

## Chapter 2

# Function Spaces and Matrices

**Abstract** This chapter refreshes such necessary algebraic knowledge as will be needed in this book. It introduces function spaces, the meaning of a linear operator, and the properties of unitary matrices. The homomorphism between operations and matrix multiplications is established, and the Dirac notation for function spaces is defined. For those who might wonder why the linearity of operators need be considered, the final section introduces time reversal, which is anti-linear.

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## 2.1 Function Spaces

In the first chapter, we saw that if we wanted to rotate the  $2p_x$  function, we automatically also needed its companion  $2p_y$  function. If this is extended to out-of-plane rotations, the  $2p_z$  function will also be needed. The set of the three  $p$ -orbitals forms a prime example of what is called a *linear vector space*. In general, this is a space that consists of components that can be combined linearly using real or complex numbers as coefficients. An  $n$ -dimensional linear vector space consists of a set of  $n$  vectors that are linearly independent. The components or basis vectors will be denoted as  $f_l$ , with  $l$  ranging from 1 to  $n$ . At this point we shall introduce the Dirac notation [1] and rewrite these functions as  $|f_l\rangle$ , which characterizes them as so-called *ket*-functions. Whenever we have such a set of vectors, we can set up a complementary set of so-called *bra*-functions, denoted as  $\langle f_k|$ . The scalar product of a bra and a ket yields a number. It is denoted as the bracket:  $\langle f_k|f_l\rangle$ . In other words, when a bra collides with a ket on its right, it yields a scalar number. A bra-vector is completely defined when its scalar product with every ket-vector of the vector space is given.

For linearly independent functions, we have

$$\forall k \neq l : \langle f_k | f_l \rangle = 0 \quad (2.1)$$

The basis is orthonormal if all vectors are in addition normalized to +1:

$$\forall k : \langle f_k | f_k \rangle = 1 \quad (2.2)$$

This result can be summarized with the help of the Kronecker delta,  $\delta_{ij}$ , which is zero unless the subscript indices are identical, in which case it is unity. Hence, for an orthonormal basis set,

$$\langle f_k | f_l \rangle = \delta_{kl} \quad (2.3)$$

In quantum mechanics, the bra-function of  $f_k$  is simply the complex-conjugate function,  $\bar{f}_k$ , and the bracket or scalar product is defined as the integral of the product of the functions over space:

$$\langle f_k | f_l \rangle = \int \int \int \bar{f}_k f_l dV \quad (2.4)$$

One thus also has

$$\overline{\langle f_k | f_l \rangle} = \langle f_l | f_k \rangle \quad (2.5)$$

## 2.2 Linear Operators and Transformation Matrices

A linear operator is an operator that commutes with multiplicative scalars and is distributive with respect to summation: this means that when it acts on a sum of functions, it will operate on each term of the sum:

$$\begin{aligned} \hat{R}c|f_k\rangle &= c\hat{R}|f_k\rangle \\ \hat{R}(|f_k\rangle + |f_l\rangle) &= \hat{R}|f_k\rangle + \hat{R}|f_l\rangle \end{aligned} \quad (2.6)$$

If the transformations of functions under an operator can be expressed as a mapping of these functions onto a linear combination of the basis vectors in the function space, then the operator is said to leave the function space *invariant*. The corresponding coefficients can then be collected in a transformation matrix. For this purpose, we arrange the components in a row vector,  $(|f_1\rangle, |f_2\rangle, \dots, |f_n\rangle)$ , as agreed upon in Chap. 1. This row precedes the transformation matrix. The usual symbols are  $\hat{R}$  for the operator and  $\mathbb{D}(R)$  for the corresponding matrix:

$$\hat{R}(|f_1\rangle|f_2\rangle \cdots |f_n\rangle) = (|f_1\rangle|f_2\rangle \cdots |f_n\rangle) \begin{pmatrix} \mathbb{D}(R) \end{pmatrix}$$

i.e.,

$$\hat{R}|f_i\rangle = \sum_{j=1}^n D_{ji}(R)|f_j\rangle \quad (2.7)$$

When multiplying this equation left and right with a given bra-function in an orthonormal basis, one obtains

