5 Operators (II)

5.1 Hermitian operators

An operator $\hat{A}$ is said to be Hermitian when

$$\langle\phi|\hat{A}|\psi\rangle = \langle\psi|\hat{A}|\phi\rangle^* \tag{5.1}$$

for any vectors $|\phi\rangle$ and $|\psi\rangle$ this operator may act on. Many of the important operators of Quantum Mechanics are Hermitian, although not quite all of them.

☞ It should be noted that this definition does not require an operator to be equal to its adjoint in order to be Hermitian — i.e., it does not say, and does not necessarily imply, that

$$\hat{A} = \hat{A}^\dagger. \tag{5.2}$$

Eq. (5.1) refers only to the action of $\hat{A}$ on the vectors in the domain of $\hat{A}$, irrespective of the domain of $\hat{A}^\dagger$. Eq. (5.2) says that $\hat{A}$ not only satisfies Eq. (5.1) but also that $\hat{A}$ and $\hat{A}^\dagger$ have the same domain. An operator satisfying Eq. (5.2) is said to be self-adjoint. An operator which is self-adjoint is also Hermitian but the converse is not true; some operators are Hermitian but not self-adjoint (an example is given below). The distinction between Hermiticity and self-adjointness is of key importance in Mathematics. Physical quantities such as the energy, the linear momentum and the orbital angular momentum correspond to operators that are self-adjoint, not merely Hermitian. Why this needs to be so will be addressed later in the course.

Let us take an example. The z-component of the angular momentum of a particle (specifically, the "orbital angular momentum" of that particle) can be shown to correspond to an operator

$$L_z = -i\hbar\,\frac{\partial}{\partial\phi}, \tag{5.3}$$

where ϕ is the azimuth angle of the particle in spherical polar coordinates. Suppose that we take the domain of L_z to be the space of all differentiable square-integrable functions $y(\phi)$ defined on $[0, 2\pi]$ and such that $y(0) = y(2\pi) = 0$. L_z is Hermitian in that space, since, if $f(\phi)$ and $g(\phi)$ are two such functions,

$$\begin{aligned}\int_0^{2\pi} f^*(\phi)\, L_z\, g(\phi)\,\mathrm{d}\phi &= -i\hbar\int_0^{2\pi} f^*(\phi)\,\frac{\partial g}{\partial\phi}\,\mathrm{d}\phi \\ &= -i\hbar\, f^*(\phi)g(\phi)\Big|_0^{2\pi} + i\hbar\int_0^{2\pi}\frac{\partial f^*}{\partial\phi}\,g(\phi)\,\mathrm{d}\phi \\ &= \left[-i\hbar\int_0^{2\pi} g^*(\phi)\frac{\partial f}{\partial\phi}\,\mathrm{d}\phi\right]^*,\end{aligned} \tag{5.4}$$

and therefore

$$\int_0^{2\pi} f^*(\phi)\, L_z\, g(\phi)\, \mathrm{d}\phi = \left[\int_0^{2\pi} g^*(\phi)\, L_z\, f(\phi)\, \mathrm{d}\phi \right]^* . \qquad (5.5)$$

(The boundary term vanishes since $g(0) = g(2\pi) = 0$ if $g(\phi)$ is in the domain of L_z.) However, so defined, L_z is not self-adjoint: The domain of the adjoint of L_z would indeed be the set of all the functions $f(\phi)$ such that, for any function $g(\phi)$ in the domain of L_z,

$$-i\hbar \int_0^{2\pi} f^*(\phi)\, \frac{\partial g}{\partial \phi}\, \mathrm{d}\phi = \left[-i\hbar \int_0^{2\pi} g^*(\phi) \frac{\partial f}{\partial \phi}\, \mathrm{d}\phi \right]^* , \qquad (5.6)$$

and this set includes functions $f(\phi)$ which are finite but non-zero at $\phi = 0$ or at $\phi = 2\pi$ and therefore do not belong to the domain of L_z (the boundary term vanishes for any function $f(\phi)$ finite at $\phi = 0$ and $\phi = 2\pi$, as long as $g(0) = g(2\pi) = 0$).

By contrast, L_z is not only Hermitian but also self-adjoint if we take its domain to be the space of all differentiable square-integrable functions $y(\phi)$ defined on $[0, 2\pi]$ and such that $y(0) = y(2\pi)$ (i.e., we do not longer require that $y(\phi)$ vanishes at $\phi = 0$ and $\phi = 2\pi$). Indeed, in order for the boundary term

$$-i\hbar\, [f^*(2\pi)g(2\pi) - f^*(0)g(0)]$$

to be zero for any function $g(\phi)$ such that $g(0) = g(2\pi)$, it is necessary that $f(0) = f(2\pi)$. The domain of the adjoint of L_z coincides with the domain of L_z in this case.

That the domain of L_z matters is illustrated by the fact that this operator has *no* eigenfunctions if we require that $y(0) = y(2\pi) = 0$, and that it has *infinitely many* eigenfunctions if we only require that $y(0) = y(2\pi)$. (Explanation: any eigenfunction of L_z must be of the form $\exp[i(\lambda/\hbar)\phi]$. There is no value of λ for which an exponential function of this form vanishes both at $\phi = 0$ and at $\phi = 2\pi$; however, $\exp[i(\lambda/\hbar)0] = \exp[i(\lambda/\hbar)2\pi]$ for $\lambda = 0,\ \pm\hbar,\ \pm 2\hbar, \ldots$)

☞ The terminology is a bit confused. In Mathematics, an operator satisfying Eq. (5.1) is said to be symmetric. The term “Hermitian” is generally used in Physics for the same. It is also used in Mathematics, often as a synonym of “symmetric” but sometimes to refer only to a particular kind of symmetric operators. Many physicists use the word “Hermitian” as a synonym of “self-adjoint” (which, as noted above, is fraught mathematically).

☞ Although it is worth keeping in mind that, mathematically speaking, “Hermitian” is not the same as “self-adjoint”, there is actually no difference between the two in finite-dimensional spaces: any Hermitian operator defined in a finite-dimensional space is also self-adjoint. This is not the case for operators defined in an infinite-dimensional space.

