Advanced Quantum Mechanics

Fall 2023

Bernat Frangi Mahiques
Physics Engineering and Industrial
Technologies Engineering

Contents

1 Mathematical Tools of Quantum Mechanics. Postulates of Quantum Mechanics

1.1 Hilbert Spaces

Hilbert spaces, also known as **complex vector spaces**, are defined in **Definition 1.1**.

Definition 1.1. Any set $\mathcal{H}$ is called a Hilbert space (or complex vector space), if:

a) it posesses an operation $\mathcal{H} \times \mathcal{H} \to \mathcal{H}$ called "addition" which obeys the rules for a commutative group.

b) it has a multiplication $\mathbb{C} \times \mathcal{H} \to \mathcal{H}$ obeying the following axioms for all $|v\rangle$, $|w\rangle \in \mathcal{H}$ and for all α, $\beta \in \mathbb{C}$:

$$(\alpha + \beta)|v\rangle = \alpha|v\rangle + \beta|v\rangle \tag{1}$$

$$\alpha(|v\rangle + |w\rangle) = \alpha|v\rangle + \alpha|w\rangle \tag{2}$$

$$(\alpha\beta)|v\rangle = \alpha(\beta|v\rangle) \tag{3}$$

$$1|v\rangle = |w\rangle \tag{4}$$

c) it posesses an inner product $\langle u|v\rangle \in \mathbb{C}$.

Check that this is rigorous

1.2 The dual space

Given any Hilbert space $\mathcal{H}$, one can construct another complex vector space $\mathcal{H}^*$, called the **dual vector space**. It contains all the linear functionals in $\mathcal{H}$, which are a special kind of operator that maps all elements of $\mathcal{H}$ onto complex numbers[1]. In general, for an abstract vector space $\mathcal{H}$:

Definition 1.2. Given a Hilbert space $\mathcal{H}$, the dual space $\mathcal{H}^*$ is the vector space of all linear functionals in $\mathcal{H}$.

Therefore, all linear functionals $L : \mathcal{H} \to \mathbb{C}$ live in $\mathcal{H}^*$ ($L \in V^*$).

The reason that the dual space is so interesting for quantum mechanics is that our goal as quantum physicists is to build a mathematical model for the real world, and in the end we want to be able to extract useful values and predictions from this model. For example, we may want to know the probability of getting a certain energy; or the average position we expect in a certain state. All these are scalar values, that we need to extract from a quantum state $|\psi\rangle$, so we know we will need a linear functional someplace or other!

This may all sound really abstract at first glance, but hopefully it will become a lot clearer in the next section when we look at the **Dirac notation**.

1.3 Dirac Notation

In quantum mechanics, we use the Dirac notation to represent wave functions:

- We call the elements of $\mathcal{H}$ "ket" vectors, and we represent them as $|\psi\rangle \in \mathcal{H}$.

[1] See Appendix **Section 2.1** for more on linear functionals.

- We call the elements of $\mathcal{H}^*$ "bra" vectors, and we represent them as $\langle\phi| \in \mathcal{H}^*$.

Bra vectors are operators that linearly map elements of $\mathcal{H}$ into complex numbers:

$$\begin{array}{rccc} \langle\phi|: & \mathcal{H} & \to & \mathbb{C} \\ \langle\phi|: & |\psi\rangle & \to & \langle\phi|\psi\rangle \end{array} \tag{5}$$

1.3.1 Inner product and bra-ket notation

Notice that, when we put a bra and a ket together ($\langle\phi||\psi\rangle$), they look suspiciously like an inner product in this notation: $\langle\phi|\psi\rangle$. If we go back at how our L_x operator in $\mathbb{R}^2$ acts on a column vector:

$$L_x \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} a \\ b \end{bmatrix} = 1 \cdot a + 0 \cdot b = a \tag{6}$$

Notice that its action is the same as if we were taking the dot product with the x unit vector:

$$x \cdot \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \cdot \begin{bmatrix} a \\ b \end{bmatrix} = 1 \cdot a + 0 \cdot b = a \tag{7}$$

In fact, when a linear functional in $\mathbb{R}^n$ acts on any vector, it can be written equivalently as a dot product with the corresponding column vector:

$$L_x \vec{v} = L_x^T \cdot \vec{v} \tag{8}$$

This is actually a very general mathematical fact, rooted within something called the **Riesz Representation Theorem**:

Theorem 1.3. (Riesz Representation Theorem) For any linear functional L_ϕ, the action of L_ϕ is equivalent to taking the inner product with some unique vector $\vec{\phi}$.

