Chapter 8
Time-Independent Schrödinger Equation

8.1 Introduction

The properties of the time-independent Schrödinger equation are introduced step by step, starting from a short discussion about its boundary conditions. Considering that the equation is seldom amenable to analytical solutions, two simple cases are examined first: that of a free particle and that of a particle in a box. The determination of the lower energy bound follows, introducing more general issues that build up the mathematical frame of the theory: norm of a function, scalar product of functions, Hermitean operators, eigenfunctions and eigenvalues of operators, orthogonal functions, and completeness of a set of functions. The chapter is concluded with the important examples of the Hamiltonian operator and momentum operator. The complements provide examples of Hermitean operators, a collection of operators' definitions and properties, examples of commuting operators, and a further discussion about the free-particle case.

8.2 Properties of the Time-Independent Schrödinger Equation

A number of properties of the time-independent Schrödinger equation are discussed in this section. The form (7.45) holds only when the force is conservative, so it is not the most general one. However, as will be shown later, many of its properties still hold in more complicated cases. Equation (7.45) is a linear, homogeneous partial-differential equation of the second order, with the zero-order coefficient depending on $\mathbf{r}$. As shown in Prob. 8.1, it is a very general form of linear, second-order equation. The boundary conditions are specified on a case-by-case basis depending on the problem under consideration. More details about the boundary conditions are discussed below. One notes that:

1. The coefficients of (7.45) are real. As a consequence, the solutions are real. In same cases, however, it is convenient to express them in complex form. An example is given in Sect. 8.2.1.

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2. The equation is linear and homogeneous and, as shown below, its boundary conditions are homogeneous as well. It follows that its solution is defined apart from a multiplicative constant. The function $w = 0$ is a solution of (7.45), however it has no physical meaning and is not considered.
3. As the equation is of the second order, its solution w and first derivatives $\partial w/\partial x_i$ are continuous. These requirements are discussed from the physical standpoint in Sect. 9.4. The second derivatives may or may not be continuous, depending on the form of the potential energy V.
4. The solution of (7.45) may contain terms that diverge as $|\mathbf{r}| \to \infty$. In this case such terms must be discarded because they are not compatible with the physical meaning of w (examples are given in Sect. 8.2.1).

Given the above premises, to discuss the boundary conditions of (7.45) it is convenient to distinguish a few cases:

A. The domain Ω of w is finite; in other terms, some information about the problem in hand is available, from which it follows that w vanishes identically outside a finite domain Ω. The continuity of w (see point 3 above) then implies that w vanishes over the boundary of Ω, hence the boundary conditions are homogeneous. After discarding possible diverging terms from the solution, the integral $\int_\Omega |w|^2 \,\mathrm{d}\Omega$ is finite (the use of the absolute value is due to the possibility that w is expressed in complex form, see point 1 above).
B. The domain of w is infinite in all directions, but the form of w is such that $\int_\Omega |w|^2 \,\mathrm{d}\Omega$ is finite. When this happens, w necessarily vanishes as $|\mathbf{r}| \to \infty$. Thus, the boundary conditions are homogeneous also in this case.[1]
C. The domain of w is infinite, and the form of w is such that $\int_\Omega |w|^2 \,\mathrm{d}\Omega$ diverges. This is not due to the fact that $|w|^2$ diverges (in fact, divergent terms in w must be discarded beforehand), but to the fact that w, e.g., asymptotically tends to a constant different from zero, or oscillates (an example of asymptotically-oscillating behavior is given in Sect. 8.2.1). These situations must be tackled separately; one finds that w is still defined apart from a multiplicative constant.

As remarked above, the time-independent Schrödinger equation is a second-order differential equation of a very general form. For this reason, an analytical solution can seldom be obtained, and in the majority of cases it is necessary to resort to numerical-solution methods. The typical situations where the problem can be tackled analytically are those where the equation is separable (compare with Sect. 10.3), so that it can be split into one-dimensional equations. Even when this occurs, the analytical solution can be found only for some forms of the potential energy. The rest of this chapter provides examples that are solvable analytically.

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[1] It may happen that the domain is infinite in some direction and finite in the others. For instance, one may consider the case where w vanishes identically for $x \geq 0$ and differs from zero for $x < 0$. Such situations are easily found to be a combination of cases A and B illustrated here.

8.2.1 Schrödinger Equation for a Free Particle

The equation for a free particle is obtained by letting $V = \text{const}$ in (7.45). Without loss of generality one may let $V = 0$, this yielding $\nabla^2 w = -(2\,m\,E/\hbar^2)\,w$. As the above can be solved by separating the variables, it is sufficient to consider here only the one-dimensional form

$$\frac{\mathrm{d}^2 w}{\mathrm{d}x^2} = -\frac{2\,m\,E}{\hbar^2}\,w. \tag{8.1}$$

The case $E < 0$ must be discarded as it gives rise to divergent solutions, which are not acceptable from the physical standpoint. The case $E = 0$ yields $w = a_1 x + a_2$, where a_1 must be set to zero to prevent w from diverging. As a consequence, the value $E = 0$ yields $w = a_2 = \text{const}$, that is one of the possibilities anticipated at point C of Sect. 8.2. The integral of $|w|^2$ diverges. Finally, the case $E > 0$ yields

$$w = c_1\,\exp(\mathrm{i}\,k\,x) + c_2\,\exp(-\mathrm{i}\,k\,x), \qquad k = \sqrt{2\,m\,E/\hbar^2} = p/\hbar > 0, \tag{8.2}$$

where c_1, c_2 are constants to be determined. Thus, the value $E > 0$ yields the asymptotically-oscillating behavior that has also been anticipated at point C of Sect. 8.2. The integral of $|w|^2$ diverges. One notes that w is written in terms of two complex functions; it could equally well be expressed in terms of the real functions $\cos(k\,x)$ and $\sin(k\,x)$. The time-dependent, monochromatic wave function $\psi = w\,\exp(-\mathrm{i}\,\omega\,t)$ corresponding to (8.2) reads

$$\psi = c_1\,\exp[\mathrm{i}\,(k\,x - \omega\,t)] + c_2\,\exp[-\mathrm{i}\,(k\,x + \omega\,t)], \qquad \omega = E/\hbar. \tag{8.3}$$

The relations $k = p/\hbar$, $\omega = E/\hbar$ stem from the analogy described in Sect. 7.4.5. The total energy E and momentum's modulus p are fully determined; this outcome is the same as that found for the motion of a free particle in Classical Mechanics: for a free particle the kinetic energy equals the total energy; if the latter is prescribed, the momentum's modulus is prescribed as well due to $E = p^2/(2\,m)$. The direction of the motion, instead, is not determined because both the forward and backward motions, corresponding to the positive and negative square root of p^2 respectively, are possible solutions. To ascertain the motion's direction it is necessary to acquire more information; specifically, one should prescribe the initial conditions which, in turn, would provide the momentum's sign.

The quantum situation is similar, because the time-dependent wave function (8.2) is a superposition of a planar wave $c_1\,\exp[\mathrm{i}\,(k\,x - \omega\,t)]$ whose front moves in the positive direction, and of a planar wave $c_2\,\exp[-\mathrm{i}\,(k\,x + \omega\,t)]$ whose front moves in the negative direction. Here to ascertain the motion's direction one must acquire the information about the coefficients in (8.2): the forward motion corresponds to $c_1 \neq 0$, $c_2 = 0$, the backward motion to $c_1 = 0$, $c_2 \neq 0$. Obviously (8.2) in itself does not provide any information about the coefficients, because such an expression is the general solution of (8.1) obtained as a combination of the two linearly-independent, particular solutions $\exp(\mathrm{i}\,k\,x)$ and $\exp(-\mathrm{i}\,k\,x)$; so, without further information about c_1 and c_2, both the forward and backward motions are possible.

