Quantum Mechanics

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Contents

Chapter 1

Hilbert Spaces and Dirac's Notation

1.1 Hilbert Space & Inner Product

Let us start by briefly defining the Hilbert space (usually denoted as $\mathscr{H}$), which plays a key role in the world of quantum mechanics. Basically, the Hilbert space is just a vector space as we know it from the course of Linear Algebra with one additional operation – the *inner product* – that we will inspect later.

First, the elements of the Hilbert space $\mathscr{H}$ are still called vectors. But here comes the first big difference in the notation. Most of you are probably familiar with vectors being denoted as something like $\boldsymbol{v}$, or $\overrightarrow{v}$. In quantum mechanics, however, we use the so called *Dirac's notation* (Paul dirac, 1937–1984) that uses the following symbol for a vector

$$|\psi\rangle \in \mathscr{H}\,. \tag{1.1}$$

To make things even weirder, we are going to call such object as a *Ket-vector* (I will explain why later in the text). As usual, for Ket-vectors, we define the two operations:

1. *addition* : $\mathscr{H} \times \mathscr{H} \to \mathscr{H}$ (this rather fancy formula states that the operation takes two Ket-vectors in $\mathscr{H}$ and produces another Ket-vector in $\mathscr{H}$)

$$|\psi\rangle + |\phi\rangle \in \mathscr{H}\,, \tag{1.2}$$

2. *multiplication by scalar* : $\mathbb{C} \times \mathscr{H} \to \mathscr{H}$, where by scalar in this context we mean a complex number

$$\alpha\,|\psi\rangle \in \mathscr{H}\,, \quad \alpha \in \mathbb{C}\,. \tag{1.3}$$

We can, of course, combine the two preceding operations to express a general *linear combination* as

$$\alpha\,|\psi\rangle + \beta\,|\phi\rangle + \cdots \in \mathscr{H}\,. \tag{1.4}$$

Note that the output of both the operations (or their combination) results always in another Ket-vector in $\mathscr{H}$. We say that $\mathscr{H}$ is *closed* under addition and scalar multiplication.

Up to this point, everything should seem quite normal (except from the weird notation, perhaps). But now comes the key difference between our Hilbert space $\mathscr{H}$ and the common vector space – the Hilbert space includes one additional operation called the *inner product* : $\mathscr{H} \times \mathscr{H} \to \mathbb{C}$, denoted as

$$\langle \phi | \psi \rangle \in \mathbb{C} \,. \tag{1.5}$$

Note that the result of this operation is not another object in $\mathscr{H}$ but rather a scalar (complex number). The inner product is then defined by the following properties

1. $\langle \psi | \psi \rangle \geq 0$,
2. $\langle \phi | \psi \rangle = \langle \psi | \phi \rangle^*$ (* denotes the complex conjugation),
3. $\langle \phi | \psi + \xi \rangle = \langle \phi | \psi \rangle + \langle \phi | \xi \rangle$,
4. $\langle \phi | \alpha \psi \rangle = \alpha \, \langle \phi | \psi \rangle$, $\alpha \in \mathbb{C}$.

Before we move on, note the confusion in the Dirac's notation here. First, regarding the third property, the $|\psi + \xi\rangle$ term stands for $|\psi\rangle + |\xi\rangle$. Second, when we defined the multiplication operation by Eq. (1.3) we used $\alpha \, |f\rangle$ and now when dealing with inner product we write $|\alpha f\rangle$. Unfortunately, the Dirac's notation is sometimes a bit inconsistent. The best thing you can do here is just to get used to it. We will encounter a similar confusion soon when talking about operators.

The first property ensures that the norm of a Ket-vector defined as

$$\| |\psi\rangle \| = \sqrt{\langle \psi | \psi \rangle} \tag{1.6}$$

is always a non-negative real number while $\langle \psi | \psi \rangle = 0$ implies $|\psi\rangle = 0$. This is another ambiguity in the Dirac's notation - the 0 here stands for the zero Ket-vector, while $|0\rangle$ will usually have different meaning. Like I said, just get used to it.

By combining the second property with the third and fourth, one can then easily show that the following holds

$$\langle \psi + \xi | \phi \rangle = \langle \psi | \phi \rangle + \langle \xi | \phi \rangle \;, \quad \langle \alpha \psi | \phi \rangle = \alpha^* \, \langle \psi | \phi \rangle \;. \tag{1.7}$$

Now is the appropriate time to explain why do we uste the term Ket-vectors. According to the above definition, the inner products is an operation that takes two Ket-vectors as an input and produces a complex number at the output. But there is a different way to

look at this. We can define the so called Hermitian adjoint to the Ket-vector $|\phi\rangle$ denoted as

$$|\phi\rangle^\dagger \equiv \langle\phi| \tag{1.8}$$

which now represents a different object living in a different vector space (formally it is called a dual space to our Hilbert space and has a formal mathematical definition which I am not going to bother with here). Such an object is then called a *Bra-vector* and will be treated as follows: whenever a Bra-vector meets a Ket-vector (in this exact ordering), together they form an inner product as

$$\boxed{\langle\phi|\,|\psi\rangle \equiv \langle\phi|\psi\rangle}\,. \tag{1.9}$$

As you can see: Bra meets Ket $\rightarrow$ BraKet $\rightarrow$ *bracket*, which symbolises the inner product notation.

Up to this point everything was defined rather formally. Now let's concretize things a little bit.

1.2 Bases and Representations

The first time you encountered vectors was probably in high school where you were told that vector is something like an arrow which has a direction and length (this reminds me of the animated movie "Despicable Me"). Now look at Fig. 1.1 depicting a 2D vector $\boldsymbol{v}$ (for now, ignore the red axes). The teacher at the high school would then write

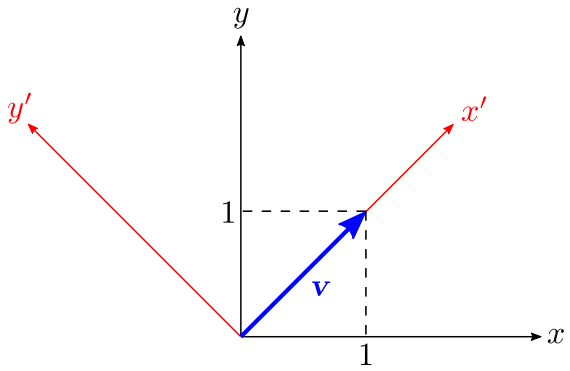

Figure 1.1: 2D vector

something like

$$\boldsymbol{v} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}\,. \tag{1.10}$$

After a while you visited your first course of linear algebra and (hopefully) someone explained to you that this is not correct. A vector is not a column of numbers. This is

only the representation of the vector in a specifically chosen *basis* - a set of n linearly independent vectors where n is the dimension of the corresponding vector space. The correct way to express $\boldsymbol{v}$ would be

$$\boldsymbol{v} = 1\boldsymbol{e}_1 + 1\boldsymbol{e}_2\,, \tag{1.11}$$

where $\boldsymbol{e}_i$ stand for the basis vectors - unit vectors pointing along the x and y axes in this case. One can then represent the vector as a column of numbers but only if the basis is known a priori. If someone would then take a different basis such as $\boldsymbol{e}'_i$ (corresponding to the red x' and y' axes in Fig. 1.1), the vector $\boldsymbol{v}$ would be expressed as

$$\boldsymbol{v} = \sqrt{2}\boldsymbol{e}'_1 + 0\boldsymbol{e}'_2\,. \tag{1.12}$$

The corresponding column representation would then be

$$\boldsymbol{v} = \begin{pmatrix} \sqrt{2} \\ 0 \end{pmatrix}\,, \tag{1.13}$$

which is something completely different than the expression (1.10), even though it represents the same object (the vector $\boldsymbol{v}$)! Hence, we can (and will do) use the representations but at the same time we need to be sure to understand the difference between a vector and it's representation, otherwise QM would not make any sense to us.

Now let's get back to our favourite Hilbert space and define an appropriate basis. We must divide the text into two subsections based on the choice of either discrete or continuous basis. We start with the discrete case.

1.2.1 Discrete Basis

By a discrete basis we mean that the basis vectors can be indexed by a discrete index n (typically an integer) such as $|n\rangle$. Further, we will require the following condition to be met:

$$\boxed{\langle m|n\rangle = \delta_{mn}}\,, \tag{1.14}$$

where δ_{mn} stands for the Kronecker's delta defined as

$$\delta_{mn} = \begin{cases} 1\,, & m = n \\ 0\,, & \text{otherwise} \end{cases}\,. \tag{1.15}$$

A basis with this property is called *orthonormal* (it is trivial to show that $\||\psi\rangle\| = 1$). Any Ket-vector can now be expressed as an appropriate linear combination of such basis Ket-vectors

$$|\psi\rangle = \sum_n \psi_n\,|n\rangle\,, \tag{1.16}$$

where ψ_n are called *coefficients of the expansion*. We can now represent $|\psi\rangle$ as a column (of complex numbers) in the following way:

$$|\psi\rangle \rightarrow \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} , \tag{1.17}$$

which will be further referred to as the *discrete basis representation* of $|\psi\rangle$. Now pause for a minute and note a few things. First, I used "$\rightarrow$" instead of "$=$" to stress out that this is only the representation of $|\psi\rangle$ in the respective basis $\{|n\rangle\}$ and not $|\psi\rangle$ itself. Second, the first component of the column definitely does not have to start with the index 1, it is just a convention to write it this way. Third, N can go (and usually will go) to infinity, so the column will have infinitely (countably) many components.

At this point just one question remains - how to determine the respective coefficients of the expansion? To answer this we proceed as follows:

$$\langle n|\psi\rangle = \langle n| \left(\sum_{n'} \psi_{n'} \left|n'\right\rangle \right) = \sum_{n'} \psi_{n'} \left\langle n\middle|n'\right\rangle = \sum_{n'} \psi_{n'} \delta_{n,n'} = \psi_n \, . \tag{1.18}$$

By comparing the LHS with the RHS we get

$$\psi_n = \langle n|\psi\rangle \ . \tag{1.19}$$

Finally, we can write down the complete formula

$$\boxed{|\psi\rangle = \sum_n \psi_n \, |n\rangle \quad \text{where} \quad \psi_n = \langle n|\psi\rangle}, \tag{1.20}$$

which we will frequently use later in the the upcoming sections.

As the Ket-vectors live in $\mathscr{H}$, we should inspect of how to add two Ket-vectors together and further how to multiply a Ket-vector by a scalar. First, we deal with the addition by writing

$$|\psi\rangle + |\phi\rangle = \sum_n \psi_n \, |n\rangle + \sum_n \phi_n \, |n\rangle = \sum_n (\psi_n + \phi_n) \, |n\rangle \ . \tag{1.21}$$

Hence, to add $|\psi\rangle + |\phi\rangle$ one simply adds the respective components $\psi_n + \phi_n$ as usual. To multiply a Ket-vector by a scalar we write

$$\alpha \, |\psi\rangle = \alpha \sum_n \psi_n \, |n\rangle = \sum_n \alpha \psi_n \, |n\rangle \ , \tag{1.22}$$

so basically we just multiply each component ψ_n by α.

Moving on, we define the corresponding Bra-vector as

$$\boxed{\langle\psi| = \sum_n \psi_n^* \langle n|}, \tag{1.23}$$

To see why, let's express $\langle\phi|\psi\rangle$ as

$$\begin{aligned}\langle\phi|\psi\rangle = \langle\phi|\,|\psi\rangle = \left(\sum_n \phi_n^* \langle n|\right)\left(\sum_{n'} \psi_{n'} \left|n'\right\rangle\right) &= \sum_{n,n'} \phi_n^* \psi_{n'} \left\langle n\middle|n'\right\rangle \\ &= \sum_{n,n'} \phi_n^* \psi_{n'} \delta_{nn'} = \sum_n \phi_n^* \psi_n\,, \end{aligned} \tag{1.24}$$

where we have used the property that once a Bra-vector meets a Ket-vector they form an inner product. Since this result is very important, let's put it in a box

$$\boxed{\langle\phi|\psi\rangle = \sum_n \phi_n^* \psi_n}. \tag{1.25}$$

It should be stressed out that this simple expression holds only due to the orthonormal property of the basis! It is pretty straightforward to show that such an expression for the inner product meets exactly the properties as defined above in the previous section, which justifies the definition (1.23). E.g., the norm of the Ket-vector is given by

$$\||\psi\rangle\| = \sqrt{\langle\psi|\psi\rangle} = \sqrt{\sum_n \psi_n^* \psi_n} = \sqrt{\sum_n |\psi_n|^2}\,, \tag{1.26}$$

which is a perfectly good (and standardly used) norm. To prove the remaining properties is let up to the reader as an exercise.

Based on Eqs. (1.23) and (1.25), one can represent the respective Bra-vector as a row

$$\langle\phi| \to \begin{pmatrix} \phi_1^* & \cdots & \phi_N^* \end{pmatrix}, \tag{1.27}$$

which enables us to express the inner product only by the representations of the respective vectors as

$$\langle\phi|\psi\rangle = \begin{pmatrix} \phi_1^* & \cdots & \phi_N^* \end{pmatrix} \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} = \sum_n \phi_n^* \psi_n\,, \tag{1.28}$$

where the standard matrix multiplication rule is used. Note that in the above expression, there is no need to use "$\to$" anymore since these are truly equal.

1.2.2 An Aside - Dirac Distribution

Perhaps before doing the continuous case, it might be useful to define the Dirac delta function (distribution, to be mathematically correct), since it plays a very important role in QM and we are going to use it a lot in this chapter. Let's start by defining the following function

$$\delta_\varepsilon(x) = \begin{cases} \frac{1}{\varepsilon}\,, & \text{if } |x| \leq \frac{\varepsilon}{2} \\ 0\,, & \text{otherwise} \end{cases}\,. \tag{1.29}$$

The function is plotted in Fig. 1.2. Now there is one important property to this function:

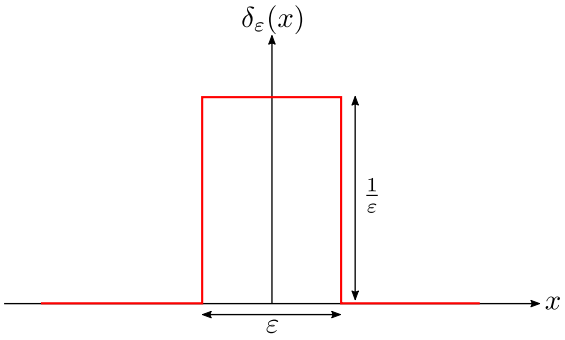

Figure 1.2: Dirac distribution

no matter what the value of ε is, the area under the curve is always equal to unity, i.e.,

$$\int_{-\infty}^{\infty} \mathrm{d}x\, \delta_\varepsilon(x) = 1\,. \tag{1.30}$$

Now the Dirac distribution is simply defined as

$$\delta(x) = \lim_{\varepsilon \to 0} \delta_\varepsilon(x)\,. \tag{1.31}$$

Please note that this is not a correct mathematical way to define such object, but it is sufficient for the purpose of this text. Now based on that definition we can write

$$\delta(x) = \begin{cases} \infty\,, & \text{if } x = 0 \\ 0\,, & \text{otherwise} \end{cases}\,. \tag{1.32}$$

but the infinity value at $x = 0$ is a very specific infinity such that the following condition still holds

$$\int_{-\infty}^{\infty} \mathrm{d}x\, \delta(x) = 1\,. \tag{1.33}$$

Strictly speaking, such object we have just defined is not a function - a function cannot have a nonzero value at only one point and at the same time nonzero area under the

curve - and therefore it is called the *Dirac distribution*.

Before moving on, there is one additional important property of the Dirac distribution. To present it we perform the following calculation

$$\int_{-\infty}^{\infty} \mathrm{d}x\, f(x)\delta(x-x_0) = \int_{-\infty}^{\infty} \mathrm{d}x\, f(x_0)\delta(x-x_0) = f(x_0)\int_{-\infty}^{\infty} \mathrm{d}x\, \delta(x-x_0) = f(x_0)\,, \quad (1.34)$$

where in the first equality we have used the fact that the Dirac distribution is nonzero only at $x = x_0$, which enables us to replace $f(x)$ with just $f(x_0)$, and the last equality just follows from the fact that the Dirac distribution has a unity are under the curve. As this is an important property, let's put it in the box

$$\boxed{\int_{-\infty}^{\infty} \mathrm{d}x\, f(x)\delta(x-x_0) = f(x_0)}\,. \quad (1.35)$$

This property is sometimes called the *sampling property* of the Dirac distribution as it takes the whole function $f(x)$ as an input and produces just one "sample" at $x = x_0$, i.e., $f(x_0)$.