In our example of L_x, we have that $\vec{\phi} = \vec{x} = [1\ 0]^T$:

$$L_x \vec{v} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \cdot \vec{v} \tag{9}$$

This is the reason for the suggestive notation for bra vectors: they are operators whose action on a ket is mathematically equivalent to taking the inner product with said ket:

$$\langle\phi||\psi\rangle = \langle\phi|\psi\rangle \tag{10}$$

That is the power of bra-ket notation: it has the Riesz Representation Theorem baked right into it. Whatever you do, breaking apart inner products and putting together bras and kets, you will always have something that makes mathematical sense. Although bra and the inner product are two entities that are completely different mathematically, the bra-ket notation makes their connection completely seamless, thanks to the Riesz Representation Theorem.

1.3.2 Properties of bras and kets

Some properties that arise naturally from the Dirac notation:

$$\langle\psi|\lambda_1\phi_1 + \lambda_2\phi_2\rangle = \lambda_1\langle\psi|\phi_1\rangle + \lambda_2\langle\psi|\phi_2\rangle \tag{11}$$

$$\langle \lambda_1 \psi + \lambda_2 \psi_2 | \phi \rangle = \lambda_1^* \langle \psi_1 | \phi \rangle + \lambda_2^* \langle \psi_2 | \phi \rangle \tag{12}$$

$$\langle \psi | \phi \rangle = \langle \phi | \psi \rangle^* \tag{13}$$

$$\langle \psi | \psi \rangle \text{ is real, positive and only zero if } |\psi\rangle = 0 \tag{14}$$

1.4 Linear operators

A linear map is defined as:

Definition 1.4. A linear map (or linear operator) is a mathematical entity A that associates a function with another function such that:

$$A(\lambda_1 \psi_1 + \lambda_2 \psi_2) = \lambda_1 A \psi_1 + \lambda_2 A \psi_2 \tag{15}$$

In the quantum mechanical context, we can see them as entities that transform a ket into another ket. Some example linear operators are:

- **Commutator:** $[A, B] \equiv AB - BA$ (in general, $AB \neq BA$).
- **Projector:** $P_\phi = |\phi\rangle\langle\phi|$. The projector operator P_ϕ acting on a ket $|\psi\rangle$ gives a new ket that is proportional to $|\phi\rangle$. The coefficient of proportionality is the scalar product $\langle\phi|\psi\rangle$.[2]
- **Inverse:** assuming it exists, the inverse operator A^{-1} of the operator A, when applied to A, gives the identity operator. Also, A is the inverse of A^{-1}, so that $AA^{-1} = A^{-1}A = \mathbb{1}$.
- **Hermitian conjugation:** the hermitian conjugate (or adjoint) $A^\dagger$ of an operator A is obtained by interchanging the columns of the operator by its rows, and taking the complex conjugate of all elements. For example:

  $$A = \begin{bmatrix} i & 1 \\ 3-i & -i \end{bmatrix} \to A^\dagger = \begin{bmatrix} -i & 3+i \\ 1 & i \end{bmatrix} \tag{16}$$

  Some properties of the adjoint are:

  a) $\left(A^\dagger\right)^\dagger = A$.
  b) $(\lambda A)^\dagger = \lambda^* A^\dagger$.
  c) $(A+B)^\dagger = A^\dagger + B^\dagger$.
  d) $(AB)^\dagger = B^\dagger A^\dagger$.
  e) $(|u\rangle\langle v|)^\dagger = |v\rangle\langle u|$.[3]

  The adjoint of a bra is its ket, and the adjoint of a ket is its bra. To obtain the hermitian conjugate of an expression:

  a) Replace constants with their complex conjugate: $\lambda \to \lambda^*$.
  b) Replace operators with their Hermitian conjugates: $A \to A^\dagger$.
  c) Replace kets with bras: $|\phi\rangle \to \langle\phi|$.
  d) Replace bras with kets: $\langle\phi| \to |\phi\rangle$.
  e) Reverse the order of factors: $A|\phi\rangle \to \langle\phi|A^\dagger$.