Another similarity between the classical and quantum cases is that no constraint is imposed on the total energy, apart from the prescription $E \geq 0$. From this viewpoint one concludes that (8.1) is an eigenvalue equation with a continuous distribution of eigenvalues in the interval $E \geq 0$.

8.2.2 Schrödinger Equation for a Particle in a Box

Considering again the one-dimensional case of (7.45),

$$\frac{\mathrm{d}^2 w}{\mathrm{d}x^2} = -\frac{2\,m}{\hbar^2}\,(E - V)\,w, \qquad V = V(x), \tag{8.4}$$

let $V = \text{const} = 0$ for $x \in [0, a]$ and $V = V_0 > 0$ elsewhere. The form of the potential energy is that of a square well whose counterpart of Classical Mechanics is illustrated in Sect. 3.2. Here, however, the limit $V_0 \to \infty$ is considered for the sake of simplicity. This limiting case is what is referred to with the term *box*. As shown in Sect. 11.5, here w vanishes identically outside the interval $[0, a]$: this is one of the possibilities that were anticipated in Sect. 8.2 (point A). The continuity of w then yields $w(0) = w(a) = 0$. It is easily found that if $E \leq 0$ the only solution of (8.4) is $w = 0$, which is not considered because it has no physical meaning. When $E > 0$, the solution reads

$$w = c_1\, \exp\,(\mathrm{i}\,k\,x) + c_2\, \exp\,(-\,\mathrm{i}\,k\,x), \qquad k = \sqrt{2\,m\,E/\hbar^2} > 0. \tag{8.5}$$

Letting $w(0) = 0$ yields $c_1 + c_2 = 0$ and $w = 2\,\mathrm{i}\,c_1\, \sin\,(k\,x)$. Then, $w(a) = 0$ yields $k\,a = n\,\pi$ with n an integer whence, using the relation $k = k_n = n\,\pi/a$ within those of E and w,

$$E = E_n = \frac{\hbar^2\,\pi^2}{2\,m\,a^2}\,n^2, \qquad w = w_n = 2\,\mathrm{i}\,c_1\, \sin\left(\frac{n\,\pi}{a}\,x\right). \tag{8.6}$$

This result shows that (8.4) is an eigenvalue equation with a discrete distribution of eigenvalues, given by the first relation in (8.6). For this reason, the energy is said to be *quantized*. To each index n it corresponds one and only one eigenvalue E_n, and one and only one eigenfunction w_n; as a consequence, this case provides a one-to-one-correspondence between eigenvalues and eigenfunctions.[2] Not every integer should be used in (8.6) though; in fact, $n = 0$ must be discarded because the corresponding eigenfunction vanishes identically. Also, the negative indices are to be excluded because $E_{-n} = E_n$ and $|w_{-n}|^2 = |w_n|^2$, so they do not add information with respect to the positive ones. In conclusion, the indices to be used are $n = 1, 2, \ldots$

[2] The one-to-one correspondence does not occur in general. Examples of the Schrödinger equation are easily given (Sect. 9.6) where to each eigenvalue there corresponds more than one—even infinite— eigenfunctions.

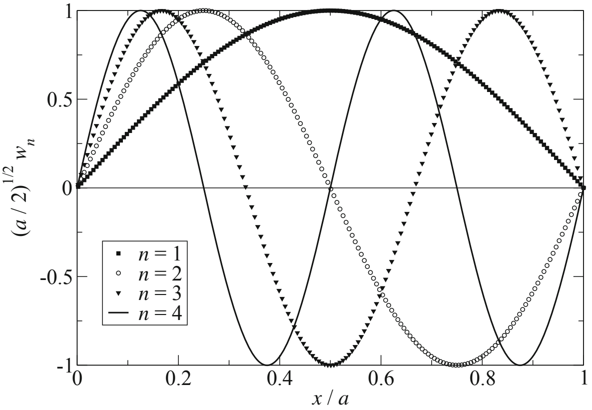

Fig. 8.1 The first eigenfunctions of the Schrödinger equation in the case of a particle in a box

As expected, each eigenfunction contains a multiplicative constant; here the integral of $|w|^2$ converges, so the constant can be exploited to normalize the eigenfunction by letting $\int_0^a |w_n|^2\,\mathrm{d}x = 1$. One finds

$$\int_0^a |w_n|^2\,\mathrm{d}x = 4\,|c_1|^2 \int_0^a \sin^2\left(\frac{n\,\pi}{a}\,x\right)\,\mathrm{d}x = \frac{4\,|c_1|^2 a}{n\,\pi} \int_0^{n\,\pi} \sin^2(y)\,\mathrm{d}y. \tag{8.7}$$

Integrating by parts shows that the last integral equals $n\,\pi/2$, whence the normalization condition yields $4\,|c_1|^2 = 2/a$. Choosing $2\,c_1 = -j\,\sqrt{2/a}$ provides the eigenfunctions

$$w_n = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\,\pi}{a}\,x\right). \tag{8.8}$$

The first eigenfunctions are shown in Fig. 8.1. Remembering that $w = 0$ outside the interval $[0, a]$, one notes that $\mathrm{d}w/\mathrm{d}x$ is discontinuous at $x = 0$ and $x = a$. This apparently contradicts the continuity property of the first derivative mentioned in Sect. 8.2, point 3. However, in the case considered here the limit $V_0 \to \infty$ has introduced a discontinuity of the second kind into the potential energy; for this reason, the property mentioned above does not apply.

8.2.3 Lower Energy Bound in the Schrödinger Equation

In the example of Sect. 8.2.1, where the free particle is considered, the lower bound for the particle's total energy is $E \ge V_{\min}$, with $V_{\min}$ the minimum[3] of the potential energy; in contrast, in the example of the particle in a box illustrated in Sect. 8.2.2, the lower bound is $E > V_{\min}$. A more general analysis of the lower bound for the total energy in the Schrödinger equation is carried out here.

[3] Such a minimum is set to zero in the example of Sect. 8.2.1.

Consider the time-independent Schrödinger equation in a conservative case, (7.45), and let Ω be the domain of w (which may extend to infinity), with Σ the boundary of Ω. Recasting (7.45) as $-\nabla^2 w = 2\,m\,(E - V)\,w/\hbar^2$ and integrating it over Ω after multiplying both sides by w^* yields

$$-\int_\Omega w^*\,\nabla^2 w\,\mathrm{d}\Omega = \frac{2m}{\hbar^2}\int_\Omega (E - V)\,|w|^2\,\mathrm{d}\Omega. \tag{8.9}$$

It is implied that w is a physically meaningful solution of (7.45), whence w does not vanish identically within Ω. Thanks to the identity (A.17) and the divergence theorem (A.23) the above becomes

$$\frac{2\,m}{\hbar^2}\int_\Omega (E - V)\,|w|^2\,\mathrm{d}\Omega = \int_\Omega |\mathrm{grad} w|^2\,\mathrm{d}\Omega - \int_\Sigma w^*\,\frac{\partial w}{\partial n}\,\mathrm{d}\Sigma, \tag{8.10}$$

with $\partial w/\partial n$ the derivative of w in the direction normal to Σ. Consider now the case where w vanishes over Σ; as w^* vanishes as well, the boundary integral in (8.10) is equal to zero. In contrast, the other integral at the right hand side of (8.10) is strictly positive: in fact, as w vanishes at the boundary while it is different from zero inside the domain, its gradient does not vanish identically in Ω. It follows

$$\int_\Omega (E - V)\,|w|^2\,\mathrm{d}\Omega > 0, \qquad E > \frac{\int_\Omega V\,|w|^2\,\mathrm{d}\Omega}{\int_\Omega |w|^2\,\mathrm{d}\Omega} \ge V_{\min}, \tag{8.11}$$

where the last inequality stems from the fact that $|w|^2$ is strictly positive. In conclusion, when V is such that w vanishes at the boundary, then the strict inequality $E > V_{\min}$ holds. When V does not vanish at the boundary, the reasoning leading to (8.11) does not apply and the lower bound for E must be sought by a direct examination of the solutions. An example of this examination is that of the free-particle case shown in Sect. 8.2.1.

