Time Evolution . . . . .	525
23.2.3	Example: Free Wave Packet Motion . . . . .	536
23.3	Few-State Systems . . . . .	537
23.3.1	Two-State System . . . . .	540
23.3.2	Two-State System with Time Dependent Perturbation . . . . .	543
23.3.3	Superexchange Model . . . . .	545
23.3.4	Ladder Model for Exponential Decay . . . . .	548
23.3.5	Semiclassical Curve Crossing . . . . .	551
23.3.6	Landau–Zener Model. . . . .	553
23.4	The Dissipative Two-State System . . . . .	555
23.4.1	Equations of Motion for a Two-State System . . . . .	555

23.4.2	The Vector Model . . . . .	556
23.4.3	The Spin-1/2 System . . . . .	558
23.4.4	Relaxation Processes - The Bloch Equations . . . . .	559
23.4.5	The Driven Two-State System . . . . .	561
23.4.6	Elementary Qubit Manipulation . . . . .	569
	Problems . . . . .	572
<b>24</b>	<b>Variational Methods for Quantum Systems . . . . .</b>	<b>575</b>
24.1	Variational Quantum Monte Carlo Simulation of Atomic and Molecular Systems . . . . .	577
24.1.1	The Simplest Molecule: $H_2^+$ . . . . .	579
24.1.2	The Simplest Two-Electron System: The Helium Atom . . . . .	582
24.1.3	The Hydrogen Molecule $H_2$ . . . . .	586
24.2	Exciton-Phonon Coupling in Molecular Aggregates . . . . .	589
24.2.1	Molecular Dimer . . . . .	592
24.2.2	Larger Aggregates . . . . .	598
	Problems . . . . .	601
	<b>Appendix A: Performing the Computer Experiments . . . . .</b>	<b>605</b>
	<b>Appendix B: Methods and Algorithms . . . . .</b>	<b>609</b>
	<b>References . . . . .</b>	<b>617</b>
	<b>Index . . . . .</b>	<b>627</b>