1.2.3 Continuous Basis

In the continuous case, the basis Ket-vectors can not be denoted by a discrete index n anymore but rather by a continuous inded x (typically a real number). Please note that at this points x has nothing to do with position along the x axis! Hence, we will use the notation $|x\rangle$. As in the previous case, we will require the basis to be orthonormal, which can be written as

$$\boxed{\langle x|x'\rangle = \delta(x-x')}\,, \quad (1.36)$$

where $\delta(x)$ stands for the Dirac distribution and plays essentialy the same role as the Kronecker delta in the discrete case. Now to translate from the discrete case to the continuous one, we simply replace all the sums with the corresponding integrals as

$$\sum_n \quad \to \quad \int \mathrm{d}x\ . \quad (1.37)$$

Even though not explicitly stated, the integral here runs over all possible values of x. The Ket-vector $|\psi\rangle$ can thereby be expressed in the basis $\{|x\rangle\}$ as

$$\boxed{|\psi\rangle = \int \mathrm{d}x\ \psi(x)\,|x\rangle}\,. \quad (1.38)$$

Note that when dealing with QM, we usually write the differential $\mathrm{d}x$ right after the integral symbol as opposed to what you have learned in the introductory courses of

Calculus where the differential is written at the end of the expression that is being integrated. The function $\psi(x)$ should now be thought of a continuous set of expansion coefficients w.r.t. a continuous base, similarly as ψ_n in the discrete case. Since it is not possible to express all the values of a function into a column, the representation of $|\psi\rangle$ in the basis $\{|x\rangle\}$ will be just

$$|\psi\rangle \to \psi(x)\,, \tag{1.39}$$

which will be further referred to as the *continuous basis representation* of a Ket-vector (actually, this is what we are later going to call the wavefunction).

By calculating

$$\langle x|\psi\rangle = \langle x| \int \mathrm{d}x'\, \psi(x') \left|x'\right\rangle = \int \mathrm{d}x'\, \psi(x') \left\langle x\middle|x'\right\rangle = \psi(x) \int \mathrm{d}x'\, \delta(x-x') = \psi(x) \tag{1.40}$$

and comparing the LHS with the RHS we get

$$\psi(x) = \langle x|\psi\rangle\ . \tag{1.41}$$

Therefore, we can write down the general formula for expressing a Ket-vector in terms of a continuous basis as

$$\boxed{|\psi\rangle = \int \mathrm{d}x\, \psi(x)\, |x\rangle \quad \text{where} \quad \psi(x) = \langle x|\psi\rangle}\,. \tag{1.42}$$

Moving on, the Bra-vector in the continuous case is defined as

$$\boxed{\langle\phi| = \int \mathrm{d}x\, \phi^*(x)\, \langle x|}\,. \tag{1.43}$$

We can now derive the expression for an inner product in the case of a continuous basis. To do this we express the inner product $\langle\phi|\psi\rangle$ once again as

$$\begin{aligned}\langle\phi|\,|\psi\rangle = \left(\int \mathrm{d}x\, \phi^*(x)\, \langle x|\right) \left(\int \mathrm{d}x'\, \psi(x') \left|x'\right\rangle\right) &= \int \mathrm{d}x\, \mathrm{d}x'\, \phi^*(x)\psi(x') \left\langle x\middle|x'\right\rangle \\ &= \int \mathrm{d}x\, \mathrm{d}x'\, \phi^*(x)\psi(x')\delta(x-x') = \int \mathrm{d}x\, \phi^*(x)\psi(x)\,. \end{aligned} \tag{1.44}$$

Since this expression will be important later, we put it in a box

$$\boxed{\langle\phi|\psi\rangle = \int \mathrm{d}x\, \phi^*(x)\psi(x)}\,. \tag{1.45}$$

You can check once again that the above expression meets the four properties of the inner product defined in the previous section and thus the definition (1.43) is justified.

Things get just a little bit more complicated when looking for the representation of

a Bra-vector in a continuous basis. Based on Eq. (1.45), we should probably write something like

$$\langle\phi| \to \int \mathrm{d}x\, \phi^*(x) \times \,, \tag{1.46}$$

where $\times$ denotes that this is an operation that needs another complex-valued function as an input such as $\psi(x)$ before being evaluated. Now you may ask why do we not need any sum or the "$\times$" symbol when dealing with the Bra representation in the discreet case. It is simply because the sum is implied when multiplying a row with a column (in this order) by the rules of the matrix multiplication, which is not the case here.

1.3 Operators

In this section, we introduce the objects called *operators* which play one of the key roles in the context of QM. So, what exactly is an operator? An operator on a Hilbert space $\mathscr{H}$ is something similar as a function on real numbers $\mathbb{R}$. A function f takes a real number $x \in \mathbb{R}$ as an input and produces another real number $f(x) \in \mathbb{R}$ as an output. In analogy, an operator $\hat{\mathbf{A}}$ is an object that takes a Ket-vector $|\psi\rangle \in \mathscr{H}$ as an input and produces another Ket-vector $|\phi\rangle$ belonging to the same Hilbert space $\mathscr{H}$ as an output. A mathematician would describe such object as

$$\hat{\mathbf{A}} : \mathscr{H} \to \mathscr{H} \,. \tag{1.47}$$

For pedagogical reasons (since this is an introductory text), all operators will be strictly denoted as bold characters with a hat (more advanced textbooks usually omit the notation and it is left up to you to decipher what is an operator and what is just an ordinary variable).

Now as you were warn above, there is another inconsistency in the Dirac's notation. The most logical way of how to write that $\hat{\mathbf{A}}$ takes $|\psi\rangle$ as an input - hereinafter referred to as the operator $\hat{\mathbf{A}}$ *acting on* $|\psi\rangle$ - and produces $|\phi\rangle$ is

$$\hat{\mathbf{A}}\,|\psi\rangle = |\phi\rangle \,. \tag{1.48}$$

However, you will see shortly that sometimes (even though it does not make much sense) it can be useful to denote it as

$$\left|\hat{\mathbf{A}}\psi\right\rangle = |\phi\rangle \,. \tag{1.49}$$

1.3.1 Linear Operators on $\mathscr{H}$

In this text we will deal solely with the *linear* operators, so this short paragraph is devoted to the respective definition. Basically, any linear operator $\hat{\mathbf{A}}$ on $\mathscr{H}$ meets the following two conditions:

1. linearity in vector addition

$$\hat{\mathbf{A}}(|\psi\rangle + |\phi\rangle) = \hat{\mathbf{A}}\,|\psi\rangle + \hat{\mathbf{A}}\,|\phi\rangle \,,$$

2. linearity in scalar multiplication

$$\hat{\mathbf{A}}(\alpha\,|\psi\rangle) = \alpha\hat{\mathbf{A}}\,|\psi\rangle\ ,$$

where $\alpha \in \mathbb{C}$.

Both of those properties can then be formulated together as

$$\hat{\mathbf{A}}(\alpha\,|\psi\rangle + \beta\,|\phi\rangle) = \alpha\hat{\mathbf{A}}\,|\psi\rangle + \beta\hat{\mathbf{A}}\,|\phi\rangle\ , \tag{1.50}$$

where $\alpha, \beta \in \mathbb{C}$. If this reminds you of the linear transformations defined in the course of the linear algebra then you are absolutely correct. Actually, we will see shortly that in the discrete basis representation all linear operators can be represented by matrices.

1.3.2 Operators - Discrete Basis Expansion & Representation

Similarly as in the previous section where we showed how a Ket-vector can be expressed by terms of basis Ket-vectors, here we will do the same with linear operators (it only works for the linear ones) in the discrete case. Further, we will show that any linear operator can be represented by a matrix.

First, we define the *unit operator* which we are going to use the most during this section. The definition is simple - the unit operator $\hat{\mathbf{1}}$ acting on any Ket-vector $|\psi\rangle$ leaves it unchanged. Or mathematically speaking

$$\hat{\mathbf{1}}\,|\psi\rangle = |\psi\rangle\ . \tag{1.51}$$

Now let's look on how we can express the unit operator in terms of our discrete basis $\{|n\rangle\}$. For such purpose, we use Eq. (1.20) to write

$$|\psi\rangle = \sum_n \psi_n\,|n\rangle = \sum_n \langle n|\psi\rangle\,|n\rangle\ . \tag{1.52}$$

To find the formula for the unit operator, we do the following:

$$|\psi\rangle = \sum_n \langle n|\psi\rangle\,|n\rangle = \sum_n |n\rangle\,\langle n|\psi\rangle = \left(\sum_n |n\rangle\,\langle n|\right)|\psi\rangle\ . \tag{1.53}$$

Now by comparing the LHS with the RHS and employing the definition of the unit operator, we can identify

$$\hat{\mathbf{1}} = \sum_n |n\rangle\,\langle n|\ . \tag{1.54}$$

As a next step, we use the unit operator to express any (linear) operator $\hat{\mathbf{A}}$ by terms of the basis Ket-vectors $\{|n\rangle\}$. We proceed as follows:

$$\hat{\mathbf{A}} = \hat{\mathbf{1}}\hat{\mathbf{A}}\hat{\mathbf{1}} = \sum_k |k\rangle\,\langle k|\,\hat{\mathbf{A}}\sum_l |l\rangle\,\langle l| = \sum_{k,l}\langle k|\,\hat{\mathbf{A}}\,|l\rangle\,|k\rangle\,\langle l| = \sum_{k,l} A_{kl}\,|k\rangle\,\langle l|\ , \tag{1.55}$$

where we have denoted $A_{kl} \equiv \langle k| \hat{\mathbf{A}} |l\rangle$. Since this is a very important formula, we put it in a box

$$\boxed{\hat{\mathbf{A}} = \sum_{k,l} A_{kl} |k\rangle \langle l| \quad \text{with} \quad A_{kl} \equiv \langle k| \hat{\mathbf{A}} |l\rangle} \,. \tag{1.56}$$

There is a little subtlety in (1.55) that I should explain, as it might seem that this would work for any operator. But actually, we have secretly made use of the linearity property of $\hat{\mathbf{A}}$ (1.50). Let's inspect this more carefully. If we write

$$\hat{\mathbf{A}} |\psi\rangle = \hat{\mathbf{A}} \left(\hat{\mathbf{1}} |\psi\rangle \right) = \hat{\mathbf{A}} \left(\sum_n |n\rangle \langle n|\psi\rangle \right) , \tag{1.57}$$

then the only way to be able to shift $\hat{\mathbf{A}}$ inside the sum as

$$\hat{\mathbf{A}} \left(\sum_n |n\rangle \langle n|\psi\rangle \right) = \sum_n \hat{\mathbf{A}} |n\rangle \langle n|\psi\rangle \tag{1.58}$$

is to assume $\hat{\mathbf{A}}$ linear, which is exactly what we have done in (1.55).

Next, we show how does the operator $\hat{\mathbf{A}}$ act on a Ket-vector $|\psi\rangle$. To do so, we write

$$\begin{aligned} \hat{\mathbf{A}} |\psi\rangle = \hat{\mathbf{A}} \sum_n \psi_n |n\rangle &= \sum_{k,l} A_{kl} |k\rangle \langle l| \sum_n \psi_n |n\rangle \\ &= \sum_{k,l,n} A_{kl} \psi_n \langle l|n\rangle |k\rangle = \sum_{k,l,n} A_{kl} \psi_n \delta_{ln} |k\rangle = \sum_{k,l} A_{kl} \psi_l |k\rangle \,, \end{aligned} \tag{1.59}$$

where in the first equality the expansion of $|\psi\rangle$ into the basis $\{|n\rangle\}$ was used and further in the second one the above derived expression (1.56) for $\hat{\mathbf{A}}$ was employed. Due to it's importance, the result of the above calculation is rewritten here in a compact form

$$\boxed{\hat{\mathbf{A}} |\psi\rangle = \sum_{k,l} A_{kl} \psi_l |k\rangle} \,. \tag{1.60}$$

If we now denote

$$|\phi\rangle = \hat{\mathbf{A}} |\psi\rangle \tag{1.61}$$

and further expand $|\phi\rangle$ as

$$|\phi\rangle = \sum_k \phi_k |k\rangle \,, \tag{1.62}$$

then by comparing the expressions (1.62) and (1.60) we get the following relation between the expansion coefficients

$$\phi_k = \sum_l A_{kl} \psi_l \,, \tag{1.63}$$

which you should recognise as the matrix multiplication formula. Hence, the discrete basis representation of an operator $\hat{\mathbf{A}}$ is the following matrix

$$\hat{\mathbf{A}} \to \mathbb{A} = \begin{pmatrix} A_{1,1} & A_{1,2} & \cdots \\ A_{2,1} & A_{2,2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} , \tag{1.64}$$

where once again the indexing starting here from 1 is just a conventional choice.

As an exercise, let us find a discrete basis representation of a unit operator. By employing Eq. (1.56) we find

$$1_{kl} = \langle k| \, \hat{\mathbf{1}} \, |l\rangle = \langle k|l\rangle = \delta_{kl} \, , \tag{1.65}$$

which makes sence, because any column vector multiplied by a unit matrix (from left) results in the same unit vector. (Note that in order to distinguish between the number 1 and the element of the matrix representation of $\hat{\mathbf{1}}$ I used the italics font.) Hence, the sought representation for the unit operator is

$$\hat{\mathbf{1}} \to \mathrm{diag}(1, 1, \dots) \, , \tag{1.66}$$

where "diag" stands for the diagonal matrix.

1.3.3 Operators - Continuous Basis Expansion & Representation

Following the previous subsection, here we deal with the continuous basis expansion of operators together with the corresponding representations. Let's start once again with the unit operator which (in analogy) can be expressed as

$$\boxed{\hat{\mathbf{1}} = \int \mathrm{d}x \; |x\rangle \, \langle x|} \, . \tag{1.67}$$

We can simply check this by calculating

$$\begin{aligned} \hat{\mathbf{1}} \, |\psi\rangle = \int \mathrm{d}x \; |x\rangle \, \langle x| \int \mathrm{d}x' \, \psi(x') \, |x'\rangle = \int \mathrm{d}x \, \mathrm{d}x' \; \langle x|x'\rangle \, \psi(x') \, |x\rangle \\ = \int \mathrm{d}x \, \mathrm{d}x' \, \delta(x - x') \psi(x') \, |x\rangle = \int \mathrm{d}x \, \psi(x) \, |x\rangle = |\psi\rangle \; . \end{aligned} \tag{1.68}$$

Now we focus on expressing an arbitrary operator $\hat{\mathbf{A}}$ by terms of the continuous basis $\{|x\rangle\}$. To do so we follow exactly the same procedure as in the previous case, so

$$\begin{aligned} \hat{\mathbf{A}} = \hat{\mathbf{1}}\hat{\mathbf{A}}\hat{\mathbf{1}} = \int \mathrm{d}x \; |x\rangle \, \langle x| \, \hat{\mathbf{A}} \int \mathrm{d}y \; |y\rangle \, \langle y| \\ = \int \mathrm{d}x \, \mathrm{d}y \; \langle x| \, \hat{\mathbf{A}} \, |y\rangle \, |x\rangle \, \langle y| = \int \mathrm{d}x \, \mathrm{d}y \, A(x, y) \, |x\rangle \, \langle y| \; , \end{aligned} \tag{1.69}$$

where we have denoted $A(x,y) \equiv \langle x| \hat{\mathbf{A}} |y\rangle$. (Once again, we assumed the linearity property of $\hat{\mathbf{A}}$ in the above calculation.) Note that instead of x' we used y here for the second integration variable. Of course this has absolutely no effect other than aesthetic. Due to it's importance, we put the result in a box

$$\boxed{\hat{\mathbf{A}} = \int \mathrm{d}x\, \mathrm{d}y\, A(x,y)\, |x\rangle \langle y| \quad \text{with} \quad A(x,y) \equiv \langle x| \hat{\mathbf{A}} |y\rangle}\,. \tag{1.70}$$

It is now pretty straightforward to show how does $\hat{\mathbf{A}}$ act on $|\psi\rangle$. So as with the discreet case,

$$\begin{aligned}\hat{\mathbf{A}} |\psi\rangle &= \int \mathrm{d}x\, \mathrm{d}y\, A(x,y)\, |x\rangle \langle y| \int \mathrm{d}z\, \psi(z)\, |z\rangle = \int \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z\, A(x,y)\psi(z)\, \langle y|z\rangle\, |x\rangle \\ &= \int \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z\, A(x,y)\psi(z)\delta(y-z)\, |x\rangle = \int \mathrm{d}x\, \mathrm{d}y\, A(x,y)\psi(y)\, |x\rangle\ . \end{aligned} \tag{1.71}$$

Hence,

$$\boxed{\hat{\mathbf{A}} |\psi\rangle = \int \mathrm{d}x\, \mathrm{d}y\, A(x,y)\psi(y)\, |x\rangle}\,. \tag{1.72}$$

If we further denote

$$|\phi\rangle = \hat{\mathbf{A}} |\psi\rangle \tag{1.73}$$

and expand $|\phi\rangle$ in the respective basis as

$$|\phi\rangle = \int \mathrm{d}x\, \phi(x)\, |x\rangle\ , \tag{1.74}$$

then by comparing with Eq. (1.72) we get the following relationship between $\phi(x)$ and $\psi(x)$:

$$\phi(x) = \int \mathrm{d}y\, A(x,y)\psi(y)\,, \tag{1.75}$$

which can be thought of as a continuous variant of the matrix multiplication. Thus, the representation of the operator $\hat{\mathbf{A}}$ in the continuous basis can be written as

$$\hat{\mathbf{A}} \to \int \mathrm{d}y\, A(x,y)\times\,, \tag{1.76}$$

where similarly as in the case of a continuous representation of $|\psi\rangle$ the symbol $\times$ indicates an operation which first takes another complex valued function $\psi(y)$ and only then evaluates the integral.

