Chapter 1
Introduction to Spectral/Pseudospectral Methods

Abstract This chapter introduces the basic principles of spectral/pseudospectral methods for the solution of partial differential and/or integral equations that serve to model a large number of physical processes in chemistry and physics. The first part of the chapter defines the spectral space representation of functions and the transformation to the physical space representation. A Hilbert space is defined as well as the definition of self-adjoint operators that occur in quantum mechanics and kinetic theory. The Rayleigh-Ritz variational principle and the method of weighted residuals are discussed. An historical summary of the development of pseudospectral methods in chemistry and physics is presented together with an outline of the book. The science, the mathematical models and the computer algorithms are interrelated.

1.1 Introduction

This book describes current spectral and pseudospectral methods for the solution of partial differential and/or integral equations that model a large number of systems and processes in chemistry and physics with many applications to biology, engineering, astrophysics and space science. We consider physical systems and processes that are modeled theoretically with the principles of quantum mechanics and kinetic theory. This introduction provides an overview of several physical systems for which spectral and pseudospectral methods are used to solve the differential and/or integral equations that define the problems.

The basic mathematical tools are briefly presented in Sects. 1.2 and 1.3. A more detailed presentation of the mathematics and numerical algorithms is presented in Chap. 2. There are also many comprehensive discussions of this material in the bibliography provided.

A personal historical summary of the development of pseudospectral methods with applications to physical problems in chemistry, physics, biology and engineering is presented in Sect. 1.4. This is a very broad subject that cannot be covered in detail in a single volume. The many references provided form a very important additional resource to the material presented here. This large bibliography also demonstrates the widespread use of the mathematical/numerical methods that are described.

B. Shizgal, *Spectral Methods in Chemistry and Physics*, Scientific Computation,
DOI 10.1007/978-94-017-9454-1_1

Quantum theory (Messiah 1961; Liboff 2002) based on the Schrödinger [1] equation provides the theoretical description of numerous systems in chemistry and physics. An important problem in quantum chemistry is the calculation of the electronic energy states for a molecule taking into account the electron-nuclei and electron-electron Coulombic interactions for fixed positions of the nuclei (Sherrill 2010). This is referred to as electronic structure theory (Szabo and Ostlund 1996; Friesner 1991; Helgaker et al. 2000; Levine 2009) and includes density functional theory (Jones and Gunnarsson 1989; Morgan 1996; Tsuneda 2014).

The potential from the solution of the electronic problem is used in the Schrödinger equation for the motion of the nuclei and provides the rotational and vibrational states of the molecule (Friesner et al. 1993; Light and Carrington 2000; Koput et al. 2001). A complementary problem concerns the quantum description for the continuum or scattered states that are of concern in collision theory (Child 1996; Taylor 2012) especially as applied to theoretical chemical kinetics and photochemistry (Cassam-Chenaï and Liévin 2012; Balint-Kurti 2008; Burke 2011). These applications and many others (Hu et al. 2002; Baye et al. 2008; Amore et al. 2009; Heyl and Thirumalai 2010) are active areas of research in chemistry and physics requiring efficient computational algorithms.

Statistical mechanics can be divided into equilibrium and non-equilibrium statistical mechanics which includes kinetic theory. Kinetic theory is based on the Boltzmann[2] equation (Liboff 2003; Kremer 2010) or the Fokker[3]-Planck[4] equation (Chandrasekhar 1949; Risken and Till 1996) for the particle distribution functions that define, for example, the transport coefficients in a dilute gas as well as chemical reaction rates including nuclear reactions. For collision dominated gaseous systems, the Chapman[5]-Enksog[6] method (Chapman and Cowling 1970) of solution of the Boltzmann equation yields the macroscopic equations of fluid mechanics and in

[1] Erwin Schrödinger (1887–1961) was an Austrian physicist who worked on fundamental aspects of quantum theory and developed the equation that bears his name. He also made important contributions to statistical mechanics and thermodynamics and had an interest in biology and philosophy. He was awarded the 1933 Nobel Prize for his development of wave mechanics in quantum theory.

[2] Ludwig Eduard Boltzmann (1844–1906) was an Austrian physicist who made significant contributions to statistical mechanics and proposed the kinetic equation that bears his name. The equilibrium particle distribution is the Maxwell-Boltzmann distribution.

[3] Adrian Fokker (1887–1972) was a Dutch physicist and made contributions to relativity in addition to statistical mechanics. The Fokker-Planck equation used to model numerous processes in physics, astrophysics, chemistry, finance and biology bears his name. He also made numerous contributions to music theory.

[4] Max Planck (1858–1947) was a German physicist and was awarded the 1918 Nobel Physics Prize for his contributions to quantum theory. Planck and Fokker independently derived the Fokker-Planck equation of statistical physics.

[5] Sydney Chapman (1888–1970) was a British mathematician and geophysicist developed the Chapman-Enksog method of solution of the Boltzmann equation and contributed to the theory of stochastic processes. He also made many fundamental contributions to geophysics.

[6] David Enskog (1884–1947) was a Swedish mathematical physicist who contributed to the kinetic theory of gases with the method of solution developed with Chapman.

particular the Navier[7]-Stokes[8] equation. This complements the usual derivation of the equations of fluid mechanics in terms of mass, momentum and energy conservation (Kundu et al. 2012; Durran 2010). Spectral and pseudospectral methods have been extensively applied to problems in fluid mechanics (Gottlieb and Orszag 1977; Peyret 2002; Canuto et al. 2006b).

We consider a large number of systems that includes radiative and neutron transport, astrophysics, plasma physics and space science that can be described with kinetic theory. We do not consider applications of equilibrium statistical mechanics to liquids and electrochemistry that are currently studied primarily with Monte Carlo simulations (Car and Parrinello 1985; Landau and Binder 2009). The direct simulation Monte Carlo method (Bird 1994) used for many rarefied gas dynamical problems is not discussed.

The vast number of applications of kinetic theory in many different fields is truly remarkable. If the particles of interest are photons, the Boltzmann equation is replaced with a radiative transfer equation and we find applications to the transport of radiation in atmospheric science (Liou 2002; Thomas and Stamnes 2002), radio therapy (Gifford et al. 2006) and astrophysics (Chandrasekhar 1949). The evolution of stars in globular clusters can be studied with the Fokker-Planck equation with the interstellar gravitational Coulomb interactions (Lightman and Shapiro 1978; Chavanis 2006; Binney and Tremaine 2008) analogous to the use in plasma physics (Birdsall and Langdon 2005; Anderson et al. 2004; Peeters and Strintzi 2008). The development of nuclear reactors (Hebert 2009) requires kinetic theory to understand the thermalization and transport of neutrons (Davison 1957; Williams 1966), and nuclear reaction rates (Atenzi and Meyer-Ter-Vehn 2004).

There are also important applications to the escape of atoms from planetary atmospheres (Fahr and Shizgal 1983; Shizgal and Arkos 1996) as well as the loss of charged particles from the earth (Lie-Svendsen and Rees 1996; Pierrard and Lemaire 1998) and the sun (Echim et al. 2011). A complementary problem is the escape of stars from a globular cluster (Spitzer and Härm 1958; Lemou and Chavanis 2010) and relativistic astrophysics (Bonazzola et al. 1999; Grandclément and Novak 2009). We will not be able to consider all of these applications. However, we will provide some of the basic concepts with concern to the numerical modeling of particular systems with spectral and pseudospectral methods.

In each application, the physical problem is approximated with a mathematical model which for most applications requires a numerical solution of partial differential or integral equations. The objectives can be summarized in the flow chart in Fig. 1.1. We consider a mathematical model which provides an approximate description of the physical system. A numerical algorithm is developed to solve the differential or integral equations for the model. The results are compared with observations

[7] Claude Louis Navier (1785–1836) was a French mathematician who worked in engineering science with emphasis on bridge building and also made basic contributions to fluid mechanics. He was a student and colleague of Fourier.

[8] Sir George Gabriel Stokes (1819–1903) was a Irish/English mathematical physicist and made fundamental contributions to fluid dynamics including Stokes' law and Navier-Stokes equation.

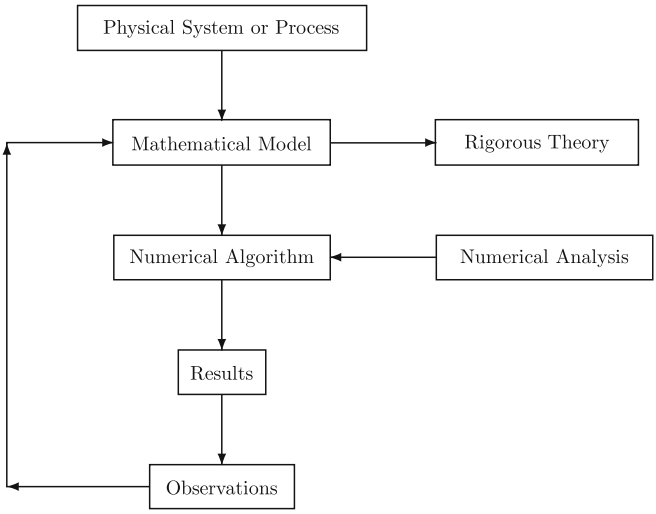

Fig. 1.1 Flow diagram of the modelling of physical systems or processes

and revisions to the mathematical model are made as required. There are often more rigorous mathematical treatments for much simplified models of the physical system. There are many discussions with concern to the numerical analysis of the algorithms used. We will not consider in detail these theoretical aspects but we will provide references to research papers that complement the presentation. The objective is to provide a utilitarian approach for the use of spectral and pseudospectral methods.