[2] *Proof:* $P_\phi|\psi\rangle = |\phi\rangle\langle\phi||\psi\rangle = |\phi\rangle\langle\phi|\psi\rangle = \langle\phi|\psi\rangle|\phi\rangle$.

[3] *Proof:* $\langle\phi|\left(|u\rangle\langle v|\right)^\dagger|\psi\rangle = \left[\langle\psi|\left(|u\rangle\langle v|\right)|\phi\rangle\right]^* = \langle\psi|u\rangle^*\langle v|\phi\rangle^* = \langle u|\psi\rangle\langle\phi|v\rangle = \langle\phi|v\rangle\langle u|\psi\rangle = \langle\phi|\left(|v\rangle\langle u|\right)|\psi\rangle$

A special case of linear operators are **unitary operators**:

Definition 1.5. A linear operator U is said to be unitary if its inverse U^{-1} is equal to its adjoint $U^\dagger$, so that $U^{-1} = U^\dagger$ and $U^\dagger U = UU^\dagger = \mathbb{1}$.

Another special case are **Hermitian operators**:

Definition 1.6. An operator A is said to be Hermitian if $A = A^\dagger$.

An example of a Hermitian operator is the projector operator, as $P_\phi^\dagger = (|\phi\rangle\langle\phi|)^\dagger = |\phi\rangle\langle\phi| = P_\phi$.

1.5 Closure relation

For a set of vectors to form a basis of a Hilbert space $\mathcal{H}$, they must fulfil the **closure relation** (also known as the completeness relation). In simple terms, if the set of vectors fulfills the closure relation, it means that with those vectors you can reach all possible directions in $\mathcal{H}$, and any $|\psi\rangle \in \mathcal{H}$ is a linear combination of those basis vectors. In our general Hilbert space:

Definition 1.7. A set of vectors $\{|A_1\rangle, |A_2\rangle, ...\}$ in a Hilbert space $\mathcal{H}$ form a basis for $\mathcal{H}$ if and only if they fulfil the closure relation:

$$\mathbb{1} = \sum_i |A_i\rangle\langle A_i|. \tag{17}$$

Proof of this relation is given in **Section 2.3**.

1.6 Basis of a Hilbert space

If $\{|\psi_i\rangle\}$ is a basis for a Hilbert space $\mathcal{H}$, we can expand every arbitrary vector $|\Psi\rangle$ according to this basis:

$$|\Psi\rangle = \sum_i c_i |\psi_i\rangle \tag{18}$$

so that we have[4]:

$$\langle\psi_i|\Psi\rangle = \sum_j c_i \langle\psi_i|\Psi\rangle = \sum_j c_i \delta_{ij} = c_i \tag{19}$$

The choice of basis is arbitrary, and depending on the choice we make, we obtain different representations of state space. There are many different representations, which often have to do with physical properties of the system.

If you are familiar with basic quantum mechanics, you will probably have seen the position representation of the wave function, $\Psi(\vec{r})$. This representation of state space is particularly useful for working with position in a quantum system. However, it is not the *only* representation of state space that can have. What does this mean? Well, here, there is an important concept to understand, which is the difference between a vector and its representation: a vector is a mathematical entity that, once defined, is the same all the time, no matter where we look at it from or which basis we express it in. Its representation, however, may differ, depending on which basis we choose to represent it in. If the basis changes, the coordinates will also change, even though the vector is still the same.