1.4 Commutator

Now that we know how does an operator act on a Ket-vector, it is time to investigate what happens when we act with two different operators on the same Ket-vector. We

will work this out only by using the discrete basis. Hence, assume

$$\hat{\mathbf{A}} = \sum_{k,l} A_{kl} \left|k\right\rangle \left\langle l\right| \quad \text{and} \quad \hat{\mathbf{B}} = \sum_{kl} B_{kl} \left|k\right\rangle \left\langle l\right| . \tag{1.77}$$

The question now arises - does the order of the operators matter? I.e., does $\hat{\mathbf{A}}\hat{\mathbf{B}} \left|\psi\right\rangle$ produce the same result as $\hat{\mathbf{B}}\hat{\mathbf{A}} \left|\psi\right\rangle$? The answer is simple: no. To show why, we compute

$$\hat{\mathbf{A}}\hat{\mathbf{B}} = \left(\sum_{k,l} A_{kl} \left|k\right\rangle \left\langle l\right| \right) \left(\sum_{m,n} B_{mn} \left|m\right\rangle \left\langle n\right| \right) = \sum_{k,n} \left(\sum_{m} A_{km} B_{mn} \right) \left|k\right\rangle \left\langle n\right| . \tag{1.78}$$

But the term in brackets can be expressed as

$$\sum_{m} A_{km} B_{mn} = (\mathbb{A}\mathbb{B})_{kn} , \tag{1.79}$$

where $\mathbb{A}, \mathbb{B}$ stand for the matrices representing the respective operators. But as we know, the matrix multiplication is not commutative, i.e.,

$$\sum_{k,l} (\mathbb{A}\mathbb{B})_{kl} \left|k\right\rangle \left\langle l\right| \neq \sum_{k,l} (\mathbb{B}\mathbb{A})_{kl} \left|k\right\rangle \left\langle l\right| , \tag{1.80}$$

and hence

$$\hat{\mathbf{A}}\hat{\mathbf{B}} \neq \hat{\mathbf{B}}\hat{\mathbf{A}} . \tag{1.81}$$

(In the continuous case the proof is similar.) We say that the operators generally do not *commute*. To determine whether two operators commute or not we define the *commutator* as

$$\boxed{\left[\hat{\mathbf{A}}, \hat{\mathbf{B}}\right] = \hat{\mathbf{A}}\hat{\mathbf{B}} - \hat{\mathbf{B}}\hat{\mathbf{A}}} . \tag{1.82}$$

The two operators then commute iff the corresponding commutator is equal to zero. We will see later that the commutator plays an important role in the context of QM.

There are three properties of commutator that will be stated without proof - that is left for the reader as an exercise:

1. Anticommutativity
$$\left[\hat{\mathbf{A}}, \hat{\mathbf{B}}\right] = - \left[\hat{\mathbf{B}}, \hat{\mathbf{A}}\right] ,$$

2. (Bi)linearity
$$\left[\alpha\hat{\mathbf{A}} + \beta\hat{\mathbf{B}}, \hat{\mathbf{C}}\right] = \alpha \left[\hat{\mathbf{A}}, \hat{\mathbf{C}}\right] + \beta \left[\hat{\mathbf{B}}, \hat{\mathbf{C}}\right] ,$$
where $\alpha, \beta \in \mathbb{C}$ and the prefix "Bi" meaning that this holds also for the second argument,

3. Jacobi identity

$$\left[\hat{\mathbf{A}}, \left[\hat{\mathbf{B}}, \hat{\mathbf{C}}\right]\right] + \left[\hat{\mathbf{B}}, \left[\hat{\mathbf{C}}, \hat{\mathbf{A}}\right]\right] + \left[\hat{\mathbf{C}}, \left[\hat{\mathbf{A}}, \hat{\mathbf{B}}\right]\right] = 0\,.$$

We then say that commutator forms the so called *Lie Algebra*. Finally, there is one additional property that might come in handy when doing algebraic operations with commutators which I am going to state here (again, without the proof):

$$\left[\hat{\mathbf{A}}\hat{\mathbf{B}}, \hat{\mathbf{C}}\right] = \hat{\mathbf{A}}\left[\hat{\mathbf{B}}, \hat{\mathbf{C}}\right] + \left[\hat{\mathbf{A}}, \hat{\mathbf{C}}\right]\hat{\mathbf{B}}\,.$$

1.5 Inverse Operator

Assume an equation in a Hilbert space of the following form

$$\hat{\mathbf{A}}\,|\psi\rangle = |\phi\rangle\ , \tag{1.83}$$

where $|x\rangle$ is the unknown Ket-vector that we would like to determine and $|b\rangle$ is the Ket-vector representing the known RHS of the above equation. To solve such equation, we define the *inverse operator* to $\hat{\mathbf{A}}$, denoted as $\hat{\mathbf{A}}^{-1}$, by the following formula

$$\hat{\mathbf{A}}^{-1}\hat{\mathbf{A}} = \hat{\mathbf{1}}\,. \tag{1.84}$$

Now - based on the previous section - we know that when acting with two operators the order generally matters. So let's take the above equation and act on both sides by $\hat{\mathbf{A}}$ - an incorrect but usual way of saying that would be that we multiply both sides by $\hat{\mathbf{A}}$ from the left. We get

$$\hat{\mathbf{A}}\hat{\mathbf{A}}^{-1}\hat{\mathbf{A}} = \hat{\mathbf{A}}\,. \tag{1.85}$$

But if we rewrite this as

$$(\hat{\mathbf{A}}\hat{\mathbf{A}}^{-1})\hat{\mathbf{A}} = \hat{\mathbf{A}}\,, \tag{1.86}$$

which we can do since acting by a linear operator can be represented by matrix multiplication which is associative, it is apparent that

$$\hat{\mathbf{A}}\hat{\mathbf{A}}^{-1} = \hat{\mathbf{1}} \tag{1.87}$$

and hence the following can be written for the inverse operator

$$\boxed{\hat{\mathbf{A}}^{-1}\hat{\mathbf{A}} = \hat{\mathbf{A}}\hat{\mathbf{A}}^{-1} = \hat{\mathbf{1}}}. \tag{1.88}$$

We can say that any (linear) operator commutes with it's own inverse, i.e.,

$$\left[\hat{\mathbf{A}}, \hat{\mathbf{A}}^{-1}\right] = 0\,. \tag{1.89}$$

The solution to Eq. (1.83) is then simply

$$|\psi\rangle = \hat{\mathbf{A}}^{-1}\,|\phi\rangle\ . \tag{1.90}$$

1.5.1 Inverse Operator - Discrete Case

To determine the form of the inverse operator in the discrete case, we want to solve the following operator equation for $\hat{\mathbf{B}}$:

$$\hat{\mathbf{B}}\hat{\mathbf{A}} = \hat{\mathbf{1}}\,. \tag{1.91}$$

The left hand side of the above equation can be expressed using (1.78) as

$$\sum_{k,l}\left(\sum_{m} B_{km}A_{ml}\right)|k\rangle\langle l| = \sum_{k}|k\rangle\langle k|\,, \tag{1.92}$$

where on the right hand side we employed the discrete basis formula for the unit operator. The above equation is then satisfied if and only if

$$\sum_{m} B_{km}A_{ml} = \delta_{kl}\,, \tag{1.93}$$

or in matrix notation

$$\mathbb{B}\mathbb{A} = \mathbb{I}\,, \tag{1.94}$$

where $\mathbb{I}$ stands for the identity matrix. But this is exactly the definition for the inverse matrix, i.e.,

$$\mathbb{B} = \mathbb{A}^{-1}\,. \tag{1.95}$$

We can then write

$$\hat{\mathbf{A}}^{-1} = \sum_{k,l}\left(\mathbb{A}^{-1}\right)_{kl}|k\rangle\langle l| \tag{1.96}$$

and

$$\hat{\mathbf{A}}^{-1} \to \mathbb{A}^{-1}\,. \tag{1.97}$$

1.5.2 Inverse Operator - Continuous Case

In the continuous case, Eq. (1.92) becomes

$$\int \mathrm{d}x\,\mathrm{d}y\,\left(\int \mathrm{d}z\,B(x,z)A(z,y)\right)|x\rangle\langle y| = \int \mathrm{d}x\,|x\rangle\langle x|\,, \tag{1.98}$$

which is then solved by imposing

$$\int \mathrm{d}z\,B(x,z)A(z,y) = \delta(x-y)\,. \tag{1.99}$$

By denoting

$$A^{-1}(x,y) \equiv B(x,y)\,, \tag{1.100}$$

(the $A^{-1}(x,y)$ does not mean an inverse to the function $A(x,y)$ in this case), we can now write

$$\hat{\mathbf{A}}^{-1} = \int \mathrm{d}x\,\mathrm{d}y\,A^{-1}(x,y)\,|x\rangle\langle y| \tag{1.101}$$

and

$$\hat{\mathbf{A}}^{-1} \to \int \mathrm{d}y\, A^{-1}(x,y) \times \ . \tag{1.102}$$

Note that in case where $\hat{\mathbf{A}}$ represents a differential operator, such function $A^{-1}(x,y)$ is usually called the *Green function*.

1.6 Adjoint Operator

Now it is time to move on to study how do the operators affect inner products. It is also the time when we revisit one of the confusions of the Dirac's notation.

Assume that we act with $\hat{\mathbf{A}}$ onto $|\psi\rangle$ and then form an inner product with $\langle\phi|$. Probably the most correct way of writing this would be something like

$$\langle\phi| \left(\hat{\mathbf{A}}\,|\psi\rangle\right) . \tag{1.103}$$

Of course there is no specific need for the round brackets so we can simplify this to

$$\langle\phi|\,\hat{\mathbf{A}}\,|\psi\rangle \tag{1.104}$$

but we need to keep in mind that when writing it this way the operator acts on the Ket-vector to the right, which is why some authors prefer the notation

$$\left\langle \phi \middle| \hat{\mathbf{A}}\psi \right\rangle . \tag{1.105}$$

Now let's ask the following question – at this point without a specific reasoning of why (that will come later) – is there a way to take the operator $\hat{\mathbf{A}}$ that acts on the right side of the inner product and somehow shift it to the other side such that the inner product stays unchanged? The answer is yes. We start by defining the so called adjoint operator to $\hat{\mathbf{A}}$ and denote it as $\hat{\mathbf{A}}^\dagger$ (the same notation as for the adjoint vector). Then, we impose the following condition on such adjoint operator

$$\boxed{\left\langle \hat{\mathbf{A}}^\dagger\phi \middle| \psi \right\rangle = \left\langle \phi \middle| \hat{\mathbf{A}}\psi \right\rangle}, \tag{1.106}$$

where

$$\left\langle \hat{\mathbf{A}}^\dagger\phi \right| \equiv \left(\hat{\mathbf{A}}^\dagger\,|\phi\rangle\right)^\dagger . \tag{1.107}$$

To proceed further, we need to (as always) separate the following derivation into the discrete and the continuous case.

1.6.1 Adjoint Operator - Discrete Case

We already know that $\hat{\mathbf{A}}$ acting on $|\psi\rangle$ results in

$$\hat{\mathbf{A}}\,|\psi\rangle = \sum_{k,l} A_{kl}\,\psi_l\,|k\rangle\ . \tag{1.108}$$

Then, by forming the inner product with

$$\langle\phi| = \sum_n \phi_n^*\,\langle n| \tag{1.109}$$

we get

$$\langle\phi|\,\hat{\mathbf{A}}\,|\psi\rangle = \sum_n \phi_n^*\,\langle n| \sum_{k,l} A_{kl}\,\psi_l\,|k\rangle = \sum_{k,l} \phi_k^*\,A_{kl}\,\psi_l\,, \tag{1.110}$$

which can be written by using the corresponding representations as

$$\begin{pmatrix}\phi_1^* & \cdots & \phi_N^*\end{pmatrix}\begin{pmatrix}A_{1,1} & A_{1,2} & \cdots\\ A_{2,1} & A_{2,2} & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\begin{pmatrix}\psi_1\\ \vdots\\ \psi_N\end{pmatrix}\ . \tag{1.111}$$

Now let's get back to the freshly defined adjoint operator $\hat{\mathbf{A}}^\dagger$. First, let it act on $|\phi\rangle$ such that

$$\hat{\mathbf{A}}^\dagger\,|\phi\rangle = \sum_{k,l} A_{kl}^\dagger\,\phi_l\,|k\rangle \tag{1.112}$$

and then follow by turning this into the corresponding Bra-vector:

$$\left\langle \hat{\mathbf{A}}^\dagger\phi\right| = \left(\hat{\mathbf{A}}^\dagger\,|\phi\rangle\right)^\dagger = \sum_{k,l}(A_{kl}^\dagger)^*\,\phi_l^*\,\langle k|\ . \tag{1.113}$$

Finally, the inner product with $|\psi\rangle$ ten gives us

$$\left\langle \hat{\mathbf{A}}^\dagger\phi\middle|\psi\right\rangle = \sum_{k,l}(A_{kl}^\dagger)^*\,\phi_l^*\,\langle k|\sum_m \psi_m\,|m\rangle = \sum_{k,l}\psi_k\,(A_{kl}^\dagger)^*\,\phi_l^*\,. \tag{1.114}$$

Now based on the definition we know that $A_{kl}^\dagger = \langle k|\,\hat{\mathbf{A}}^\dagger\,|l\rangle$. Hence, we can write

$$(A_{kl}^\dagger)^* = \langle k|\,\hat{\mathbf{A}}^\dagger\,|l\rangle^* = \left\langle k\middle|\hat{\mathbf{A}}^\dagger l\right\rangle^* = \left\langle \hat{\mathbf{A}}^\dagger l\middle|k\right\rangle = \left\langle l\middle|\hat{\mathbf{A}}k\right\rangle = \langle l|\,\hat{\mathbf{A}}\,|k\rangle = A_{lk}\,, \tag{1.115}$$

where in the third equality we used the second property of the inner product and in the fourth one the definition (1.106) of the adjoint operator. Finally, by comparing the LHS with the RHS of the above equation we get

$$A_{kl}^\dagger = A_{lk}^*\,. \tag{1.116}$$

With this knowledge we can then further manipulate the calculation (1.114) as

$$\sum_{k,l} \psi_k \, (A^\dagger_{kl})^* \, \phi^*_l = \sum_{k,l} \psi_k \, A_{lk} \, \phi^*_l = \sum_{k,l} \phi^*_k \, A_{kl} \, \psi_l \, , \tag{1.117}$$

where in the second equality we just appropriately renamed the indices. As you can see, the result is exactly the same as previously when we acted with $\hat{\mathbf{A}}$ to the right (see the calculation (1.110)), which is exactly what we wanted to achieve. Further, in the discrete representation the matrix corresponding to $\hat{\mathbf{A}}^\dagger$ is then

$$\mathbb{A}^\dagger = \left(\mathbb{A}^{\mathrm{T}}\right)^* \, , \tag{1.118}$$

where $^{\mathrm{T}}$ stands for the matrix transpose. Finally, by using Eq. (1.116) we can write the general formula for $\hat{\mathbf{A}}^\dagger$ as

$$\boxed{\hat{\mathbf{A}}^\dagger = \sum_{k,l} A^*_{lk} \, |k\rangle \, \langle l| \quad \text{with} \quad A_{kl} = \langle k| \, \hat{\mathbf{A}} \, |l\rangle} \, . \tag{1.119}$$

1.6.2 Adjoint Operator - Continuous Case

As always, to proceed with the continuous case we follow the same steps as in the discrete case. Hence, we start by reminding that acting by $\hat{\mathbf{A}}$ onto $|\psi\rangle$ while working with a continuous basis $\{|x\rangle\}$ results in

$$\hat{\mathbf{A}} \, |\psi\rangle = \int \mathrm{d}x \, \mathrm{d}y \, A(x,y) \psi(y) \, |x\rangle \, . \tag{1.120}$$

Then we form the corresponding inner product with

$$\langle \phi| = \int \mathrm{d}z \, \phi^*(z) \, \langle z| \, , \tag{1.121}$$

resulting in

$$\langle \phi| \, \hat{\mathbf{A}} \, |\psi\rangle = \int \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z \, \phi^*(z) A(x,y) \psi(y) \, \langle z|x\rangle = \int \mathrm{d}x \, \mathrm{d}y \, \phi^*(x) A(x,y) \psi(y) \, , \tag{1.122}$$

which is an continuous analogue of (1.111).

Next, we work out the formula for $\hat{\mathbf{A}}^\dagger$ as follows:

$$\left\langle \hat{\mathbf{A}}^\dagger \phi \middle| \psi \right\rangle = \int \mathrm{d}x \, \mathrm{d}y \, [A^\dagger(x,y)]^* \phi^*(y) \, \langle x| \int \mathrm{d}z \, \psi(z) \, |z\rangle = \int \mathrm{d}x \, \mathrm{d}y \, [A^\dagger(x,y)]^* \phi^*(y) \psi(x) \, , \tag{1.123}$$

where

$$[A^\dagger(x,y)]^* = \langle x| \, \hat{\mathbf{A}}^\dagger \, |y\rangle^* = \left\langle \hat{\mathbf{A}}^\dagger y \middle| x \right\rangle = \left\langle y \middle| \hat{\mathbf{A}} x \right\rangle = \langle y| \, \hat{\mathbf{A}} \, |x\rangle = A(y,x) \, . \tag{1.124}$$

Finally, by comparing both sides of the above calculation we get

$$A^\dagger(x,y) = A^*(y,x)\,. \tag{1.125}$$

Then, inserting this back into (1.123) produces

$$\int \mathrm{d}x\,\mathrm{d}y\,[A^\dagger(x,y)]^*\phi^*(y)\psi(x) = \int \mathrm{d}x\,\mathrm{d}y\,\phi^*(y)A(y,x)\psi(x) = \int \mathrm{d}x\,\mathrm{d}y\,\phi^*(x)A(x,y)\psi(y)\,, \tag{1.126}$$

which agrees with (1.122). Therefore, the general formula for $\hat{\mathbf{A}}^\dagger$ can be written as

$$\boxed{\hat{\mathbf{A}}^\dagger = \int \mathrm{d}x\,\mathrm{d}y\,A^*(y,x)\,|x\rangle\,\langle y| \quad \text{with} \quad A(x,y) = \langle x|\,\hat{\mathbf{A}}\,|y\rangle}\,. \tag{1.127}$$

The continuous representation of $\hat{\mathbf{A}}^\dagger$ is then

$$\int \mathrm{d}y\,A^*(y,x)\times\,, \tag{1.128}$$

where the $\times$ symbol has the same meaning as before.