Examples

- The spin operator represented by the matrix
$$S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{5.7}$$
is Hermitian since, for any 2-component column vectors χ and χ', $(\chi, S_y\chi') = (\chi', S_y\chi)^*$:
$$\begin{aligned}\begin{pmatrix} a^* & b^* \end{pmatrix} \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} a' \\ b' \end{pmatrix} &= \frac{\hbar}{2}\begin{pmatrix} a^* & b^* \end{pmatrix}\begin{pmatrix} -ib' \\ ia' \end{pmatrix} = -i\hbar(a^*b' - a'b^*)/2 \\ &= \left[-i\hbar(a'^*b - ab'^*)/2\right]^* = \left[\frac{\hbar}{2}\begin{pmatrix} a'^* & b'^* \end{pmatrix}\begin{pmatrix} -ib \\ ia \end{pmatrix}\right]^* \\ &= \left[\begin{pmatrix} a'^* & b'^* \end{pmatrix}\frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix}\right]^*. \end{aligned} \tag{5.8}$$

- One of the systems you have studied in your level 1 Quantum Mechanics course was that formed by a particle of mass m submitted to no force between $x = -a$ and $x = a$ but confined to that interval by impenetrable potential barriers at $x = \pm a$. The Hamiltonian for this problem can be taken to be
$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}, \tag{5.9}$$
considered as an operator acting on twice-differentiable, square-integrable functions of x which vanish at $x = -a$ and $x = a$. This operator is Hermitian since for any such functions,
$$\begin{aligned}\int_{-a}^{a}\phi^*(x)\,H\,\psi(x)\,\mathrm{d}x &= -\frac{\hbar^2}{2m}\int_{-a}^{a}\phi^*(x)\,\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x \\ &= -\frac{\hbar^2}{2m}\left[\phi^*(x)\,\frac{\mathrm{d}\psi}{\mathrm{d}x}\bigg|_{-a}^{a} - \int_{-a}^{a}\frac{\mathrm{d}\phi^*}{\mathrm{d}x}\,\frac{\mathrm{d}\psi}{\mathrm{d}x}\,\mathrm{d}x\right] \\ &= -\frac{\hbar^2}{2m}\left[\phi^*(x)\,\frac{\mathrm{d}\psi}{\mathrm{d}x}\bigg|_{-a}^{a} - \frac{\mathrm{d}\phi^*}{\mathrm{d}x}\,\psi(x)\bigg|_{-a}^{a} + \int_{-a}^{a}\frac{\mathrm{d}^2\phi^*}{\mathrm{d}x^2}\,\psi(x)\,\mathrm{d}x\right] \\ &= -\frac{\hbar^2}{2m}\left[\int_{-a}^{a}\frac{\mathrm{d}^2\phi^*}{\mathrm{d}x^2}\,\psi(x)\,\mathrm{d}x\right] \\ &= -\frac{\hbar^2}{2m}\left[\int_{-a}^{a}\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\,\psi^*(x)\,\mathrm{d}x\right]^* = \left[\int_{-a}^{a}\psi^*(x)\,H\,\phi(x)\,\mathrm{d}x\right]^*. \end{aligned} \tag{5.10}$$
(The boundary terms vanish since $\phi^*(\pm a) = \psi(\pm a) = 0$.)

- The ladder operators a_+ and a_- are non Hermitian. (The proof of this assertion is left as an exercise.)

Real eigenvalues and orthogonal eigenvectors

The eigenvalues of a Hermitian operator are always real.

> Proof: Let us suppose that $\hat{A}$ is a Hermitian operator and that there exists a non-zero vector $|\psi\rangle$ such that $\hat{A}|\psi\rangle = \lambda|\psi\rangle$. (We assume that $|\psi\rangle$ is non-zero because the zero vector is never considered to be an eigenvector.) Since $\hat{A}$ is Hermitian, we must have, from Eq. (5.1), that $\langle\psi|\hat{A}|\psi\rangle = \langle\psi|\hat{A}|\psi\rangle^*$. But $\langle\psi|\hat{A}|\psi\rangle = \lambda\langle\psi|\psi\rangle$ since $\hat{A}|\psi\rangle = \lambda|\psi\rangle$. Thus $\lambda\langle\psi|\psi\rangle = \lambda^*\langle\psi|\psi\rangle^*$, which implies that $\lambda = \lambda^*$ since $\langle\psi|\psi\rangle^* = \langle\psi|\psi\rangle \neq 0$. (Recall the axioms of the inner product and our assumption that $|\psi\rangle$ is not the zero vector). $\square$

Eigenvectors of a Hermitian operator corresponding to different eigenvalues are always orthogonal.

> Proof: Suppose that $\hat{A}$ is a Hermitian operator, and also that $\hat{A}|\psi_1\rangle = \lambda_1|\psi_1\rangle$ and $\hat{A}|\psi_2\rangle = \lambda_2|\psi_2\rangle$ with $\lambda_1 \neq \lambda_2$. Thus
>
> $$\langle\psi_2|\hat{A}|\psi_1\rangle = \lambda_1\langle\psi_2|\psi_1\rangle, \tag{5.11}$$
> $$\langle\psi_1|\hat{A}|\psi_2\rangle = \lambda_2\langle\psi_1|\psi_2\rangle. \tag{5.12}$$
>
> But $\langle\psi_1|\hat{A}|\psi_2\rangle = \langle\psi_2|\hat{A}|\psi_1\rangle^*$ since $\hat{A}$ is Hermitian, and $\lambda_2 = \lambda_2^*$ since the eigenvalues of a Hermitian operator are real. Moreover, $\langle\psi_2|\psi_1\rangle = \langle\psi_2|\psi_1\rangle^*$ from the axioms of the inner product. Complex conjugating Eq. (5.12) thus gives $\langle\psi_2|\hat{A}|\psi_1\rangle = \lambda_2\langle\psi_2|\psi_1\rangle$. Subtracting this last equation from Eq. (5.11) yields $(\lambda_1-\lambda_2)\langle\psi_2|\psi_1\rangle = 0$. Therefore $\langle\psi_2|\psi_1\rangle = 0$. (Remember that we assume that $\lambda_1 \neq \lambda_2$.) $\square$

It is worth noting that not all Hermitian operators have eigenvalues and eigenvectors and that non-Hermitian operators may also have real eigenvalues or orthogonal eigenvectors. However, if an operator is Hermitian, one can be sure that its eigenvalues and eigenvector (if any) have these two important properties.