$$\langle f_k|\hat{R}|f_i\rangle = \sum_{j=1}^n D_{ji}(R)\langle f_k|f_j\rangle = \sum_{j=1}^n D_{ji}(R)\delta_{kj} = D_{ki}(R) \quad (2.8)$$

where the summation index  $j$  has been restricted to  $k$  by the Kronecker delta. Hence, the elements of the transformation matrix are recognized as matrix elements of the symmetry operators. The transformation of bra-functions runs entirely parallel with the transformation of ket-functions, except that the complex conjugate of the transformation matrix has to be taken, and hence,

$$\hat{R}\langle f_i| = \sum_{j=1}^n \bar{D}_{ji}(R)\langle f_j| \quad (2.9)$$

For convenience, we sometimes abbreviate the row vector of the function space as  $|\mathbf{f}\rangle$ , so that the transformation is written as

$$R|\mathbf{f}\rangle = |\mathbf{f}\rangle\mathbb{D}(R) \quad (2.10)$$

When the bra-functions are also ordered in a row vector, we likewise have:

$$\hat{R}\langle\mathbf{f}| = \langle\mathbf{f}|\bar{\mathbb{D}}(R) \quad (2.11)$$

A product of two operators is executed consecutively, and hence the one closest to the ket acts first. In detail,

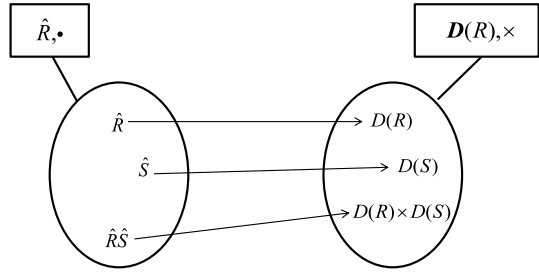
$$\begin{aligned} \hat{R}\hat{S}|f_i\rangle &= \hat{R}\sum_j D_{ji}(S)|f_j\rangle \\ &= \sum_{k,j} D_{kj}(R)D_{ji}(S)|f_k\rangle \\ &= \sum_k [\mathbb{D}(R) \times \mathbb{D}(S)]_{ki}|f_k\rangle \end{aligned} \quad (2.12)$$

Here, the symbol  $\times$  refers to the product of two matrices.

$$\hat{R}\hat{S}|\mathbf{f}\rangle = |\mathbf{f}\rangle\mathbb{D}(R) \times \mathbb{D}(S) \quad (2.13)$$

This is an important result. It shows that the consecutive action of two operators can be expressed by the product of the corresponding matrices. The matrices are said to

**Fig. 2.1** Matrix representation of a group: the operators (*left*) are mapped onto the transformations (*right*) of a function space. The consecutive action of two operators on *the left* (symbolized by  $\bullet$ ) is replaced by the multiplication of two matrices on *the right* (symbolized by  $\times$ )



*represent* the action of the corresponding operators. The relationship between both is a mapping. In this mapping the operators are replaced by their respective matrices, and the product of the operators is mapped onto the product of the corresponding matrices. In this mapping the order of the elements is kept.

$$\mathbb{D}(RS) = \mathbb{D}(R) \times \mathbb{D}(S) \quad (2.14)$$

In mathematical terms, such a mapping is called a *homomorphism* (see Fig. 2.1). In Eq. (2.14) both the operators and matrices that represent them are *right-justified*; that is, the operator (matrix) on the *right* is applied first, and then the operator (matrix) immediately to the left of it is applied to the result of the action of the right-hand operator (matrix). The conservation of the order is an important characteristic, which in the active picture entirely relies on the convention for collecting the functions in a row vector. In the column vector notation the order would be reversed. Further consequences of the homomorphism are that the unit element is represented by the unit matrix,  $\mathbb{I}$ , and that an inverse element is represented by the corresponding inverse matrix:

$$\begin{aligned} \mathbb{D}(E) &= \mathbb{I} \\ \mathbb{D}(R^{-1}) &= [\mathbb{D}(R)]^{-1} \end{aligned} \quad (2.15)$$