8.3 Norm of a Function—Scalar Product

The functions $f,\ g, \ldots$ that are considered in this section are *square-integrable* complex functions, namely, they have the property that the integrals

$$||f||^2 = \int_{\Omega'} |f|^2\,\mathrm{d}\Omega', \qquad ||g||^2 = \int_{\Omega''} |g|^2\,\mathrm{d}\Omega'', \ldots \tag{8.12}$$

converge. In (8.12), Ω' is the domain of f, Ω'' that of g, and so on. The variables in the domains Ω', Ω'', ... are real. The positive numbers $||f||$ and $||g||$ are the *norm* of f and g, respectively. If f, g are square integrable over the same domain Ω, a linear combination $\lambda\,f + \mu\,g$, with λ, μ arbitrary complex constants, is also square integrable over Ω ([78], Chap. V.2).

If a square-integrable function f is defined apart from a multiplicative constant, for instance because it solves a linear, homogeneous differential equation with homogeneous boundary conditions, it is often convenient to choose the constant such that the norm equals unity. This is accomplished by letting $\varphi = c\, f$ and $||\varphi|| = 1$, whence $|c|^2 = 1/||\varphi||^2$.

Consider two square-integrable functions f and g defined over the same domain Ω; their *scalar product* is defined as

$$\langle g|f\rangle = \int_\Omega g^*\, f\, \mathrm{d}\Omega. \tag{8.13}$$

From (8.13) it follows

$$\langle f|g\rangle = \int_\Omega f^*\, g\, \mathrm{d}\Omega = \left(\int_\Omega f\, g^*\, \mathrm{d}\Omega\right)^* = \langle g|f\rangle^*. \tag{8.14}$$

It is implied that f, g are regular enough to make the integral in (8.13) to exist; in fact, this is proved by observing that for square-integrable functions the *Schwarz inequality* holds, analogous to that found in the case of vectors (Sect. A.2): if f and g are square integrable, then

$$|\langle g|f\rangle| \le ||f|| \times ||g||, \tag{8.15}$$

where the equality holds if and only if f is proportional to g (compare with (A.5)). In turn, to prove (8.15) one observes that $\sigma = f + \mu\, g$, where μ is an arbitrary constant, is also square integrable. Then [47],

$$||\sigma||^2 = ||f||^2 + |\mu|^2\, ||g||^2 + \mu\,\langle f|g\rangle + \mu^*\,\langle g|f\rangle \ge 0. \tag{8.16}$$

The relation (8.15) is obvious if $f = 0$ or $g = 0$. Let $g \ne 0$ and choose $\mu = -\langle g|f\rangle/||g||^2$. Replacing in (8.16) yields (8.15). For the equality to hold it must be $\sigma = 0$, which implies that f and g are proportional to each other; conversely, from $f = c\, g$ the equality follows.

The symbol $\langle g|f\rangle$ for the scalar product is called *Dirac's notation*.[4] If $\langle g|f\rangle = 0$, the functions f, g are called *orthogonal*. For any complex constants b, b_1, b_2 the following hold:

$$\langle g|b\, f\rangle = b\,\langle g|f\rangle, \qquad \langle g|b_1\, f_1 + b_2\, f_2\rangle = b_1\,\langle g|f_1\rangle + b_2\,\langle g|f_2\rangle, \tag{8.17}$$

$$\langle b\, g|f\rangle = b^*\,\langle g|f\rangle, \qquad \langle b_1\, g_1 + b_2\, g_2|f\rangle = b_1^*\,\langle g_1|f\rangle + b_2^*\,\langle g_2|f\rangle, \tag{8.18}$$

namely, the scalar product is distributive and bilinear. The properties defined here are the counterpart of those defined in Sect. A.1 for vectors.

[4] The two terms $\langle g|$ and $|f\rangle$ of the scalar product $\langle g|f\rangle$ are called *bra vector* and *ket vector*, respectively.

8.3.1 Adjoint Operators and Hermitean Operators

A function appearing within a scalar product may result from the application of a linear operator, say, $\mathcal{A}$, onto another function.[5] For instance, if $s = \mathcal{A} f$, then from (8.13, 8.14) it follows

$$\langle g|s\rangle = \int_\Omega g^* \mathcal{A} f \, d\Omega, \qquad \langle s|g\rangle = \int_\Omega (\mathcal{A} f)^* g \, d\Omega = \langle g|s\rangle^*. \tag{8.19}$$

Given an operator $\mathcal{A}$ it is possible to find another operator, typically indicated with $\mathcal{A}^\dagger$, having the property that, for any pair f, g of square-integrable functions,

$$\int_\Omega \left(\mathcal{A}^\dagger g\right)^* f \, d\Omega = \int_\Omega g^* \mathcal{A} f \, d\Omega \tag{8.20}$$

or, in Dirac's notation, $\langle \mathcal{A}^\dagger g|f\rangle = \langle g|\mathcal{A} f\rangle$. Operator $\mathcal{A}^\dagger$ is called the *adjoint*[6] of $\mathcal{A}$. In general it is $\mathcal{A}^\dagger \neq \mathcal{A}$; however, for some operators it happens that $\mathcal{A}^\dagger = \mathcal{A}$. In this case, $\mathcal{A}$ is called Hermitean. Thus, for Hermitean operators the following holds:

$$\langle g|\mathcal{A} f\rangle = \langle \mathcal{A} g|f\rangle = \langle g|\mathcal{A}|f\rangle. \tag{8.21}$$

The notation on the right of (8.21) indicates that one can consider the operator as applied onto f or g. Examples of Hermitean operators are given in Sect. 8.6.1. It is found by inspection that, for any operator $\mathcal{C}$, the operators $\mathcal{S} = \mathcal{C} + \mathcal{C}^\dagger$ and $\mathcal{D} = -\mathrm{i}\,(\mathcal{C} - \mathcal{C}^\dagger)$ are Hermitean.

The following property is of use: a linear combination of Hermitean operator with real coefficients is Hermitean; considering, e.g., two Hermitean operators $\mathcal{A}$, $\mathcal{B}$ and two real numbers λ, μ, one finds

$$\int_\Omega g^* \, (\lambda\,\mathcal{A} + \mu\,\mathcal{B})\, f \, d\Omega = \int_\Omega [(\lambda\,\mathcal{A} + \mu\,\mathcal{B})\, g]^* \, f \, d\Omega. \tag{8.22}$$

8.4 Eigenvalues and Eigenfunctions of an Operator

A linear operator $\mathcal{A}$ may be used to generate a homogeneous equation (*eigenvalue equation*) in the unknown v, having the form

$$\mathcal{A} v = A\, v, \tag{8.23}$$

[5] In this context the term *operator* has the following meaning: if an operation brings each function f of a given function space into correspondence with one and only one function s of the same space, one says that this is obtained through the action of a given operator $\mathcal{A}$ onto f and writes $s = \mathcal{A} f$. A *linear* operator is such that $\mathcal{A}\,(c_1 f_1 + c_2 f_2) = c_1\,\mathcal{A} f_1 + c_2\,\mathcal{A} f_2$ for any pair of functions f_1, f_2 and of complex constants c_1, c_2 ([78], Chap. II.11).

[6] The adjoint operator is the counterpart of the conjugate-transpose matrix in vector algebra.

with A a parameter. Clearly (8.23) admits the solution $v = 0$ which, however, is of no interest; it is more important to find whether specific values of A exist (*eigenvalues*), such that (8.23) admits non-vanishing solutions (*eigenfunctions*). In general (8.23) must be supplemented with suitable boundary or regularity conditions on v.