Hermitian matrices

Matrices representing Hermitian operators are Hermitian. Recall that a Hermitian matrix is one equal to its conjugate transpose — e.g., for 2×2 matrices, a matrix such that

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} a^* & c^* \\ b^* & d^* \end{pmatrix}. \tag{5.13}$$

(The proof of this assertion is left as a short exercise.)

5.2 Projectors and the completeness relation

We start with a definition: An operator $\hat{A}$ is said to be idempotent if $\hat{A}^2 = \hat{A}$ (i.e., if $\hat{A}(\hat{A}|\psi\rangle) \equiv \hat{A}|\psi\rangle$ for any vector $|\psi\rangle$ the operator $\hat{A}$ acts on).

Now, suppose that you are interested in a certain subspace V' of the whole vector space, V. Specifying V' is also specifying another subspace of V, namely the space $V'^{\perp}$ containing all the vectors of V that are orthogonal to every vector of V'. It is intuitively clear, and can be shown rigorously, that a vector v belonging to V can always be written as the sum of a vector v' belonging to V' and a vector $v'^{\perp}$ belonging to $V'^{\perp}$, and that there is only one way of doing so. For example, arrow vectors parallel to the x-axis form a subspace of the whole vector space of 3D geometric vectors, and any 3D geometric vector $\mathbf{v}$ can be written as the sum of a vector $\mathbf{v}'$ parallel the x-direction and a vector $\mathbf{v}'^{\perp}$ orthogonal to that direction (thus parallel to the yz-plane). In terms of Cartesian components, if

$$\mathbf{v} = v_x\,\hat{\mathbf{x}} + v_y\,\hat{\mathbf{y}} + v_z\,\hat{\mathbf{z}} \tag{5.14}$$

with $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ unit vectors in the respective directions, then $\mathbf{v}'$ is necessarily $v_x\,\hat{\mathbf{x}}$ and $\mathbf{v}'^{\perp}$ is necessarily $v_y\,\hat{\mathbf{y}} + v_z\,\hat{\mathbf{z}}$. Clearly, $\mathbf{v}'$ is the projection of $\mathbf{v}$ onto the x-axis. More generally, if we write each vector v of V as the sum of a vector v' belonging to V' and a vector $v'^{\perp}$ belonging to $V'^{\perp}$, mapping v to v' amounts to projecting v onto the subspace V'. Operators effecting this transformation are called projection operators, or projectors. In the example above, projecting $\mathbf{v}$ onto the x-axis amounts to transforming this vector into the vector $\hat{\mathbf{x}}$ multiplied by the inner product of $\hat{\mathbf{x}}$ and $\mathbf{v}$ (since $v_x = \hat{\mathbf{x}} \cdot \mathbf{v}$).

Let us consider, for example, a ket vector of unit norm $|\phi\rangle$ and the operator $\hat{\mathcal{P}}_\phi$ whose action on any ket vector $|\psi\rangle$ is to project it onto the 1-dimensional subspace spanned by $|\phi\rangle$. Thus $\hat{\mathcal{P}}_\phi$ transforms $|\psi\rangle$ into the ket vector $|\phi\rangle$ multiplied by the inner product of $|\phi\rangle$ and $|\psi\rangle$:

$$\hat{\mathcal{P}}_\phi|\psi\rangle = \langle\phi|\psi\rangle|\phi\rangle. \tag{5.15}$$

Since $\langle\phi|\psi\rangle|\phi\rangle$ is just a scalar (a number), and scalars commute with vectors, this equation can also be written in the form

$$\hat{\mathcal{P}}_\phi|\psi\rangle = |\phi\rangle\langle\phi|\psi\rangle. \tag{5.16}$$

Eq. (5.16) suggests an alternative notation for $\hat{\mathcal{P}}_\phi$:

$$\hat{\mathcal{P}}_\phi \equiv |\phi\rangle\langle\phi|, \tag{5.17}$$

in the sense that the action of $|\phi\rangle\langle\phi|$ on a ket vector $|\psi\rangle$ is to transform it into $|\phi\rangle\langle\phi|\psi\rangle$. The operator $\hat{\mathcal{P}}_\phi$ so defined is a projector.

It is easy to show that $\hat{\mathcal{P}}_\phi$ is idempotent:

$$\hat{\mathcal{P}}_\phi^2 = \hat{\mathcal{P}}_\phi \hat{\mathcal{P}}_\phi = |\phi\rangle\langle\phi|\phi\rangle\langle\phi| = |\phi\rangle\langle\phi| = \hat{\mathcal{P}}_\phi, \tag{5.18}$$

where we have used our assumption that $\langle\phi|\phi\rangle = 1$. It is also possible to show that $\hat{\mathcal{P}}_\phi$ is Hermitian.

Proof: $\hat{\mathcal{P}}_\phi$ is Hermitian since $\langle\psi_a|\hat{\mathcal{P}}_\phi|\psi_b\rangle = \langle\psi_b|\hat{\mathcal{P}}_\phi|\psi_a\rangle^*$ for any ket $|\psi_a\rangle$, $|\psi_b\rangle$:

$$\begin{aligned}
\langle\psi_a|\hat{\mathcal{P}}_\phi|\psi_b\rangle &= \langle\psi_a|\phi\rangle\langle\phi|\psi_b\rangle \\
&= \langle\phi|\psi_b\rangle\langle\psi_a|\phi\rangle \\
&= \langle\psi_b|\phi\rangle^*\langle\phi|\psi_a\rangle^* \\
&= \big(\langle\psi_b|\phi\rangle\langle\phi|\psi_a\rangle\big)^* \\
&= \langle\psi_b|\hat{\mathcal{P}}_\phi|\psi_a\rangle^*.
\end{aligned}$$

Hence, $\hat{\mathcal{P}}_\phi$ fulfils the definition of a Hermitian operator. □

It is not extremely difficult to show that any projection operator is idempotent and Hermitian, and that the converse is also true: any operator which is both idempotent and Hermitian is a projection operator.