Computer power has become readily available and inexpensive and fairly large complex systems can be modeled numerically with ease. The advances made in this area parallels advances made in the development of numerical methods and algorithms for the numerical solution for a large number of applied problems. Our main objective in this book is to demonstrate the ease of use of spectral and pseudospectral methods in the efficient numerical modeling of many systems and processes.

1.2 Spectral and Pseudospectral Methods

We provide in this section a brief overview of spectral and pseudospectral methods. The origin of the terminology, "spectral" is not entirely clear but probably arises from the original use of Fourier[9] sines and cosines as basis functions (Gottlieb and Orszag 1977; Brown and Churchill 1993) especially in connection with a time series analysis and the fundamental frequencies of a process, namely the "spectrum" (Shen et al. 2011).

[9] Jean Baptiste Joseph Fourier (1768–1830) was a French mathematician and physicist best known for the development of Fourier series and the solution of differential equations notably heat transfer.

Spectral methods are generally based on the representation of a real, continuous, "well-behaved" function, $f(x)$, on some interval not necessarily bounded as an expansion in an orthonormal set of functions, $P_n(x)$, that is,

$$f(x) = \sum_{n=0}^{\infty} a_n P_n(x), \quad x \in [a, b] \tag{1.1}$$

where the polynomials are orthonormal

$$\int_a^b w(x) P_n(x) P_m(x) dx = \delta_{nm}, \tag{1.2}$$

with respect to some appropriate weight function, $w(x)$, and the Kronecker[10] delta is defined by

$$\delta_{nm} = \begin{cases} 1, & m = n \\ 0, & m \neq m. \end{cases} \tag{1.3}$$

Examples of such polynomial basis sets are the well-known classical polynomials listed in Chap. 2, Table 2.1 and several nonclassical polynomials in Table 2.2. Whereas the non-classical polynomials are constructed to be orthonormal as in Eq. (1.2), the classical polynomials are generally not normalized to unity.

The term "pseudospectral" refers to the solution of the defining equations on a grid of discrete points, $\{x_i\}$, and the solution, $f(x_i)$, as determined at the grid points. This is often referred to as a collocation. Pseudospectral methods are discussed further in Sect. 1.4.

1.2.1 The Spectral Space Representation

We approximate the function of interest, $f(x)$, with the finite sum

$$f^{(N)}(x) = \sum_{n=0}^{N-1} a_n P_n(x), \quad x \in [a, b] \tag{1.4}$$

where with the orthonormality condition, Eq. (1.2), the expansion coefficients are given by

$$a_n = \int_a^b w(x) P_n(x) f(x) dx, \tag{1.5}$$

[10] Leopold Kronecker (1823–1891) was a German mathematician who specialized in algebra and number theory. His studies of mathematics was originally a hobby and he did not hold a university position untill 1883 at the University of Berlin.

and occasionally referred to as the generalized Fourier coefficients. The a_n coefficients, Eq. (1.5), represent the "spectral space representation" of $f(x)$. We choose an appropriate basis set so that the series Eq. (1.1) provides an accurate approximation of $f(x)$ with a small number of terms. If the method is efficient, the absolute values of the coefficients, $|a_n|$, should decrease rapidly with increasing n as will be demonstrated for particular functions and basis sets in Chap. 4.

An alternate choice of basis functions are the functions $p_n(x) = \sqrt{w(x)}P_n(x)$, orthonormal according to

$$\int_a^b p_n(x)p_m(x)dx = \delta_{nm}. \tag{1.6}$$

We have the alternate expansion

$$f^{(N)}(x) = \sum_{n=0}^{N-1} b_n p_n(x), \tag{1.7}$$

with the expansion coefficients,

$$b_n = \int_a^b f(x)p_n(x)dx. \tag{1.8}$$

We can also choose the expansion

$$f^{(N)}(x) = w(x)\sum_{n=0}^{N-1} c_n P_n(x), \tag{1.9}$$

for which the expansion coefficients are

$$c_n = \int_a^b f(x)P_n(x)dx.$$

The convergence of the expansions Eqs. (1.4), (1.7) and (1.9) (each designated with the same $f^{(N)}$(x)!) can be very different as dependent on the behaviour of $f(x)$. Several examples are presented in Chap. 4. For basis sets with unit weight function such as Legendre polynomials and Fourier sines and cosines, these expansions are identical.

The main concern regarding the approximations Eqs. (1.4), (1.7) and (1.9) is whether the series converges and how quickly. Often these two concerns are unrelated except when the series does not converge and then the rapidity of the convergence is irrelevant. The knowledge that the series expansion is convergent does not provide the practical information as to how many terms, N, are required for the approximation, $f^{(N)}(x)$, to be a good approximation to the function, $f(x)$.

There are many discussions of the mathematics concerning the convergence of such expansions. The interested reader can consult several references (Cheney 1966; Rivlin 1969; Trefethen 2013) for a more detailed mathematical treatment of this subject. A discussion of approximation theory from an historical perspective is provided by Steffens (2006).

A very important aspect of approximation theory (Pinkus 2000) is how to measure the difference between $f(x)$ and $f^{(N)}(x)$. We measure the error of the series expansion, Eq. (1.4), with the least squares norm, that is,

$$E_2^{(N)} = \int_a^b w(x)\Big[f(x) - f^{(N)}(x)\Big]^2 dx. \tag{1.10}$$

We write out the square in Eq. (1.10) and use Eq. (1.4) that is

$$\begin{aligned} E_2(N) = &\int_a^b w(x) f^2(x) dx - 2\sum_{n=0}^{N-1} a_n \int_a^b w(x) P_n(x) f(x) dx \\ &+ \sum_{n=0}^{N-1}\sum_{m=0}^{N-1} a_n a_m \int_a^b w(x) P_n P_m dx. \end{aligned} \tag{1.11}$$

With the orthonormality of the basis functions in the last term and the minimization of $E_2(N)$ with respect to all a_n, that is

$$\frac{\partial E_2^{(N)}}{\partial a_n} = 0, \tag{1.12}$$

give the same expansion coefficients as obtained using orthogonality, Eq. (1.5). With Eq. (1.5) in (1.11)

$$E_2^{(N)} = \|f\|^2 - \sum_{n=0}^{N-1} a_n^2, \tag{1.13}$$

where the norm of the function is defined as

$$\|f\|^2 = \int_a^b w(x) f^2(x) dx < \infty, \tag{1.14}$$

and which must be finite. Since $E_2^{(N)} \geq 0$, Bessel's inequality follows as

$$\sum_{n=0}^{N-1} a_n^2 \leq \|f\|. \tag{1.15}$$

For $N \to \infty$, we have Parseval's theorem

$$\sum_{n=0}^{N-1} a_n^2 = \|f\|^2. \tag{1.16}$$

A more detailed mathematical proof of the results, Eqs. (1.15) and (1.16), can be found in the book by Brown and Churchill (1993) on Fourier series expansions.

Another important result is obtained with Eq. (1.8) substituted into Eq. (1.7) which gives

$$f(x) = \int_a^b f(x') \sum_{n=0}^{\infty} p_n(x) p_n(x') dx', \tag{1.17}$$

where

$$\sum_{n=0}^{\infty} p_n(x) p_n(x') = \delta(x - x'), \tag{1.18}$$

and $\delta(x - x')$ is the Dirac delta function defined in terms of the integral

$$\int_0^{\infty} f(x') \delta(x - x') dx' = f(x). \tag{1.19}$$

The basis set $\{p_n\}$ is then considered to be "complete" and Eq. (1.18) is referred to as the completeness relation.

1.2.2 The Physical Space Representation

We have referred to the set of expansion coefficients $\{a_n\}$ in the expansion, Eq. (1.1), as the spectral space representation of the function. The expansion coefficients are determined from orthogonality, Eq. (1.5). In Chap. 2, we introduce Gaussian[11] quadratures for the efficient evaluation of integrals. This is the algorithm

$$\int_a^b w(x) F(x) dx \approx \sum_{i=1}^{N} w_i F(x_i), \tag{1.20}$$

[11] Carl Friedrich Gauss (1777–1855) was a German mathematician and physical scientist. He was a child prodigy and made many fundamental contributions to geometry, number theory and algebra at a very young age. He is also well known for his work on planetary science, geomagnetism and Gaussian probability distributions.

where the set of "quadrature points" $\{x_i\}$ are the roots $P_N(x_i) = 0$ and $\{w_i\}$ are the corresponding set of "quadrature weights". The polynomials that define the quadrature are orthogonal with respect to $w(x)$ as given by Eq. (1.2). With Eq. (1.20), in (1.5), the Gaussian quadrature approximation of the $\{a_n\}$ coefficients is

$$a_n = \sum_{i=1}^{N} w_i P_n(x_i) f_(x_i). \tag{1.21}$$

The set of function values, $f_i \equiv f(x_i)$, is the representation of $f(x)$ in the "physical space representation" and can be written as

$$f_i = \sum_{n=0}^{N-1} a_n P_n(x_i). \tag{1.22}$$

We label the first grid point and the first expansion coefficient as x_1 and a_0, respectively. Equations (1.21) and (1.22) are the transformations from physical space to spectral space and from spectral space to physical space, respectively.

