

Preface

Spectral and pseudospectral methods have become increasingly popular as higher order methods for the solution of partial differential and integral equations (Azañez et al. 2013). A spectral method refers to the representation of the solution of some problem in a basis set of orthogonal functions, whereas a pseudospectral approach, sometimes referred to as a collocation, is based on the representation of the solution with the function values at a set of discrete points. For the smooth solutions of particular problems, these methods can provide exponential convergence of the solutions versus the number of basis functions or the number of grid points retained.

Books devoted to these methods include the monographs by Shen et al. (2011), Kopriva (2009), Hesthaven et al. (2007) and the new edition of the book by Canuto et al. (2006). Other textbooks include those by Peyret (2002), Deville et al. (2002), Boyd (2001), Trefethen (2000), Shu (2000), Fornberg (1996), Funaro (1992), Guo (1998) and Gottlieb and Orszag (1977).

In view of the availability of texts on spectral/pseudospectral methods, it might be appropriate to question whether another book on this subject is justified. The aforementioned books are devoted primarily to problems in fluid mechanics and to the solutions of the Navier-Stokes, Helmholtz, Poisson equations and related problems most often for bounded intervals. At the present time, a textbook that covers the fundamental aspects of spectral and pseudospectral methods with applications to problems in chemistry and physics does not exist.

The main objective is to provide the basic concepts of spectral and pseudospectral methods to the solution of problems in diverse fields of interest to a wide audience, and to demonstrate the improved convergence obtained with nonclassical basis functions for certain problems. Perhaps the first application of a collocation method in physics was the solution of the integro-differential radiative transfer equation by Chandrasekhar (1944, 1960) based on Gauss-Legendre quadrature points. There are many applied problems in chemistry, physics, astrophysics, engineering, biology, economics and other fields for which spectral/pseudospectral methods can be used to advantage.

The basic mathematics and numerical methods used in the book are presented in Chaps. 1–4, whereas Chaps. 5 and 6 summarize the applications of spectral and

pseudospectral methods to several specialized topics in nonequilibrium statistical mechanics and quantum mechanics. A brief overview of the background physics is provided for some of the topics.

Chapter 1 presents the basic concepts of spectral space and physical space for the representations of functions and the unitary transformation between the two spaces. A Hilbert space is defined as are hermitian operators, Sturm-Liouville eigenvalue problems and the Rayleigh-Ritz variational theorem, which might also be referred to as a method of weighted residuals or a Galerkin method. A personal historical summary of the development of pseudospectral methods in chemistry and physics is also presented with an overview of the topics in the book.

Chapter 2 provides the fundamental mathematics used throughout the book. The construction of orthogonal polynomials in terms of the three term recurrence relation is discussed. The numerical instability inherent in the Gram-Schmidt orthogonalization to construct basis sets is demonstrated with applications to Legendre, Hermite and the nonclassical Rys polynomials. Numerical round-off errors in scientific computations can sometimes be very subtle as is demonstrated in several applications. Lagrange interpolation is introduced as the basis for Newton-Cotes integration algorithms and Gaussian quadrature. The Gaussian quadrature points are the eigenvalues of the Jacobi matrix, the matrix representation of the continuous multiplicative coordinate operator and defined in terms of the recurrence coefficients in the three term recurrence relation. From a quantum mechanical perspective, the Jacobi matrix is the discrete approximation to the continuous eigenvalues of the coordinate operator. The quadrature weights are determined from the eigenvectors of the Jacobi matrix.

In addition to a summary of the properties of the classical polynomials, several nonclassical basis sets such as the Maxwell polynomials orthogonal with respect to weight function $w(x) = x^p e^{-x^2}$ on the semi-infinite axis, the Rys polynomials with $w(x) = e^{-cx^2}$ on the interval $[-1, 1]$ and bimodal polynomials with $w(x) = \exp(-(x^4/(4\epsilon) - x^2/(2\epsilon)))$ for both the infinite and semi-infinite axes are presented. These polynomial basis sets and associated quadratures are used in kinetic theory, quantum mechanics and chemical kinetics. Alternate interpolation algorithms such as the sinc function, B-splines and radial basis functions are also discussed.

In Chap. 3, the convergence of the integration algorithms of Chap. 2 versus the number of quadrature points is compared for integrals that occur for several physical systems. The systems include chemical and nuclear reaction rates, the integral over the “cusp” in the Boltzmann integral collision operator as well as for quantum mechanical scattering phase shifts. The calculation of matrix elements of multiplicative operators, namely the collision frequency in the Boltzmann equation and the interaction potential in the Schrödinger equation are compared. Several challenging integrals such as integrals with oscillating integrands and electron repulsion integrals in quantum chemistry are reviewed. The last section describes the discrete matrix representation of derivative operators employed in pseudospectral methods. The exact pseudospectral solutions of Sturm-Liouville eigenvalue equations for the classical polynomials is demonstrated.

Chapter 4 illustrates spectral convergence in the expansion of selected functions in different basis sets. The expansions of simple Gaussians, as well as the Kappa distribution of space physics, in Hermite and Laguerre polynomials are presented with an analysis of the spectral convergence. Fourier series expansions are included and applied to the construction of wave packets in quantum mechanics and the resolution of a free induction decay curve typical in Fourier Transform spectroscopy. Also presented is the resolution of the oscillations at a jump discontinuity, known as the Gibbs phenomenon, that arise in the Fourier series representation of a piecewise continuous function. A brief description of the Runge phenomenon is also discussed.

