10.2 HERMITIAN OPERATORS

Hermitian, or self-adjoint, operators with appropriate boundary conditions have three properties

1. The eigenvalues of a Hermitian operator are real.

Real eigenvalues of Hermitian operators have a fundamental significance in quantum mechanics . With the theory formulated in terms of Hermitian operators, this proof of real eigenvalues guarantees that the theory will predict real numbers for these measurable physical quantities.

2. A Hermitian operator possesses an orthogonal set of eigenfunctions.

If we now take *i ≠ j and if λi ≠ λj in, the integral of the product of the two* different eigenfunctions must vanish:

$$\int_a^b u_i u_j^* w \, dx = 0$$

This condition, called **orthogonality, but** This proof of orthogonality is not quite complete. because we may have *ui ≠ uj but still have λi = λj . Such a case is labeled* ***degenerate, the*** the integral need not vanish.

This means that linearly independent eigenfunctions corresponding to the same eigenvalue are not automatically orthogonal, but linear combinations of degenerate functions can be formed that will be orthogonal to each other.

3. The eigenfunctions of a Hermitian operator form a complete set.

10.3 GRAM–SCHMIDT ORTHOGONALIZATION

The Gram–Schmidt orthogonalization is a method that takes a nonorthogonal set of linearly independent functions and constructs an orthogonal set of functions over an arbitrary interval and with respect to an arbitrary weight or density function.

We consider three sets of functions:

$u_n(x)$	$\psi_n(x)$	$\varphi_n(x)$
Linearly independent	*Linearly independent*	*Linearly independent*
Nonorthogonal	*Orthogonal*	*Orthogonal*
Unnormalized	Unnormalized	*Normalized* (orthonormal)

where

$$\psi_i(x) = u_i + a_{i,0}\varphi_0 + a_{i,1}\varphi_1 + \cdots + a_{i,i-1}\varphi_{i-1}.$$

The coefficients $a_{i,j}$ are given by

$$a_{i,j} = -\int u_i \varphi_j w\, dx.$$

Example 10.3.1 LEGENDRE POLYNOMIALS BY GRAM–SCHMIDT ORTHOGONALIZATION

Let us form an orthonormal set from the set of functions $u_n(x) = x^n$, $n = 0, 1, 2 \ldots$. The interval is $-1 \le x \le 1$ and the density function is $w(x) = 1$.

In accordance with the Gram–Schmidt orthogonalization process described,

$$u_0 = 1, \qquad \text{hence} \qquad \varphi_0 = \frac{1}{\sqrt{2}}. \tag{10.50}$$

Then

$$\psi_1(x) = x + a_{1,0}\frac{1}{\sqrt{2}} \tag{10.51}$$

and

$$a_{1,0} = -\int_{-1}^{1} \frac{x}{\sqrt{2}} dx = 0 \tag{10.52}$$

by symmetry. We normalize ψ_1 to obtain

$$\varphi_1(x) = \sqrt{\frac{3}{2}}x. \tag{10.53}$$

Then we continue the Gram–Schmidt procedure with

$$\psi_2(x) = x^2 + a_{2,0}\frac{1}{\sqrt{2}} + a_{2,1}\sqrt{\frac{3}{2}}x, \tag{10.54}$$

where

$$a_{2,0} = -\int_{-1}^{1} \frac{x^2}{\sqrt{2}} dx = -\frac{\sqrt{2}}{3}, \tag{10.55}$$

$$a_{2,1} = -\int_{-1}^{1} \sqrt{\frac{3}{2}} x^3 \, dx = 0, \tag{10.56}$$

again by symmetry. Therefore

$$\psi_2(x) = x^2 - \frac{1}{3}, \tag{10.57}$$

and, on normalizing to unity, we have

$$\varphi_2(x) = \sqrt{\frac{5}{2}} \cdot \frac{1}{2}\left(3x^2 - 1\right). \tag{10.58}$$

The next function, $\varphi_3(x)$, becomes

$$\varphi_3(x) = \sqrt{\frac{7}{2}} \cdot \frac{1}{2}\left(5x^3 - 3x\right). \tag{10.59}$$

Reference to Chapter 12 will show that

$$\varphi_n(x) = \sqrt{\frac{2n+1}{2}} P_n(x), \tag{10.60}$$

where $P_n(x)$ is the nth-order Legendre polynomial. Our Gram–Schmidt process provides a possible but very cumbersome method of generating the Legendre polynomials. It illustrates how a power-series expansion in $u_n(x) = x^n$, which is not orthogonal, can be converted into an orthogonal series. ■

Table 10.3 Orthogonal Polynomials Generated by Gram–Schmidt Orthogonalization of $u_n(x) = x^n, n = 0, 1, 2, \ldots$