## 2.3 Unitary Matrices

A matrix is unitary if its rows and columns are orthonormal. In this definition the scalar product of two rows (or two columns) is obtained by adding pairwise products of the corresponding elements,  $\bar{A}_{ij} A_{kj}$ , one of which is taken to be complex conjugate:

$$\sum_j \bar{A}_{ij} A_{kj} = \sum_j \bar{A}_{ji} A_{jk} = \delta_{ik} \leftrightarrow \mathbb{A} \text{ is unitary} \quad (2.16)$$

A unitary matrix has several interesting properties, which can easily be checked from the general definition:

- The inverse of a unitary matrix is obtained by combining complex conjugation and transposition:

$$\mathbb{A}^{-1} = \bar{\mathbb{A}}^T \quad (2.17)$$

Here, T denotes transposition of rows and columns. This result implies that  $A_{ij}^{-1} = \bar{A}_{ji}$ .

- The inverse and the transpose of a unitary matrix are unitary.
- The product of unitary matrices is a unitary matrix.
- The determinant of a unitary matrix has an absolute value of unity.

To prove the final property, we note that the determinant of a product of matrices is equal to the product of the determinants of the individual matrices, and we also note that the determinant does not change upon transposition of a matrix. By definition,  $\mathbb{I} = \mathbb{A} \times \mathbb{A}^{-1}$ , and it then follows:

$$\begin{aligned} \det(\mathbb{A} \times \mathbb{A}^{-1}) &= \det(\mathbb{A}) \det(\mathbb{A}^{-1}) \\ &= \det(\mathbb{A}) \det(\bar{\mathbb{A}}^T) \\ &= \det(\mathbb{A}) \det(\bar{\mathbb{A}}) \\ &= \det(\mathbb{A}) \overline{\det(\mathbb{A})} \\ &= |\det(\mathbb{A})|^2 = \det(\mathbb{I}) = 1 \end{aligned} \quad (2.18)$$

Now consider a function space  $|\mathbf{f}\rangle$  and a linear transformation matrix,  $\mathbb{A}$ , which recombines the basis functions to yield a transformed basis set, say  $|\mathbf{f}'\rangle$ . Such a linear transformation of an orthonormal vector space preserves orthonormality *if and only if the transformation matrix  $\mathbb{A}$  is unitary*. Assuming that  $\mathbb{A}$  is unitary, the forward implication is easily proven:

$$\begin{aligned} \langle f'_k | f'_l \rangle &= \sum_{ij} \bar{A}_{ik} A_{jl} \langle f_i | f_j \rangle \\ &= \sum_{ij} \bar{A}_{ik} A_{jl} \delta_{ij} \\ &= \sum_i \bar{A}_{ik} A_{il} \\ &= \delta_{kl} \end{aligned} \quad (2.19)$$

The converse implication is that if a transformation preserves orthonormality, the corresponding representation matrix will be unitary. Here, the starting point is the assumption that the basis remains orthonormal after transformation:

$$\sum_i \bar{A}_{ik} A_{il} = \delta_{kl} \quad (2.20)$$

This result may be recast in a matrix multiplication as

$$\sum_i \bar{A}_{ki}^T A_{il} = [\bar{\mathbb{A}}^T \times \mathbb{A}]_{kl} = \delta_{kl} \quad (2.21)$$

or  $\bar{\mathbb{A}}^T \times \mathbb{A} = \mathbb{I}$ . In order to prove the unitary property, we also have to prove that the matrix order in this multiplication may be switched. This is achieved<sup>1</sup> as follows:

$$\begin{aligned} \bar{\mathbb{A}}^T \times \mathbb{A} &= \mathbb{I} \\ \mathbb{A} \times \bar{\mathbb{A}}^T \times \mathbb{A} &= \mathbb{A} \\ \mathbb{A} \times \bar{\mathbb{A}}^T &= \mathbb{A} \times \mathbb{A}^{-1} \\ \mathbb{A} \times \bar{\mathbb{A}}^T &= \mathbb{I} \end{aligned} \quad (2.22)$$