This transformation can by symmetrized with the definition $\hat{f}_i = \sqrt{w_i} f_i$ and gives

$$\begin{aligned} \hat{f}_i &= \sum_{n=0}^{N-1} a_n \sqrt{w_i} P_n(x_i), \quad i = 1, 2, \ldots, N, \\ a_n &= \sum_{j=1}^{N} \sqrt{w_j} P_n(x_j) \hat{f}_j, \quad n = 0, 1, \ldots, N-1. \end{aligned} \tag{1.23}$$

The transformation matrix between the spectral space representation a_n and the physical space representation $\hat{f}_i$ is defined by

$$T_{in} = \sqrt{w_i} P_n(x_i), \tag{1.24}$$

and we rewrite Eq. (1.23) as

$$\begin{aligned} \hat{f}_i &= \sum_{n=0}^{N-1} T_{in} a_n, \\ a_n &= \sum_{i=1}^{N} T_{ni} \hat{f}_i. \end{aligned} \tag{1.25}$$

With the second of these equations for a_n substituted in the first, gives

$$\hat{f}_i = \sum_{j=1}^{N} \left(\sum_{n=0}^{N-1} T_{in} T_{nj} \right) \hat{f}_j. \tag{1.26}$$

The transformation matrix **T** is unitary, that is,

$$\sum_{n=0}^{N-1} T_{in} T_{nj} = \delta_{ij} \tag{1.27}$$

which is equivalent to

$$\begin{aligned} w_i \sum_{n=0}^{N-1} P_n^2(x_i) &= 1, \quad i = j, \\ \sum_{n=0}^{N-1} P_n(x_j) P_n(x_i) &= 0, \quad i \neq j, \end{aligned} \tag{1.28}$$

valid for all N.

With the substitution of Eq. (1.21) into (1.4) and interchange of the summations, we obtain the basic interpolation result

$$f^{(N)}(x) = \sum_{i=1}^{N} I_i(x) f(x_i), \tag{1.29}$$

where the interpolation function is given by

$$I_i^{(N)}(x) = w_i \sum_{n=0}^{N-1} P_n(x) P_n(x_i), \tag{1.30}$$

which satisfies,

$$I_i^{(N)}(x_j) = \delta_{ij}, \tag{1.31}$$

referred to as the "Cardinality" condition. What is remarkable is that this result is satisfied for any N, consistent with Eq. (1.27). These interpolation functions play a central role in pseudospectral methods of solution.

It is of interest to notice that the interpolation functions, Eq. (1.30), are orthogonal, that is,

$$\begin{aligned} \int_a^b w(x) I_i(x) I_j(x) dx &= w_i w_j \sum_{n=0}^{N-1} P_n(x_i) P_n(x_j), \\ &= \delta_{ij}, \end{aligned} \tag{1.32}$$

where the orthonormality of the basis functions, $P_n(x)$, has been used. The use of similar basis function interpolants has been employed by Baye (2006) and co-workers

(Baye and Heenen 1986; Baye and Vincke 1999; Baye et al. 2002) in the development of the Lagrange mesh method for the solution of differential equations, notably the Schrödinger equation. A more detailed discussion is presented in Chap. 6 with comparisons made with other pseudospectral methods.

1.2.3 A Hilbert Space

In this section, we present a few elementary principles associated with the use of a Hilbert space. We first make comparison with a real vector space defined by the set of three mutually perpendicular unit cartesian vectors $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$. We define a scalar or dot product between these unit vectors as $\mathbf{e}_\alpha \cdot \mathbf{e}_\beta = \delta_{\alpha\beta}$, $(\alpha, \beta) \equiv (x, y, z)$. An arbitrary vector can be represented by $\mathbf{v} = v_x\mathbf{e}_x + v_y\mathbf{e}_y + v_z\mathbf{e}_z$ where v_x, v_y and v_z are the cartesian components of $\mathbf{v}$, given by $v_x = \mathbf{e}_x \cdot \mathbf{v}$, by $v_y = \mathbf{e}_y \cdot \mathbf{v}$ and by $v_z = \mathbf{e}_z \cdot \mathbf{v}$. The scalar or dot product of two different vectors is $\mathbf{u} \cdot \mathbf{v} = u_x v_x + u_y v_y + u_x v_z$ and is zero if the vectors are orthogonal. The length of a vector or the *norm* is defined in terms of the scalar product $||\mathbf{v}|| = \sqrt{\mathbf{v} \cdot \mathbf{v}} = \sqrt{v_x^2 + v_y^2 + v_z^2} \geq 0$ with the equality if and only if $\mathbf{v} = 0$. The distance between two vectors is simply the norm $||\mathbf{v} - \mathbf{u}||$. This cartesian space is said to be linear since $\mathbf{u} \cdot (a\mathbf{v}_1 + b\mathbf{v}_2) = a\mathbf{u} \cdot \mathbf{v}_1 + b\mathbf{u} \cdot \mathbf{v}_2$. Moreover, we can define a linear operator $\mathbf{R}$ which transforms or maps one vector into another, that is $\mathbf{u} = \mathbf{R} \cdot \mathbf{v}$. In the $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)$ representation, the operator $\mathbf{R}$ is the familiar three-dimensional rotation matrix. We consider this space as complete as we can express any vector as a linear combination of the three unit vectors.

We consider a Hilbert[12] space with the orthogonal basis functions $p_n(x)$, $n = 0, 1, \ldots, \infty$ as unit vectors that are in general complex. We introduce the Dirac[13] *bra*, $\langle n|$, and *ket*, $|n\rangle$ notation (Messiah 1961) to make the connection with a vector space clearer by associating the basis function, $p_n(x)$, with the symbolic vector $|n\rangle$. The basis functions, $p_n(x)$, are in fact the components of the vector $|n\rangle$ in the coordinate representation of basis vectors $|x\rangle$, such that

$$|n\rangle = \int p_n(x)|x\rangle dx. \tag{1.33}$$

There is also the dual space of complex vectors written as $\langle m|$ and the scalar product satisfies, $\langle m|n\rangle = \langle n|m\rangle^*$, where the asterisk denotes the complex conjugate. Thus we

[12] David Hilbert (1862–1943) was a German mathematician who worked on many fundamental problems including functional analysis and integral equations with a deep interest in mathematical physics.

[13] Paul Adrien Maurice Dirac (1902–1984) was an English mathematical physicist who shared the 1933 Nobel Physics Prize with Irwin Schrödinger for their contributions to atomic theory. He made seminal contributions to quantum mechanics and relativity.

consider the representation of the function $f(x)$ or the vector $|f\rangle$ in terms of the basis functions or unit vectors. We include N basis functions and obtain the approximation $|f^{(N)}\rangle$ given by,

$$|f^{(N)}\rangle = \sum_{n=0}^{N-1} c_n |n\rangle, \tag{1.34}$$

where the expansion coefficients are obtained from the projection of $|n\rangle$ onto $|f\rangle$, that is

$$c_n = \langle n|f\rangle \equiv \int_a^b p_n^*(x) f(x) dx. \tag{1.35}$$

Although we have written $p_n^*(x)$ in Eq. (1.35), for most of the applications considered the basis functions are real. We include linear differential operators denoted by L and the eigenvalue problem of the form

$$L|\psi_n\rangle = \lambda_n |\psi_n\rangle, \tag{1.36}$$

where λ_n is the eigenvalue, assumed to be discrete. We will find it useful to also denote the scalar product as

$$\langle f|g\rangle = \int_a^b w(x) f^*(x) g(x) dx, \tag{1.37}$$

with the weight function $w(x)$. The matrix element of some operator, L, is denoted by

$$\langle f|Lg\rangle = \int_a^b w(x) f^*(x) Lg(x) dx. \tag{1.38}$$

For the scalar products, $\langle f|g\rangle$ and $\langle f|Lg\rangle$, the weight function is not shown explicitly to simplify the notation. We summarize the properties of a Hilbert space for our purposes as

1. $\langle f|ag + bh\rangle = a\langle f|g\rangle + b\langle f|h\rangle$, a and b are numbers,
2. $\langle f|g\rangle = \langle g|f\rangle^*$,
3. $\langle f|f\rangle \geq 0$,
4. $||f|| = \langle f|f\rangle = 0$ if and only if $f = 0$.
5. $L(|f\rangle + |g\rangle) = L|f\rangle + L|g\rangle$, L is a linear operator.

More detailed discriptions of a Hilbert space are in the book by Helmberg (2008) and especially Chap. 6 in the book by Hunter and Nachtergaele (2001).