To put the above in a mathematically rigorous framework, it is necessary for the subspace V' to have the property of being closed; what this means cannot be explained within the scope of the course, is relevant only for infinite-dimensional spaces, and can normally be ignored in applications of this formalism to Quantum Mechanics. In the jargon of Linear Algebra, the set $V'^{\perp}$ of all the vectors orthogonal to a closed subspace V' of a Hilbert space V is called the orthogonal complement of V', and V is said to be the direct sum of the two subspaces V' and $V'^{\perp}$ (in the sense that any vector of V can be written in one and only one way as the sum of a vector of V' and a vector of $V'^{\perp}$). This relation is expressed by the equation $V = V' \oplus V'^{\perp}$, where the symbol $\oplus$ denotes the direct sum.

☞ Projection operators projecting ket vectors onto a higher-dimensional subspace are also used. For example, let us consider the unit vectors $|\phi_1\rangle$, $|\phi_2\rangle$,..., $|\phi_M\rangle$, with $\langle\phi_i|\phi_j\rangle = \delta_{ij}$. The operator

$$\hat{\mathcal{P}} = \sum_{i=1}^{M} |\phi_i\rangle\langle\phi_i| \tag{5.19}$$

projects any vector it acts on onto the M-dimensional subspace spanned by the M unit vectors $|\phi_n\rangle$.

☞ Suppose that we would use wave functions instead of ket vectors. E.g., $|\psi\rangle$ and $|\phi\rangle$ would correspond, respectively, to a wave function $\psi(\mathbf{r})$ and a wave function $\phi(\mathbf{r})$. In this case, the operator $\hat{\mathcal{P}}_\phi$ would correspond to an operator $\mathcal{P}_\phi$ defined by the following equation:

$$\mathcal{P}_\phi\,\psi(\mathbf{r}) = \phi(\mathbf{r})\left[\int \mathrm{d}^3r'\,\phi^*(\mathbf{r}')\psi(\mathbf{r}')\right]. \tag{5.20}$$

We can therefore write the operator $\mathcal{P}_\phi$ as $\phi(\mathbf{r})\phi^*(\mathbf{r}')$ in this representation, being understood that $\phi(\mathbf{r})\phi^*(\mathbf{r}')$ is actually an operator, not a mere product of two functions, and that this operator transforms any $\psi(\mathbf{r})$ it acts on into $\phi(\mathbf{r})$ times the inner product of $\phi(\mathbf{r})$ and $\psi(\mathbf{r})$.

☞ Suppose that in a certain basis the ket vector $|\phi\rangle$ is represented by the column vector c. Then, in that basis, the operator $|\phi\rangle\langle\phi|$ is represented by the matrix P_ϕ formed by taking the outer product of c with itself:

$$\mathsf{P}_\phi = \mathsf{c}\mathsf{c}^\dagger, \tag{5.21}$$

where $\mathsf{c}^\dagger$ denotes the row vector obtained by transposing the column vector c and complex-conjugating all its elements. (The proof of this assertion is left as an exercise for the reader. See Appendix A of these notes for the calculation of the outer product of two column vectors.)

The completeness relation

By a "complete set" of vectors one means a set of vectors spanning the whole of the vector space considered. By definition, a basis set is always a complete set.

Consider a finite-dimensional Hilbert space of dimension N, spanned by the orthonormal basis $\{|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_N\rangle\}$. Any vector of that space can be written as a linear superposition of these $|\phi_n\rangle$'s; e.g.,

$$|\psi\rangle = \sum_{n=1}^{N} c_n|\phi_n\rangle. \tag{5.22}$$

Since the basis is orthonormal, each coefficient c_n can be calculated as the inner product of $|\psi\rangle$ with the respective basis vector: $c_n = \langle\phi_n|\psi\rangle$. Therefore one can also write

$$|\psi\rangle = \sum_{n=1}^{N}\langle\phi_n|\psi\rangle|\phi_n\rangle, \tag{5.23}$$

or, writing the scalar $\langle\phi_n|\psi\rangle$ on the right rather than on the left of the vector $|\phi_n\rangle$ (this is just a change of notation),

$$|\psi\rangle = \sum_{n=1}^{N}|\phi_n\rangle\langle\phi_n|\psi\rangle. \tag{5.24}$$

Hence

$$|\psi\rangle = \sum_{n=1}^{N} \hat{P}_n |\psi\rangle \tag{5.25}$$

where $\hat{P}_n = |\phi_n\rangle\langle\phi_n|$. Since Eq. (5.25) must be true for any vector $|\psi\rangle$, the sum of the projectors $\hat{P}_n$ over all the vectors in the basis can only be the identity operator:

$$\sum_{n=1}^{N} |\phi_n\rangle\langle\phi_n| = \hat{I}. \tag{5.26}$$

This last equation is an important result called the completeness relation, or closure relation. (We stress that the $|\phi_n\rangle$'s must be orthonormal and form a complete set for it to hold.)

5.3 Bases of eigenvectors: I. Finite-dimensional spaces

Not all Hermitian operators acting in infinite-dimensional spaces — e.g., in spaces of functions— have eigenvectors and eigenvalues. However, Hermitian operators acting in finite-dimensional spaces, such as spin operators, always have eigenvectors and eigenvalues. In fact, if $\hat{A}$ is a Hermitian operator acting in a finite-dimensional Hilbert space, then it is always possible to form an orthonormal basis of eigenvectors of $\hat{A}$ spanning the whole of this Hilbert space.

Proof: We start by showing that the eigenvectors of a Hermitian operator acting in a finite-dimensional Hilbert space always span that Hilbert space.

First, let us recall the general result that any square matrix has at least one eigenvalue (possibly complex), and therefore has eigenvectors. (You may have seen this theorem in a previous course; if not, see, e.g., "Advanced Engineering Mathematics" by E. Kreyszig.]