Left or right multiplication by  $\bar{\mathbb{A}}^T$  thus turns the matrix  $\mathbb{A}$  into the unit matrix, and the inverse of a matrix is unique; it thus follows that the inverse of  $\mathbb{A}$  is obtained by taking the complex-conjugate transposed form, which means that the matrix is unitary. Note that the result in Eq. (2.22) is valid only if the matrix  $\mathbb{A}$  is nonsingular. However, this will certainly be the case since

$$\det(\bar{\mathbb{A}}^T) \det(\mathbb{A}) = |\det(\mathbb{A})|^2 = 1 \quad (2.23)$$

Spatial symmetry operations are linear transformations of a coordinate function space. When choosing the space in orthonormal form, symmetry operations will conserve orthonormality, and hence all transformations will be carried out by unitary matrices. This will be the case for all spatial representation matrices in this book. When all elements of a unitary matrix are real, it is called an *orthogonal* matrix. As unitary matrices, orthogonal matrices have the same properties except that complex conjugation leaves them unchanged. The determinant of an orthogonal matrix will thus be equal to  $\pm 1$ . The rotation matrices in Chap. 1 are all orthogonal and have determinant +1.

## 2.4 Time Reversal as an Anti-linear Operator

The fact that an operator cannot change a scalar constant in front of the function on which it operates seems to be evident. However, in quantum mechanics there is one important operator that does affect a scalar constant and turns it into its complex conjugate. This is the operator of *time reversal*, i.e., the operator which inverts time,  $t \rightarrow -t$ , and sends the system back to its own past. If we are looking at a stationary

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<sup>1</sup>Adapted from: [2, Problem 8, p. 59].

state, with no explicit time dependence, time inversion really means reversal of the direction of motion, where all angular momenta will be changing sign, including the “spinning” of the electrons. We shall denote this operator as  $\hat{\vartheta}$ . It has the following properties:

$$\begin{aligned}\hat{\vartheta}(|f_k\rangle + |f_l\rangle) &= \hat{\vartheta}|f_k\rangle + \hat{\vartheta}|f_l\rangle \\ \hat{\vartheta}c|f_k\rangle &= \bar{c}\hat{\vartheta}|f_k\rangle\end{aligned}\tag{2.24}$$

These properties are characteristic of an *anti-linear* operator. As a rationale for the complex conjugation upon commutation with a multiplicative constant, we consider a simple case-study of a stationary quantum state. The time-dependent Schrödinger equation, describing the time evolution of a wavefunction,  $\Psi$ , defined by a Hamiltonian  $\mathcal{H}$ , is given by

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi\tag{2.25}$$

For a stationary state, the Hamiltonian is independent of time, and the wavefunction is characterized by an eigenenergy,  $E$ ; hence the right-hand side of the equation is given by  $\mathcal{H}\Psi = E\Psi$ . The solution for the stationary state then becomes

$$\Psi(t) = \Psi(t_0) \exp\left(-\frac{iE(t-t_0)}{\hbar}\right)\tag{2.26}$$

Hence, the phase of a stationary state is “pulsating” at a frequency given by  $E/\hbar$ . Now we demonstrate the anti-linear character, using Wigner’s argument that a perfect looping in time would bring a system back to its original state.<sup>2</sup> Such a process can be achieved by running backwards in time over a certain interval and then returning to the original starting time. Let  $T_{\Delta t}$  represent a displacement in time toward the future over an interval  $\Delta t$ , and  $T_{-\Delta t}$  a displacement over the same interval but toward the past. The consecutive action of  $T_{\Delta t}$  and  $T_{-\Delta t}$  certainly describes a perfect loop in time, and thus we can write:

$$\hat{T}_{\Delta t} \hat{T}_{-\Delta t} = \hat{E}\tag{2.27}$$

The reversal of the translation in time is the result of a reversal of the time variable. We thus can apply the operator transformation under  $\hat{\vartheta}$ , in line with the previous results in Sect. 1.3:

$$\hat{T}_{-\Delta t} = \hat{\vartheta} \hat{T}_{\Delta t} \hat{\vartheta}^{-1}\tag{2.28}$$

The complete loop can thus be written as follows:

$$T_{\Delta t} \hat{\vartheta} T_{\Delta t} \hat{\vartheta}^{-1} = \hat{E}\tag{2.29}$$

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<sup>2</sup>Adapted from [3, Chap. 26].