Polynomials	Interval	Weighting function $w(x)$	Standard normalization
Legendre	$-1 \le x \le 1$	1	$\int_{-1}^{1} [P_n(x)]^2\,dx = \frac{2}{2n+1}$
Shifted Legendre	$0 \le x \le 1$	1	$\int_{0}^{1} [P_n^*(x)]^2\,dx = \frac{1}{2n+1}$
Chebyshev I	$-1 \le x \le 1$	$(1-x^2)^{-1/2}$	$\int_{-1}^{1} \frac{[T_n(x)]^2}{(1-x^2)^{1/2}}\,dx = \begin{cases} \pi/2, & n \ne 0 \\ \pi, & n = 0 \end{cases}$
Shifted Chebyshev I	$0 \le x \le 1$	$[x(1-x)]^{-1/2}$	$\int_{0}^{1} \frac{[T_n^*(x)]^2}{[x(1-x)]^{1/2}}\,dx = \begin{cases} \pi/2, & n > 0 \\ \pi, & n = 0 \end{cases}$
Chebyshev II	$-1 \le x \le 1$	$(1-x^2)^{1/2}$	$\int_{-1}^{1} [U_n(x)]^2 (1-x^2)^{1/2}\,dx = \frac{\pi}{2}$
Laguerre	$0 \le x < \infty$	e^{-x}	$\int_{0}^{\infty} [L_n(x)]^2 e^{-x}\,dx = 1$
Associated Laguerre	$0 \le x < \infty$	$x^k e^{-x}$	$\int_{0}^{\infty} [L_n^k(x)]^2 x^k e^{-x}\,dx = \frac{(n+k)!}{n!}$
Hermite	$-\infty < x < \infty$	e^{-x^2}	$\int_{-\infty}^{\infty} [H_n(x)]^2 e^{-x^2}\,dx = 2^n \pi^{1/2} n!$

10.4 COMPLETENESS OF EIGENFUNCTIONS

The third important property of an Hermitian operator is that its eigenfunctions form a complete set. This completeness means that any well-behaved function *F(x) can be approximated by a series*

$$F(x) = \sum_{n=0}^{\infty} a_n \varphi_n(x)$$

the set *ϕn(x) is called* ***complete if*** the limit of the mean square error convergence to zero:

$$\lim_{m\to\infty} \int_a^b \left[F(x) - \sum_{n=0}^{m} a_n \varphi_n(x) \right]^2 w(x)\, dx = 0$$

the expansion coefficients *am may be determined by*

$$a_m = \int_a^b F(x) \varphi_m^*(x) w(x)\, dx$$

For a known function *F(x), Eq. gives am as a* ***definite integral that can always*** be evaluated, by computer if not analytically.

Setting the weight function *w(x) = 1 for simplicity, completeness in operator form for*

a discrete set of eigenfunctions $|\phi i>$ *becomes*

$$\sum_i |\varphi_i\rangle\langle\varphi_i| = 1$$

Multiplying the completeness relation by $|F>$ *we obtain the eigenfunction expansion*

$$|F\rangle = \sum_i |\varphi_i\rangle\langle\varphi_i|F\rangle$$

with the generalized Fourier coefficient $ai = <\phi i\ |F>$.

It may also happen that the eigenfunction expansion, Eq. (|F>), is the expansion of an unknown *F(x) in a series of known eigenfunctions* $\phi n(x)$ *with unknown coefficients an.* An example would be the quantum chemist's attempt to describe an (unknown) molecular wave function as a linear combination of known atomic wave functions. The unknown coefficients *an would be determined by a variational technique—Rayleigh–Ritz*

The concept of **completeness has been developed for finite vector spaces** and carries over into infinite vector spaces.

For summarizing some properties of vector spaces ,

Vector Space	Function Space
1v. We shall describe our vector space with a set of *n linearly independent vectors ei ,* *i = 1, 2, . . . , n. If n = 3, then* ***e1 = ˆx, e2 = ˆy, and e3 = ˆz. The nei span the linear vector*** space.	**1f. We shall describe our vector (function) space with a set of *n linearly independent*** functions, *φi(x), i = 0, 1, . . . , n − 1. The index i starts with 0 to agree with the labeling* of the classical polynomials. Here *φi(x) is assumed to be a polynomial of degree i. The nφi(x) span the linear vector (function) space.*