Suppose that the operator $\hat{A}$ acts in a finite-dimensional Hilbert space $\mathcal{H}$ of dimension N. Let $\mathcal{H}_A$ be the subspace of $\mathcal{H}$ spanned by the eigenvectors of $\hat{A}$ and $\mathcal{H}^\perp$ the subspace of $\mathcal{H}$ formed by the vectors orthogonal to all the vectors of $\mathcal{H}_A$. The dimension of $\mathcal{H}_A$ is a certain number $N_A \leq N$. This subspace can thus be spanned by a basis of N_A vectors. Let $\{|\phi_n\rangle\}$ $(n = 1, \ldots, N_A)$ be such a basis.

We first consider the possibility that $N_A < N$. If $N \neq N_A$, it is always possible to find a linearly independent set of $N - N_A$ non-zero vectors of $\mathcal{H}$ orthogonal to all these N_A vectors (recall that linearly independent vectors can always be made orthogonal to each other using the Gram-Schmidt method). These $N - N_A$ vectors span $\mathcal{H}_\perp$. Let us denote them by $|\phi_n\rangle$, $n = N_A + 1, \ldots, N$. Joining them to the N_A basis vectors spanning $\mathcal{H}_A$ gives a set of N basis vectors spanning the whole of $\mathcal{H}$, $\{|\phi_n\rangle\}$, $n = 1, \ldots, N$.

By definition, any vector $|\gamma\rangle$ in $\mathcal{H}_A$ can be written as a linear combination of eigenvectors of $\hat{A}$:

$$|\gamma\rangle = \sum_i c_i |\psi_i\rangle, \tag{5.27}$$

where each vector $|\psi_i\rangle$ is such that $\hat{A}|\psi_i\rangle = \lambda_i |\psi_i\rangle$ for some number λ. But then

$$\hat{A}|\gamma\rangle = \sum_i c_i \hat{A}|\psi_i\rangle = \sum_i c_i \lambda_i |\psi_i\rangle. \tag{5.28}$$

The operator $\hat{A}$ thus transforms vectors belonging to $\mathcal{H}_A$ into vectors belonging to $\mathcal{H}_A$.

Next we show that $\hat{A}$ also transforms vectors belonging to $\mathcal{H}_\perp$ into vectors belonging to $\mathcal{H}_\perp$: Suppose, as above, that $|\gamma\rangle$ is in $\mathcal{H}_A$. Then, as just shown, $|\gamma_A\rangle = \hat{A}|\gamma\rangle$ is also in $\mathcal{H}_A$. Now, suppose that $|\beta\rangle$ is in $\mathcal{H}_\perp$ and consider $|\beta_A\rangle = \hat{A}|\beta\rangle$. Since $\hat{A}$ is Hermitian,

$$\langle\gamma|\beta_A\rangle = \langle\gamma|\hat{A}|\beta\rangle = \langle\beta|\hat{A}|\gamma\rangle^* = \langle\beta|\gamma_A\rangle^*. \tag{5.29}$$

However, since $|\gamma_A\rangle$ is in $\mathcal{H}_A$ and $|\beta\rangle$ is in $\mathcal{H}_\perp$, $\langle\beta|\gamma_A\rangle^* = 0$ and therefore $\langle\psi|\beta_A\rangle$=0. Since this is true for any vector $|\gamma\rangle$ belonging to $\mathcal{H}_A$, $\hat{A}|\beta\rangle$ must be in $\mathcal{H}_\perp$ if $|\beta\rangle$ is in $\mathcal{H}_\perp$. Thus $\hat{A}$ transforms vectors in $\mathcal{H}_\perp$ into vectors in $\mathcal{H}_\perp$.

The upshot is that $\langle\phi_i|\hat{A}|\phi_j\rangle = 0$ if $i \leq N$ and $j \geq N+1$ or if $i \geq N+1$ and $j \geq N$. The matrix A representing the operator $\hat{A}$ in the $\{|\phi_n\rangle\}$ basis is therefore block-diagonal:

$$\mathsf{A} = \begin{pmatrix} \times & \times & \ldots & \times & \times & 0 & \ldots & 0 \\ \times & \times & \ldots & \times & \times & 0 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ \times & \times & \ldots & \times & \times & 0 & \ldots & 0 \\ \times & \times & \ldots & \times & \times & 0 & \ldots & 0 \\ 0 & 0 & \ldots & 0 & 0 & \times & \ldots & \times \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & 0 & 0 & \times & \ldots & \times \end{pmatrix}, \tag{5.30}$$

where the crosses indicate which elements of A may be non-zero. The upper and lower diagonal blocks of A are, respectively, $N_A \times N_A$ and $(N-N_A)\times(N-N_A)$ square matrices. Any eigenvector of A corresponds to an eigenvector of $\hat{A}$; indeed, if the numbers c_n, $n = 1, \ldots, N$ are the components of a vector c such that $\mathsf{A}\mathsf{c} = \lambda\mathsf{c}$, then $\hat{A}|\psi\rangle = \lambda|\psi\rangle$ for

$$|\psi\rangle = \sum_{n=1}^{N} c_n |\phi_n\rangle. \tag{5.31}$$

Now, that $\mathcal{H}_A$ is spanned by the eigenvectors of $\hat{A}$ implies that any eigenvector of the matrix A is such that $c_n = 0$ for all $n \geq N+1$ and $c_n \neq 0$ for at least one value of $n \leq N$. However, as any square matrix has at least one eigenvalue, the lower diagonal block of A must have eigenvectors. Hence A must have eigenvectors such that $c_n \neq 0$ for at least one value of $n \geq N+1$ and $c_n = 0$ for all $n \leq N$.

The contradiction implies that it is impossible that $N_A < N$. Instead, N_A must be equal to N, which means that $\mathcal{H}_A$ is the whole Hilbert space $\mathcal{H}$ in which the operator $\hat{A}$ acts.

Let us now show that an orthonormal basis of eigenvectors of $\hat{A}$ can always be found. First, recall that if an eigenvalue λ of an operator $\hat{A}$ is M-fold degenerate, then, (1) it is possible to find M linearly independent non-zero vectors $|\psi_1\rangle$, $|\psi_2\rangle$,..., $|\psi_M\rangle$ such that $\hat{A}|\psi_n\rangle = \lambda|\psi_n\rangle$, $(n = 1, 2, \ldots, M)$, and (2) any eigenvector belonging to that eigenvalue can be written as a linear combination of these M linearly independent vectors. As the latter can always be orthonormalized, it is always possible to form a basis of M orthogonal unit eigenvectors spanning the subspace formed by all the eigenvectors belonging to that eigenvalue.