For example, a vector $\vec{v}_B = (a, b)$ expressed in the basis $B = \{(1, 0),\ (0, 1)\}$ will change to $\vec{v}_{B'} = (b/2, a)$ $B' = \{(0, 2),\ (1, 0)\}$. The coordinates of the vector have changed, but we can see that both representations refer to the same vector:

[4] δ_{ij} is known as Kronecker's delta, and is equal to 1 if $i = j$ and 0 otherwise.

$$\vec{v}_B = a \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b \cdot \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{b}{2} \cdot \begin{pmatrix} 0 \\ 2 \end{pmatrix} + a \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \vec{v}_{B'} \tag{20}$$

Just as in this example, the position representation of the wave function vector space is only one of its many possible representations. The functions $\psi_i(\vec{r})$ form the basis for the position representation of state space. Other representations, like the momentum representation, can be useful in certain situations, as we will see later on.

1.7 Representations in state space

When studying quantum mechanical systems, we need a way to represent quantum states. We do that by choosing an orthonormal basis, either discrete or continuous, in the state space E. Vectors and operators are then represented in this basis by numbers: components for the vectors and matrix elements for the operators.

As we mentioned before, the choice of a representation is, in principle, arbitrary. In fact, it depends on the particular problem being studied: in each case, one chooses the representation that leads to the simplest calculations.

Most useful bases come as eigenstates of some pertinent operator[5]. So far, we have mentioned the position and the momentum representation. These bases deal with the position and momentum operators, but you can think of many others. For example, the eigenstates of the Hamiltonian for some physical system are often used, especially when solving the Schrödinger equation. These might also be infinite dimensional but can be discrete, as opposed to the continuous bases of position and momentum.

1.7.1 General representation

For a general representation of state space E (wave function space), the elements of E are functions $\psi(\vec{\xi}),\ \phi(\vec{\xi})$, and the inner product in E is defined as:

$$\left(\phi(\vec{\xi}),\ \psi(\vec{\xi})\right) \equiv \int \phi^*(\vec{\xi})\psi(\vec{\xi})d\vec{\xi} \tag{21}$$

The length (norm) of a vector is given by:

$$\text{length}\left(\psi(\vec{\xi})\right) = \sqrt{\left(\psi(\vec{\xi}),\ \psi(\vec{\xi})\right)} = \sqrt{\int \psi^*(\vec{\xi})\psi(\vec{\xi})d\vec{\xi}} = \sqrt{\int \left|\psi(\vec{\xi})\right|^2 d\vec{\xi}} \tag{22}$$

As the vectors of the basis $\{\phi_i\}$ of E are orthonormal, we have that:

$$\left(\phi_i(\vec{\xi}),\ \phi_j(\vec{\xi})\right) = \delta_{ij} \tag{23}$$

1.8 Discrete orthonormal bases

A **discrete orthonormal basis** is defined as:

[5] More on this lateradd link, but the idea is that, if we represent the state space in the basis of eigenstates (analogous to eigenvectors) of an operator, then that operator will be expressed in that basis as a diagonal matrix, where the elements of the diagonals are the eigenvalues of the operator. This makes calculations very easy.

Definition 1.8. A countable set of functions $\{u_i\}$ is called orthonormal if:

$$\Big(u_i(\vec{\xi}),\ u_j(\vec{\xi})\Big) = \delta_{ij} \tag{24}$$

And it constitutes a basis for the Hilbert space E if every function in E can be written as a linear combination of the functions of the basis in exactly one way:

$$\psi(\vec{\xi}) = \sum_i c_i u_i(\vec{\xi}) \tag{25}$$

with the coefficients being:

$$c_i = \Big(u_i(\vec{\xi}),\ \psi(\vec{\xi})\Big) = \int u_i^*(\vec{\xi})\psi(\vec{\xi})d\vec{\xi} \tag{26}$$

For a discrete orthonormal basis, we can express the **scalar product in terms of the components** as:

$$\Big(\phi(\vec{\xi}),\ \psi(\vec{\xi})\Big) = \left(\sum_i b_i u_i(\vec{\xi}),\ \sum_j c_j u_j(\vec{\xi})\right) = \sum_{i,\ j} b_i^* c_j \Big(u_i(\vec{\xi}),\ u_j(\vec{\xi})\Big) = \sum_{i,\ j} b_i^* c_i \delta_{ij} = \sum_i b_i^* c_i \tag{27}$$