Lastly, we ask ourselves the question - what is the appropriate formula for an adjoint operator to a multiple of two (or more) operators? Fortunately, the answer is trivial and follows directly from the definition (1.106):

$$\left\langle \phi \middle| \hat{\mathbf{A}}\hat{\mathbf{B}}\psi \right\rangle = \left\langle \hat{\mathbf{A}}^\dagger\phi \middle| \hat{\mathbf{B}}\psi \right\rangle = \left\langle \hat{\mathbf{B}}^\dagger\hat{\mathbf{A}}^\dagger\phi \middle| \psi \right\rangle\,, \tag{1.129}$$

and therefore

$$\boxed{(\hat{\mathbf{A}}\hat{\mathbf{B}})^\dagger = \hat{\mathbf{B}}^\dagger\hat{\mathbf{A}}^\dagger}\,. \tag{1.130}$$

This can then be simply extended to a multiple of N operators as

$$(\hat{\mathbf{A}}_1\cdots\hat{\mathbf{A}}_N)^\dagger = \hat{\mathbf{A}}_N^\dagger\cdots\hat{\mathbf{A}}_1^\dagger\,. \tag{1.131}$$

To sum up, we have shown how do operators affect the inner products when acting on the Ket-vector to the right, followed by deriving formulas for the adjoint operators that preserve the inner product while acting on the Bra-vector to the left.

1.7 Eigenvalues and Eigenvectors

Each one of you were surely at least once given the task to calculate the eigenvalues and the corresponding eigenvectors to a specific matrix. No we will just generalise this task to operators. First, assume there exist $\hat{\mathbf{A}}$, $|\lambda\rangle$ and $\lambda \in \mathbb{C}$ such that

$$\hat{\mathbf{A}}\,|\lambda\rangle = \lambda\,|\lambda\rangle\ . \tag{1.132}$$

Then we call λ the *eigenvalue* and $|\lambda\rangle$ the corresponding (to that λ) *eigenvector* of $\hat{\mathbf{A}}$ (we do not use the term eigen-Ket-vector because that looks horrible). There is not much more we can say about the eigenvalue problem in general. But we will further inspect the properties of eigenvalues and the corresponding eigenvectors for a very special class of so called *hermitian operators*, in which case things are going to get much more interesting.

1.8 Hermitian Operators

Now is the time to explain why did we define the adjoint operators. Let's start with a definition. The operator $\hat{\mathbf{A}}$ with the following property:

$$\hat{\mathbf{A}}^\dagger = \hat{\mathbf{A}} \tag{1.133}$$

is called *hermitian*. Or in terms of the inner products we can write

$$\left\langle \hat{\mathbf{A}}\phi \middle| \psi \right\rangle = \left\langle \phi \middle| \hat{\mathbf{A}}\psi \right\rangle = \langle \phi | \, \hat{\mathbf{A}} \, | \psi \rangle \ . \tag{1.134}$$

In other words, it does not matter if $\hat{\mathbf{A}}$ acts on either the right or the left side of the inner product, the result will be the same. Such operators play a key role in quantum mechanics and have some amazing properties that we are going to explore now.

First, we focus on the eigenvalue problem for the hermitian operators, i.e.,

$$\hat{\mathbf{A}} \, | \lambda \rangle = \lambda \, | \lambda \rangle \ . \tag{1.135}$$

First, note that there can (and most typically will) be more then just one eigenvalue to each hermitian operator. The complete set of all the eigenvalues of $\hat{\mathbf{A}}$ is then called the *spectrum* of $\hat{\mathbf{A}}$. And such spectrum can be either discrete or continuous as usual.

Let's now calculate the following inner product:

$$\left\langle \lambda \middle| \hat{\mathbf{A}}\lambda \right\rangle = \lambda \, \langle \lambda | \lambda \rangle \ . \tag{1.136}$$

However, since the operator is hermitian, then

$$\left\langle \lambda \middle| \hat{\mathbf{A}}\lambda \right\rangle = \left\langle \hat{\mathbf{A}}\lambda \middle| \lambda \right\rangle = \lambda^* \, \langle \lambda | \lambda \rangle \ , \tag{1.137}$$

where the second equality follows from the third property of the inner product. By comparing those two results, we arrive at

$$\boxed{\lambda = \lambda^*} . \tag{1.138}$$

In other words, all the eigenvalues of a Hermitian operator are real

$$\lambda \in \mathbb{R} \, . \tag{1.139}$$

And that is a powerful statement!

Next, assume two distinct eigenvalues (and the corresponding eigenvectors) as

$$\hat{\mathbf{A}} \, | \lambda \rangle = \lambda \, | \lambda \rangle \ , \quad \hat{\mathbf{A}} \, | \mu \rangle = \mu \, | \mu \rangle \ , \tag{1.140}$$

where $\lambda \neq \mu$. We then consider the following inner product

$$\left\langle \lambda \middle| \hat{\mathbf{A}}\mu \right\rangle = \mu \left\langle \lambda | \mu \right\rangle \, . \tag{1.141}$$

Once again, we make use of the hermitian property of $\hat{\mathbf{A}}$ to express

$$\left\langle \lambda \middle| \hat{\mathbf{A}}\mu \right\rangle = \left\langle \hat{\mathbf{A}}\lambda \middle| \mu \right\rangle = \lambda \left\langle \lambda | \mu \right\rangle \, , \tag{1.142}$$

while there is no need for the * symbol anymore since λ is real. If we then take the preceding two equations and subtract the first one from the second we get

$$(\lambda - \mu) \left\langle \lambda | \mu \right\rangle = 0 \, , \tag{1.143}$$

but since $\lambda \neq \mu$, the only possibility to fulfill the above equation is that

$$\boxed{\left\langle \lambda | \mu \right\rangle = 0 \quad \text{for} \quad \lambda \neq \mu} \, . \tag{1.144}$$

In other words, all the eigenvectors of $\hat{\mathbf{A}}$ corresponding to distinct eigenvalues are mutually orthogonal. Another powerful statement here!

Let's now make use of the two found properties to express an appropriate orthonormal basis by the set of all the eigenvectors of $\hat{\mathbf{A}}$, hereinafter referred to as the *eigenbasis*.

1.8.1 Orthonormal Eigenbasis - Discrete Case

In the discrete case, i.e., the case where the spectrum of $\hat{\mathbf{A}}$ is discrete, we can label each eigenvalue and the corresponding eigenvector by a discrete index k as

$$\hat{\mathbf{A}} \left| \lambda_k \right\rangle = \lambda_k \left| \lambda_k \right\rangle \, . \tag{1.145}$$

By applying Eq. (1.144), we get

$$\left\langle \lambda_k | \lambda_l \right\rangle = 0 \quad \text{for} \quad k \neq l \, . \tag{1.146}$$

Then, it must hold that

$$\left\langle \lambda_k | \lambda_l \right\rangle = \alpha_k \delta_{kl} \, , \tag{1.147}$$

since there is no reason for the eigenvectors to be automatically normalized to unit norm. Note that even if there are two indices k, l present at the left hand side of the above equation, we only need one of them for α_k due to the presence of δ_{kl} on the right hand side. Also, due to the first property of the inner product, $\alpha_k \in \mathbb{R}$. So at this point, we have an orthogonal basis. To make it further orthonormal, we simply define

$$\left| k \right\rangle = \frac{\left| \lambda_k \right\rangle}{\sqrt{\alpha_k}} \, . \tag{1.148}$$

By calculating

$$\langle k|l\rangle = \frac{\langle \lambda_k|\lambda_l\rangle}{\sqrt{\alpha_k\alpha_l}} = \frac{\alpha_k\delta_{kl}}{\sqrt{\alpha_k\alpha_l}} = \delta_{kl}\,, \tag{1.149}$$

we come to a conclusion that such renormalized eigenvectors form an appropriate orthonormal eigenbasis. Actually, to be completely honest, there is one additional think we ought to do. Formally, we must show that the basis $\{|k\rangle\}$ is complete, which basically means that any $|\psi\rangle \in \mathscr{H}$ can be expressed just by those. But the proof is generally complicated, so you have to blindly believe me that it is true.

1.8.2 Orthonormal Eigenbasis - Continuous Case

In case of the continuous spectrum of $\hat{\mathbf{A}}$, we use a continuous index x to label the eigenvalues and the corresponding eigenvectors as

$$\hat{\mathbf{A}}\,|\lambda(x)\rangle = \lambda(x)\,|\lambda(x)\rangle\ . \tag{1.150}$$

Based on Eq. (1.144) we then have

$$\langle\lambda(x)|\lambda(y)\rangle = 0 \quad \text{for} \quad x \neq y\,, \tag{1.151}$$

which means that

$$\langle\lambda(x)|\lambda(y)\rangle = \alpha(x)\delta(x-y)\,. \tag{1.152}$$

By following the same steps as in the discrete case, we can now normalize the respective eigenvectors to

$$|x\rangle = \frac{|\lambda(x)\rangle}{\sqrt{\alpha(x)}}\,. \tag{1.153}$$

By checking

$$\langle x|y\rangle = \frac{\langle\lambda(x)|\lambda(y)\rangle}{\sqrt{\alpha(x)\alpha(y)}} = \frac{\alpha(x)\delta(x-y)}{\sqrt{\alpha(x)\alpha(y)}} = \delta(x-y)\,, \tag{1.154}$$

and therefore we have just proven that such renormalization (again) leads to an appropriate orthonormal eigenbasis $\{|x\rangle\}$.

1.8.3 Hermitian Operator in it's Eigenbasis - Discrete Case

We proceed further to show how does one express a general linear hermitian operator $\hat{\mathbf{A}}$ in it's own eigenbasis. Based on the above discussions, we assume an orthonormal basis $\{|k\rangle\}$ formed by the eigenvalues of $\hat{\mathbf{A}}$, i.e.,

$$\hat{\mathbf{A}}\,|k\rangle = \lambda_k\,|k\rangle\ . \tag{1.155}$$

By employing the general formula for expressing any operator in terms of a discrete basis (1.56) we write

$$\hat{\mathbf{A}} = \sum_{k,l}\langle k|\,\hat{\mathbf{A}}\,|l\rangle\,|k\rangle\,\langle l| = \sum_{k,l}\lambda_l\,\delta_{kl}\,|k\rangle\,\langle l| = \sum_k \lambda_k\,|k\rangle\,\langle k|\ , \tag{1.156}$$

Due to the importance of this formula we put it in a box

$$\boxed{\hat{\mathbf{A}} = \sum_k \lambda_k \left|k\right\rangle \left\langle k\right|} . \tag{1.157}$$

By acting with $\hat{\mathbf{A}}$ on $\left|\psi\right\rangle$ then results in

$$\hat{\mathbf{A}} \left|\psi\right\rangle = \sum_k \lambda_k \left|k\right\rangle \left\langle k\right| \sum_l \psi_l \left|l\right\rangle = \sum_k \lambda_k \psi_k \left|k\right\rangle \ , \tag{1.158}$$

and the discrete representation of $\hat{\mathbf{A}}$ is therefore

$$\hat{\mathbf{A}} \to \mathrm{diag}(\lambda_1, \lambda_2, \dots) \, . \tag{1.159}$$

1.8.4 Hermitian Operator in it's Eigenbasis - Continuous Case

In the continuous case, we assume a continuous orthonormal basis $\{\left|x\right\rangle\}$ formed by the eigenvectors of $\hat{\mathbf{A}}$, i.e.,

$$\hat{\mathbf{A}} \left|x\right\rangle = \lambda(x) \left|x\right\rangle \ . \tag{1.160}$$

Now we use the general formula (1.70) to calculate

$$\hat{\mathbf{A}} = \int \mathrm{d}x \, \mathrm{d}y \ \left\langle x\right| \hat{\mathbf{A}} \left|y\right\rangle \left|x\right\rangle \left\langle y\right| = \int \mathrm{d}x \, \mathrm{d}y \, \lambda(y) \delta(x-y) \left|x\right\rangle \left\langle y\right| = \int \mathrm{d}x \, \lambda(x) \left|x\right\rangle \left\langle x\right| \ . \tag{1.161}$$

Another important formula here – let's put it in a box:

$$\boxed{\hat{\mathbf{A}} = \int \mathrm{d}x \, \lambda(x) \left|x\right\rangle \left\langle x\right|} . \tag{1.162}$$

Now by acting with $\hat{\mathbf{A}}$ onto $\left|\psi\right\rangle$ we get

$$\hat{\mathbf{A}} \left|\psi\right\rangle = \int \mathrm{d}x \, \lambda(x) \left|x\right\rangle \left\langle x\right| \int \mathrm{d}y \, \psi(y) \left|y\right\rangle = \int \mathrm{d}x \, \lambda(x) \psi(x) \left|x\right\rangle \ . \tag{1.163}$$

Hence, the corresponding continuous representation of $\hat{\mathbf{A}}$ is just

$$\hat{\mathbf{A}} \to \lambda(x) \, . \tag{1.164}$$

And that basically covers all the basic properties of the Hermitian operators we need for the purpose of this text.

1.9 Spectral Decomposition

The last bit of mathematics we are going to need in order to solve the famous Schrödinger equation is called the *spectral decomposition theorem*. But first, we need to introduce a new concept called the function of an operator. All of us are familiar with functions of

the variable $x \to f(x)$, such as $\sin(x), \exp(x)$, etc. But what if I asked you to evaluate the respective function while replacing x with a operator $\hat{\mathbf{A}}$, i.e.,

$$f(\hat{\mathbf{A}}) = ? \tag{1.165}$$

Fortunately, the answer to this is simple. We just use the fact that each "well behaved" (analytic, to be precise) function can be expressed by the respective Taylor series as

$$f(x) = \sum_n c_n x^n \,. \tag{1.166}$$

The same function but now evaluated at $\hat{\mathbf{A}}$ is then defined by the same Taylor series as

$$f(\hat{\mathbf{A}}) = \sum_n c_n \hat{\mathbf{A}}^n \,. \tag{1.167}$$

If we now assume a general hermitian operator $\hat{\mathbf{A}}$ and the corresponding basis of normalised eigenvectors $\{|n\rangle\}$ (for the purpose of this text we need only the discrete version), the spectral decomposition theorem then states the following:

$$\boxed{f(\hat{\mathbf{A}}) = \sum_k f(\lambda_k) \, |k\rangle \, \langle k|} \,. \tag{1.168}$$

To prove this, we proceed as follows:

$$\begin{aligned} f(\hat{\mathbf{A}}) &= \sum_{k,l} \langle k| \, f(\hat{\mathbf{A}}) \, |l\rangle \, |k\rangle \, \langle l| = \sum_{k,l} \langle k| \left(\sum_n c_n \hat{\mathbf{A}}^n \right) |l\rangle \, |k\rangle \, \langle l| = \sum_{k,l,n} c_n \, \langle k| \, \hat{\mathbf{A}}^n \, |l\rangle \, |k\rangle \, \langle l| \\ &= \sum_{k,l} \left(\sum_n c_n \lambda_l^n \right) \langle k|l\rangle \, |k\rangle \, \langle l| = \sum_{k,l} f(\lambda_l) \delta_{kl} \, |k\rangle \, \langle l| = \sum_k f(\lambda_k) \, |k\rangle \, \langle k| \,, \end{aligned} \tag{1.169}$$

where in the first equality we have used the fact that $f(\hat{\mathbf{A}})$ is itself an operator and therefore it must be able to be expressed using (1.56).

1.10 Unitary Operators

The last type of operators that are important for QM are the *unitary operators* that are defined by the property

$$\boxed{\langle \psi | \phi \rangle = \left\langle \hat{\mathbf{U}} \psi \middle| \hat{\mathbf{U}} \phi \right\rangle} \,, \tag{1.170}$$

where $\hat{\mathbf{U}}$ stands for an unitary operator and $|\psi\rangle$, $|\phi\rangle$ are arbitrary Ket-vectors. The above statement is then usually described by the statement that a unitary operator does not change the inner product. There is now an important property of the eigenvalues of

such operators that we are going to inspect. First, assume the eigenvalue problem of a unitary operator formulated as

$$\hat{\mathbf{U}}\,|\lambda\rangle = \lambda\,|\lambda\rangle\ , \tag{1.171}$$

where (as always) λ is the eigenvalue and the corresponding eigenvector $|\lambda\rangle$ is normalized to unity, i.e.,

$$\langle\lambda|\lambda\rangle = 1\,. \tag{1.172}$$

At this point, it does not matter if the whole eigenvalue spectrum of $\hat{\mathbf{U}}$ is discrete or continuous. Then, we can calculate

$$\left\langle \hat{\mathbf{U}}\lambda \middle| \hat{\mathbf{U}}\lambda \right\rangle = |\lambda|^2\,\langle\lambda|\lambda\rangle = |\lambda|^2\,. \tag{1.173}$$

But at the same time, according to the definition (1.170), we must have

$$\left\langle \hat{\mathbf{U}}\lambda \middle| \hat{\mathbf{U}}\lambda \right\rangle = \langle\lambda|\lambda\rangle = 1\,. \tag{1.174}$$

By combining both the above results, we arrive at

$$\boxed{|\lambda| = 1}\,. \tag{1.175}$$

This means that all the eigenvalues of an unitary operator lie on the unit circle in the complex plane, and due to this, they can always be written as

$$\lambda = \mathrm{e}^{\mathrm{i}\mu}\,, \tag{1.176}$$

where $\mu \in \mathbb{R}$. As we will see later, the most important unitary operator in QM is the evolution operator, that describes how does a system evolve in time.