This equation decomposes the closed path in time in four consecutive steps. Reading Eq. (2.29) from right to left, one sets off at time  $t_0$  and reverses time ( $\hat{\vartheta}^{-1}$ ). Now time runs for a certain interval  $\Delta t$  along the reversed time axis. A positive interval actually means that we are returning in time since the time axis has been oriented toward the past. This operation is presented by the displacement  $\hat{T}_{\Delta t}$ . Then one applies the time reversal again and now runs forward over the same interval to close the loop. The forward translation corresponds to the same  $\hat{T}_{\Delta t}$  operator since again the interval is positive. Now multiply both sides of the equation, on the right, by  $\hat{\vartheta} \hat{T}_{-\Delta t}$ :

$$\hat{T}_{\Delta t} \hat{\vartheta} = \hat{\vartheta} \hat{T}_{-\Delta t} \quad (2.30)$$

The actions of the translations on the wavefunction are given by

$$\begin{aligned} T_{\Delta t} \Psi(t_0) &= \Psi(t_0) \exp\left(-\frac{i E \Delta t}{\hbar}\right) \\ T_{-\Delta t} \Psi(t_0) &= \Psi(t_0) \exp\left(\frac{i E \Delta t}{\hbar}\right) \end{aligned} \quad (2.31)$$

Applying now both sides of Eq. (2.30) to the initial state yields

$$\begin{aligned} T_{\Delta t} \vartheta \Psi(t_0) &= \vartheta T_{-\Delta t} \Psi(t_0) \\ &= \vartheta \exp\left(\frac{i E \Delta t}{\hbar}\right) \Psi(t_0) \end{aligned} \quad (2.32)$$

Since the Hamiltonian that we have used is invariant under time reversal, the function  $\vartheta \Psi(t_0)$  on the left-hand side of Eq. (2.32) will be characterized by the same energy,  $E$ , and thus translate in time with the same phase factor as  $\Psi(t_0)$  itself. Then the equation becomes

$$\exp\left(-\frac{i E \Delta t}{\hbar}\right) \vartheta \Psi(t_0) = \vartheta \exp\left(\frac{i E \Delta t}{\hbar}\right) \Psi(t_0) \quad (2.33)$$

which shows that time reversal will invert scalar constants to their complex conjugate, and hence it will be an anti-linear operator.

Note that in the present derivation we avoided providing an explicit form for the inverse of the time reversal operator. As a matter of fact, while space inversion is its own inverse, applying time reversal twice may give rise to an additional phase factor, which is  $+1$  for systems with an even number of electrons, but  $-1$  for systems with an odd number of electrons. We shall demonstrate this point later in Sect. 7.6. Hence,  $\vartheta^{-1} = \pm \vartheta$ , or

$$\hat{\vartheta}^2 = \pm 1 \quad (2.34)$$



## 2.5 Problems

- 2.1 A complex number can be characterized by an absolute value and a phase. A  $2 \times 2$  complex matrix thus contains eight parameters, say

$$\mathbb{C} = \begin{pmatrix} |a|e^{i\alpha} & |b|e^{i\beta} \\ |c|e^{i\gamma} & |d|e^{i\delta} \end{pmatrix}$$

Impose now the requirement that this matrix is unitary. This will introduce relationships between the parameters. Try to solve these by adopting a reduced set of parameters.

- 2.2 The cyclic waves  $e^{ik\phi}$  and  $e^{-ik\phi}$  are defined in a circular interval  $\phi \in [0, 2\pi[$ . Normalize these waves over the interval. Are they mutually orthogonal?
- 2.3 A matrix  $\mathbb{H}$  which is equal to its complex-conjugate transpose,  $\mathbb{H} = \bar{\mathbb{H}}^T$ , is called *Hermitian*. It follows that the diagonal elements of such a matrix are real, while corresponding off-diagonal elements form complex-conjugate pairs:

$$\mathbb{H} \text{ Hermitian} \rightarrow H_{ii} \in \mathcal{R}; \quad H_{ij} = \bar{H}_{ji}$$

Prove that the eigenvalues of a Hermitian matrix are real. If the matrix is *skew-Hermitian*,  $\mathbb{H} = -\bar{\mathbb{H}}^T$ , the eigenvalues are all imaginary.

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