1.2.4 Hermitian and Self-adjoint Operators: The Sturm-Liouville Problem

Consider the eigenvalue problem

$$L\psi_n(x) = \lambda_n \psi_n(x), \tag{1.39}$$

where L is a linear operator which includes the Hamiltonian for a quantum problem or the linear integral operator in the Boltzmann equation or the differential Fokker-Planck operator. The eigenfunction, $\psi_n(x)$, defined on the interval $[a, b]$ is subject to two homogeneous boundary conditions which are linear combinations of the value of the function and derivative at the two interval end points and are of the form

$$\begin{aligned} A_1\psi_n(a) + B_1\psi_n'(a) &= 0, \\ A_2\psi_n(b) + B_2\psi_n'(b) &= 0, \end{aligned} \tag{1.40}$$

where for $A_k = 0$ we have a Neumann boundary condition and if $B_k = 0$ we have a Dirichlet boundary condition.

The Hermitian conjugate or the adjoint of L denoted by $L^\dagger$ is defined by the eigenvalue problem

$$L^\dagger \psi_m^*(x) = \lambda_m^* \psi_m^*(x). \tag{1.41}$$

The Hermitian conjugate of the matrix representative of an operator with elements L_{nm} is the complex conjugate of each element of the transpose matrix, that is L_{mn}^*.

We now show that for a self-adjoint operator, the eigenvalues, λ_n, are real and the eigenfunctions, $\psi_n(x)$, of different eigenvalues are orthogonal. Multiply Eq. (1.41) by $\psi_n(x)$ and Eq. (1.39) by $\psi_m^*(x)$, subtract the two equations and integrate to get

$$\int_a^b \left[\psi_n(x) L^\dagger \psi_m^*(x) - \psi_m^*(x) L\psi_n(x)\right] dx = (\lambda_m^* - \lambda_n) \int_a^b \psi_m^*(x)\psi_n(x)dx \tag{1.42}$$

If L, is self-adjoint or Hermitian, the left hand side of Eq. (1.42) is zero. Thus the right hand side of Eq. (1.42) is also zero. If $m = n$ we have that $\lambda_n^* = \lambda_n$ since the integral is not zero. The eigenvalues of a self-adjoint operator are real. For $n \neq m$ we have the orthogonality of the eigenfunctions, that is,

$$\int_a^b \psi_m^*(x)\psi_n(x)dx = \gamma_n \delta_{nm}, \tag{1.43}$$

where the norm is

$$\gamma_n = ||\psi_n||^2 = \int_a^b \psi_n^2(x)dx. \tag{1.44}$$

The Sturm[14]-Liouville[15] problem (Pryce 1993; Al-Gwaiz 2008) is the eigenvalue problem defined by the differential equation

$$L\psi_n(x) = \frac{d}{dx}\left[p(x)\frac{d\psi_n(x)}{dx}\right] + q(x)\psi_n(x) = \lambda_n w(x)\psi_n(x), \tag{1.45}$$

where $p(x)$, $q(x)$ are real and $w(x) > 0$ is a real weight function. The interval may be bounded, $x \in [a, b]$, semi-infinite $x \in [0, \infty)$, or infinite $x \in (-\infty, \infty)$. Any linear second order differential equation can be written in this form. The classical polynomials such as the Legendre, Hermite and Laguerre polynomials defined in Chap. 2 satisfy Sturm-Liouville eigenvalue equations. These polynomials are often chosen as the basis functions in spectral solutions of particular problems. Alternatively, the quadrature weights and points associated with these classical polynomials are used in pseudospectral solutions.

To show that L defined by Eq. (1.45) is self-adjoint, we consider the matrix element

$$\langle\phi|L|\psi\rangle = \int_a^b \phi(x)\left[p(x)\psi'(x)\right]' dx + \int_a^b q(x)\phi(x)\psi(x)dx, \tag{1.46}$$

and perform an integration by parts for the first integral on the right hand side. The result is

$$\langle\phi|L|\psi\rangle = p(x)\psi'(x)\phi'(x)\Big|_a^b - \int_a^b p(x)\psi'(x)\phi'(x)dx + \int_a^b q(x)\phi(x)\psi(x)dx. \tag{1.47}$$

The boundary term is zero owing to the chosen boundary conditions, Eqs. (1.40), and

$$\langle\phi|L|\psi\rangle = \langle\psi|L|\phi\rangle.$$

Thus the Sturm-Liouville operator, L, is self-adjoint, and the importance of the specified boundary conditions is clear. The Schrödinger and the Fokker-Planck eigenvalue equations are Sturm-Liouville problems and considered in Chap. 6. In Chap. 5, we consider the eigenvalues of the integral collision operator of the Boltzmann equation.

[14] Jacques Charles François Sturm (1803–1855) was a French mathematician who made important contributions to algebra and the numerical evaluation of the roots of polynomials. The differential eigenvalue equation that bears his name defines the classical polynomials.

[15] Joseph Liouville (1809–1882) was a French mathematician who made fundamental contributions to complex analysis, algebra, mechanics, and many other topics. He is well known for Liouville's theorem in classical Hamiltonian mechanics.

1.2.5 Rayleigh-Ritz Variational Theorem

We are interested in solving the operator eigenvalue problem

$$L|\psi_n\rangle = \lambda_n|\psi_n\rangle, \tag{1.48}$$

where L is a self-adjoint positive definite operator in a square integrable Hilbert space of real functions. The Rayleigh[16]-Ritz[17] variational approach is based on the representation of the eigenvectors $|\psi_n\rangle$ in terms of N orthogonal vectors $|k\rangle$ each weighted linearly with a variational parameter, a_k. Thus we write,

$$|\psi_n\rangle = \sum_{k=0}^{N-1} a_k|k\rangle, \tag{1.49}$$

where $\langle k|\ell\rangle = \delta_{k\ell}$. A functional dependent on the set of variational parameters, a_k, is defined by

$$\begin{aligned} F(\{a_k\}) &= \langle\psi_n|L|\psi_n\rangle - \lambda\langle\psi_n|\psi_n\rangle, \\ &= \sum_{k=0}^{N-1}\sum_{\ell=0}^{N-1}\left[a_k a_\ell L_{k\ell} - \lambda a_k^2\right], \end{aligned} \tag{1.50}$$

where $L_{k\ell} = \langle k|L|\ell\rangle$ are the matrix elements of the operator in the chosen basis set. We determine the extremum of $F(\{a_k\})$ with respect to the set of expansion coefficients $\{a_k\}$ by setting

$$\frac{\partial F(\{a_k\})}{\partial a_k} = 0. \tag{1.51}$$

The result is the set of linear equations for the variational parameters, a_k, that is,

$$\sum_{k=0}^{N-1} a_k\left[L_{k\ell} - \lambda\delta_{k\ell}\right] = 0, \tag{1.52}$$

and the eigenvalues are the roots of the "secular" equation resulting from the requirement that the solution of homogeneous linear equations, Eq. (1.52), exists, that is

$$\det\left[\mathbf{L}^{(N)} - \Lambda\right] = 0, \tag{1.53}$$

---

[16] John William Strutt, third Baron Rayleigh (1842–1919) was an English physicist who discovered argon for which he was awarded 1904 Nobel Physics Prize. His named is associated with kinetic theory, electrodynamics, light scattering, sound propagation and other subjects.

[17] Walther Ritz (1878–1909) was a Swiss theoretical physicist. His name is associated with the Rydberg Ritz combination principle for atomic spectral lines and the Rayleigh-Ritz variational method.

where the matrix Λ is diagonal, $\Lambda_{k\ell} = \lambda_k \delta_{k\ell}$. Equation (1.53) is the secular equation, a polynomial of degree N in λ and the roots are λ_k.

A good overall discussion of the different approximation methods for applications in physics and engineering can be found in the book by Finlayson (1972). The review paper by Finlayson and Scriven (1966) with 187 references provides an overview of the development of these methods. A more rigrous mathematical discussion has been presented by Hill (1985).

The Rayleigh-Ritz variational theorem has been applied extensively in numerous fields including quantum mechanics (Bhattacharyya 2009), kinetic theory (Cuperman et al. 1982; Driessler 1981; Present and Morris 1969; Snider 1964; Shizgal and Karplus 1971; Bobylev and Cercignani 1999), radio science (Sarkar 1983) and other fields. The common aspect of all these applications is the approximate representation of the solution of a differential equation in a set of orthogonal basis functions.

1.3 An Overview of Spectral Methods

In Chap. 2, we develop the basic concepts of spectral and pseudospectral methods with application to physical problems. In this section, we provide an overview of the development of these methods which are discussed in greater detail in the chapters that follow.

We consider the time dependent differential equation,

$$\frac{\partial f(x,t)}{\partial t} = Lf(x,t) + S(x) \quad x \in [a,b], \tag{1.54}$$

where L is a linear operator and $S(x)$ is a source term. We impose Dirichlet boundary conditions, $f(a,t) = 0, f(b,t) = 0$ and provide an initial condition $f(x,0) = g(x)$. The operator L could be the operator in the linear Boltzmann equation, Eq. (5.41), or in a Fokker-Planck equation, Eq. (6.7). The eigenvalue problem $L\psi_n(x) = \lambda_n \psi_n(x)$ is of interest for the time dependent solution of Eq. (1.54). We are also interested in a similar eigenvalue problem for the Schrödinger equation, Eq. (6.78), defined with a linear self-adjoint Hamiltonian operator H.