1.11 Summary

I understand that this was probably a bit overwhelming for someone who encountered the Dirac's notation and Hilbert spaces for the first time. Therefore, here I present two tables (for the discrete and the continuous case) with the most important formulae while strictly distinguishing between the real objects and their respective representations.

Object	True Form	Representation
Ket-vector	$\|\psi\rangle = \sum_n \psi_n \|n\rangle$	$\begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \end{pmatrix}$
Bra-vector	$\langle\psi\| = \sum_n \psi_n \langle n\|$	$\begin{pmatrix} \psi_1^* & \psi_2^* & \cdots \end{pmatrix}$
Operator	$\hat{\mathbf{A}} = \sum_{k,l} A_{kl} \|k\rangle \langle l\|$	$\mathbb{A} = \begin{pmatrix} A_{1,1} & A_{1,2} & \cdots \\ A_{2,1} & A_{2,2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$
Inverse operator	$\hat{\mathbf{A}}^{-1} = \sum_{k,l} (\mathbb{A}^{-1})_{kl} \|k\rangle \langle l\|$	$\mathbb{A}^{-1} = \begin{pmatrix} A_{1,1} & A_{1,2} & \cdots \\ A_{2,1} & A_{2,2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}^{-1}$
Adjoint operator	$\hat{\mathbf{A}}^\dagger = \sum_{k,l} A_{lk}^* \|k\rangle \langle l\|$	$\mathbb{A}^\dagger = \left(\mathbb{A}^{\mathrm{T}}\right)^* = \begin{pmatrix} A_{1,1}^* & A_{2,1}^* & \cdots \\ A_{1,2}^* & A_{2,2}^* & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$
Operator in eigenbasis	$\hat{\mathbf{A}} = \sum_k \lambda_k \|k\rangle \langle k\|$	$\mathbb{A} = \operatorname{diag}(\lambda_1, \lambda_2, \dots)$

Table 1.1: Discrete basis formulas

Object	True Form	Representation
Ket-vector	$\|\psi\rangle = \int \mathrm{d}x\, \psi(x) \|x\rangle$	$\psi(x)$
Bra-vector	$\langle\psi\| = \int \mathrm{d}x\, \psi^*(x) \langle x\|$	$\int \mathrm{d}x\, \psi^*(x)\times$
Inner product	$\langle\phi\|\psi\rangle$	$\int \mathrm{d}x\, \phi^*(x)\psi(x)$
Operator	$\hat{\mathbf{A}} = \int \mathrm{d}x\, \mathrm{d}y\, A(x,y) \|x\rangle \langle y\|$	$\int \mathrm{d}y\, A(x,y)\times$
Inverse operator	$\hat{\mathbf{A}}^{-1} = \int \mathrm{d}x\, \mathrm{d}y\, A^{-1}(x,y) \|x\rangle \langle y\|$	$\int \mathrm{d}y\, A^{-1}(x,y)\times$
Adjoint operator	$\hat{\mathbf{A}}^\dagger = \int \mathrm{d}x\, \mathrm{d}y\, A^*(y,x) \|x\rangle \langle y\|$	$\int \mathrm{d}y\, A^*(y,x)\times$
Operator in eigenbasis	$\hat{\mathbf{A}} = \int \mathrm{d}x\, \lambda(x) \|x\rangle \langle x\|$	$\lambda(x)$

Table 1.2: Continuous basis formulas

Chapter 2

Postulates of Quantum Mechanics

In this chapter we focus on developing the framework of QM based on the postulates which will be stated in their general form by using the Dirac's notation. And only then, based on those postulates together with what we have learnt in the preceding chapter, we will derive the formulas in the famous wavefunction representation.

2.1 Postulate I. - Physical System

Each physical system is represented by a corresponding Hilbert space $\mathscr{H}$. The state of such system is fully described by $\|\psi\rangle \in \mathscr{H}$.

I can imagine that for someone that has never seen QM before this probably makes absolutely zero sense. Please be prepared that all the postulates of QM are just weird when you go through them for the first time and it seems like there is no correspondence to the classical physics as you have learnt it so far. But don't worry - after we deal with all the postulates, I will show you that there is actually a very direct correspondence with the Hamilton formulation of classical mechanics that we will make use of.

Let's compare this postulate with what do we know from the classical dynamics. In classical dynamics, a physical system is represented by the phase space consisting of the generalised coordinates and the conjugate momenta. The state of the system is then represented by a point in such phase space. On the other hand, in the world of QM, the system is represented by an abstract Hilbert space $\mathscr{H}$ and the state is then given by $|\psi\rangle \in \mathscr{H}$. Maybe it is worth reminding ourselves of what do we mean by the state of the system – to know the state of a system means that we possess all the necessary information to be able to calculate how will the system evolve in time.

There is not much more we can do here at this point. But before moving on, for the purpose of this text, we will require that the Ket-vectors representing the states will be always normalised, i.e.,

$$\langle\psi|\psi\rangle = 1\,. \tag{2.1}$$

This is by no means necessary, but it is a standard convention that will make our life a bit easier.

2.2 Postulate II. - Observables

The generalised coordinates and the conjugate momenta are replaced by the linear hermitian operators

$$q \to \hat{\mathbf{q}}\,, \quad p \to \hat{\mathbf{p}}\,.$$

Any dynamical variable is then replaced by the linear hermitian operator by the following rule

$$A(q,p,t) \to \hat{\mathbf{A}} = A(\hat{\mathbf{q}},\hat{\mathbf{p}},t)\,.$$

First, in the context of QM, dynamical variables are usually referred to as the *observables* (we can observe them by the act of measurement). Second, at this point we are not going to specify how to define the $\hat{\mathbf{q}}$ and $\hat{\mathbf{p}}$ operators – that will come later, but it is important to understand the latter formula for $\hat{\mathbf{A}}$. In classical dynamics, any observable (dynamical variable) is a function of the generalised coordinates, conjugate momenta and time, i.e., $A = A(q,p,t)$. The formula $\hat{\mathbf{A}} = A(\hat{\mathbf{q}},\hat{\mathbf{p}},t)$ then means that to express the operator $\hat{\mathbf{A}}$ we take the the function $A(q,p,t)$ and replace $q \to \hat{\mathbf{q}}$ and $p \to \hat{\mathbf{p}}$. Some authors use the notation $\hat{\mathbf{A}}(\hat{\mathbf{q}},\hat{\mathbf{p}},t)$, which is perfectly correct, since (of course) the resulting object is an operator. But I wanted to stress out that the operator arises by taking the same function as in the classical case and only then replacing the arguments with the corresponding operators. So please keep that in mind. Now moving on to the next postulate.

2.3 Postulate III. - Measurements

When measuring the observable A, the only possible outcomes are the eigenvalues of the corresponding operator $\hat{\mathbf{A}}$.

Now things start to get interesting. First, we should specify more clearly what do we mean by "measuring". In the context of QM, by measuring we simply mean that we somehow determine the value of the observable a. Do not think of of some elaborate method including various expensive measurement tools. On the contrary, think of it in a more abstract way.

So the postulate states that the only allowed results of the measurement are the eigenvalues of the corresponding operator. This explains why did we require all the operators to be hermitian in the preceding postulate – they have purely real eigenvalues, and of course the measurement of a real physical quantity cannot have a complex result.

We should emphasise that this is something completely different than what we are used to in the world of classical dynamics. In QM, one of the most important operators is the

Hamilton operator $\hat{\mathbf{H}}$ representing the total energy of the system. And in many cases, the spectrum of $\hat{\mathbf{H}}$ will be discrete. Then, according to this postulate, only discrete values of energy can be measured on the system! But more on this later. Now, let's move on to the next postulate.

2.4 Postulate IV. - Mean Value of Measurements

> When repeatedly measuring the observable A on a system in state $|\psi\rangle$, the mean value is equal to $\langle\psi|\,\hat{\mathbf{A}}\,|\psi\rangle$.

This is probably the most complicated postulate to understand, so let me make a few comments here. First, I should probably explain what do we mean by repeatedly measuring on a system in state $|\psi\rangle$. But it would not make much sence until we learn the Postulate V, so let me postpone this for now. Second, the previously mentioned postulate tells us that the only possible outcomes when measuring the observable A are eigenvalues of $\hat{\mathbf{A}}$. And now this postulate actually specifies the probabilities of the individual outcomes, and will now show how.

2.4.1 Mean Value - Discrete Case

Assume a basis $\{|n\rangle\}$ of eigenvectors of $\hat{\mathbf{A}}$, i.e.,

$$\hat{\mathbf{A}}\,|n\rangle = a_n\,|n\rangle\ , \tag{2.2}$$

where a_n denotes the corresponding eigenvalue. Since the system is in a state $|\psi\rangle$, we can expand it in our basis as

$$|\psi\rangle = \sum_n \psi_n\,|n\rangle\ . \tag{2.3}$$

According to the postulate, the mean value of the results when repeatedly measuring A is equal to

$$\bar{A} = \langle\psi|\,\hat{\mathbf{A}}\,|\psi\rangle = \sum_{m,n}\psi_m^*\psi_n\,\langle m|\,\hat{\mathbf{A}}\,|n\rangle = \sum_{m,n}\psi_m^*\psi_n a_n\delta_{mn} = \sum_n |\psi_n|^2 a_n\,. \tag{2.4}$$

Note that I have used the overline to denote a mean value. Some authors prefer to use $\langle A\rangle$, but (at least to me) this is unpractical, since we already use the pointy brackets for the inner product. From the theory of probability we can now identify that

$$\boxed{w_n \equiv |\psi_n|^2 = |\,\langle n|\psi\rangle\,|^2} \tag{2.5}$$

represents the probability that the output of the individual measurement will be a_n. Since the probabilities must always add up to 1, we can write

$$\sum_n w_n = \sum_n |\psi_n|^2 = \sum_n \psi_n^*\psi_n = \langle\psi|\psi\rangle = 1\,, \tag{2.6}$$

which is why we required all the physical states to be normalised to unity.

2.4.2 Mean Value - Continuous Case

In the continuous case, the following applies for the continuous basis $\{|x\rangle\}$ of eigenvectors

$$\hat{\mathbf{A}}\,|x\rangle = a(x)\,|x\rangle\ , \tag{2.7}$$

where $a(x)$ denotes the continuous spectrum of eigenvalues. The state $|\psi\rangle$ is now expressed as

$$|\psi\rangle = \int \mathrm{d}x\,\psi(x)\,|x\rangle \tag{2.8}$$

while the following applies for the mean value $\bar{a}$:

$$\bar{A} = \langle\psi|\,\hat{\mathbf{A}}\,|\psi\rangle = \int \mathrm{d}x\,\mathrm{d}y\,\psi^*(x)\psi(y)\,\langle x|\,\hat{\mathbf{A}}\,|y\rangle = \int \mathrm{d}x\,|\psi(x)|^2 a(x)\,, \tag{2.9}$$

whereas we can identify

$$\boxed{w(x) \equiv |\psi(x)|^2 = |\,\langle x|\psi\rangle\,|^2} \tag{2.10}$$

as the probability density for the measurement result to be equal to $a(x)$. Similarly as in the previous case, the probability density must always give 1 when integrated over all the possible values of x. Hence,

$$\int \mathrm{d}x\,w(x) = \int \mathrm{d}x\,|\psi(x)|^2 = \int \mathrm{d}x\,\psi^*(x)\psi(x) = \langle\psi|\psi\rangle = 1\,, \tag{2.11}$$

which once again explains the necessity of normalised states.

So now we know that the outputs of any measurement can be only the eigenvalues of the corresponding hermitian operator and at the same time if we know the state $|\psi\rangle$ we are able to predict the probabilities of the individual outcomes. But even though all of this sounds nice and easy, we should be shocked - the QM dictates that the world as we know id does not behave in a deterministically as Newton thought but rather stochastically! To paraphrase Forrest Gump – "Quantum mechanics is like a box of chocolates. You never know what you're gonna get."

2.5 Postulate V. - System Collapse

By measuring a specific value of the observable A, the system transitions (collapses) to the corresponding eigenstate.

Now, as promised, let me explain what do we mean by the repeated measurement on a system in the state $|\psi\rangle$ in the context of the preceding postulate. Assume we want to measure the observable A on a system in a general state $|\psi\rangle$. But this postulate states that whenever we conduct the measurement, the system collapses to the eigenstate corresponding to the measured eigenvalue. Hence, we cannot conduct the measurement again, since the system is now in a different state then before! Hence, the only way

to conduct repeated measurements is to have (infinitely) many identical copies of the system, each one prepared in the same state $|\psi\rangle$. The measurement is then conducted on each such system exactly once. The mean value of all such measurements then gives $\langle\psi|\,\hat{\mathbf{A}}\,|\psi\rangle$ as stated above.

2.6 Postulate VI. - Schrödinger Picture of Time Evolution

The the time evolution of a system is contained in the state Ket-vector $|\psi\rangle = |\psi(t)\rangle$ while the operators $\hat{\mathbf{q}}$ and $\hat{\mathbf{p}}$ are time independent. The equation of motion is called the Schrödinger's equation and is expressed as

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\psi(t)\rangle = \hat{\mathbf{H}}\,|\psi(t)\rangle\ ,$$

where

$$\hat{\mathbf{H}} = H(\hat{\mathbf{q}}, \hat{\mathbf{p}}, t)$$

is the Hamilton operator corresponding to the Hamiltonian and

$$\hbar \approx 1.054571817 \cdot 10^{-34}\,\mathrm{J\,s}$$

is the reduced Planck constant.

A few notes here. First, the $\hat{\mathbf{q}}$ and $\hat{\mathbf{p}}$ stand for the whole set of $\{\hat{\mathbf{q}}_k\}, \{\hat{\mathbf{p}}_k\}$, but we will use this simplified notation for the sake of readability. Second, the fact that the time evolution of a system is contained in the respective state Ket-vector is just a standardly used convention called the *Schrödinger picture*. Later in the text, we will also present a different convention called the *Heisenberg picture* where (on the contrary) the states are time independent and $\hat{\mathbf{q}} = \hat{\mathbf{q}}(t)$, $\hat{\mathbf{p}} = \hat{\mathbf{p}}(t)$ instead. Third, even though $\hat{\mathbf{q}}$, $\hat{\mathbf{p}}$ are time independent, a general observable $\hat{\mathbf{A}} = A(\hat{\mathbf{q}}, \hat{\mathbf{p}}, t)$ can depend on time explicitly as

$$\frac{\mathrm{d}\hat{\mathbf{A}}(t)}{\mathrm{d}t} = \frac{\partial A(\hat{\mathbf{q}}, \hat{\mathbf{p}}, t)}{\partial t}\,, \tag{2.12}$$

where the notation on the RHS means

$$\frac{\partial A(\hat{\mathbf{q}}, \hat{\mathbf{p}}, t)}{\partial t} \equiv \left.\frac{\partial A(q, p, t)}{\partial t}\right|_{\substack{q\to\hat{\mathbf{q}}\\ p\to\hat{\mathbf{p}}}}\,. \tag{2.13}$$

(This is why I prefer not to use the operator symbol for $A(\hat{\mathbf{q}}, \hat{\mathbf{p}}, t)$ – to stress out that e.g., when dealing with derivatives, we treat A as a standard multivariable function and only then replace q, p with the corresponding operators.) Hence, an observable $\hat{\mathbf{A}}$ depends on time iff the dynamical variable A has an explicit time dependence, which (mostly) won't be the case in this text.

Now we have covered all the postulates of QM. And even though they might seem a bit random at first sight, in the following section, I will show you that there is actually a nice correspondence between QM and the classical dynamics.