The same also applies to non-degenerate eigenvalues, i.e., to "1-fold degenerate" eigenvalues ($M = 1$): If the eigenvalue λ is non-degenerate, then any of its eigenvectors can be written as the linear combination $c|\psi\rangle$, where c is a non-zero complex number and $|\psi\rangle$ is a unit vector such that $\hat{A}|\psi\rangle = \lambda|\psi\rangle$.

Thus any eigenvector of a Hermitian operator $\hat{A}$ can be written as a linear combination of unit eigenvectors of $\hat{A}$. These unit eigenvectors are mutually orthogonal (both by construction, in the case of degenerate eigenvalues, and because eigenvectors of Hermitian operators corresponding to different eigenvalues are always orthogonal). As any vector of the Hilbert space in which this operator acts can be written as a linear combination of its eigenvectors, this set of orthonormal eigenvectors is a basis for that space. $\square$

Matrix representation in a basis of eigenvectors

Suppose that $\{|\psi_1\rangle, |\psi_2\rangle, \ldots, |\psi_N\rangle\}$ is an orthonormal basis formed by eigenvectors of a Hermitian operator $\hat{A}$. Let us denote by λ_j the eigenvalue the eigenvector $|\psi_j\rangle$ corresponds to. We then have that

$$\langle\psi_i|\hat{A}|\psi_j\rangle = \lambda_j\langle\psi_i|\psi_j\rangle = \lambda_j\delta_{ij}. \tag{5.32}$$

(We replaced $\langle\psi_i|\psi_j\rangle$ by δ_{ij} in the last step since the ket vectors $|\psi_j\rangle$ are assumed to be orthonormal.) Therefore, the off-diagonal elements of the matrix

A representing $\hat{A}$ in that basis are all zero, and the diagonal elements are the eigenvalues λ_j:

$$\mathsf{A} = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \vdots & \lambda_N \end{pmatrix}. \tag{5.33}$$

A matrix representing an operator in an orthonormal basis of its own eigenvectors is always diagonal, and each diagonal element is the eigenvalue the respective basis vector corresponds to.

Spectral decomposition of an operator

As just seen, given a Hermitian operator $\hat{A}$ acting in a finite-dimensional Hilbert space, it is always possible to form an orthonormal basis spanning this space with eigenvectors of that operator. Let $\{|\psi_1\rangle, |\psi_2\rangle, \ldots, |\psi_N\rangle\}$ be such a basis, with $\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle$. As this set is complete, we can invoke the completeness relation (Section 5.2) and write $\hat{I} = \sum_{n=1}^{N} |\psi_n\rangle\langle\psi_n|$. However, since $\hat{I}$ is the identity operator, $\hat{A} \equiv \hat{A}\hat{I}$ and thus $\hat{A} = \sum_{n=1}^{N} \hat{A}\,|\psi_n\rangle\langle\psi_n|$. Therefore, given that $\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle$,

$$\hat{A} = \sum_{n=1}^{N} \lambda_n\,|\psi_n\rangle\langle\psi_n|. \tag{5.34}$$

This last equation expresses the operator $\hat{A}$ in terms of its eigenvalues and of the projectors $|\psi_n\rangle\langle\psi_n|$. The right-hand side of this equation is called the spectral decomposition of $\hat{A}$.

☞ We have seen in Section 3.3 that the exponential of an operator can be defined by a series of powers of that operator. More general functions can also be defined in terms of the spectral decomposition of that operator. I.e., given Eq. (5.34), a function $f(\hat{A})$ of the operator $\hat{A}$ can be taken to be the operator defined by the equation

$$f(\hat{A}) = \sum_{n=1}^{N} f(\lambda_n)\,|\psi_n\rangle\langle\psi_n|. \tag{5.35}$$

For example,

$$\frac{1}{\hat{A} - \lambda\hat{I}} = \sum_{n=1}^{N} \frac{1}{\lambda_n - \lambda}\,|\psi_n\rangle\langle\psi_n|. \tag{5.36}$$

(It is clear from this last equation that the operator $\hat{A} - \lambda\hat{I}$ is not invertible when λ is an eigenvalue of $\hat{A}$.)

Eigenvalues and eigenvectors of commuting operators

Consider two Hermitian operators, $\hat{A}$ and $\hat{B}$, acting in the same finite-dimensional Hilbert space, and suppose that $\hat{A}$ and $\hat{B}$ commute. That they commute has important implications:

1. If $\hat{A}$ and $\hat{B}$ commute and $|\psi_n\rangle$ is an eigenvector of $\hat{A}$, then the vector $\hat{B}|\psi_n\rangle$ is also an eigenvector of $\hat{A}$ corresponding to the same eigenvalue.

> Proof: If $\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle$ and $\hat{A}$ commutes with $\hat{B}$, then $\hat{A}\hat{B}|\psi_n\rangle = \hat{B}\hat{A}|\psi_n\rangle = \lambda_n\hat{B}|\psi_n\rangle$ and therefore $\hat{B}|\psi_n\rangle$ is an eigenvector of $\hat{A}$ with eigenvalue λ_n (the same eigenvalue as that $|\psi_n\rangle$ corresponds to). □

As an example, take the case of an atom of hydrogen exposed to an external time-varying electric field oriented in the z-direction. The wave function of this system evolves according to the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = H(t)\Psi(r,\theta,\phi,t), \tag{5.37}$$

where $H(t)$ is the Hamiltonian of the atom+field system. Thus, given $\Psi(r,\theta,\phi,t)$ at a time $t = t_0$,

$$\Psi(r,\theta,\phi,t=t_0+\mathrm{d}t) = \Psi(r,\theta,\phi,t=t_0) + \frac{1}{i\hbar}H(t_0)\Psi(r,\theta,\phi,t=t_0)\,\mathrm{d}t. \tag{5.38}$$

One can show that $H(t)$ commutes with the angular momentum operator L_z. Thus, if $\Psi(r,\theta,\phi,t=t_0)$ is an eigenfunction of L_z, then $\Psi(r,\theta,\phi,t=t_0+\mathrm{d}t)$ is also an eigenfunction of L_z corresponding to the same eigenvalue. The upshot is that the wave function $\Psi(r,\theta,\phi,t)$ then remains an eigenfunction of L_z at all times, even though it may change in a very complicated way under the effect of this time-varying electric field.