In Chap. 5, the applications to the solution of integral equations with particular emphasis on the Boltzmann equation of kinetic theory are presented. The use of spectral and pseudospectral methods in the determination of the eigenvalue spectra of the linearized (one component) and linear (two component) integral collision operators is presented. The spectra of both operators consist of discrete and continuous eigenvalues as can also occur for the eigenvalue spectrum of the Hamiltonian in the Schrödinger equation for particular potentials. A brief summary is provided of the Chapman-Enskog method of solution of the Boltzmann equation that yields the integral equations that define the transport coefficients in a dilute gas. The relaxation of initial nonequilibrium distributions, including anisotropic initial distributions, is studied versus the mass ratio of the two components in a binary gaseous mixture. The classic Milne problem of astrophysics and kinetic theory is presented and applied to a study of the nonequilibrium effects associated with the escape of light atoms from planetary atmospheres. As can be ascertained from this overview, there are several different applications included and the presentation shifts quickly from topic to topic.

Chapter 6 consists of applications of spectral and pseudospectral methods for the solution of the Fokker-Planck equation (Riskin and Till 1996) in nonequilibrium statistical mechanics and the Schrödinger equation (Liboff 2002) in quantum mechanics. Fokker-Planck equations can be transformed to Schrödinger equations and the potentials that result belong to supersymmetric quantum mechanics (Comtet et al. 1985; Dutt et al. 1988; Cooper et al. 1995). The nonclassical basis sets and quadrature points are chosen based on the equilibrium probability density functions for the Fokker-Planck equations. Fokker-Planck equations for Brownian motion, for relaxation in the disparate mass limits of the linear Boltzmann equation known as the Rayleigh and Lorentz limits and for models of cis-trans isomerization reactions are solved with both spectral and pseudospectral methods. Pseudospectral methods are used for the solution of Sturm-Liouville eigenvalue problems for simple systems. With the appropriate choice of weight function, a quadrature can be constructed for which the pseudospectral representation of the Hamiltonian in the Schrödinger equation does not include an explicit reference to the potential. As is the case for Chap. 5, the topics in this chapter also change quickly from topic to topic.

I have deliberately limited the use of acronyms as they are often not unique. A good example is DFT which can be either Density Functional Theory or Discrete Fourier Transform. In kinetic theory, BGK refers to the Bhatnager-Gross-Krook

model of the Boltzmann collision operator, whereas in plasma physics it signifies Bernstein-Green-Kruskal solitary waves. The subject matter of the book spans several disciplines and the use of acronyms would defeat the purpose of reaching a broad audience.

I have provided in footnotes very brief biographies of the scientists and mathematicians who have provided the mathematical and physical concepts upon which much of the current research is based. As an example, Josiah Willard Gibbs (1839–1903) is familiar to mathematicians for his contributions to the understanding of the slow convergence of the Fourier series for functions with jump discontinuities leading to oscillations referred to as the Gibbs phenomenon. Gibbs is very well known to chemists and physicists as a thermodynamicist and his name is associated with the Gibbs free energy and for his contributions to entropy concepts in physical systems. The biography of Gibbs at aps.org mentions that, “When his publications were read, they were considered too mathematically complex for most chemists and too scientific for many mathematicians”. Much of the current applied work by chemists and physicists could not be done without the mathematics developed by mathematicians and scientists. More detailed and interesting discourses of the contributions of many people and their personal careers can be found on the Internet and published biographies.

MATLAB[®] codes are provided for many of the numerical results reported in the book. These were developed on a 64 bit personal computer with an Intel i5 CPU at 2.50 GHz and 8 GB RAM. The computational time in most cases was of the order of several seconds and usually less than one minute. The codes in some instances are not completely vectorized and a few “for” loops remain. As a consequence, the codes are hopefully more transparent to the user for a very small cost in the computational time. Although several short MATLAB codes are listed in the text, the vast majority of the codes were finalized after submission of the manuscript. The codes and accompanying documentation are available at www.springer.com and at spectralmethods.chem.ubc.ca.

The book is intended for use by upper year undergraduates, graduate students as well as established researchers working on applied problems in chemistry, physics, astrophysics, space science, plasma physics, biology, engineering and in other related fields. The large bibliography provided is to current research in these diverse fields. Although many mathematical results are proved and the fundamental principles are illustrated with numerical examples, the presentation is utilitarian and not meant to be mathematically rigorous. I provide references to textbooks and review papers where more rigorous mathematical approaches are presented. I have also included very brief derivations of the integral and/or differential equations defining the physical problems considered with references to more detailed discussions. The large bibliography provided is the evidence of the wide applicability of spectral/pseudospectral methods in science and engineering.

This book is the result of 30 years of research employing spectral and pseudospectral methods for the solution of a wide range of different physical problems. I have not benefited from the opportunity to teach this material to several cohorts of undergraduate and/or graduate students. However, I am indebted to

numerous graduate students, postdoctoral fellows and other collaborators, who are cited in the references provided, for their contributions to this research. I am also very grateful to several colleagues who proofread portions of a preliminary version of the book. The people involved are Patrick Casasm-Chenai, Daniel Hubert, Joseph Lemaire, Joseph Lo, Norman McCormick, Gren Patey, Viviane Pierrard, Bob Snider and Larry Viehland. My heartfelt thanks are extended especially to Daniel Baye, Livio Gibelli, Jae-Hun Jung, Konstantin Kabin and Mark Thachuk for their conscientious reading of several chapters. The many constructive comments of these people are very much appreciated and their contributions to the book cannot be underestimated. However, I am solely responsible for any errors that remain and I encourage readers of the book to report any further corrections to me at shizgal@chem.ubc.ca. A list of errata and MATLAB codes will be posted periodically at the websites provided. I thank Maria Bellantone and Mieke van der Fluit at Springer for their advice and their extreme patience with this project. Very special thanks to my wife, Judy, for putting up with my preoccupation with this effort for several years.

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