2.7 Correspondence between QM and classical dynamics

There is a different way of how to look at the time evolution in the context of QM. Instead of considering the state of the system to be time dependent, we can define the *evolution operator* in the following way

$$|\psi(t)\rangle = \hat{\mathbf{U}}(t, t_0)\,|\psi(t_0)\rangle\ . \tag{2.14}$$

where $t_0 = const.$ represents an arbitrary (let's call it initial) time and $|\psi_0\rangle$ stands for the state Ket-vector evaluated at t_0. (Note that due to the Schrödinger equation being linear, $\hat{\mathbf{U}}(t, t_0)$ must also be linear.) Hence, the time evolution is then represented by acting with this operator onto the initial state. For simplicity and without the loss of generality, we set $t_0 = 0$ and relabel

$$\hat{\mathbf{U}}(t, 0) \to \hat{\mathbf{U}}(t)\,, \quad |\psi(t_0)\rangle = |\psi(0)\rangle \to |\psi_0\rangle\ . \tag{2.15}$$

Hence, we can rewrite (2.14) as

$$|\psi(t)\rangle = \hat{\mathbf{U}}(t)\,|\psi_0\rangle\ . \tag{2.16}$$

Since we require the state vector to be normalised at any time, which we can write as

$$\langle\psi_0|\psi_0\rangle = \langle\psi(t)|\psi(t)\rangle = \left\langle \hat{\mathbf{U}}(t)\psi_0 \middle| \hat{\mathbf{U}}(t)\psi_0 \right\rangle = 1\,, \tag{2.17}$$

the time evolution operator must be unitary, i.e.,

$$\hat{\mathbf{U}}^\dagger(t)\hat{\mathbf{U}}(t) = \hat{\mathbf{1}}\,. \tag{2.18}$$

By using the formula (2.14) and substituting into the Schrödinger's equation we obtain

$$\mathrm{i}\hbar\frac{\mathrm{d}\hat{\mathbf{U}}(t)}{\mathrm{d}t} = \hat{\mathbf{H}}\hat{\mathbf{U}}(t)\,, \tag{2.19}$$

which holds since $|\psi_0\rangle$ does not depend on time. We will also need the adjoint version of the above equation, which we can write as

$$-\mathrm{i}\hbar\frac{\mathrm{d}\hat{\mathbf{U}}^\dagger(t)}{\mathrm{d}t} = \hat{\mathbf{U}}^\dagger(t)\hat{\mathbf{H}}^\dagger\,. \tag{2.20}$$

Now assume an arbitrary observable $\hat{\mathbf{A}}$. According to the fourth postulate, the mean value of A at the time t is given as

$$\langle\psi(t)|\,\hat{\mathbf{A}}\,|\psi(t)\rangle = \langle\psi_0|\,\hat{\mathbf{U}}^\dagger(t)\hat{\mathbf{A}}\hat{\mathbf{U}}(t)\,|\psi_0\rangle\ , \tag{2.21}$$

where we have used (2.16). Now we apply the total time derivative onto this expression, resulting in

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\psi_0\middle|\hat{\mathbf{U}}^\dagger(t)\hat{\mathbf{A}}\hat{\mathbf{U}}(t)\middle|\psi_0\right\rangle &= \left\langle\psi_0\middle|\frac{\mathrm{d}\hat{\mathbf{U}}^\dagger(t)}{\mathrm{d}t}\hat{\mathbf{A}}\hat{\mathbf{U}}(t) + \hat{\mathbf{U}}^\dagger(t)\frac{\mathrm{d}\hat{\mathbf{A}}}{\mathrm{d}t}\hat{\mathbf{U}}(t) + \hat{\mathbf{U}}^\dagger(t)\hat{\mathbf{A}}\frac{\mathrm{d}\hat{\mathbf{U}}(t)}{\mathrm{d}t}\middle|\psi_0\right\rangle \\ &= \left\langle\psi_0\middle|\hat{\mathbf{U}}^\dagger(t)\frac{1}{\mathrm{i}\hbar}\left[\hat{\mathbf{A}}, \hat{\mathbf{H}}\right]\hat{\mathbf{U}}(t) + \hat{\mathbf{U}}^\dagger(t)\frac{\mathrm{d}\hat{\mathbf{A}}}{\mathrm{d}t}\hat{\mathbf{U}}(t)\middle|\psi_0\right\rangle = \left\langle\psi(t)\middle|\frac{1}{\mathrm{i}\hbar}\left[\hat{\mathbf{A}}, \hat{\mathbf{H}}\right] + \frac{\mathrm{d}\hat{\mathbf{A}}}{\mathrm{d}t}\middle|\psi(t)\right\rangle\ .\end{aligned} \tag{2.22}$$

Finally, we get

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\psi(t)\right|\hat{\mathbf{A}}\left|\psi(t)\right\rangle=\left\langle\psi(t)\right|\frac{1}{\mathrm{i}\hbar}\left[\hat{\mathbf{A}},\hat{\mathbf{H}}\right]+\frac{\mathrm{d}\hat{\mathbf{A}}}{\mathrm{d}t}\left|\psi(t)\right\rangle}. \tag{2.23}$$

To clearly demonstrate the correspondence to the classical case, we further rewrite the above result as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\psi(t)\right|A(\hat{\mathbf{q}},\hat{\mathbf{p}},t)\left|\psi(t)\right\rangle=\left\langle\psi(t)\right|\frac{1}{\mathrm{i}\hbar}\left[A(\hat{\mathbf{q}},\hat{\mathbf{p}},t),H(\hat{\mathbf{q}},\hat{\mathbf{p}},t)\right]+\frac{\partial A(\hat{\mathbf{q}},\hat{\mathbf{p}},t)}{\partial t}\left|\psi(t)\right\rangle. \tag{2.24}$$

If you go now through your lecture notes from the course of classical dynamics, you should be able to find a most general equation of motion for an arbitrary dynamical variable $A(q,p,t)$ expressed by using the Poisson brackets:

$$\frac{\mathrm{d}A(q,p,t)}{\mathrm{d}t}=\{A(q,p,t),H(q,p,t)\}+\frac{\partial A(q,p,t)}{\partial t}. \tag{2.25}$$

As you can see when comparing this with Eq. (2.24), those equations are remarkably similar! Actually, Paul Dirac was one of the first people who noted this resemblance. And most importantly, based on this observation, he came up with the following idea: it seems that if we want to translate from the language of classical dynamics into QM, we shall replace

$$\boxed{\{A,B\}\rightarrow\frac{1}{\mathrm{i}\hbar}\left[\hat{\mathbf{A}},\hat{\mathbf{B}}\right]}, \tag{2.26}$$

which actually makes quite a bit of sense, since both the Poisson brackets and the commutator form the Lie algebra.

Based on Eq. (2.26), we can now derive (actually more like postulate) the three fundamental relations that determine the relationships between $\hat{\mathbf{q}}$ and $\hat{\mathbf{p}}$. In classical mechanics, we have

$$\{q_k,q_l\}=0\,,\quad\{p_k,p_l\}=0\,,\quad\{q_k,p_l\}=\delta_{kl}\,. \tag{2.27}$$

Hence, the QM version of the above statement is that

$$\boxed{[\hat{\mathbf{q}}_k,\hat{\mathbf{q}}_l]=0\,,\quad[\hat{\mathbf{p}}_k,\hat{\mathbf{p}}_l]=0\,,\quad[\hat{\mathbf{q}}_k,\hat{\mathbf{p}}_l]=\mathrm{i}\hbar\delta_{kl}}. \tag{2.28}$$

These are called the *canonical quantization* formulas and they play a key role not just in QM but also in the quantum field theory (QFT). In case where we deal only with a 1D problem with $\hat{\mathbf{q}}=\hat{\mathbf{x}}$, we can write a simplified version as

$$\boxed{[\hat{\mathbf{x}},\hat{\mathbf{p}}]=\mathrm{i}\hbar}. \tag{2.29}$$

2.8 Ehrenfest Theorems

Here we make use of the above section to show another nice correspondence between QM and the Newton's second law of motion. We assume a single point particle that can move only along the x axis. Let's start by computing how does $\bar{x}$ change in time. According to (2.23), we have

$$\frac{\mathrm{d}\bar{x}}{\mathrm{d}t} = \left\langle \psi(t) \middle| \frac{1}{\mathrm{i}\hbar} \left[\hat{\mathbf{x}}, \hat{\mathbf{H}}\right] \middle| \psi(t) \right\rangle . \tag{2.30}$$

To further expand $\left[\hat{\mathbf{x}}, \hat{\mathbf{H}}\right]$, we make use of the Postulate II. to replace

$$H(x,p) = \frac{p^2}{2m} + V(x) \quad \rightarrow \quad \hat{\mathbf{H}} = H(\hat{\mathbf{x}}, \hat{\mathbf{p}}) = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}}) \,. \tag{2.31}$$

By employing the properties of the commutator and the canonical quantisation formula (2.29) we get

$$\left[\hat{\mathbf{x}}, \hat{\mathbf{H}}\right] = \left[\hat{\mathbf{x}}, \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}})\right] = \frac{1}{2m}\left[\hat{\mathbf{x}}, \hat{\mathbf{p}}^2\right] + \left[\hat{\mathbf{x}}, V(\hat{\mathbf{x}})\right] = \frac{1}{2m}\left(\hat{\mathbf{p}}\left[\hat{\mathbf{x}}, \hat{\mathbf{p}}\right] + \left[\hat{\mathbf{x}}, \hat{\mathbf{p}}\right]\hat{\mathbf{p}}\right) = \frac{\mathrm{i}\hbar}{m}\hat{\mathbf{p}} \,. \tag{2.32}$$

To check that $[\hat{\mathbf{x}}, V(\hat{\mathbf{x}})] = 0$, we expand $V(x)$ by a Taylor series and further replace $x \rightarrow \hat{\mathbf{x}}$, resulting in

$$V(\hat{\mathbf{x}}) = \sum_n c_n \hat{\mathbf{x}}^n \,, \tag{2.33}$$

and since $[\hat{\mathbf{x}}, \hat{\mathbf{x}}^n] = 0$, the original commutator must vanish. After substituting the result of (2.31) into (2.30), we arrive at

$$\frac{\mathrm{d}\bar{x}}{\mathrm{d}t} = \frac{\bar{p}}{m} \,, \tag{2.34}$$

which is the *first Ehrenfest theorem*.

Moving on, we calculate

$$\frac{\mathrm{d}\bar{p}}{\mathrm{d}t} = \left\langle \psi(t) \middle| \frac{1}{\mathrm{i}\hbar} \left[\hat{\mathbf{p}}, \hat{\mathbf{H}}\right] \middle| \psi(t) \right\rangle . \tag{2.35}$$

The commutator $\left[\hat{\mathbf{p}}, \hat{\mathbf{H}}\right]$ can be written as

$$\left[\hat{\mathbf{p}}, \hat{\mathbf{H}}\right] = \left[\hat{\mathbf{p}}, \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}})\right] = \left[\hat{\mathbf{p}}, V(\hat{\mathbf{x}})\right] . \tag{2.36}$$

We now show that

$$\left[\hat{\mathbf{p}}, \hat{\mathbf{x}}^n\right] = -\mathrm{i}\hbar n \hat{\mathbf{x}}^{n-1} \quad \text{for} \quad n \geq 0 \,. \tag{2.37}$$

For such purpose, we use the mathematical induction. First, for $n = 0$ we have $\left[\hat{\mathbf{p}}, \hat{\mathbf{1}}\right] = 0$. Second, we assume $[\hat{\mathbf{p}}, \hat{\mathbf{x}}^n] = -\mathrm{i}\hbar n \hat{\mathbf{x}}^{n-1}$ (the induction assumption) and need to show that

$$\left[\hat{\mathbf{p}}, \hat{\mathbf{x}}^{n+1}\right] = -\mathrm{i}\hbar(n+1)\hat{\mathbf{x}}^n \,. \tag{2.38}$$

To do so, we proceed as

$$\left[\hat{\mathbf{p}}, \hat{\mathbf{x}}^{n+1}\right] = [\hat{\mathbf{p}}, \hat{\mathbf{x}}^n \hat{\mathbf{x}}] = \hat{\mathbf{x}}^n [\hat{\mathbf{p}}, \hat{\mathbf{x}}] + [\hat{\mathbf{p}}, \hat{\mathbf{x}}^n] \hat{\mathbf{x}} = -\mathrm{i}\hbar \hat{\mathbf{x}}^n - \mathrm{i}\hbar n \hat{\mathbf{x}}^{n-1} \hat{\mathbf{x}} = -\mathrm{i}\hbar(n+1)\hat{\mathbf{x}}^n \,, \tag{2.39}$$

where in the third equality we have used the induction assumption and the canonical quantization formula. The proof by induction is now complete. It is now left for the reader to show that

$$[\hat{\mathbf{p}}, V(\hat{\mathbf{x}})] = -\mathrm{i}\hbar \frac{\mathrm{d}V(\hat{\mathbf{x}})}{\mathrm{d}x} \,. \tag{2.40}$$

By inserting the above result into (2.35), we arrive at

$$\frac{\mathrm{d}\bar{p}}{\mathrm{d}t} = \overline{-\frac{\mathrm{d}V}{\mathrm{d}x}} \,, \tag{2.41}$$

where we can interpret the term on the RHS as the mean value of the acting force, i.e.,

$$\frac{\mathrm{d}\bar{p}}{\mathrm{d}t} = \bar{F} \,. \tag{2.42}$$

This is the *second Ehrenfest theorem*.

After a careful inspection, we can see that both of the presented theorems are just the QM version of the Newton's second law statement

$$\frac{\mathrm{d}p}{\mathrm{d}t} = F \,, \quad \text{where} \quad p = m\frac{\mathrm{d}x}{\mathrm{d}t} \,. \tag{2.43}$$

Another nice correspondence here. We can now see that the QM – when taken on average – exactly reproduces the results that we know from classical dynamics.

2.9 Time evolution

We will now explore the time evolution in the most simple case where $\hat{\mathbf{H}}$ does not depend on time (and we will assume this contidion to hold for the rest of this text). First, let us assume an eigenbasis $\{|n\rangle\}$ corresponding to the Hamilton operator (this is mostly the discrete case) as

$$\hat{\mathbf{H}} |n\rangle = E_n |n\rangle \,, \tag{2.44}$$

where (according to the Postulate III.) E_n represent the only measureable values of energy. Further, since $\hat{\mathbf{H}}$ is time independent, the corresponding eigenvectors $|n\rangle$ also do not depend on time. Now we would like to determine how does a system that initially starts at one of the energy eigenstates, i.e.,

$$|\psi_0\rangle = |n\rangle \,, \tag{2.45}$$

evolve in time. We propose that the time evolution is given by

$$|n(t)\rangle = \alpha(t)\,|n\rangle \ , \tag{2.46}$$

where $|n(t)\rangle \equiv |\psi(t)\rangle$. By plugging the above ansatz into the SE, we get

$$\mathrm{i}\hbar\frac{\mathrm{d}\alpha(t)}{\mathrm{d}t}\,|n\rangle = E_n\alpha(t)\,|n\rangle \ . \tag{2.47}$$

Hence, we obtain an ordinary differential equation for the function $\alpha(t)$ as

$$\mathrm{i}\hbar\frac{\mathrm{d}\alpha(t)}{\mathrm{d}t} = E_n\alpha(t)\,, \tag{2.48}$$

whose solution is simply

$$\alpha(t) = \exp\left(-\mathrm{i}\frac{E_n}{\hbar}t\right) \ , \tag{2.49}$$

and therefore,

$$|n(t)\rangle = \exp\left(-\mathrm{i}\frac{E_n}{\hbar}t\right)|n\rangle \ . \tag{2.50}$$

It can be easily shown (and the reader is encouraged to do so) that a general time evolving state Ket-vector can then be expressed as

$$|\psi(t)\rangle = \sum_n \psi_{0n}\,|n(t)\rangle \ , \tag{2.51}$$

where

$$\psi_{0n} = \langle n|\psi_0\rangle \ . \tag{2.52}$$

We can further rearrange this to get

$$|\psi(t)\rangle = \sum_n \exp\left(-\mathrm{i}\frac{E_n}{\hbar}t\right)|n\rangle\,\langle n|\psi_0\rangle = \exp\left(-\mathrm{i}\frac{\hat{\mathbf{H}}}{\hbar}t\right)|\psi_0\rangle \ , \tag{2.53}$$

where in the last equality we used the spectral decomposition of $\hat{\mathbf{H}}$, see Eq. (1.168). Hence, the time evolution of an arbitrary state is simply

$$\boxed{|\psi(t)\rangle = \exp\left(-\mathrm{i}\frac{\hat{\mathbf{H}}}{\hbar}t\right)|\psi_0\rangle}\,. \tag{2.54}$$

Now pause for a while and think about what we have just done. Basically, we have demonstrated that in the case of time-independent Hamiltonian we do not need to care about the time evolution what so ever. This is an amazing simplification, since (as you probably know) to find the time evolution of a studied system is the key quest in the kingdom of classical mechanics.

Finally, note that by comparing Eqs. (2.16) and (2.54), we can identify

$$\hat{\mathbf{U}}(t) = \exp\left(-\mathrm{i}\frac{\hat{\mathbf{H}}}{\hbar}t\right) . \tag{2.55}$$

By employing the Taylor series for $\exp(x)$ it can be shown that in this case

$$\hat{\mathbf{U}}^{\dagger}(t) = \exp\left(\mathrm{i}\frac{\hat{\mathbf{H}}}{\hbar}t\right) \tag{2.56}$$

and

$$\hat{\mathbf{U}}^{\dagger}(t)\hat{\mathbf{U}}(t) = \exp\left(\mathrm{i}\frac{\hat{\mathbf{H}}}{\hbar}t - \mathrm{i}\frac{\hat{\mathbf{H}}}{\hbar}t\right) = \exp(0) = \hat{\mathbf{1}} , \tag{2.57}$$

by which we immediately see that $\hat{\mathbf{U}}(t)$ is truly unitary. But be careful, since the rule

$$\exp\left(\hat{\mathbf{A}}\right)\exp\left(\hat{\mathbf{B}}\right) = \exp\left(\hat{\mathbf{A}} + \hat{\mathbf{B}}\right) \tag{2.58}$$

holds only in case where

$$\left[\hat{\mathbf{A}}, \hat{\mathbf{B}}\right] = 0 , \tag{2.59}$$

which (fortunately) is the case here (we will not prove this).