For these problems, we approximate the solution in terms of the finite expansion in a set of orthonormal functions, $p_n(x) = \sqrt{w(x)}P_n(x)$, Eq. (1.7), involving N terms and we have the Nth approximation to $f(x,t)$, that is

$$f^{(N)}(x,t) = \sum_{n=0}^{N-1} b_n(t) p_n(x). \tag{1.55}$$

We discuss the choice of basis set from the large set of classical and nonclassical polynomials in Chap. 2. This choice determines the rate of convergence of the expansion, Eq. (1.55).

The initial values of the expansion coefficients are provided from the expansion of the initial condition, that is,

$$g(x) = \sum_{n=0}^{N-1} b_n(0) p_n(x). \tag{1.56}$$

With the substitution of Eq. (1.56) into (1.54), we have that

$$\sum_{n=0}^{N-1} p_n(x) \frac{db_n(t)}{dt} = \sum_{n=0}^{N-1} b_n(t) L p_n(x) + S(x). \tag{1.57}$$

The departure of the approximate solution from the actual solution is measured by the "residue" defined by

$$\begin{aligned} R_N(x,t) &= \frac{\partial f^{(N)}(x,t)}{\partial t} - L f^{(N)}(x,t) - S(x), \\ &= \sum_{n=0}^{N-1} p_n(x) \frac{db_n(t)}{dt} - \sum_{n=0}^{N-1} b_n(t) L p_n(x) - S(x). \end{aligned} \tag{1.58}$$

The method of weighted residuals (Finlayson and Scriven 1966; Finlayson 1972) is a procedure to calculate $b_n(t)$ so as to minimize the residual $R_N(x,t)$ in some average way. We impose the condition that the residue is minimized subject to

$$\int_a^b t(x) R_N(x,t) dx = 0, \tag{1.59}$$

where there are several different choices for the "test" function $t(x)$ and each choice gives rise to a different approximation. If we choose $t(x) = p_n(x)$, $n = 0, 1, \ldots, N-1$, the partial differential equation is converted to a set of N coupled ordinary differential equations, that is,

$$\frac{db_m(t)}{dt} = \sum_{n=0}^{N-1} L_{mn} b_n(t) + s_m \quad m = 0, 1, \ldots, N-1, \tag{1.60}$$

where the matrix representation of L in this basis set is,

$$L_{mn} = \int_a^b p_m(x) L p_n(x) dx, \tag{1.61}$$

and

$$s_n = \int_a^b p_n(x) S(x) dx, \tag{1.62}$$

are the expansion coefficients for the source term, $S(x)$. This approach is referred to as a spectral or a "Galerkin"[18] solution.

The set of coupled ordinary differential equations, Eq. (1.60), can be advanced in time from the initial values, $c_n(0)$, with the appropriate time integration algorithm. An important aspect regarding the stability of the direct time integration of the set of equations, Eq. (1.60), is the eigenvalue spectrum of the matrix, L_{mn}, and the condition number, $\kappa(\mathbf{L}) = \lambda_{max}/\lambda_{min}$.

The condition number is also very important with regards to the inversion of the steady state matrix equations

$$\sum_{n=0}^{N-1} L_{nm} C_m = -s_n \quad m = 0, 1, \ldots, N-1, \tag{1.63}$$

for the time independent coefficients denoted by C_m. If the condition number of the matrix $\mathbf{L}$ is large, the inversion of Eq.(1.63) can be contaminated with numerical errors. We can also consider the related eigenvalue problem

$$\sum_{n=0}^{N-1} L_{nm} d_m = \lambda_n d_n \quad n = 0, 1, \ldots, N, \tag{1.64}$$

for the eigenvalues, λ_n, and eigenvector coefficients $\mathbf{d}$ with the proviso that the eigenvalue spectrum of the operator L is discrete.

For the Boltzmann, Fokker-Planck and Schrödinger equations, the linear operators involved can have discrete spectra, or a combination of a discrete spectrum plus a continuum or just a continuum. We discuss these properties of eigenvalue problems with specific applications in Chaps. 5 and 6 (Reinhardt 1979).

1.4 The Development of Pseudospectral Methods in Chemistry and Physics: An Overview of the Book

A preliminary introduction to pseudospectral methods is provided by the eigenvalue problem

$$\int_a^b k(x, y)\psi_n(y)dy = \lambda_n \psi_n(x), \tag{1.65}$$

where the integral operator on the left hand side is defined by the kernel, $k(x, y)$, which is assumed to be well behaved in both arguments. The integral equation

[18] Boris Galerkin (1871–1945) was a Russian mathematician and developed the Galerkin method for solving partial differential equations associated with problems in mechanical engineering.

is reduced to a set of linear equations with the use of the appropriate quadrature. Equation (1.20), defined with the quadrature points, $\{x_i\}$. The result is

$$\sum_{i=1}^{N} W_i k(x_j, x_i)\psi_n(x_i) = \lambda_n \psi_n(x_j), \tag{1.66}$$

where $W_i = w_i/w(x_i)$ and $w(x)$ is the weight function that defines the polynomials, Eq. (1.2). The eigenfunctions are evaluated at the set of quadrature points and are represented by the physical space representation, $\psi_n(x_i)$. Extensive use of this pseudospectral method is discussed in Chap. 5 for the solution of the Boltzmann equation.

For differential equations, a derivative matrix operator is derived in Chap. 2 in terms of the interpolation function, Eq. (2.32),

$$D_{ij} = \left.\frac{dI_i^{(N)}(x)}{dx}\right|_{x=x_i}, \tag{1.67}$$

as well as an analogous matrix operator for the second derivative. Second order differential equations such as the Fokker-Planck and Schrödinger equations can be reduced to linear algebraic equations or time dependent ordinary differential equations. Pseudospectral methods are used extensively in Chaps. 5 and 6. The history of the development of pseudospectral methods in chemistry, physics and other fields is outlined in Table 1.1. This chronology of events is a personal view and people with different backgrounds may well have other interpretations.

As discussed in Chap. 5, the first use of a pseudospectral method appears to be the work of Wick (1943) and Chandrasekhar (1944) in the solution of

Table 1.1 The development of pseudospectral methods in chemistry and physics

1943	Gaussian quadrature solution for Radiative Transfer	Wick (1943)
1944	Gaussian quadrature solution for Radiative Transfer	Chandrasekhar (1944)
1953	The Discrete Ordinate Method (DOM) in Neutron Transport	Carlson (1955)
1972	Differential Quadrature (DQ)	Bellman et al. (1972)
1973	Spline methods for the Schrödinger equation	Shore (1973, 1975)
1977	Numerical Analysis of Spectral Methods	Gottlieb and Orszag (1977)
1982	Nonclassical basis functions for the Boltzmann equation	Shizgal (1981a)
1984	A DOM for the solution of differential equations	Shizgal and Blackmore (1984)
1985	Pseudospectral methods for electronic structure	Friesner (1985)
1985	Discrete Variable Representation (DVR)	Light et al. (1985)
1985	Fourier techniques	Schwartz (1985)
1986	Lagrange mesh method	Baye and Heenen (1986)
1987	Spectral methods in fluid mechanics	Canuto et al. (1998)

the integro-differential radiative transfer equation (Chandrasekhar 1960). They introduced Gauss-Legendre quadratures to reduce the radiative transfer equation to a set of linear ordinary differential equations. The problem was originally considered by Milne[19] (Milne 1930) as a problem in astrophysics as well as in rarefied gas dynamics where it is referred to as a half-space problem (Williams 1971; Cercignani 1988). A spectral solution of the Milne problem based on the Boltzmann equation is discussed in Chap. 5 (Lindenfeld and Shizgal 1983) and a pseudospectral method of solution for an electron Fokker-Planck equation was presented by Vasenkov and Shizgal (2000).

The radiative transfer and neutron transport community exploited the pseudospectral approach (Chandrasekhar 1960; Rybicki 1996) and it was referred to as the Discrete Ordinate Method (DOM) (Carlson 1955). Other designations are the S_N (Lathrop 1992) and P_N methods (Liou 2002; Thomas and Stamnes 2002). The S_N method appears to refer to the "segmentation" of the interval of interest with N quadrature points and can be considered as a spectral element method (Deville et al. 2002) or a discontinuous Galerkin method (Cockburn et al. 2000) originally developed in neutron transport theory (Reed and Hill 1973). The P_N method refers to a spectral method with the expansion of the angular dependence of the velocity distribution functions in Legendre polynomials (Liou 2002; Thomas and Stamnes 2002). Similar Laguerre and Hermite expansions of functions that occur in kinetic theory are presented in Chap. 4.

The pseudospectral solution of differential equations is based on the global approximation of the derivative operator in terms of the function values on a grid. Interpolation, Eq. (1.30), and the discrete matrix derivative operator, Eq. (1.67), are the basis for the development of these collocation type solutions of differential equations. Bellman et al. (1972) developed the differential quadrature (DQ) method for the solution of differential equations. This appears to be the first introduction of pseudospectral methods applied primarily to problems in engineering (Shu 2000). Pseudospectral methods based on the discrete physical space representation of derivative operators is presented in Chap. 3, Sect. 3.9.2 and defined with the Lagrange interpolation in Chap. 2, Sect. 2.3.1.