The set of the eigenvalues of an operator found from (8.23) is the operator's *spectrum*. It may happen that the eigenvalues are distinguished by an index, or a set of indices, that take only discrete values; in this case the spectrum is called *discrete*. If, instead, the eigenvalues are distinguished by an index, or a set of indices, that vary continuously, the spectrum is *continuous*. Finally, it is *mixed* if a combination of discrete and continuous indices occurs.

An eigenvalue is *simple* if there is one and only one eigenfuction corresponding to it, while it is *degenerate of order s* if there are s linearly independent eigenfuctions corresponding to it. The order of degeneracy may also be infinite. By way of example, the Schrödinger equation for a free particle in one dimension discussed in Sect. 8.2.1 has a continuous spectrum of eigenvalues $E = \hbar^2 k^2/(2\,m)$ of index k, namely, $E = E_k$. Each eigenvalue is degenerate of order 2 because to each E there correspond two linearly-independent eigenfunctions $\exp(\mathrm{i}\,k\,x)$, $\exp(-\mathrm{i}\,k\,x)$, with $k = \sqrt{2\,m\,E}/\hbar$. Instead, the Schrödinger equation for a particle in a box discussed in Sect. 8.2.2 has a discrete spectrum of eigenvalues E_n given by the first relation in (8.6). Each eigenvalue is simple as already indicated in Sect. 8.2.2.

Let $v^{(1)}, \dots, v^{(s)}$ be the linearly-independent eigenfunctions belonging to an eigenvalue A degenerate of order s; then a linear combination of such eigenfunctions is also an eigenfunction belonging to A. In fact, letting $\alpha_1, \dots, \alpha_s$ be the coefficients of the linear combination, from $\mathcal{A}v^{(k)} = A\,v^{(k)}$ it follows

$$\mathcal{A}\sum_{k=1}^{s}\alpha_k\,v^{(k)} = \sum_{k=1}^{s}\alpha_k\mathcal{A}v^{(k)} = \sum_{k=1}^{s}\alpha_k\,A\,v^{(k)} = A\,\sum_{k=1}^{s}\alpha_k\,v^{(k)}. \tag{8.24}$$

8.4.1 Eigenvalues of Hermitean Operators

A fundamental property of the Hermitean operators is that their eigenvalues are real. Consider, first, the case where the eigenfunctions are square integrable, so that $\langle v|v\rangle$ is different from zero and finite. To proceed one considers the discrete spectrum, where the eigenvalues are A_n. Here n indicates a single index or also a set of indices. If the eigenvalue is simple, let v_n be the eigenfunction belonging to A_n; if it is degenerate, the same symbol v_n is used here to indicate any eigenfunction belonging to A_n. Then, two operations are performed: in the first one, the eigenvalue equation $\mathcal{A}v_n = A_n\,v_n$ is scalarly multiplied by v_n on the left, while in the second one the conjugate equation $(\mathcal{A}v_n)^* = A_n^*\,v_n^*$ is scalarly multiplied by v_n on the right. The operations yield, respectively,

$$\langle v_n|\mathcal{A}v_n\rangle = A_n\,\langle v_n|v_n\rangle, \qquad \langle\mathcal{A}v_n|v_n\rangle = A_n^*\,\langle v_n|v_n\rangle. \tag{8.25}$$

The left hand sides in (8.25) are equal to each other due to the hermiticity of $\mathcal{A}$; as a consequence, $A_n^* = A_n$, that is, A_n is real.

Another fundamental property of the Hermitean operators is that two eigenfunctions belonging to different eigenvalues are orthogonal to each other. Still considering the discrete spectrum, let A_m, A_n be two different eigenvalues and let v_m (v_n) be an eigenfunction belonging to A_m (A_n). The two eigenvalues are real as demonstrated earlier. Then, the eigenvalue equation $\mathcal{A}v_n = A_n\, v_n$ is scalarly multiplied by v_m on the left, while the conjugate equation for the other eigenvalue, $(\mathcal{A}v_m)^* = A_m\, v_m^*$, is scalarly multiplied by v_n on the right. The operations yield, respectively,

$$\langle v_m|\mathcal{A}v_n\rangle = A_n\,\langle v_m|v_n\rangle, \qquad \langle \mathcal{A}v_m|v_n\rangle = A_m\,\langle v_m|v_n\rangle. \tag{8.26}$$

The left hand sides in (8.26) are equal to each other due to the hermiticity of $\mathcal{A}$; as a consequence, $(A_m - A_n)\,\langle v_m|v_n\rangle = 0$. But $A_n \neq A_m$, so it is $\langle v_m|v_n\rangle = 0$.

8.4.2 Gram–Schmidt Orthogonalization

When two eigenfunctions belonging to a degenerate eigenvalue are considered, the reasoning that proves their orthogonality through (8.26) is not applicable because $A_n = A_m$. In fact, linearly-independent eigenfunctions of an operator $\mathcal{A}$ belonging to the same eigenvalue are not mutually orthogonal in general. However, it is possible to form mutually-orthogonal linear combinations of the eigenfunctions. As shown by (8.24), such linear combinations are also eigenfunctions, so their norm is different from zero. The procedure (*Gram–Schmidt orthogonalization*) is described here with reference to the case of the nth eigenfunction of a discrete spectrum, with a degeneracy of order s. Let the non-orthogonal eigenfunctions be $v_n^{(1)}, \dots, v_n^{(s)}$, and let $u_n^{(1)}, \dots, u_n^{(s)}$ be the linear combinations to be found. Then one prescribes $u_n^{(1)} = v_n^{(1)}$, $u_n^{(2)} = v_n^{(2)} + a_{21}\, u_n^{(1)}$ where a_{21} is such that $\langle u_n^{(1)}|u_n^{(2)}\rangle = 0$; thus

$$\langle u_n^{(1)}|v_n^{(2)}\rangle + a_{21}\,\langle u_n^{(1)}|u_n^{(1)}\rangle = 0, \qquad a_{21} = -\frac{\langle u_n^{(1)}|v_n^{(2)}\rangle}{\langle u_n^{(1)}|u_n^{(1)}\rangle}. \tag{8.27}$$

The next function is found be letting $u_n^{(3)} = v_n^{(3)} + a_{31}\, u_n^{(1)} + a_{32}\, u_n^{(2)}$, with $\langle u_n^{(1)}|u_n^{(3)}\rangle = 0$, $\langle u_n^{(2)}|u_n^{(3)}\rangle = 0$, whence

$$\langle u_n^{(1)}|v_n^{(3)}\rangle + a_{31}\,\langle u_n^{(1)}|u_n^{(1)}\rangle = 0, \qquad a_{31} = -\frac{\langle u_n^{(1)}|v_n^{(3)}\rangle}{\langle u_n^{(1)}|u_n^{(1)}\rangle}, \tag{8.28}$$

$$\langle u_n^{(2)}|v_n^{(3)}\rangle + a_{32}\,\langle u_n^{(2)}|u_n^{(2)}\rangle = 0, \qquad a_{32} = -\frac{\langle u_n^{(2)}|v_n^{(3)}\rangle}{\langle u_n^{(2)}|u_n^{(2)}\rangle}. \tag{8.29}$$

Similarly, the kth linear combination is built up recursively from the combinations of indices $1, \dots, k-1$:

$$u_n^{(k)} = v_n^{(k)} + \sum_{i=1}^{k-1} a_{ki}\, u_n^{(i)}, \qquad a_{ki} = -\frac{\langle u_n^{(i)}|v_n^{(k)}\rangle}{\langle u_n^{(i)}|u_n^{(i)}\rangle}. \tag{8.30}$$

The denominators in (8.30) are different from zero because they are the squared norms of the previously-defined combinations.