2.10 Heisenberg Picture

I will just briefly mention here what does the Heisenberg picture mean since you will need it in your future studies of QM and quantum field theory (QFT). The Heisenberg picture is basically just a convenient relabel in Eq. (2.21), where we denote

$$\hat{\mathbf{A}}_{\mathrm{H}} \equiv \hat{\mathbf{U}}^{\dagger}(t)\hat{\mathbf{A}}\hat{\mathbf{U}}(t) \tag{2.60}$$

and call this new operator as the operator $\hat{\mathbf{A}}$ in the Heisenberg picture. We can then simply rewrite Eq. (2.21) as

$$\langle\psi(t)|\,\hat{\mathbf{A}}\,|\psi(t)\rangle = \langle\psi_0|\,\hat{\mathbf{A}}_{\mathrm{H}}\,|\psi_0\rangle . \tag{2.61}$$

The LHS then represents the *Schrödinger picture* where the time evolution of the system is included in the state Ket-vector and the RHS represents the *Heisenberg picture* where, on the contrary, the state Ket-vector is time independent and the time evolution is included in the respective operator. Note that there is also a hybrid of the two pictures called the interaction picture, but that is beyond the scope of this text.

2.11 Heisenberg Uncertainty Principle

Last but not least, in this chapter, we will discuss a very important topic regarding the possibility of determining (measuring) two observables on the system at the same time. To be honest, I personally do not like the derivation, since it is quite a tedious one and not very elegant. Nevertheless, the resulting formula is beautiful!

The Postulate IV. tells us that the mean value of a repeated measurement of the observable A on a system in the state $|\psi\rangle$ is equal to $\langle\psi|\,\hat{\mathbf{A}}\,|\psi\rangle$. Now we would like to express a similar formula for the variance of such measurement. The classical formula for variance is given by

$$\sigma_A^2 = \overline{\left(A - \bar{A}\right)^2}\,. \tag{2.62}$$

Hence, the QM version of this must be

$$\sigma_A^2 = \left\langle \psi \middle| \left(\hat{\mathbf{A}} - \bar{A}\right)^2 \middle| \psi \right\rangle\,. \tag{2.63}$$

Assume now that we would like to measure two observables A and B on the system. It would be wise once again to explain what do we mean by measuring repeatedly on a system in the state $|\psi\rangle$ – now with the extension that we are measuring not one, but two different observables. As we have stated before, we need infinite many copies of the studied system, each one prepared in exactly the same state $|\psi\rangle$. Then, on each one of those copies we can conduct only one measurement. So if we measure e.g., the observable A and next we would like to measure B, we still need to take another copy, since the previous one already collapsed to the respective eigenstate of $\hat{\mathbf{A}}$ which is generally different than the original state $|\psi\rangle$. Our task now is to determine the lower bound of the product $\sigma_A^2\sigma_B^2$. First, we denote

$$\Delta\hat{\mathbf{A}} \equiv \hat{\mathbf{A}} - \bar{A}\,. \tag{2.64}$$

Then we proceed as follows

$$\sigma_A^2\sigma_B^2 = \langle\psi|\,\Delta\hat{\mathbf{A}}^2\,|\psi\rangle\,\langle\psi|\,\Delta\hat{\mathbf{B}}^2\,|\psi\rangle = \\ \left\langle \Delta\hat{\mathbf{A}}\psi \middle| \Delta\hat{\mathbf{A}}\psi \right\rangle \left\langle \Delta\hat{\mathbf{B}}\psi \middle| \Delta\hat{\mathbf{B}}\psi \right\rangle = \left\| \left| \Delta\hat{\mathbf{A}}\psi \right\rangle \right\|^2 \cdot \left\| \left| \Delta\hat{\mathbf{B}}\psi \right\rangle \right\|^2\,, \tag{2.65}$$

while it is trivial to check that $\Delta\hat{\mathbf{A}}^\dagger = \Delta\hat{\mathbf{A}}$. For the next step we need the following lemma:

$$|\,\langle\phi|\psi\rangle\,| \leq \||\phi\rangle\| \cdot \||\psi\rangle\|\,. \tag{2.66}$$

We will not prove this for a general Hilbert space, but at least show the proof for $\mathbb{R}^3$. From the introductory course of Linear Algebra we know that

$$\boldsymbol{a}\cdot\boldsymbol{b} = \|\boldsymbol{a}\|\|\boldsymbol{b}\|\cos(\varphi)\,, \tag{2.67}$$

where φ is the angle between $\boldsymbol{a}$ and $\boldsymbol{b}$. By applying the absolute value operation on both sides of the above expression and further noting that $0 \leq |\cos(\varphi)| \leq 1$, we immediately get

$$|\boldsymbol{a} \cdot \boldsymbol{b}| \leq \|\boldsymbol{a}\| \|\boldsymbol{b}\| \,, \tag{2.68}$$

which is just a special case of (2.66). We can now continue our calculation as

$$\left\| \left| \Delta\hat{\mathbf{A}}\psi \right\rangle \right\|^2 \cdot \left\| \left| \Delta\hat{\mathbf{B}}\psi \right\rangle \right\|^2 \geq \left| \left\langle \Delta\hat{\mathbf{A}}\psi \middle| \Delta\hat{\mathbf{B}}\psi \right\rangle \right|^2 . \tag{2.69}$$

The next inequality we are going to need is as follows:

$$|z|^2 = \mathrm{Re}[z]^2 + \mathrm{Im}[z]^2 \geq \mathrm{Im}[z]^2 = \left[\frac{1}{2\mathrm{i}} (z - z^*) \right]^2 , \tag{2.70}$$

where $z \in \mathbb{C}$. By assigning

$$z = \left\langle \Delta\hat{\mathbf{A}}\psi \middle| \Delta\hat{\mathbf{B}}\psi \right\rangle , \tag{2.71}$$

we proceed further as

$$\begin{aligned} \left| \left\langle \Delta\hat{\mathbf{A}}\psi \middle| \Delta\hat{\mathbf{B}}\psi \right\rangle \right|^2 \geq \left[\frac{1}{2\mathrm{i}} \left(\left\langle \Delta\hat{\mathbf{A}}\psi \middle| \Delta\hat{\mathbf{B}}\psi \right\rangle - \left\langle \Delta\hat{\mathbf{A}}\psi \middle| \Delta\hat{\mathbf{B}}\psi \right\rangle^* \right) \right]^2 = \\ \left[\frac{1}{2\mathrm{i}} \left(\left\langle \Delta\hat{\mathbf{A}}\psi \middle| \Delta\hat{\mathbf{B}}\psi \right\rangle - \left\langle \Delta\hat{\mathbf{B}}\psi \middle| \Delta\hat{\mathbf{A}}\psi \right\rangle \right) \right]^2 = \left[\frac{1}{2\mathrm{i}} \left\langle \psi \middle| \left[\Delta\hat{\mathbf{A}}, \Delta\hat{\mathbf{B}} \right] \middle| \psi \right\rangle \right]^2 . \end{aligned} \tag{2.72}$$

It is left for the reader to check that

$$\left[\Delta\hat{\mathbf{A}}, \Delta\hat{\mathbf{B}} \right] = \left[\hat{\mathbf{A}}, \hat{\mathbf{B}} \right] . \tag{2.73}$$

Finally, by employing the above equality, equating the LHS of (2.65) with the RHS of (2.72) and taking the square root, we arrive at

$$\boxed{\sigma_A \sigma_B \geq \left| \frac{1}{2\mathrm{i}} \left\langle \psi \middle| \left[\hat{\mathbf{A}}, \hat{\mathbf{B}} \right] \middle| \psi \right\rangle \right|}, \tag{2.74}$$

which is the famous formula for the so called *Heisenberg uncertainity principle*.

The derivation process (even though quite tedious) should be pretty straightforward and clear. But now comes the trickier part: we need to interpret the result somehow. First, refer back to the Postulate IV., where we discovered that the outputs of a measurement on a quantum system are stochastic – i.e., each possible result has a certain probability of happening. But there is actually one singular case where this is not true. Assume (without the loss of generality we show this for the discrete case) that the system is in the k-th eigenstate of $\hat{\mathbf{A}}$:

$$|\psi\rangle = |k\rangle \,. \tag{2.75}$$

By employing Eq. (2.10), we get

$$w_k = \langle k|\psi\rangle = |\,\langle k|k\rangle\,|^2 = 1\,. \tag{2.76}$$

This means that if we measure A on the system, the output will be a_k. By employing the concept of repeated measurement on the system (we prepare infinitely many identical copies, each in the state $|k\rangle$), the mean value becomes

$$\bar{A} = a_k \tag{2.77}$$

and the corresponding standard deviation (the square root of the variance) is equal to

$$\sigma_A = 0\,. \tag{2.78}$$

In such case, we can say that the system has $A = a_k$, since we know that the measurement of A must always result in a_k. So e.g., when the studied system is an electron in a presence of a central Coulomb field and the electron is in the eigenstate $|k\rangle$ of $\hat{\mathbf{H}}$, we say that the electron has energy $E = E_k$. But if the electron is in a general superposition of the eigenstates, such a statement does not make sense anymore.

Now we ask ourselves the following question: is there a possibility for a specific state to exist to which we can assign two values of two distinct observables A and B? Or in other words a state for which

$$\sigma_A = \sigma_B = 0\,? \tag{2.79}$$

The answer is provided by the Heisenberg uncertainity formula (2.74), which tells us that in such case the following condition must hold:

$$0 \geq \left|\frac{1}{2\mathrm{i}}\left\langle\psi\right|\left[\hat{\mathbf{A}},\hat{\mathbf{B}}\right]\left|\psi\right\rangle\right|\,, \tag{2.80}$$

which is true only if $\hat{\mathbf{A}}$ and $\hat{\mathbf{B}}$ commute, i.e.,

$$\left[\hat{\mathbf{A}},\hat{\mathbf{B}}\right] = 0\,. \tag{2.81}$$

Same as before, assume $|k\rangle$ being an eigenvector of $\hat{\mathbf{A}}$:

$$\hat{\mathbf{A}}\,|k\rangle = a_k\,|k\rangle\ . \tag{2.82}$$

Now we act with $\hat{\mathbf{B}}$ on both sides:

$$\hat{\mathbf{B}}\hat{\mathbf{A}}\,|k\rangle = a_k\hat{\mathbf{B}}\,|k\rangle\ . \tag{2.83}$$

Since $\hat{\mathbf{A}}$ and $\hat{\mathbf{B}}$ commute, we can rearrange this as

$$\hat{\mathbf{A}}\left(\hat{\mathbf{B}}\,|k\rangle\right) = a_k\left(\hat{\mathbf{B}}\,|k\rangle\right)\,, \tag{2.84}$$

which implies that

$$\hat{\mathbf{B}}\,|k\rangle \propto |k\rangle\ . \tag{2.85}$$

So by acting with $\hat{\mathbf{B}}$ onto $|k\rangle$, we get something proportional to $|k\rangle$. But this is exactly the definition of an eigenvector of $\hat{\mathbf{B}}$. Hence, by identifying the proportionality constant with the eigenvalue b_k, we have

$$\hat{\mathbf{B}}\,|k\rangle = b_k\,|k\rangle\ . \tag{2.86}$$

We have therefore proven that if the two operators commute, they have the same set of all eigenvectors! (Actually, we have just shown that if $|k\rangle$ is an eigenvector of $\hat{\mathbf{A}}$, it must be also an eigenvector of $\hat{\mathbf{B}}$. But since the whole argument can be reversed, i.e., we start with an eigenvector of $\hat{\mathbf{B}}$ and show that it must be also an eigenvector of $\hat{\mathbf{A}}$, then the statement must be true.) Note that regardless of the same set of eigenvectors, the corresponding eigenvalues are different for each operator ($a_k \neq b_k$).

Now let's demonstrate how does this explain our previous question. Imagine that the system is prepared in one of the eigenstates $|k\rangle$ of $\hat{\mathbf{A}}$. This means that if we would measure A on the system, we will get a_k. But $|k\rangle$ is also an eigenstate of $\hat{\mathbf{B}}$, so if we measure B instead, we would get b_k. And for that reason we can say that the system has simultaneously $A = a_k$ and $B = b_k$. Once again, such a statement would not make sense anymore if the system would be in a general superposition of eigenstates.

Before moving on, we present the most famous case of the Heisenberg uncertainity principle, and that is by considering $\hat{\mathbf{A}} = \hat{\mathbf{x}}$ and $\hat{\mathbf{B}} = \hat{\mathbf{p}}$ for a particle moving only in 1D. In such case, we get

$$\sigma_x\sigma_p \geq \left|\frac{1}{2\mathrm{i}}\,\langle\psi|[\hat{\mathbf{x}},\hat{\mathbf{p}}]|\psi\rangle\right| = \left|\frac{\mathrm{i}\hbar}{2\mathrm{i}}\,\langle\psi|\psi\rangle\right| = \frac{\hbar}{2}\,. \tag{2.87}$$

We put the result in a box

$$\boxed{\sigma_x\sigma_p \geq \frac{\hbar}{2}}\,. \tag{2.88}$$

What is important here, the RHS of the above formula does not depend on the actual state $|\psi\rangle$ and hence the statement is universally true. But do not get mislead here as this is not the general case!

To conclude this section, we make use of the standard nomenclature and (from now on) denote any two observables that commute as *compatible*. And note that there does not need to be just two of those. E.g., when we solve the previously mentioned system constituting of an electron in a spherically symmetric Coulomb field, there will be three compatible observables, namely the energy, the magnitude of the angular momentum and the z-component of the angular momentum.

2.12 Summary

Now that we have covered all the postulates and discovered the canonical quantization formula, we are finally ready to move on to the famous "wavefunction representation" of QM.

Chapter 3

Continuous Representation of QM

This chapter is devoted to the formulation of QM in the continuous x-representation. To make things easier, we assume a simple system consisting of a point particle (or – to be more precise – something that we would call a point particle in the context of classical mechanics) moving in one dimension that would be described by one coordinate x with the conjugate momentum p in the classical case.

3.1 Position Operator & Wavefunction

We start by employing the Postulate II. and introduce the linear hermitian *position operator* $\hat{\mathbf{x}}$ corresponding to the coordinate x. Let's continue by formulating the eigenvalue problem for such operator as

$$\hat{\mathbf{x}}\,|x\rangle = x\,|x\rangle\ . \tag{3.1}$$

Now first of all, since $\hat{\mathbf{x}}$ is hermitian, $x \in \mathbb{R}$ and based on the Postulate III. it represents all the possible outcomes when measuring the position of the particle. The Postulate V. further tells us that whenever we measure the position to be x, no matter what the initial state was, the system collapses to $|x\rangle$. Hence, the eigenstate $|x\rangle$ has the interpretation that the particle is located at x. Moreover, once again due to $\hat{\mathbf{x}}$ being hermitian,

$$\langle x|x'\rangle = \delta(x - x') \tag{3.2}$$

(the eigenbasis can always be normalized according to the discussion presented in Chapter 1), and therefore we can use $\{|x\rangle\}$ as an appropriate basis to express any general state as

$$|\psi\rangle = \int \mathrm{d}x\,\psi(x)\,|x\rangle\ . \tag{3.3}$$

The function

$$\psi(x) = \langle x|\psi\rangle \tag{3.4}$$

is then called the *wavefunction* of the particle. If we now have a particle in a general state $|\psi\rangle$, then according to the Postulate IV.,

$$w(x) = |\psi(x)|^2 \tag{3.5}$$

represents the probability density that the particle can be found at x. Note that this is something completely different from the classical mechanics, where the particle's position is strictly defined whereas in QM the position of a particle is not deterministic. This is sometimes referred to as the *non-locality*. Given the state $|\psi\rangle$, we can only determine the probability that the particle can be found in the range $\langle a, b\rangle$ as

$$P[x \in \langle a, b\rangle] = \int_a^b \mathrm{d}x \, |\psi(x)|^2 \,. \tag{3.6}$$

Moving on, by using the formula (1.162) we can express the position operator as

$$\hat{\mathbf{x}} = \int \mathrm{d}x \, x \, |x\rangle \, \langle x| \,. \tag{3.7}$$

Finally, based on the formulae given in Tab. 1.11 we will now use the continuous representation as

$$\boxed{|\psi\rangle \to \psi(x) \,, \quad \hat{\mathbf{x}} \to x} \,, \tag{3.8}$$

hereinafter referred to as the *x-representation*.