The numerical methods of solution based on B-Splines (Shore 1973) also belong to the class of collocation Galerkin type solutions for quantum problems (Bachau et al. 2001) as well as for the Boltzmann equation (Pitchford and Phelps 1982; Siewert 2002; Khurana and Thachuk 2012) and many other applications. The introduction of spectral methods with Fourier and Chebyshev basis functions for fluid mechanics problems was developed by Gottlieb and Orszag (1977).

Shizgal and Blackmore (1984) applied a combination of the Gaussian quadratures for integrals, Eq. (1.20), and the discrete physical space matrix representations for derivatives, Eq. (1.67), for the solution of the integro-differential Boltzmann equation, presented in Chap. 5. A nonclassical quadrature based on polynomials orthogonal with weight function, $w(x) = x^p e^{-x^2}, \quad x \in [0, \infty)$, was used (Shizgal 1981a). The

[19] Edward Arthur Milne (1896–1950) was a British astrophysicist and mathematician who contributed to stellar structure and the thermodynamics of stars.

method of Gaussian quadrature for the evaluation of integrals is used to solve integral equations (Delves and Mohamed 1985; Jerri 1999; Eskola 2012) and is referred to as the Nyström method. Gaussian quadratures are developed in Chap. 2 and applied to the numerical evaluation of integrals in Chap. 3 and to the determination of the eigenvalue spectra for the collision operators of the Boltzmann equation in Chap. 5.

Nonclassical polynomials and associated quadratures were subsequently applied to the Fokker-Planck and Schrödinger equations and referred to as the quadrature discretization method (Shizgal and Chen 1996, 1997; Lo and Shizgal 2006, 2008a). The choice of basis functions arises from the transformation of the Fokker-Planck equation to a Schrödinger equation with potentials that belong to the class of problems in supersymmetric quantum mechanics (Comtet et al. 1985; Dutt et al. 1988). The pseudospectral algorithms discussed in Chap. 6, Sect. 6.3.2, provide a representation of the Hamiltonian in the Schrödinger equation that is not contaminated by nonphysical ghost levels (Wei 1997; Willner et al. 2004; Kallush and Kosloff 2006).

Friesner (1985) applied pseudospectral methods to the solution of the electronic structure equations (the Schrödinger equation) for the electronic states of the neon atom following on the pioneering work of Gottlieb and Orszag (1977) on spectral methods for fluid mechanics. For the quantum chemistry community involved with the calculation of the vibrational states of polyatomic molcules, pseudospectral methods originated from the quadrature evaluation of matrix elements of a multiplicative operator, namely the potential in the Schrödinger equation (Harris et al. 1965; Dickinson and Certain 1968). Following on this work, Light and coworkers (Hamilton and Light 1986; Bacic and Light 1989; Light and Carrington 2000) developed a pseudospectral method referred to as the Discrete Variable Representation (DVR).

Baye (1995, 2006) and coworkers (Baye and Heenen 1986; Baye and Vincke 1999; Baye et al. 2002) developed the Lagrange mesh method for similar quantum problems. Mention should be made of the work of Schwartz (1985) on Fourier methods. The second derivative operator representation in this paper was later reported by Colbert and Miller (1992) and Amore (2006).

In Chap. 3, we discuss the representations of multiplicative operators for both kinetic theory as well as for quantum problems and the transformation between spectral space and physical space, Eq. (1.25). This provides insight into the success of pseudospectral methods from the inexact calculation of matrix elements of the potentials in the Schrödinger equation (Baye et al. 2002; Szalay et al. 2012).

Fourier methods for quantum problems were developed by Balint-Kurti and coworkers (Marston and Balint-Kurti 1989; Balint-Kurti and Pulay 1995; Stare and Balint-Kurti 2003) and by Kosloff (Kosloff and Kosloff 1983; Kosloff 1993, 1994). Mention should be made of the distributed approximating functional (DAF) method of Hoffman et al. (1998) and the discrete singular convolution (DSC) method (Wei 2000a, b; Amore et al. 2009).

In Chap. 5, we employ Gaussian quadratures for the representation of integral operators such as in the Boltzmann equation (Shizgal and Blackmore 1983; Sospedra-Alfonso and Shizgal 2012). Quadratures are used to reduce integral equations to algebraic form. In Chap. 6, interpolation serves to define a matrix derivative operator

to reduce differential equations such as the Fokker-Planck and Schrödinger equations to algebraic equations. In both situations, nonclassical basis functions are often used. The original version of the book by Canuto et al. (1998), which has since been republished in two volumes (Canuto et al. 2006a, b), is noted in the table as representative of the many textbooks on spectral methods in fluid dynamics that have been referenced in the Preface.

References

Al-Gwaiz, M.A.: Sturm-Liouville Theory and its Applications. Springer, Berlin (2008)
Amore, P.: A variational Sinc collocation method for strong-coupling problems. J. Phys. A: Math. Gen. **39**, L349–L355 (2006)
Amore, P., Fernandez, F.M., Saenz, R.A., Salvo, K.: Collocation on uniform grids. J. Phys. A: Math. Theor. **42**, 115302 (2009)
Anderson, D., Lisak, M., Andersson, F., Fülöp, T.: Slowing down dynamics of fast particles in plasmas via the Fokker-Planck equation. Nucl. Sci. Eng. **146**, 99–105 (2004)
Atenzi, S., Meyer-Ter-Vehn, J.: The Physics of Inertial Fusion. Clarendon Press, Oxford (2004)
Bachau, H., Cormier, E., Decleva, P., Hansen, J.E., Martin, F.: Application of B-Splines in atomic and molecular physics. Rep. Prog. Phys. **64**, 1815–1942 (2001)
Bacic, Z., Light, J.C.: Theoretical methods for rovibrational states of floppy molecules. Annu. Rev. Phys. Chem. **40**, 469–498 (1989)
Balint-Kurti, G.G.: Time-dependent and time-independent wavepacket approaches to reactive scattering and photodissociation dynamics. Int. Rev. Phys. Chem. **27**, 507–539 (2008)
Balint-Kurti, G.G., Pulay, P.: A new grid-based method for the direct computation of excited molecular vibrational-states: test application to formaldehyde. J. Mol. Struct. (Theochem) **341**, 1–11 (1995)
Baye, D.: Constant-step Lagrange meshes for central potentials. J. Phys. B: At. Mol. Opt. Phys. **28**, 4399–4412 (1995)
Baye, D.: Lagrange-mesh method for quantum-mechanical problems. Phys. Stat. Sol. B **243**, 1095–1109 (2006)
Baye, D., Heenen, P.H.: Generalized meshes for quantum-mechanical problems. J. Phys. A: Math. Gen. **19**, 2041–2059 (1986)
Baye, D., Vincke, V.: Lagrange meshes from nonclassical orthogonal polynomials. Phys. Rev. E **59**, 7195–7199 (1999)
Baye, D., Hesse, M., Vincke, M.: The unexplained accuracy of the Lagrange-mesh method. Phys. Rev. E **65**, 026701 (2002)
Baye, D., Vincke, M., Hesse, M.: Simple and accurate calculations on a Lagrange mesh of the hydrogen atom in a magnetic field. J. Phys. B: At. Mol. Opt. Phys. **41**, 055005 (2008)
Bellman, R.E., Kashef, B.G., Casti, J.: Differential quadrature: a technique for the rapid solution of nonlinear partial differential equations. J. Comput. Phys. **10**, 40–52 (1972)
Bhattacharyya, B.: Bounds on the ground state energy: application of the variational principle. Am. J. Phys. **77**, 44–47 (2009)
Binney, J., Tremaine, S.: Galactic Dynamics, 2nd edn. Princeton University Press, New Jersey (2008)
Bird, G.A.: Molecular Gas Dynamics and the Direct Simulation of Gas Flows. Clarendon, Oxford (1994)
Birdsall, C.K., Langdon, A.B.: Plasma Physics via Computer Simulation. Taylor and Francis, New York (2005)