8.4.3 Completeness

As discussed in Sect. 8.2.1, the eigenfunctions of the Schrödinger equation for a free particle, for a given $k = \sqrt{2\,m\,E}/\hbar$ and apart from a multiplicative constant, are $w_{+k} = \exp(\mathrm{i}\,k\,x)$ and $w_{-k} = \exp(-\mathrm{i}\,k\,x)$. They may be written equivalently as $w(x,k) = \exp(\mathrm{i}\,k\,x)$, with $k = \pm\sqrt{2\,m\,E}/\hbar$. Taking the multiplicative constant equal to $1/\sqrt{2\,\pi}$, and considering a function f that fulfills the condition (C.19) for the Fourier representation, one applies (C.16) and (C.17) to find

$$f(x) = \int_{-\infty}^{+\infty} \frac{\exp(\mathrm{i}\,k\,x)}{\sqrt{2\,\pi}}\,c(k)\,\mathrm{d}k, \qquad c(k) = \int_{-\infty}^{+\infty} \frac{\exp(-\mathrm{i}\,k\,x)}{\sqrt{2\,\pi}}\,f(x)\,\mathrm{d}x. \quad (8.31)$$

Using the definition (8.13) of scalar product one recasts (8.31) as

$$f(x) = \int_{-\infty}^{+\infty} c(k)\,w(x,k)\,\mathrm{d}k, \qquad c(k) = \langle w|f\rangle. \quad (8.32)$$

In general the shorter notation $w_k(x)$, c_k is used instead of $w(x,k)$, $c(k)$. A set of functions like $w_k(x)$ that allows for the representation of f given by the first relation in (8.32) is said to be *complete*. Each member of the set is identified by the value of the continuous parameter k ranging from $-\infty$ to $+\infty$. To each k it corresponds a *coefficient* of the expansion, whose value is given by the second relation in (8.32).

Expressions (8.31) and (8.32) hold true because they provide the Fourier transform or antitransform of a function that fulfills (C.19). On the other hand, $w_k(x)$ is also the set of eigenfunctions of the free particle. In conclusion, the eigenfunctions of the Schrödinger equation for a free particle form a complete set.

The same conclusion is readily found for the eigenfunctions of the Schrödinger equation for a particle in a box. To show this, one considers a function $f(x)$ defined in an interval $[-\alpha/2, +\alpha/2]$ and fulfilling $\int_{-\alpha/2}^{+\alpha/2} |f(x)|\,\mathrm{d}x < \infty$. In this case the expansion into a Fourier series holds:

$$f(x) = \frac{1}{2}\,a_0 + \sum_{n=1}^{\infty} \left[a_n\,\cos(2\,\pi\,n\,x/\alpha) + b_n\,\sin(2\,\pi\,n\,x/\alpha)\right], \quad (8.33)$$

with $a_0/2 = \bar{f} = (1/\alpha)\int_{-\alpha/2}^{+\alpha/2} f(x)\,\mathrm{d}x$ the average of f over the interval, and

$$\begin{Bmatrix} a_n \\ b_n \end{Bmatrix} = \frac{2}{\alpha}\int_{-\alpha/2}^{+\alpha/2} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} \left(\frac{2\,\pi\,n\,x}{\alpha}\right) f(x)\,\mathrm{d}x, \qquad n = 1, 2, \ldots \quad (8.34)$$

Equality (8.33) indicates convergence in the mean, namely, using $g = f - \bar{f}$ for the sake of simplicity, (8.33) is equivalent to

$$\lim_{N\to\infty} \int_{-\alpha/2}^{+\alpha/2} \left\{ g - \sum_{n=1}^{N} \left[a_n\,\cos(2\,\pi\,n\,x/\alpha) + b_n\,\sin(2\,\pi\,n\,x/\alpha)\right] \right\}^2 \mathrm{d}x = 0. \quad (8.35)$$

Defining the auxiliary functions

$$\chi_n = \sqrt{2/\alpha}\,\cos(2\,\pi\,n\,x/\alpha), \qquad \sigma_n = \sqrt{2/\alpha}\,\sin(2\,\pi\,n\,x/\alpha), \tag{8.36}$$

a more compact notation is obtained, namely, $f = \bar{f} + \sum_{n=1}^{\infty} (\langle\chi_n|f\rangle\,\chi_n + \langle\sigma_n|f\rangle\,\sigma_n)$ or, observing that $\langle\sigma_n|\text{const}\rangle = \langle\chi_n|\text{const}\rangle = 0$,

$$g = \sum_{n=1}^{\infty} (\langle\chi_n|g\rangle\,\chi_n + \langle\sigma_n|g\rangle\,\sigma_n)\,. \tag{8.37}$$

The norm of the auxiliary functions (8.36) is unity, $\langle\chi_n|\chi_n\rangle = \langle\sigma_n|\sigma_n\rangle = 1$ for $n = 1, 2, \ldots$, and all auxiliary functions are mutually orthogonal: $\langle\chi_m|\chi_n\rangle = \langle\sigma_m|\sigma_n\rangle = 0$ for $n, m = 0, 1, 2, \ldots,\ m \neq n$, and $\langle\sigma_m|\chi_n\rangle = 0$ for $n, m = 0, 1, 2, \ldots$ A set whose functions have a norm equal to unity and are mutually orthogonal is called *orthonormal*. Next, (8.37) shows that the set $\chi_n, \sigma_n, n = 0, 1, 2, \ldots$ is complete in $[-\alpha/2, +\alpha/2]$ with respect to any g for which the expansion is allowed. Letting $c_{2n-1} = \langle\chi_n|g\rangle$, $c_{2n} = \langle\sigma_n|g\rangle$, $w_{2n-1} = \chi_n$, $w_{2n} = \sigma_n$, (8.37) takes the even more compact form

$$g = \sum_{m=1}^{\infty} c_m\,w_m, \qquad c_m = \langle w_m|g\rangle. \tag{8.38}$$

From the properties of the Fourier series it follows that the set of the σ_n functions alone is complete with respect to any function that is odd in $[-\alpha/2, +\alpha/2]$, hence it is complete with respect to any function over the half interval $[0, +\alpha/2]$. On the other hand, letting $a = \alpha/2$ and comparing with (8.8) shows that σ_n (apart from the normalization coefficient) is the eigenfunction of the Schrödinger equation for a particle in a box. In conclusion, the set of eigenfunctions of this equation is complete within $[0, a]$.

One notes the striking resemblance of the first relation in (8.38) with the vector-algebra expression of a vector in terms of its components c_m. The similarity is completed by the second relation in (8.38), that provides each component as the projection of g over w_m. The latter plays the same role as the unit vector in algebra, the difference being that the unit vectors here are functions and that their number is infinite. A further generalization of the same concept is given by (8.32), where the summation index k is continuous.

Expansions like (8.32) or (8.38) hold because $w_k(x)$ and $w_m(x)$ are complete sets, whose completeness is demonstrated in the theory of Fourier's integral or series; such a theory is readily extended to the three-dimensional case, showing that also the three-dimensional counterparts of $w_k(x)$ or $w_m(x)$ form complete sets (in this case the indices k or m are actually groups of indices, see, e.g., (9.5)). One may wonder whether other complete sets of functions exist, different from those considered in this section; the answer is positive: in fact, completeness is possessed by many other sets of functions,[7] and those of interest in Quantum Mechanics are made of the eigenfunctions of equations like (8.23). A number of examples will be discussed later.