☞ Suppose that $\hat{A}$ and $\hat{B}$ commute and that $\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle$. The eigenvalue λ_n may or may not be degenerate.

It follows from the fact that $|\psi_n\rangle$ and $\hat{B}|\psi_n\rangle$ are both eigenvectors of $\hat{A}$ corresponding to a same eigenvalue that this eigenvalue is degenerate if these two vectors are linearly independent. In fact, most eigenvalue degeneracies arise from the fact that the operator of interest commutes with another operator.

On the other hand, if λ_n is not degenerate, then $|\psi_n\rangle$ is an eigenvector of $\hat{B}$ as well as of $\hat{A}$. Indeed, $|\psi_n\rangle$ and $\hat{B}|\psi_n\rangle$ cannot be linearly independent if λ_n is not degenerate; instead, these two vectors must differ at most by a scalar factor. Hence, if λ_n is not degenerate, there must exist a number μ_n such that $\hat{B}|\psi_n\rangle = \mu_n|\psi_n\rangle$, which means that $|\psi_n\rangle$ is an eigenvector of $\hat{B}$.

2. One can find a basis constructed from vectors which are eigenvectors both of $\hat{A}$ and of $\hat{B}$ if and only if $\hat{A}$ and $\hat{B}$ commute. I.e., there exists a basis set $\{|\psi_1\rangle, |\psi_2\rangle, \ldots, |\psi_N\rangle\}$ and scalars λ_n and μ_n, $n = 1, 2 \ldots, N$, such that

$$\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle \qquad \text{and} \qquad \hat{B}|\psi_n\rangle = \mu_n|\psi_n\rangle.$$

Proof: Suppose that $\hat{A}$ and $\hat{B}$ commute and that λ is an eigenvalue of $\hat{A}$. Let us suppose that λ is M-fold degenerate (M could be any number between 1 and N). This means that one can find up to M linearly independent eigenvectors of $\hat{A}$, all corresponding to this eigenvalue. M such eigenvectors span a M-dimensional subspace of the Hilbert space in which $\hat{A}$ and $\hat{B}$ are defined. The vectors belonging to that subspace are all eigenvectors of $\hat{A}$ corresponding to the eigenvalue λ. Moreover, since $\hat{A}$ and $\hat{B}$ commute, the action of $\hat{B}$ on any of these eigenvectors results in an eigenvector of $\hat{A}$ also corresponding to this eigenvalue. Thus $\hat{B}$ transforms vectors of that subspace into vectors of the same subspace. Within that subspace $\hat{B}$ is therefore equivalent to a Hermitian operator acting in a Hilbert space of dimension M. Hence it is always possible to form an orthonormal basis of eigenvectors of $\hat{B}$ spanning this M-dimensional subspace, and each vector in that basis is also an eigenvector of $\hat{A}$ corresponding to the eigenvalue λ. This process can be repeated for each eigenvalue of $\hat{A}$ in turn, resulting in a basis of N vectors that are eigenvectors of both $\hat{A}$ and of $\hat{B}$.

We now prove the converse, that $\hat{A}$ and $\hat{B}$ commute if one can find a basis constructed from vectors which are eigenvectors both of $\hat{A}$ and of $\hat{B}$. Suppose that there exists a basis set $\{|\psi_1\rangle, |\psi_2\rangle, \ldots, |\psi_N\rangle\}$ and scalars λ_n and μ_n, $n = 1, 2 \ldots, N$, such that

$$\hat{A}|\psi_n\rangle = \lambda_n|\psi_n\rangle \qquad \text{and} \qquad \hat{B}|\psi_n\rangle = \mu_n|\psi_n\rangle.$$

Because $\{|\psi_1\rangle, |\psi_2\rangle, \ldots, |\psi_N\rangle\}$ is a basis, any vector $|\psi\rangle$ can be written as a linear combination of these vectors; e.g., $|\psi\rangle = \sum_{n=1}^{N} c_n|\psi_n\rangle$. Now,

$$\begin{aligned}\hat{A}\hat{B}|\psi\rangle = \sum_{n=1}^{N} c_n\hat{A}\hat{B}|\psi_n\rangle &= \sum_{n=1}^{N} c_n\lambda_n\mu_n|\psi_n\rangle \\ &= \sum_{n=1}^{N} c_n\mu_n\lambda_n|\psi_n\rangle \\ &= \sum_{n=1}^{N} c_n\hat{B}\hat{A}|\psi_n\rangle = \hat{B}\hat{A}|\psi\rangle. \end{aligned} \tag{5.39}$$

Since $\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle$ for any $|\psi\rangle$, $\hat{A}$ and $\hat{B}$ commute. □

If each pair of eigenvalues (λ_n, μ_n) corresponds to a unique $|\psi_n\rangle$ (up to a scalar factor), one says that the operators $\hat{A}$ and $\hat{B}$ form a complete set of commuting operators. This means, in practice, that any joint eigenvector of $\hat{A}$ and $\hat{B}$ can be unambiguously defined by a pair of quantum numbers.

This definition generalizes to sets of more than two operators and to infinite-dimensional spaces. For example, the non-relativistic Hamiltonian of an atom hydrogen, $\hat{H}$, commutes with the angular momentum operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ and the latter two also commute with each other:

$$[\hat{H}, \hat{\mathbf{L}}^2] = [\hat{H}, \hat{L}_z] = [\hat{\mathbf{L}}^2, \hat{L}_z] = 0. \tag{5.40}$$

The wave functions $\Psi_{nlm}(r, \theta, \phi)$ you have studied in Term 1 are simultaneous eigenfunctions of $\hat{H}$, $\hat{\mathbf{L}}^2$ and $\hat{L}_z$. The corresponding eigenvalues completely define these joint eigenfunctions (up to a constant factor), and therefore $\hat{H}$, $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ form a complete set of commuting operators.