With a similar proof as in **Section 2.3**, we can find the closure relation for a discrete orthonormal basis:

$$\psi(\vec{\xi}) = \sum_i c_i u_i(\vec{\xi}) = \sum_i \Big(u_i(\vec{\xi}),\ \psi(\vec{\xi})\Big) u_i(\vec{\xi}) = \sum_i \left(\int u_i^*(\vec{\xi}')\psi(\vec{\xi}')d\vec{\xi}'\right) u_i(\vec{\xi}) =$$

$$= \int \left(\sum_i u_i^*(\vec{\xi}')u_i(\vec{\xi})\right)\psi(\vec{\xi}')d\vec{\xi}' \tag{28}$$

Therefore, the term in the parenthesis must be equal to 1 for $\vec{\xi} = \vec{\xi}'$ and zero for every other case, so we obtain the **closure relation for a discrete orthonormal basis**[6]:

$$\sum_i u^*(\vec{\xi}')u_i(\vec{\xi}) = \delta(\vec{\xi} - \vec{\xi}') \tag{29}$$

1.9 Continuous orthonormal bases

A **continuous orthonormal basis** is defined as:

Definition 1.9. A continuous set of functions $\{\omega_\alpha\}$, labelled by a continuous index α, is called orthonormal if:

$$\Big(\omega_\alpha(\vec{\xi}),\ \omega_{\alpha'}(\vec{\xi})\Big) = \delta(\alpha - \alpha') \tag{30}$$

And it constitutes a basis for the Hilbert space E if every function in E can be written as a linear combination of the functions of the basis in exactly one way:

$$\psi(\vec{\xi}) = \int c(\alpha)\omega_\alpha(\vec{\xi})d\alpha \tag{31}$$

with the continuous coefficient being:

$$c(\alpha) = \Big(\omega_\alpha(\vec{\xi}),\ \psi(\vec{\xi})\Big) = \int \omega_\alpha^*(\vec{\xi})\psi(\vec{\xi})d\vec{\xi} \tag{32}$$

[6] $\delta(\vec{\xi} - \vec{\xi}')$ is known as Dirac's delta function, and it is equal to 1 if $\vec{\xi} = \vec{\xi}'$ and 0 otherwise.

For a continuous orthonormal basis, we can express the **scalar product in terms of the continuous coefficients** as:

$$\Big(\phi(\vec{\xi}),\ \psi(\vec{\xi})\Big) = \left(\int b(\alpha)\omega_\alpha(\vec{\xi})d\alpha,\ \int c(\alpha')\omega_{\alpha'}(\vec{\xi})d\alpha'\right) = \sum_{i,\ j} b_i^* c_j \Big(u_i(\vec{\xi}),\ u_j(\vec{\xi})\Big) =$$

$$= \int \left(\int b^*(\alpha)c(\alpha')(\omega_\alpha(\vec{\xi}), \omega_{\alpha'}(\vec{\xi}))d\alpha\right) d\alpha' = \int \left(\int b^*(\alpha)c(\alpha')\delta(\alpha-\alpha')d\alpha\right) d\alpha'$$

$$= \int b^*(\alpha)c(\alpha)d\alpha \tag{33}$$

With a similar proof as in **Section 2.3**, we can find the closure relation for a continuous orthonormal basis:

$$\psi(\vec{\xi}) = \int c(\alpha)\omega_\alpha(\vec{\xi})d\alpha = \int \Big(\omega_\alpha(\vec{\xi}),\ \psi(\vec{\xi})\Big)\, \omega_\alpha(\vec{\xi})d\alpha = \int \left(\int \omega_\alpha^*(\vec{\xi'})\psi(\vec{\xi'})d\vec{\xi'}\right) \omega_\alpha(\vec{\xi})d\alpha =$$

$$= \int \left(\int \omega_\alpha^*(\vec{\xi'})\omega_\alpha(\vec{\xi})d\alpha\right) \psi(\vec{\xi'})d\vec{\xi'} \tag{34}$$