8.4.4 Parseval Theorem

Consider the expansion of a complex function f with respect to a complete and orthonormal set of functions w_n,

$$f = \sum_n c_n\, w_n, \qquad c_n = \langle w_n | f \rangle, \qquad \langle w_n | w_m \rangle = \delta_{nm}, \tag{8.39}$$

where the last relation on the right expresses the set's orthonormality. As before, m indicates a single index or a group of indices. The squared norm of f reads

$$||f||^2 = \int_\Omega |f|^2\, d\Omega = \left\langle \sum_n c_n\, w_n | \sum_m c_m\, w_m \right\rangle. \tag{8.40}$$

Applying (8.17, 8.18) yields

$$||f||^2 = \sum_n c_n^* \sum_m c_m \langle w_n | w_m \rangle = \sum_n c_n^* \sum_m c_m\, \delta_{nm} = \sum_n |c_n|^2, \tag{8.41}$$

namely, the norm of the function equals the norm of the vector whose components are the expansion's coefficients (*Parseval theorem*). The result applies irrespective of the set that has been chosen for expanding f. The procedure leading to (8.41) must be repeated for the continuous spectrum, where the expansion reads

$$f = \int_\alpha c_\alpha\, w_\alpha\, d\alpha, \qquad c_\alpha = \langle w_\alpha | f \rangle. \tag{8.42}$$

Here a difficulty seems to arise, related to expressing the counterpart of the third relation in (8.39). Considering for the sake of simplicity the case where a single index is present, the scalar product $\langle w_\alpha | w_\beta \rangle$ must differ from zero only for $\beta = \alpha$, while it must vanish for $\beta \neq \alpha$ no matter how small the difference $\alpha - \beta$ is. In other terms, for a given value of α such a scalar product vanishes for any β apart from a null set. At the same time, it must provide a finite value when used as a factor within an integral. An example taken from the case of a free particle shows that the requirements listed above are mutually compatible. In fact, remembering the analysis of Sect. 8.4.3, the scalar product corresponding to the indices α and β reads

$$\langle w_\alpha | w_\beta \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\left[i\,(\beta - \alpha)\, x\right] dx = \delta(\alpha - \beta), \tag{8.43}$$

[7] The completeness of a set of eigenfunctions must be proven on a case-by-case basis.

where the last equality is taken from (C.43). As mentioned in Sect. C.4, such an equality can be used only within an integral. In conclusion,[8]

$$\int_{\Omega} |f|^2 \, \mathrm{d}\Omega = \langle f | f \rangle = \int_{-\infty}^{+\infty} c_\alpha^* \, \mathrm{d}\alpha \int_{-\infty}^{+\infty} c_\beta \, \delta(\alpha - \beta) \, \mathrm{d}\beta = \int_{-\infty}^{+\infty} |c_\alpha|^2 \, \mathrm{d}\alpha. \tag{8.44}$$

One notes that (8.44) generalizes a theorem of Fourier's analysis that states that the norm of a function equals that of its transform.

8.5 Hamiltonian Operator and Momentum Operator

As mentioned in Sect. 7.5, the form (7.45) of the time-independent Schrödinger equation holds only when the force is conservative. It is readily recast in the more compact form (8.23) by defining the *Hamiltonian operator*

$$\mathcal{H} = -\frac{\hbar^2}{2\,m} \nabla^2 + V, \tag{8.45}$$

that is, a linear, real operator that gives (7.45) the form

$$\mathcal{H} w = E\, w. \tag{8.46}$$

The term used to denote $\mathcal{H}$ stems from the formal similarity of (8.46) with the classical expression $H(\mathbf{p}, \mathbf{q}) = E$ of a particle's total energy in a conservative field, where $H = T + V$ is the Hamiltonian function (Sect. 1.5). By this similarity, the classical kinetic energy $T = p^2/(2m)$ corresponds to the kinetic operator $\mathcal{T} = -\hbar^2/(2\,m)\,\nabla^2$; such a correspondence reads

$$T = \frac{1}{2\,m} \left(p_1^2 + p_2^2 + p_3^2 \right) \quad \Longleftrightarrow \quad \mathcal{T} = -\frac{\hbar^2}{2\,m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right). \tag{8.47}$$

The units of $\mathcal{T}$ are those of an energy, hence $\hbar^2 \nabla^2$ has the units of a momentum squared. One notes that to transform T into $\mathcal{T}$ one must replace each component of momentum by a first-order operator as follows:

$$p_i \Leftarrow \hat{p}_i = -\mathrm{i}\,\hbar \frac{\partial}{\partial x_i}, \tag{8.48}$$

where $\hat{p}_i$ is called *momentum operator*. The correspondence (8.47) would still hold if the minus sign in (8.48) were omitted. However, the minus sign is essential for

[8] The relation (8.44) is given here with reference to the specific example of the free particle's eigenfunctions. For other cases of continuous spectrum the relation $\langle w_\alpha | w_\beta \rangle = \delta(\alpha - \beta)$ is proven on a case-by-case basis.

a correct description of the particle's motion.[9] From the results of Sect. 8.6.1 one finds that the momentum operator and its three-dimensional form $\hat{\mathbf{p}} = -\mathrm{i}\,\hbar\,\mathrm{grad}$ are Hermitean for square-integrable functions. Their units are those of a momentum. The Hamiltonian operator (8.45) is a real-coefficient, linear combination of ∇^2 and V; combining (8.22) with the findings of Sect. 8.6 shows that (8.45) is Hermitean for square-integrable functions.

The one-dimensional form of the momentum operator yields the eigenvalue equation

$$-\mathrm{i}\,\hbar\,\frac{\mathrm{d}v}{\mathrm{d}x} = \tilde{p}\,v, \tag{8.49}$$

where $\tilde{p}$ has the units of a momentum. The solution of (8.49) is $v = \text{const} \times \exp(\mathrm{i}\,\tilde{p}/\hbar)$, where $\tilde{p}$ must be real to prevent the solution from diverging. Letting $\text{const} = 1/\sqrt{2\,\pi}$, $k = \tilde{p}/\hbar$ yields $v = v_k(x) = \exp(\mathrm{i}\,k\,x)/\sqrt{2\,\pi}$, showing that the eigenfunctions of the momentum operator form a complete set (compare with (8.31)) and are mutually orthogonal (compare with (8.43)). As $|v_k(x)|^2 = 1/(2\,\pi)$, the eigenfunctions are not square integrable; the spectrum is continuous because the eigenvalue $\hbar\,k$ can be any real number.

8.6 Complements

8.6.1 Examples of Hermitean Operators

A real function V, depending on the spatial coordinates over the domain Ω, and possibly on other variables $\alpha, \beta, \ldots$, may be thought of as a purely multiplicative operator. Such an operator is Hermitean; in fact,

$$\int_\Omega g^*\,V\,f\,\mathrm{d}\Omega = \int_\Omega V\,g^*\,f\,\mathrm{d}\Omega = \int_\Omega (V g)^*\,f\,\mathrm{d}\Omega. \tag{8.50}$$

In contrast, an imaginary function $W = \mathrm{i}\,V$, with V real, is not Hermitean because

$$\langle g|W\,f\rangle = -\langle W\,g|f\rangle. \tag{8.51}$$

Any operator that fulfills a relation similar to (8.51) is called *anti-Hermitean* or *skew-Hermitean*.