Bobylev, A.V., Cercignani, C.: On the rate of entropy production for the Boltzmann equation. J. Stat. Phys. **94**, 603–618 (1999)
Bonazzola, S., Gourgoulhon, E., Marck, J.-A.: Spectral methods in general relativistic astrophysics. J. Comput. Appl. Math. **109**, 433–473 (1999)
Brown, J.W., Churchill, R.V.: Fourier Series and Boundary Value Problems. McGraw Hill, New Jersey (1993)
Burke, P.G.: R-Matrix Theory of Atomic Collisions: Application to Atomic, Molecular and Optical Processes. Springer, New York (2011)
Canuto, C., Hussaini, M.Y., Quarteroni, A., Zang, T.A.: Spectral Methods in Fluid Dynamics. Springer, New York (1998)
Canuto, C., Hussaini, M.Y., Quarteroni, A., Zang, T.A.: Spectral Methods: Evolution to Complex Geometries and Applications to Fluid Mechanics. Springer, New York (2006a)
Canuto, C., Hussaini, M.Y., Quarteroni, A., Zang, T.A.: Spectral Methods: Fundamentals in Single Domains. Springer, New York (2006b)
Car, R., Parrinello, M.: Unified approach for molecular dynamics and density functional theory. Phys. Rev. Lett. **55**, 2471–2474 (1985)
Carlson, B.G.: Solution of the Transport Equation by S_n Approximation. Technical Report LA-1891, Los Alamos Scientific Laboratory (1955)
Cassam-Chenaï, P., Liévin, J.: Ab initio calculation of the rotational spectrum of methane vibrational ground state. J. Chem. Phys. **136**, 174309 (2012)
Cercignani, C.: The Boltzmann Equation and its Applications. Springer, New York (1988)
Chandrasekhar, S.: On the radiative equilibrium of a stellar atmosphere II. Astrophys. J. **100**, 76–86 (1944)
Chandrasekhar, S.: Brownian motion, dynamical friction, and stellar dynamics. Rev. Mod. Phys. **21**, 383–388 (1949)
Chandrasekhar, S.: Radiative Transfer. Dover, New York (1960)
Chapman, S., Cowling, T.G.: The Mathematical Theory of Nonuniform Gases. Cambridge University Press, Cambridge (1970)
Chavanis, P.H.: Relaxation of a test particle in systems with long-range interactions: diffusion coefficient and dynamical friction. Eur. J. Phys. B **52**, 61–82 (2006)
Cheney, E.W.: Introduction to Approximation Theory. McGraw-Hill, New York (1966)
Child, M.S.: Molecular Collision Theory. Dover, New York (1996)
Cockburn, B., Karniadakis, G.E., Shu, C.-W.: Discontinuous Galerkin Methods: Theory, Computation and Applications. Springer, Berlin (2000)
Colbert, D.T., Miller, W.H.: A novel discrete variable representation for quantum-mechanical reactive scattering via the S-Matrix Kohn method. J. Chem. Phys. **96**, 1982–1991 (1992)
Comtet, A., Bandrauk, A.D., Campbell, D.K.: Exactness of semiclassical bound-state energies for supersymmetric quantum-mechanics. Phys. Lett. B **150**, 159–162 (1985)
Cuperman, S., Weiss, J., Dryer, M.: A variational derivation of the velocity distribution functions for nonequilibrium, multispecies, weakly interacting, spherically symmetric many-body systems. J. Stat. Phys **29**, 803–812 (1982)
Davison, B.: Neutron Transport. Oxford University Press, Oxford (1957)
Delves, L.M., Mohamed, J.L.: Computational Methods for Integral Equations. Cambridge University Press, Cambridge (1985)
Deville, M.O., Fisher, P.F., Mund, E.H.: High Order Methods for Incompressible Fluid Flow. Cambridge University Press, Cambridge (2002)
Dickinson, A.S., Certain, P.R.: Calculation of matrix elements for one-dimensional quantum-mechanical problems. J. Chem. Phys. **49**, 4209–4211 (1968)
Driessler, W.: On the spectrum of the Rayleigh piston. J. Stat. Phys. **24**, 595–606 (1981)
Durran, D.R.: Numerical Methods for Fluid Dynamics: With Applications to Geophysics. Springer, Berlin (2010)
Dutt, R., Khare, A., Sukhatme, U.P.: Supersymmetry, shape invariance and exactly solvable potentials. Am. J. Phys. **56**, 163–168 (1988)

Echim, M.M., Lemaire, J., Lie-Svendsen, O.: A review on solar wind modeling: kinetic and fluid aspects. Surv. Geophys. **32**, 1–70 (2011)
Eskola, L.: Geophysical Interpretation Using Integral Equations. Springer, Netherlands (2012)
Fahr, F.J., Shizgal, B.: Modern exospheric theories and their observational relevance. Rev. Geophys. Space Phys. **21**, 75–124 (1983)
Finlayson, B.A.: The Method of Weighted Residuals and Variational Principles. Academic Press, New York (1972)
Finlayson, B.A., Scriven, L.E.: The method of weighted residuals—a review. Appl. Mech. Rev. **19**, 735–748 (1966)
Friesner, R.A.: Solution of self-consistent field electronic structure equations by a pseudospectral method. Chem. Phys. Lett. **116**, 39–43 (1985)
Friesner, R.A.: New methods for electronic structure calculations on large molecules. Annu. Rev. Phys. Chem. **42**, 341–367 (1991)
Friesner, R.A., Bentley, J.A., Menou, M., Leforestier, C.: Adiabatic pseudospectral methods for multidimensional vibrational potentials. J. Chem. Phys. **99**, 324–335 (1993)
Gifford, K.A., Horton Jr, J.L., Wareing, T.A., Failla, G., Mourtada, F.: Comparison of a finite-element multigroup discrete-ordinates code with Monte Carlo for radiotherapy calculations. Phys. Med. Biol. **51**, 2253–2265 (2006)
Gottlieb, D., Orszag, S.: Numerical Analysis of Spectral Methods: Theory and Applications. SIAM, Philadelphia (1977)
Grandclément, P., Novak, J.: Spectral methods for numerical relativity. Living Rev. Relativ. **12**(1), 103 (2009)
Hamilton, I.P., Light, J.C.: On distributed Gaussian bases for simple model multidimensional vibrational problems. J. Chem. Phys. **84**, 306–317 (1986)
Harris, D.O., Engerholm, G.G., Gwinn, W.D.: Calculation of matrix elements for one-dimensional quantum-mechanical problems and the application to anharmonic oscillators. J. Chem. Phys. **43**, 1515–1517 (1965)
Hebert, A.: Applied Reactor Physics. Presse Int. Polytechnique, Montréal (2009)
Helgaker, T., Jorgensen, P., Olsen, J.: Molecular Electronic Structure Theory. Wiley, New York (2000)
Helmberg, G.: Introduction to Spectral Theory in Hilbert Space. Dover, New York (2008)
Heyl, J.S., Thirumalai, A.: Pseudo-spectral methods for atoms in strong magnetic fields. Mon. Not. R. Astron. Soc. **407**, 590–598 (2010)
Hill, R.N.: Rates of convergence and error estimation formulas for the Rayleigh-Ritz variational methods. J. Chem. Phys. **83**, 1173–1196 (1985)
Hoffman, D.K., Wei, G.W., Zhang, D.S., Kouri, D.J.: Interpolating distributed approximating functionals. Phys. Rev. E **57**, 6152–6160 (1998)
Hu, X.G., Ho, T.S., Rabitz, H., Askar, A.: Multivariate radial basis interpolation for solving quantum fluid dynamical equations. Comput. Math. Appl. **43**, 525–537 (2002)
Hunter, J.K., Nachtergaele, B.: Applied Analysis. World Scientific, Singapore (2001)
Jerri, A.J.: Introduction to Integral Equations with Applications, 2nd edn. Wiley, New York (1999)
Jones, R.O., Gunnarsson, O.: The density functional formalism, its applications and prospects. Rev. Mod. Phys. **61**, 689–746 (1989)
Kallush, S., Kosloff, R.: Improved methods for mapped grids: applied to highly excited vibrational states of diatomic molecules. Chem. Phys. Lett. **433**, 221–227 (2006)
Khurana, S., Thachuk, M.: A numerical solution of the linear Boltzmann equation using cubic B-splines. J. Chem. Phys. **136**, 094103 (2012)
Koput, J., Carter, S., Handy, N.C.: Ab initio prediction of the vibrational-rotational energy levels of hydrogen peroxide and its isotopomers. J. Chem. Phys. **115**, 8345–8350 (2001)
Kosloff, R.: The fourier method. In: Cerjan, C. (ed.) Numerical Grid Methods and Their Application to Schrödinger's Equation, pp. 175–194. Kluwer Academic, The Netherlands (1993)
Kosloff, R.: Propagation methods for quantum molecular dynamics. Annu. Rev. Phys. Chem. **45**, 145–178 (1994)