As we will see in Part 6 of these notes, that two Hermitian operators representing measurable physical quantities commute means that there is no uncertainty relation limiting the predictions one can make about what values these quantities could be found to have if measured jointly.

5.4 Bases of eigenvectors: II. Infinite-dimensional spaces

The mathematical theory of Hermitian operators acting in an infinite-dimensional Hilbert space is considerably more difficult than that of finite matrices and other operators acting in finite-dimensional spaces. Stating (let alone proving) general results for the infinite-dimensional case would go much beyond the scope of this course. However, the following is worth bearing in mind:

1. As seen in Section 5.1, the Hamiltonian operator defined by Eq. (5.9) is Hermitian if taken as acting in the Hilbert space of the square-integrable functions which vanish at $x = \pm a$. It is possible to form an orthonormal basis set of eigenfunctions of that operator, such that any element $\phi(x)$ of that Hilbert space can be written in the form of an expansion on that set of eigenfunctions. I.e., denoting the orthonormal basis functions by $\psi_n(x)$, $n = 0, 1, 2, \ldots$, one can write $\phi(x)$ in the form

$$\phi(x) = \sum_{n=0}^{\infty} c_n \psi_n(x), \tag{5.41}$$

where the $\psi_n(x)$ functions are eigenfunctions of H of unit norm and are such that

$$\int_{-a}^{a} \psi_i^*(x) \psi_j(x) \, \mathrm{d}x = \delta_{ij}. \tag{5.42}$$

☞ As can be checked easily,

$$\psi_n(x) = \begin{cases} A_n \cos(k_n x) & n = 0, 2, 4, \dots \\ A_n \sin(k_n x) & n = 1, 3, 5, \dots \end{cases} \tag{5.43}$$

with $k_n = (n+1)\pi/(2a)$ and A_n a normalization factor. These functions satisfy the differential equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2} = E_n \psi_n(x), \tag{5.44}$$

where E_n is a constant (in fact, $E_n = \hbar^2 k_n^2/2m$). Since they are also square-integrable on $[-a, a]$ and zero at $x = \pm a$, they qualify as eigenvectors of this operator. These functions are orthogonal to each other since they all correspond to different eigenvalues and H is Hermitian. Moreover, they can be made to have unit norm by an appropriate choice of the normalization factors A_n. That any function $\phi(x)$ belonging to that Hilbert space can be written as an expansion in these $\psi_n(x)$ functions is a standard result of Fourier analysis.

2. Consider a particle of mass m confined to the x-axis but submitted to no force in the x-direction and free to move to arbitrarily large distances from the origin The Hamiltonian of this system is also given by Eq. (5.9), as in the previous example, but here this operator is taken as acting in the Hilbert space of square-integrable functions on $(-\infty, \infty)$. This operator is still Hermitian. However, contrary to the previous example, it has no eigenfunctions in the mathematical definition of the term.

☞ To be an eigenfunction of H, a function $\psi(x)$ should be a non-trivial solution of the differential equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\,\psi(x) \tag{5.45}$$

for a certain value of the constant E and should also be square-integrable on $(-\infty, \infty)$. (By non-trivial solution one means a solution other than $\psi(x) \equiv 0$.) Let $k = (2mE/\hbar^2)^{1/2}$. Any non-trivial solution of Eq. (5.45) is of the form

$$\psi(x) = c_+ \exp(ikx) + c_- \exp(-ikx) \tag{5.46}$$

with c_+ and c_- two arbitrary complex numbers (not both zero), and such solutions exist for any real or complex value of E. However, none of these solutions go to zero both for $x \to \infty$ and $x \to -\infty$. Hence, no function of that form is square-integrable on $(-\infty, \infty)$.

3. Adding a potential energy term $m\omega^2x^2/2$ to the Hamiltonian of the previous example changes it into the Hamiltonian of a linear harmonic oscillator,

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{m}{2}\,\omega^2x^2. \tag{5.47}$$

Taken as acting in the Hilbert space of the square-integrable functions on $(-\infty,\infty)$, this Hamiltonian is Hermitian and has infinitely many eigenvalues. It is possible to form an orthonormal basis set of eigenfunctions of that operator, such that any square-integrable function can be written in the form of an expansion on that set of eigenfunctions. (You have studied this system in the Term 1 Quantum Mechanics course, and we will come back to it a little later in these notes.)

☞ Advanced mathematical concepts are necessary to prove the important result, stated above, that any square-integrable function can be written in terms of eigenfunctions of that Hamiltonian.

4. We have already mentioned the angular moment operator L_z (actually, the z-component of the orbital angular operator $\hat{\mathbf{L}}$, about which there will be much more later in the course). This operator takes on the very simple form given in Eq. (5.3) when written in terms of the polar angle ϕ of a system of spherical polar co-ordinates. Recall that this polar angle varies between 0 and 2π. As we have seen in Section 5.1, L_z is a Hermitian operator in the space of all differentiable square-integrable functions $y(\phi)$ defined on $[0,2\pi]$ and such that $y(0) = y(2\pi)$. The (normalized) eigenfunctions of L_z are the complex exponentials

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}\exp(im\phi), \qquad m = 0, \pm1, \pm2, \ldots \tag{5.48}$$

These eigenfunctions form an orthonormal basis set, in the sense that any function belonging to that Hilbert space can be written in the form of an expansion on this set of eigenfunctions.

☞ The functions $\psi_m(\phi)$ are orthonormal since (check this as an exercise!)

$$\int_0^{2\pi}\psi_m^*(\phi)\psi_n(\phi)\,\mathrm{d}\phi = \frac{1}{2\pi}\int_0^{2\pi}\exp[i(n-m)\phi]\,\mathrm{d}\phi = \delta_{nm}. \tag{5.49}$$

These functions are also eigenfunctions of L_z since

$$L_z\psi_m(\phi) = -i\hbar\frac{\mathrm{d}}{\mathrm{d}\phi}\frac{\exp(im\phi)}{\sqrt{2\pi}} = m\hbar\frac{\exp(im\phi)}{\sqrt{2\pi}} = m\hbar\,\psi_m(\phi). \tag{5.50}$$

We will come back to this issue later in the course, when studying the position and momentum operators and other operators with a continuous spectrum.