As a second example consider a one-dimensional case defined over a domain Ω belonging to the x axis. It is easily shown that the operator $(\mathrm{i}\,\mathrm{d}/\mathrm{d}x)$ is Hermitean: in

[9] Consider for instance the calculation of the expectation value of the momentum of a free particle based on (10.18). If the minus sign were omitted in (8.48), the direction of momentum would be opposite to that of the propagation of the wave front associated to it.

fact, integrating by parts and observing that the integrated part vanishes because f and g are square integrable, yields

$$\int_\Omega g^* \,\mathrm{i}\, \frac{\mathrm{d}f}{\mathrm{d}x}\, \mathrm{d}\Omega = \left[g^* \,\mathrm{i}\, f\right]_\Omega - \int_\Omega \mathrm{i}\, \frac{\mathrm{d}g^*}{\mathrm{d}x}\, f\, \mathrm{d}\Omega = \int_\Omega \left(\mathrm{i}\, \frac{\mathrm{d}g}{\mathrm{d}x}\right)^* f\, \mathrm{d}\Omega. \tag{8.52}$$

By the same token one shows that the operator $\mathrm{d}/\mathrm{d}x$ is skew-Hermitean. The three-dimensional generalization of $(\mathrm{i}\,\mathrm{d}/\mathrm{d}x)$ is $(\mathrm{i}\,\mathrm{grad})$. Applying the latter onto the product $g^* f$ yields $g^* \,\mathrm{i}\,\mathrm{grad} f - (\mathrm{i}\,\mathrm{grad} g)^* f$. Integrating over Ω with Σ the boundary of Ω and $\mathbf{n}$ the unit vector normal to it, yields

$$\int_\Omega g^* \,\mathrm{i}\,\mathrm{grad} f\, \mathrm{d}\Omega - \int_\Omega (\mathrm{i}\,\mathrm{grad} g)^*\, f\, \mathrm{d}\Omega = \mathrm{i} \int_\Sigma g^* f\, \mathbf{n}\, \mathrm{d}\Sigma. \tag{8.53}$$

The form of the right hand side of (8.53) is due to (A.25). As f, g vanish over the boundary, it follows $\langle g|\mathrm{i}\,\mathrm{grad} f\rangle = \langle \mathrm{i}\,\mathrm{grad} g|f\rangle$, namely, (i grad) is Hermitean.

Another important example, still in the one-dimensional case, is that of the operator $\mathrm{d}^2/\mathrm{d}x^2$. Integrating by parts twice shows that the operator is Hermitean. Its three-dimensional generalization in Cartesian coordinates is ∇^2. Using the second Green theorem (A.25) and remembering that f, g vanish over the boundary provides $\langle g|\nabla^2 f\rangle = \langle \nabla^2 g|f\rangle$, that is, ∇^2 is Hermitean.

8.6.2 A Collection of Operators' Definitions and Properties

A number of definitions and properties of operator algebra are illustrated in this section. The *identity operator* $\mathcal{I}$ is such that $\mathcal{I} f = f$ for all f; the *null operator* $\mathcal{O}$ is such that $\mathcal{O} f = 0$ for all f. The product of two operators, $\mathcal{AB}$, is an operator whose action on a function is defined as follows: $s = \mathcal{AB} f$ is equivalent to $g = \mathcal{B} f$, $s = \mathcal{A} g$; in other terms, the operators $\mathcal{A}$ and $\mathcal{B}$ act in a specific order. In general, $\mathcal{BA} \ne \mathcal{AB}$. The operators $\mathcal{AA}$, $\mathcal{AAA}, \dots$ are indicated with $\mathcal{A}^2$, $\mathcal{A}^3, \dots$

An operator $\mathcal{A}$ may or may not have an *inverse*, $\mathcal{A}^{-1}$. If the inverse exists, it is unique and has the property $\mathcal{A}^{-1}\mathcal{A} f = f$ for all f. Left multiplying the above by $\mathcal{A}$ and letting $g = \mathcal{A} f$ yields $\mathcal{A}\mathcal{A}^{-1} g = g$ for all g. The two relations just found can be recast as

$$\mathcal{A}^{-1}\mathcal{A} = \mathcal{A}\mathcal{A}^{-1} = \mathcal{I}. \tag{8.54}$$

From (8.54) it follows $(\mathcal{A}^{-1})^{-1} = \mathcal{A}$. If $\mathcal{A}$ and $\mathcal{B}$ have an inverse, letting $\mathcal{C} = \mathcal{B}^{-1}\mathcal{A}^{-1}$ one finds, for all f and using the associative property, the two relations $\mathcal{BC} f = \mathcal{B}\mathcal{B}^{-1}\mathcal{A}^{-1} f = \mathcal{A}^{-1} f$ and $\mathcal{ABC} f = \mathcal{A}\mathcal{A}^{-1} f = f$, namely, $\mathcal{ABC} = \mathcal{I}$; in conclusion,

$$(\mathcal{AB})^{-1} = \mathcal{B}^{-1}\mathcal{A}^{-1}. \tag{8.55}$$

From (8.55) one defines the inverse powers of $\mathcal{A}$ as

$$\mathcal{A}^{-2} = (\mathcal{A}^2)^{-1} = (\mathcal{A}\mathcal{A})^{-1} = \mathcal{A}^{-1}\mathcal{A}^{-1}, \tag{8.56}$$

and so on. Let $\mathcal{A}v = \lambda v$ be the eigenvalue equation of $\mathcal{A}$. Successive left multiplications by $\mathcal{A}$ yield

$$\mathcal{A}^2 v = \lambda^2 v, \quad \mathcal{A}^3 v = \lambda^3 v, \quad \dots \tag{8.57}$$

As a consequence, an operator of the polynomial form

$$P_n(\mathcal{A}) = c_0\,\mathcal{A}^n + c_1\,\mathcal{A}^{n-1} + c_2\,\mathcal{A}^{n-2} + \dots + c_n \tag{8.58}$$

fulfills the eigenvalue equation

$$P_n(\mathcal{A})\,v = P_n(\lambda)\,v, \qquad P_n(\lambda) = c_0\,\lambda^n + \dots + c_n. \tag{8.59}$$

By definition, an eigenfunction can not vanish identically. If $\mathcal{A}$ has an inverse, left-multiplying the eigenvalue equation $\mathcal{A}v = \lambda v$ by $\mathcal{A}^{-1}$ yields $v = \lambda\,\mathcal{A}^{-1}v \neq 0$, whence $\lambda \neq 0$. Dividing the latter by λ and iterating the procedure shows that

$$\mathcal{A}^{-2} v = \lambda^{-2} v, \quad \mathcal{A}^{-3} v = \lambda^{-3} v, \quad \dots \tag{8.60}$$

An operator may be defined by a series expansion, if the latter converges:

$$\mathcal{C} = \sigma(\mathcal{A}) = \sum_{k=-\infty}^{+\infty} c_k\,\mathcal{A}^k. \tag{8.61}$$

By way of example,

$$\mathcal{C} = \exp(\mathcal{A}) = \mathcal{I} + \mathcal{A} + \frac{1}{2!}\,\mathcal{A}^2 + \frac{1}{3!}\,\mathcal{A}^3 + \dots \tag{8.62}$$

Given an operator $\mathcal{A}$, its adjoint $\mathcal{A}^\dagger$ is defined as in Sect. 8.3.1. Letting $\mathcal{C} = \mathcal{A}^\dagger$, applying the definition of adjoint operator to $\mathcal{C}$, and taking the conjugate of both sides shows that $(\mathcal{A}^\dagger)^\dagger = \mathcal{A}$. From the definition of adjoint operator it also follows

$$(\mathcal{A}\mathcal{B})^\dagger = \mathcal{B}^\dagger\mathcal{A}^\dagger. \tag{8.63}$$

An operator is *unitary* if its inverse is identical to its adjoint for all f:

$$\mathcal{A}^{-1} f = \mathcal{A}^\dagger f. \tag{8.64}$$

Left multiplying (8.64) by $\mathcal{A}$, and left multiplying the result by $\mathcal{A}^\dagger$, yields for a unitary operator

$$\mathcal{A}\mathcal{A}^\dagger = \mathcal{A}^\dagger\mathcal{A} = \mathcal{I}. \tag{8.65}$$

The application of a unitary operator to a function f leaves the norm of the latter unchanged. In fact, using definition (8.12), namely, $||f||^2 = \langle f| \, f\rangle$, and letting $g = \mathcal{A} f$ with $\mathcal{A}$ unitary, yields

$$||g||^2 = \int_\Omega (\mathcal{A} f)^* \mathcal{A} f \, \mathrm{d}\Omega = \int_\Omega (\mathcal{A}^\dagger \mathcal{A} f)^* f \, \mathrm{d}\Omega = \int_\Omega f^* f \, \mathrm{d}\Omega = ||f||^2, \quad (8.66)$$

where the second equality holds due to the definition of adjoint operator, and the third one holds because $\mathcal{A}$ is unitary. The inverse also holds true: if the application of $\mathcal{A}$ leaves the function's norm unchanged, that is, if $||\mathcal{A} f|| = ||f||$ for all f, then

$$\int_\Omega (\mathcal{A}^\dagger \mathcal{A} f - f)^* f \, \mathrm{d}\Omega = 0. \quad (8.67)$$