Therefore, the term in the parenthesis must be equal to 1 for $\vec{\xi} = \vec{\xi'}$ and zero for every other case, so we obtain the **closure relation for a continuous orthonormal basis**:

$$\int \omega_\alpha^*(\vec{\xi'})\omega_\alpha(\vec{\xi})d\alpha = \Big(\omega_\alpha(\vec{\xi'}),\ \omega_\alpha(\vec{\xi})\Big) = \delta(\vec{\xi} - \vec{\xi'}) \tag{35}$$

2 Appendix

2.1 Linear functionals

In order to understand the mathematical background of the dual space, it is interesting to know the definitions of **linear maps** and **linear functionals**. We already defined linear operators in **Definition 1.4**. As for linear functionals:

Definition 2.1. A linear functional is a linear map L that associates a function with a scalar value, which may be real or complex.

An example of a linear functional could be the linear map $L_x : \mathbb{R}^2 \to \mathbb{R}$ that returns the x-coordinate of the vector it is given. For example:

$$L_x \begin{bmatrix} a \\ b \end{bmatrix} = a \tag{36}$$

In this case, L_x takes us from $\mathbb{R}^2$ to $\mathbb{R}^1$, so its matrix will be 1 by 2 in dimension:

$$L_x = \begin{bmatrix} 1 & 0 \end{bmatrix} \tag{37}$$

so that:

$$L_x \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} a \\ b \end{bmatrix} = a \tag{38}$$

Taking a step back, we know that all linear functionals in $\mathbb{R}^2$ take us from $\mathbb{R}^2$ to $\mathbb{R}^1$. Therefore, by definition, all linear functionals in $\mathbb{R}^2$ are represented by 1×2 matrices. In other words, the set of all linear functionals in $\mathbb{R}^2$ consists of the set of all row matrices. More generally, the set of all linear functionals in $\mathbb{R}^n$ consists of the set of all $1 \times n$ row matrices. In fact, the set of all row matrices, much like column matrices, form their own vector space, which is known as the dual space[7].

2.2 Matrix element of an operator

The matrix element of an operator A is:

Definition 2.2. The matrix element of an operator A expressed in the basis $B = \{u_1, u_2, ...\}$ is defined as:

$$A_{ij} = \langle u_i | A | u_j \rangle \tag{39}$$

where u_i and u_j are the i-th and j-th vectors of the basis, respectively.

2.3 Proof of the Closure relation

The closure relation states that, for a set of vectors $\{|A_1\rangle, |A_2\rangle, ...\}$ to form a basis of a Hilbert space $\mathcal{H}$, they must fulfil the following relation:

If $B = \{\psi_1, \psi_2, ...\}$ is a basis for a Hilbert space $\mathcal{H}$, we can write any vector $|\psi\rangle \in \mathcal{H}$ as:

$$|\psi\rangle = \sum_i c_i |A_i\rangle \tag{40}$$

[7]See **Section 1.2** for more on the dual space

Where the coefficients are $c_i = \langle A_i|\psi\rangle$[8]. If we substitute this expression:

$$|\psi\rangle = \sum_i \langle A_i|\psi\rangle |A_i\rangle \tag{41}$$

As the coefficient is a complex number, we can move it to the end of the expression and separate the inner product:

$$|\psi\rangle = \sum_i |A_i\rangle\langle A_i||\psi\rangle \tag{42}$$

As $|\psi\rangle$ is the same for every element of the sum, we can pull it out of the sum:

$$|\psi\rangle = \left(\sum_i |A_i\rangle\langle A_i|\right)|\psi\rangle \tag{43}$$

And it is now easy to see that this relation will hold if and only if the closure relation holds:

$$\sum_i |A_i\rangle\langle A_i| = \mathbb{1} \tag{44}$$

The inverse argument is easy to follow.

[8] *Proof:* As A_i form an orthonormal basis: $\langle A_i|\psi\rangle = \langle A_i|\sum_j c_i|A_j\rangle = \sum_j c_i\langle A_i|A_j\rangle = \sum_j c_i\delta_{ij} = c_i$