Vector Space	Function Space
2v. The vectors in our vector space satisfy the following relations a. Vector addition is commutative **u+ v = v+u** b. Vector addition is associative [**u +v] + w = u + [v+ w]** c. There is a null vector **0+ v = v** d. Multiplication by a scalar Distributive $a[\mathbf{u}+ \mathbf{v}] = a\mathbf{u}+a\mathbf{v}$ Distributive $(a +b)\mathbf{u} = a\mathbf{u}+ b\mathbf{u}$ Associative $a[b\mathbf{u}] = (ab)\mathbf{u}$ e. Multiplication By unit scalar 1**u = u** By zero 0**u = 0** f. Negative vector $(-1)\mathbf{u}=-\mathbf{u}.$	**2f. The functions in our linear function space satisfy the properties listed for vectors:** $f(x) +g(x) = g(x)+ f(x)$ $f(x)+ g(x) + h(x) = f(x)+ g(x)+h(x)$ $0 +f(x) = f(x)$ $a[f(x)+ g(x)] = af(x)+ ag(x)$ $(a + b)f(x) = af(x)+ bf(x)$ $abf(x)= (ab)f(x)$ $1 \cdot f(x) = f(x)$ $0 \cdot f(x) = 0$ $(-1) \cdot f(x)=-f(x).$

Vector Space	Function Space
3v. In *n-dimensional vector space an arbitrary vector c is described by its n components* $\mathbf{c} = \sum_{i=1}^{n} c_i \mathbf{e}_i$ When *n***ei *(1) are linearly independent and (2) span the n-dimensional vector space, then*** the **ei *form a basis and constitute a complete set.***	**3f. In *n-dimensional function space a polynomial of degree m ≤ n −1 is described by*** $f(x) = \sum_{i=0}^{n-1} c_i \varphi_i(x).$ When the *nϕi(x) (1) are linearly independent and (2) span the n-dimensional function* space, then the *ϕi(x) form a basis and constitute a* ***complete set (for describing polynomials*** of degree *m ≤ n− 1).*

Vector Space	Function Space
4v. An inner product (scalar, dot product) of a vector space is defined by $$\mathbf{c} \cdot \mathbf{d} = \sum_{i=1}^{n} c_i d_i$$ If **c and d have complex components in an orthogonal coordinate system, the inner product** is defined as $$\sum_{i=1}^{n} c_i^* d_i$$ The inner product has the properties of a. Distributive law of addition **c · *(d +e) = c · d+c · e*** b. Scalar multiplication **c · *ad = ac · d*** c. Complex conjugation **c · d = *(d · c)*** $*$.	**4f. An inner product of a linear space of functions is defined by** The choice of the weighting function *w(x) and the interval (a, b) follows from the differential* equation satisfied by *ϕi(x) and the boundary conditions* The inner product has the properties listed for vectors: a. *<f |g +h> =< f |g + f |h>* b. *<f |ag> = <af |g>* c. *<f |g = g|f >*$*$.

Vector Space	Function Space
5v. Orthogonality: $\mathbf{e}_j \cdot \mathbf{e}_j = 0, \qquad i \neq j.$ If the *n**ei are not already orthogonal, the Gram–Schmidt process may be used to create*** an orthogonal set.	**5f. Orthogonality:** $\langle \varphi_i \vert \varphi_j \rangle = \int_a^b \varphi_i^*(x)\varphi_j(x)w(x)\,dx = 0, \qquad i \neq j$ If the *nϕi(x) are not already orthogonal, the Gram–Schmidt process may be* used to create an orthogonal set.

Vector Space	Function Space
6v. Definition of norm: $$\|\mathbf{c}\| = (\mathbf{c}\cdot\mathbf{c})^{1/2} = \left(\sum_{i=1}^{n} c_i^2\right)^{1/2}.$$ The basis vectors **e*i* *are taken to have unit norm (length) ei · ei = 1. The components of c*** are given by $$c_i = \mathbf{e}_i \cdot \mathbf{c}, \qquad i = 1, 2, \ldots, n.$$	**6f. Definition of norm:** $$\|f\| = \langle f\,|\,f\rangle^{1/2} = \left[\int_a^b |f(x)|^2 w(x)\,dx\right]^{1/2} = \left[\sum_{i=0}^{n-1} |c_i|^2\right]^{1/2}$$ The basis functions *ϕi(x)* may be taken to have unit norm (unit normalization), $$\|\varphi_i\| = 1$$ The expansion coefficients of our polynomial *f (x) are given by* $$c_i = \langle\varphi_i\,|\,f\rangle, \qquad i = 0, 1, \ldots, n-1.$$

Expansion Coefficients

For a function f its expansion coefficients are defined as

$$c_i = \langle \varphi_i | f \rangle, \qquad i = 0, 1, \ldots, \infty,$$

exactly as in a finite-dimensional vector space. Hence

$$f(x) = \sum_i \langle \varphi_i | f \rangle \varphi_i(x).$$

A linear space (finite- or infinite-dimensional) that (1) has an inner product defined ($\langle f | g \rangle$) and (2) is complete is a **Hilbert space**.

Infinite-dimensional Hilbert space provides a natural mathematical frame-work for modern quantum mechanics. Away from quantum mechanics.

Exercises:

10.2.3

10.2.6

10.3.7