As a consequence, the quantity in parenthesis must vanish, whence the operator is unitary. The product of two unitary operators is unitary:

$$(\mathcal{A}\mathcal{B})^{-1} = \mathcal{B}^{-1}\mathcal{A}^{-1} = \mathcal{B}^\dagger \mathcal{A}^\dagger = (\mathcal{A}\mathcal{B})^\dagger, \quad (8.68)$$

where the second equality holds because $\mathcal{A}$ and $\mathcal{B}$ are unitary. The eigenvalues of a unitary operator have the form $\exp(\mathrm{i}\,\nu)$, with ν a real number. Let an eigenvalue equation be $\mathcal{A} v = \lambda v$, with $\mathcal{A}$ unitary. The following hold,

$$\int_\Omega |\mathcal{A} v|^2 \, \mathrm{d}\Omega = |\lambda|^2 \int_\Omega |v|^2 \, \mathrm{d}\Omega, \qquad \int_\Omega |\mathcal{A} v|^2 \, \mathrm{d}\Omega = \int_\Omega |v|^2 \, \mathrm{d}\Omega, \quad (8.69)$$

the first one because of the eigenvalue equation, the second one because $\mathcal{A}$ is unitary. As an eigenfunction can not vanish identically, it follows $|\lambda|^2 = 1$ whence $\lambda = \exp(\mathrm{i}\,\nu)$. It is also seen by inspection that, if the eigenvalues of an operator have the form $\exp(\mathrm{i}\,\nu)$, with ν a real number, then the operator is unitary.

It has been anticipated above that in general it is $\mathcal{B}\mathcal{A} \neq \mathcal{A}\mathcal{B}$. Two operators $\mathcal{A}$, $\mathcal{B}$ are said to *commute* if

$$\mathcal{B}\mathcal{A} f = \mathcal{A}\mathcal{B} f \quad (8.70)$$

for all f. The *commutator* of $\mathcal{A}$, $\mathcal{B}$ is the operator $\mathcal{C}$ such that

$$\mathrm{i}\,\mathcal{C} f = (\mathcal{A}\mathcal{B} - \mathcal{B}\mathcal{A})\, f \quad (8.71)$$

for all f. The definition (8.71) is such that, if both $\mathcal{A}$ and $\mathcal{B}$ are Hermitean, then $\mathcal{C}$ is Hermitean as well. The commutator of two commuting operators is the null operator. A very important example of non-commuting operators is the pair q, $-\mathrm{i}\,\mathrm{d}/\mathrm{d}q$, where q is any dynamical variable. One finds

$$\mathrm{i}\,\mathcal{C} f = -\mathrm{i}\, q \,\frac{\mathrm{d}f}{\mathrm{d}q} + \mathrm{i}\,\frac{\mathrm{d}(q\, f)}{\mathrm{d}q} = \mathrm{i}\, f, \quad (8.72)$$

namely, the commutator is in this case the identity operator $\mathcal{I}$.

8.6.3 Examples of Commuting Operators

Operators that contain only spatial coordinates commute; similarly, operators that contain only momentum operators commute. The operators $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ defined in (10.4) commute because they act on different coordinates; note that the definition of $\mathcal{A}$ is such that it may contain both x and $\hat{p}_x = -\mathrm{i}\,\hbar\,\partial/\partial x$, and so on.

As an example of operators containing only momentum operators one may consider the Hamiltonian operator $-(\hbar^2/2\,m)\,\nabla^2$ of a free particle discussed in Sect. 8.2.1 and the momentum operator $-\mathrm{i}\,\hbar\,\nabla$ itself (Sect. 8.5). As for a free particle they commute, a measurement of momentum is compatible in that case with a measurement of energy (Sect. 8.6.4). Considering a one-dimensional problem, the energy is $E = p^2/(2\,m)$, where the modulus of momentum is given by $p = \hbar\,k$; for a free particle, both energy and momentum are conserved. The eigenfunctions are const $\times \exp(\pm\,\mathrm{i}\,p\,x/\hbar)$ for both operators.

Remembering (8.72) one concludes that two operators do not commute if one of them contains one coordinate q, and the other one contains the operator $-\mathrm{i}\,\hbar\,\partial/\partial q$ associated to the momentum conjugate to q.

8.6.4 Momentum and Energy of a Free Particle

The eigenfunctions of the momentum operator are the same as those of the Schrödinger equation for a free particle. More specifically, given the sign of $\tilde{p}$, the solution of (8.49) concides with either one or the other of the two linearly-independent solutions of (8.1). This outcome is coherent with the conclusions reached in Sect. 8.2.1 about the free particle's motion. For a free particle whose momentum is prescribed, the energy is purely kinetic and is prescribed as well, whence the solution of (8.49) must be compatible with that of (8.1). However, prescribing the momentum, both in modulus and direction, for a free particle, provides the additional information that allows one to eliminate one of the two summands from the linear combination (8.2) by setting either c_1 or c_2 to zero. For a given eigenvalue $\tilde{p}$, (8.49) has only one solution (apart from the multiplicative constant) because it is a first-order equation; in contrast, for a given eigenvalue E, the second-order equation (8.1) has two independent solutions and its general solution is a linear combination of them.

In a broader sense the momentum operator $\hat{p}_x = -\mathrm{i}\,\hbar\,\mathrm{d}/\mathrm{d}x$ is Hermitean also for functions of the form $v_k(x) = \exp(\mathrm{i}\,k\,x)/\sqrt{2\,\pi}$, which are not square integrable. In fact, remembering (C.43) one finds

$$\langle v_{k'}|\hat{p}_x v_k\rangle = -\frac{\mathrm{i}\,\hbar}{2\,\pi}\int_{-\infty}^{+\infty}\exp(-\,\mathrm{i}\,k'\,x)\,\frac{\mathrm{d}}{\mathrm{d}x}\exp(\mathrm{i}\,k\,x)\,\mathrm{d}x = \hbar\,k\,\delta(k'-k). \quad (8.73)$$

Similarly it is $\langle \hat{p}_x v_{k'}|v_k\rangle = \hbar\,k'\,\delta(k'-k)$. As mentioned in Sect. C.4, the two equalities just found can be used only within an integral over k or k'. In that case, however, they yield the same result $\hbar\,k$. By the same token one shows that

$$\langle v_{k'}|\hat{p}_x^2 v_k\rangle = \hbar^2\,k^2\,\delta(k'-k), \qquad \langle \hat{p}_x^2 v_{k'}|v_k\rangle = \hbar^2\,(k')^2\,\delta(k'-k), \quad (8.74)$$

hence the Laplacian operator is Hermitean in a broader sense for non-square-integrable functions of the form $v_k(x) = \exp(\mathrm{i}\,k\,x)/\sqrt{2\,\pi}$.

Problems

8.1 The one-dimensional, time-independent Schrödinger equation is a homogeneous equation of the form

$$w'' + q\,w = 0, \qquad q = q(x), \tag{8.75}$$

where primes indicate derivatives. In turn, the most general, linear equation of the second order with a non-vanishing coefficient of the highest derivative is

$$f'' + a\,f' + b\,f = c, \qquad a = a(x), \quad b = b(x), \quad c = c(x). \tag{8.76}$$

Assume that a is differentiable. Show that if the solution of (8.75) is known, then the solution of (8.76) is obtained from the former by simple integrations.