Kosloff, D., Kosloff, R.: A Fourier method solution for the time-dependent Schrödinger-equation as a tool in molecular dynamics. J. Comput. Phys. **52**, 35–53 (1983)
Kremer, G.M.: An Introduction to the Boltzmann Equation and Transport Processes in Gases. Springer, New York (2010)
Kundu, P., Cohen, I.M., Dowling, D.R.: Fluid Mechanics, 6th edn. Academic Press, Waltham (2012)
Landau, D.P., Binder, K.: A Guide to Monte Carlo Simulations in Statistical Physics, 3rd edn. Cambridge University Press, Cambridge (2009)
Lathrop, K.D.: The early days of the S_N method. Trans. Am. Nucl. Soc. **66**, 241–242 (1992)
Lemou, M., Chavanis, P.H.: Escape of stars from gravitational clusters in the Chandrasekhar model. Phys. A **389**, 1021–1040 (2010)
Levine, I.N.: Quantum Chemistry, 6th edn. Prentice Hall, New Jersey (2009)
Liboff, R.L.: Introductory Quantum Mechanics, 4th edn. Addison-Wesley, New York (2002)
Liboff, R.L.: Kinetic Theory: Classical, Quantum, and Relativistic Descriptions, 3rd edn. Springer, New York (2003)
Lie-Svendsen, O., Rees, M.H.: An improved kinetic model for the polar outflow of a minor ion. J. Geophys. Res. **101**, 2415–2433 (1996)
Light, J.C., Carrington Jr, T.: Discrete variable representations and their utilization. Adv. Chem. Phys. **114**, 263–310 (2000)
Light, J.C., Hamilton, I.P., Lill, J.V.: Generalized discrete variable approximation in quantum mechanics. J. Chem. Phys. **82**, 1400–1409 (1985)
Lightman, A.P., Shapiro, S.L.: The dynamical evolution of globular clusters. Rev. Mod. Phys. **50**, 437–481 (1978)
Lindenfeld, M.J., Shizgal, B.: The Milne problem: a study of the mass dependence. Phys. Rev. **A27**, 1657–1670 (1983)
Liou, K.N.: An Introduction to Atmospheric Radiation. Elsevier, Amsterdam (2002)
Lo, J.Q.-W., Shizgal, B.D.: Spectral convergence of the quadrature discretization method in the solution of the Schrödinger and Fokker-Planck equations: comparison with Sinc methods. J. Chem. Phys. **125**, 194108 (2006)
Lo, J.Q.-W., Shizgal, B.D.: An efficient mapped pseudospectral method for weakly bound states: vibrational states of He_2, Ne_2, Ar_2 and Cs_2. J. Phys. B: At. Mol. Opt. Phys. **41**, 185103 (2008)
Marston, C.C., Balint-Kurti, G.G.: The Fourier grid Hamiltonian method for bound state eigenvalues and eigenfunctions. J. Chem. Phys. **91**, 3571–3576 (1989)
Messiah, A.: Quantum Mechanics, vol. I. North Holland, Amsterdam (1961)
Milne, E.A.: Thermodynamics of the stars. Handbuch der Astrophysik **3**, 65–255 (1930)
Morgan, J.D.: Thomas-Fermi and other density—functional theories. In: Drake, G.W.F. (ed.) Atomic, Molecular and Optical Physics Handbook, pp. 233–242. AIP Press, New York (1996)
Peeters, A.G., Strintzi, D.: The Fokker-Planck equation, and its application in plasma physics. Ann. Phys. (Berlin) **17**, 142–157 (2008)
Peyret, R.: Spectral Methods for Incompressible Viscous Flow. Springer, New York (2002)
Pierrard, V., Lemaire, J.: A collisional model of the polar wind. J. Geophys. Res. **103**, 11701–11709 (1998)
Pinkus, A.: Weierstrass and approximation theory. J. Approx. Theory **107**, 1–66 (2000)
Pitchford, L.C., Phelps, A.V.: Comparative calculations of electron-swarm properties in N_2 at moderate E/N values. Phys. Rev. A **25**, 540–554 (1982)
Present, R.D., Morris, B.M.: Variational solution of the chemical kinetic Boltzmann equation. J. Chem. Phys. **50**, 151–160 (1969)
Pryce, J.D.: Numerical Solution of Sturm-Liouville Problems. Oxford University Press, Oxford (1993)
Reed, W. H., Hill T.R.: Triangular Mesh Methods for the Neutron Transport Equation. Technical Report LA-UR-73-479, Los Alamos Scientific Laboratory (1973)
Reinhardt, W.P.: L^2 discretization of atomic and molecular electronic continua: moment, quadrature and J-matrix techniques. Comput. Phys. Commun. **17**, 1–21 (1979)

Risken, H., Till, F.: The Fokker-Planck Equation: Methods of Solution and Applications, 2nd edn. Springer, Berlin (1996)
Rivlin, T.J.: An Introduction to the Approximation of Functions. Blaisdell Publishing Co., Toronto (1969)
Rybicki, G.B.: Radiative transfer. J. Astrophys. Astron. **17**, 95–112 (1996)
Sarkar, T.K.: A note on the variational method (Rayleigh-Ritz), Galerkin's methods and the method of weighted residuals. Radio Sci. **18**, 1207–1224 (1983)
Schwartz, C.: High-accuracy approximation techniques for analytic functions. J. Math. Phys. **26**, 411–415 (1985)
Shen, J., Tang, T., Wang, L.-L.: Spectral Methods: Algorithms, Analysis and Applications. Springer, Berlin (2011)
Sherrill, C.D.: Frontiers in electronic structure theory. J. Chem. Phys. **132**, 110902 (2010)
Shizgal, B.: A Gaussian quadrature procedure for the use in the solution of the Boltzmann equation and related problems. J. Comput. Phys. **41**, 309–328 (1981)
Shizgal, B., Blackmore, R.: Eigenvalues of the Boltzmann collision operator for binary gases and relaxation of anisotropic distributions. Chem. Phys. **77**, 417–427 (1983)
Shizgal, B., Blackmore, R.: A discrete ordinate method of solution of linear boundary value and eigenvalue problems. J. Comput. Phys. **55**, 313–327 (1984)
Shizgal, B., Karplus, M.: Nonequilibrium contributions to the rate of reaction. II. Isolated multicomponent systems. J. Chem. Phys. **54**, 4345–4356 (1971)
Shizgal, B.D., Arkos, G.G.: Nonthermal escape of the atmospheres of Venus, Earth, and Mars. Rev. Geophys. **34**, 483–505 (1996)
Shizgal, B.D., Chen, H.: The quadrature discretization method (QDM) in the solution of the Schrödinger equation with nonclassical basis functions. J. Chem. Phys. **104**, 4137–4150 (1996)
Shizgal, B.D., Chen, H.: The quadrature discretization method in the solution of the Fokker-Planck equation with nonclassical basis functions. J. Chem. Phys. **107**, 8051–8063 (1997)
Shore, B.W.: Solving the radial Schrödinger equation by using cubic-spline basis functions. J. Chem. Phys. **58**, 3855–3866 (1973)
Shore, B.W.: B-spline expansion bases for excited states and discretized scattering states. J. Chem. Phys. **63**, 3835–3840 (1975)
Shu, C.: Differential Quadrature and Its Application in Engineering. Springer, Berlin (2000)
Siewert, C.E.: On computing the Chapman-Enskog functions for viscosity and heat transfer and the Burnett functions. JQRST **74**, 789–796 (2002)
Snider, R.F.: Variational methods for solving the Boltzmann equation. J. Chem. Phys. **41**, 591–595 (1964)
Sospedra-Alfonso, R., Shizgal, B.D.: Henyey-Greenstein model in the shape relaxation of dilute gas mixtures. Trans. Theory Stat. Phys. **41**, 368–388 (2012)
Spitzer, L.J., Härm, R.: Evaporation of stars from open clusters. Astrophys. J. **127**, 544–550 (1958)
Stare, J., Balint-Kurti, G.G.: Fourier grid Hamiltonian method for solving the vibrational Schrödinger equation in internal coordinates: theory and test applications. J. Phys. Chem. A **107**, 7204–7214 (2003)
Steffens, K.G.: The History of Approximation Theory, from Euler to Bernstein. Birkhäuser, Boston (2006)
Szabo, A., Ostlund, N.S.: Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory. Dover, New York (1996)
Szalay, V., Szidarovsky, T., Czakó, G., Császár, A.G.: A paradox of grid-based representation techniques: accurate eigenvalues from inaccurate matrix elements. J. Math. Chem. **50**, 636–651 (2012)
Taylor, J.R.: Scattering Theory: the quantum Theory on Nonrelativistic Collisions. Dover, New York (2012)
Thomas, G.E., Stamnes, K.: Radiative Transfer in the Atmosphere and Ocean. Cambridge University Press, Cambridge (2002)
Trefethen, L.N.: Approximation Theory and Approximation Practice. SIAM, Philadelphia (2013)

Tsuneda, T.: Density Functional Theory in Quantum Chemistry. Springer, New York (2014)
Vasenkov, A., Shizgal, B.D.: Nonhydrodynamic aspects of electron transport near a boundary: the milne problem. Phys. Rev. E **63**, 016401 (2000)
Wei, H.: Ghost levels and near-variational forms of the discrete variable representation: application to H_2O. J. Chem. Phys. **106**, 6885–6900 (1997)
Wei, G.W.: Solving quantum eigenvalue problems by discrete singular convolution. J. Phys. B: At. Mol. Opt. Phys. **33**, 343–352 (2000a)
Wei, G.W.: Wavelets generated by using discrete singular convolution kernels. J. Phys. A: Math. Gen. **33**, 8577–8596 (2000b)
Wick, G.C.: Über ebene diffusionsprobleme. Z. Phys. **121**, 702–718 (1943)
Williams, M.M.R.: The Slowing Down and Thermalization of Neutrons. North-Holland, Amsterdam (1966)
Williams, M.M.R.: Mathematical Methods in Particle Transport Theory. Wiley-Interscience, New York (1971)
Willner, K., Dulieu, O., Masnou-Seeuws, F.: Mapped grid methods for long-range molecules and cold collisions. J. Chem. Phys. **120**, 548–561 (2004)

http://www.springer.com/978-94-017-9453-4

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