3.2 Momentum Operator

Now that we have derived the x-representation for a state Ket-vector (the wavefunction) and the position operator, it is time to determine the form and the corresponding representation for the (conjugate) *momentum operator*. And the recipe of how to do so lies in the canonical quantisation formula presented in the previous chapter. Recall that the operators $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ must satisfy

$$[\hat{\mathbf{x}}, \hat{\mathbf{p}}] = \mathrm{i}\hbar \,. \tag{3.9}$$

Further, $\hat{\mathbf{p}}$ can be expressed in terms of the eigenbasis $\{|x\rangle\}$ as

$$\hat{\mathbf{p}} = \int \mathrm{d}x \, \mathrm{d}y \, p(x, y) \, |x\rangle \, \langle y| \,. \tag{3.10}$$

We will now show that the correct expression for $p(x, y)$ is

$$p(x, y) = -\mathrm{i}\hbar \lim_{\varepsilon \to 0} \frac{\delta(y - (x + \varepsilon)) - \delta(y - x)}{\varepsilon} \,. \tag{3.11}$$

We start by investigating how does $\hat{\mathbf{p}}$ act on $|\psi\rangle$. This can be written as

$$\hat{\mathbf{p}} \, |\psi\rangle = -\mathrm{i}\hbar \int \mathrm{d}x \, \mathrm{d}y \, \lim_{\varepsilon \to 0} \frac{\delta(y - (x + \varepsilon)) - \delta(y - x)}{\varepsilon} \, |x\rangle \, \langle y| \int \mathrm{d}z \, \psi(z) \, |z\rangle \,. \tag{3.12}$$

After a bit of algebra we get

$$\hat{\mathbf{p}} \, |\psi\rangle = -\mathrm{i}\hbar \int \mathrm{d}x \, \lim_{\varepsilon \to 0} \frac{\psi(x + \varepsilon) - \psi(x)}{\varepsilon} = \int \mathrm{d}x \, \left(-\mathrm{i}\hbar \frac{\partial \psi(x)}{\partial x} \right) |x\rangle \,. \tag{3.13}$$

The partial differentiation symbol is used since the wavefunction depends also on time, which is not denoted explicitly here for the sake of readability. The continuous representation of $\hat{\mathbf{p}}$ in the eigenbasis $\{|x\rangle\}$ is therefore

$$\boxed{\hat{\mathbf{p}} \to -\mathrm{i}\hbar\frac{\partial}{\partial x}}\,. \tag{3.14}$$

Now let's calculate the commutator between $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$.

$$[\hat{\mathbf{x}}, \hat{\mathbf{p}}]\,|\psi\rangle = \int \mathrm{d}x\, x \left(-\mathrm{i}\hbar\frac{\partial\psi(x)}{\partial x}\right)|x\rangle - \int \mathrm{d}x \left(-\mathrm{i}\hbar\frac{\partial[x\psi(x)]}{\partial x}\right)|x\rangle = \mathrm{i}\hbar\,|\psi\rangle\ . \tag{3.15}$$

By comparing the LHS with the RHS we get $[\hat{\mathbf{x}}, \hat{\mathbf{p}}] = \mathrm{i}\hbar$, which is exactly what we wanted to achieve.

3.3 Schrödinger equation in the continuous representation

Being equipped with the continuous representation for $\hat{\mathbf{x}}$, $\hat{\mathbf{p}}$ and $|\psi\rangle$ we can now work out the form of the corresponding form of the Schrödinger equation. We start with the Hamilton operator $\hat{\mathbf{H}}$. In classical non-relativistic mechanics of one particle the Hamiltonian is given as

$$H(x,p) = \frac{p^2}{2m} + V(x)\,. \tag{3.16}$$

According to the second postulate, the corresponding Hamilton operator then must possess the following form

$$\hat{\mathbf{H}} = H(\hat{\mathbf{x}}, \hat{\mathbf{p}}) = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}})\,, \tag{3.17}$$

where m stands for the mass of the particle. By using the formulae derived in the sections above we can immediately write down the continuous representation of the Hamilton operator as

$$\boxed{\hat{\mathbf{H}} \to -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)}\,. \tag{3.18}$$

Now let's focus on the LHS of the Schrödinger equation. We have

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\psi\rangle = \mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\int \mathrm{d}x\,\psi(t,x)\,|x\rangle = \int \mathrm{d}x \left(\mathrm{i}\hbar\frac{\partial\psi(t,x)}{\partial t}\right)|x\rangle\ , \tag{3.19}$$

where we have now explicitly denoted the time dependence of the wavefunction $\psi(t,x)$. By combining the above expressions we can now write down the Schrödinger equation in the $\{|x\rangle\}$ representation as

$$\boxed{\mathrm{i}\hbar\frac{\partial\psi(t,x)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(t,x)}, \tag{3.20}$$

which is the form you will most certainly find in most of the introductory textbooks on QM.

3.4 Time evolution once again

As we have demonstrated in the previous chapter, since in this introductory text we will deal only with time independent hamiltonians, we do not need to care about the Schrödinger equation anymore as the time evolution is given simply by Eq. (2.54). However, this expression - even though being beautiful mathematically - is not particularly useful for real calculations, since (at least to my knowledge) you cannot insert an operator including derivatives into exponential function and assume it to produce some results in a typical Computer Algebra System (CAS) such as Maple or Mathematica. Hence, the expression that you would use in a real life scenario is

$$\boxed{\psi(x,t) = \sum_n \exp\left(-\mathrm{i}\frac{E_n}{\hbar}t\right)\psi_n(x)}, \tag{3.21}$$

where $\psi_n(x)$ stand for the (time independent) eigenvectors of the Hamilton operator in the x-representation satisfying

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi_n(x) = E_n\psi_n(x)\,. \tag{3.22}$$

Note that $\psi_n(x)$ is now a single variable function of x and hence we should use the total derivative symbol instead of the partial one. Nevertheless, we will stick with the partial differentiation, since in more complicated problems involving 3D and possibly more than one particle, the wavefunction will include additional coordinates. This is now a perfectly valid formula that any CAS should be able to work with.

I could have ended this section right here, since the formula (3.21) is basically all we need for the purpose of this text. However, I would like to comment on the nomenclature regarding the Schrödinger equation. Sometimes, Eq. (3.20) is referred to as the *time dependent Schrödinger equation* due to the presence of time. A standard method for solving such partial differential equation is to assume a time harmonic solution (a general time dependence can then be obtained by applying the Fourier transform) in the form

$$\psi(t,x) = \psi(x)\exp(-\mathrm{i}\omega t)\,, \tag{3.23}$$

which is a little bit confusing, since we have used the same symbol ψ for the two different functions (but at this point, I believe, you should be used to all sort of notation inconsistencies). By inserting this into (3.20) we obtain

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x)\,, \tag{3.24}$$

where we have identified $E = \hbar\omega$. Eq. (3.24) is then sometimes called the *time independent Schrödinger equation*, as it no longer includes time. Now here comes the problem (or at least my personal problem) with this designation. In real life, people like to abbreviate long terms. So it is typical that both of Eqs. (3.20) and (3.24) are simply called

the Schrödinger equation. But even though one could be technically derived from the other (as we have shown above), they have completely different meanings! The original Schrödinger equation represents a QM version of the equation of motion, while the time independent one is actually just the x-representation of the eigenvalue problem

$$\hat{\mathbf{H}} |\psi\rangle = E |\psi\rangle \tag{3.25}$$

which we could have written right away completely without any relevance to the time dependent form. Hence, in this text the only equation that is going to be referred to as the Schrödinger equation will be the one giving the time evolution.

3.5 Summary

It is finally here! At this point, we have covered all the necessary theoretical basics and are now ready to get into some simple introductory problems.

Chapter 4

Simple 1D Examples

In this chapter, we take all the theory that we have developed so far and apply it on selected problems in QM which are all one-dimensional and (relatively) easy to solve. The covered topics are: free particle, particle in a box, particle in a realistic box, harmonic oscillator and periodic potential.

4.1 An Aside: Fourier Transform & Dirac Distribution

Before we proceed with the study of a free particle, it would be wise to remind ourselves some of the key points about the Fourier transform. For a "well behaved" function $f(x)$ that meets the Dirichlet-Jordan conditions, which is mostly the case in physics, the following relations hold

$$\boxed{f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k\, f(k) \exp(\mathrm{i}kx)\,, \quad f(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x\, f(x) \exp(-\mathrm{i}kx)}\,, \tag{4.1}$$

where $f(k)$ is typically denoted as the *spectrum* of $f(x)$. (Note that despite $f(x)$ and $f(k)$ being represented by the same symbol, mathematically they are different functions.) The above formulas are then usually referred to as the inverse Fourier transform and Fourier transform, respectively. Sometimes, the following notation is also used

$$f(x) = \mathcal{F}^{-1}\left[f(k)\right]\,, \quad f(k) = \mathcal{F}\left[f(x)\right]\,. \tag{4.2}$$

We will now make use of the Fourier transform to express the Dirac distribution as

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}k\, \exp\left[-\mathrm{i}k(x - x')\right]\,. \tag{4.3}$$

To prove this, we proceed as

$$f(x') = \int_{-\infty}^{\infty} \mathrm{d}x\, \delta(x-x') f(x) = \int_{-\infty}^{\infty} \mathrm{d}x \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}k\, \exp\left[-\mathrm{i}k(x-x')\right] \right) f(x)$$
$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k\, \exp(\mathrm{i}kx') \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x\, f(x) \exp(-\mathrm{i}kx) \right) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k\, f(k) \exp(\mathrm{i}kx')$$
$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k\, f(k) \exp\left[\mathrm{i}k(x+x')\right] \Big|_{x=0} = f(x+x')\Big|_{x=0} = f(x'). \quad (4.4)$$

Our proof is now complete. By interchanging $x \leftrightarrow k$ (which we can do since at this point x and k stand for arbitrary continuous variables with no physical interpretation), the formula (4.3) can be restated as

$$\boxed{\delta(k-k') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}x\, \exp\left[-\mathrm{i}(k-k')x\right]}\,. \quad (4.5)$$

(If you want to ask then yes, we could have just proven this directly, but the proof is a bit more cumbersome due to some minuses.)

4.2 Free Particle

In classical physics, the problem of a free particle is typically the easiest one to solve. This is not quite the case in QM, where the free particle actually hides a lot of subtleties. Many authors therefore prefer to postpone this section and start usually by infinite quantum well – the truly simplest QM problem. Nevertheless, in my opinion, even though this would be quite a rough start, we will get a lot of important insight into the further problems, which would otherwise be missing. So let's get into it.

We start by determining the corresponding wavefunction of a particle that sits at $x = x_\star$, i.e.,

$$|\psi\rangle = |x_\star\rangle\ . \quad (4.6)$$

Since each state can be expressed in the basis $\{|x\rangle\}$, we can write

$$|x_\star\rangle = \int \mathrm{d}x\, \psi(x)\, |x\rangle\ . \quad (4.7)$$

Then, the only possible way to satisfy (4.6) is

$$\psi(x) = \delta(x - x_\star)\,. \quad (4.8)$$

This might seem intuitive at first, since if the particle sits at $x_\star$ and $|\psi(x)|^2$ represents the probability density of finding the particle at x, we would then expect the wavefunction to be zero everywhere except for $x = x_\star$, which is exactly what the Dirac distribution does. But there is one crucial problem. Recall from the previous chapter that we require each state to be normalized: $\langle\psi|\psi\rangle = 1$. But with $|\psi\rangle = |x_\star\rangle$ we have

$$\langle\psi|\psi\rangle = \langle x_\star|x_\star\rangle = \delta(0)\,! \tag{4.9}$$

So each eigenstate $|x\rangle$ of $\hat{\mathbf{x}}$ with the interpretation that the particle sits at x has infinite norm. I assume that you – the reader – must now await for me to show you some cool trick to resolve this issue. I will probably disappoint you, as there is no such trick. The free particle cannot exist at a defined position, it's that simple. Fortunately, nobody forces us to have the particle at one exact spot, and we can always express the particle as a general superposition of the position eigenstates, i.e.,

$$|\psi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, \psi(x)\, |x\rangle \ , \tag{4.10}$$

with

$$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, |\psi(x)|^2 = 1\,. \tag{4.11}$$

Now such a state is perfectly good.

Let's now look at how do the eigenstates of $\hat{\mathbf{p}}$ look like. To find those, one must solve the eigenvalue problem

$$\hat{\mathbf{p}}\,|p\rangle = p\,|p\rangle \ , \tag{4.12}$$

which in the x-representation takes on the following form:

$$-\mathrm{i}\hbar\frac{\partial\phi(x)}{\partial x} = p\phi(x)\,, \tag{4.13}$$

where $\phi(x) \leftarrow |p\rangle$ represents the momentum eigenstate expressed in the $\{|x\rangle\}$ basis. Note that in the above equation we have $p \in \mathbb{R}$. (The reason why I used $\phi(x)$ instead of $\psi(x)$ is that $\psi(x)$ was already used for the representation of the position eigenstate.) The solution is then simply

$$\phi(x) = \alpha \exp\left(\mathrm{i}\frac{p}{\hbar}x\right) \ , \tag{4.14}$$

where the integration constant α is to be chosen in order for the momentum eigenstates to satisfy the orthonormality condition. To make our life a bit easier, we will define the so called *wavenumber* $k = p/\hbar$ and express our momentum states as

$$|k\rangle \to \alpha\, \mathrm{e}^{\mathrm{i}kx}\,. \tag{4.15}$$

Further, we impose the orthonormality condition as

$$\langle k|k'\rangle = \delta(k-k')\,. \tag{4.16}$$

By calculating

$$\langle k|k'\rangle = |\alpha|^2 \int_{-\infty}^{\infty} \mathrm{d}x\, \mathrm{e}^{-\mathrm{i}(k-k')x} = |\alpha|^2\, 2\pi\delta(k-k')\,, \tag{4.17}$$

where Eq. (4.5) was used in the last equality, we get $\alpha = 1/\sqrt{2\pi}$ and the resulting normalized momentum eigenstates become

$$|k\rangle \to \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}kx}\,. \tag{4.18}$$

Assume now that we have a general state $|\Psi\rangle \to \Psi(x)$ and would like to express is in the $\{|k\rangle\}$ basis, i.e., $|\Psi\rangle \to \Psi(k) =?$ To do so, we remind ourselves that

$$|\Psi\rangle = \int_{-\infty}^{\infty} \mathrm{d}k\, \Psi(k)\,|k\rangle\ , \tag{4.19}$$

where

$$\Psi(k) = \langle k|\Psi\rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x\, \Psi(x)\,\mathrm{e}^{-\mathrm{i}kx}\,. \tag{4.20}$$

We then immediately see that

$$\boxed{\Psi(k) = \mathcal{F}\left[\Psi(x)\right]}, \tag{4.21}$$

and vice versa. In other words, the relationship between a state expressed in the $\{|x\rangle\}$ and the $\{|k\rangle\}$ basis is given by the Fourier transform. We would then call such function $\Psi(k)$ as the k-representation of $|\Psi\rangle$.

Now lets get back to our position eigenstate $\psi(x) = \delta(x - x_\star)$. Based on Eq. (4.21), we can immediately write

$$\psi(k) = \mathcal{F}\left[\psi(x)\right] = \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{-\mathrm{i}kx_\star}\,. \tag{4.22}$$

This is the k-representation of the position eigenstate $|x_\star\rangle$, i.e.,

$$|x_\star\rangle = \int_{-\infty}^{\infty} \mathrm{d}k\, \psi(k)\,|k\rangle\ . \tag{4.23}$$

Now we will show how the whole calculation can be reversed from the beginning. We start with the momentum eigenstate $|k_\star\rangle$ in the k-representation as

$$|\phi\rangle = |k_\star\rangle \to \phi(k) = \delta(k - k_\star). \tag{4.24}$$

By applying Eq. (4.21), we get the corresponding x-representation:

$$\phi(x) = \mathcal{F}^{-1}\left[\phi(k)\right] = \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}k_\star x}\,. \tag{4.25}$$

This is exactly the result (4.18).

I think that all of this might get a bit confusing, since we have been using here two representations for the same objects. Hence, all the results so far are summarised in Tab. 4.1.

Object	x-representation	k-representation
$\lvert x_\star\rangle$	$\delta(x - x_\star)$	$\frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{-\mathrm{i}kx_\star}$
$\lvert k_\star\rangle$	$\frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}k_\star x}$	$\delta(k - k_\star)$
$\lvert\Psi\rangle$	$\Psi(x) = \mathcal{F}^{-1}\left[\Psi(k)\right]$	$\Psi(k) = \mathcal{F}\left[\Psi(x)\right]$

Table 4.1: Summarised results for the free particle.

Assume now the particle to be in the state

$$\psi(x) = \left(2\pi\sigma_x^2\right)^{-\frac{1}{4}} \exp\left[-\frac{(x-\mu)^2}{4\sigma_x^2}\right]. \tag{4.26}$$

The corresponding probability density is then

$$w(x) = |\psi(x)|^2 = \frac{1}{\sqrt{2\pi\sigma_x^2}} \exp\left[-\frac{(x-\mu)^2}{2\sigma_x^2}\right]. \tag{4.27}$$

This is the so called *normal distribution* with $\bar{x} = \mu$ and width $2\sigma_x$, see Fig. 4.1.

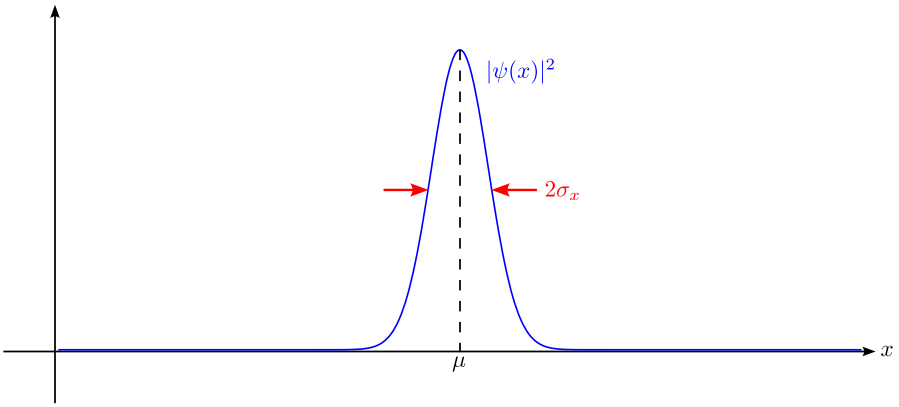

Figure 4.1: Normal distribution in the x-representation.

It can be easily checked that $\langle\psi|\psi\rangle = 1$ by employing Eq. (B.6) derived in Appendix 2. Now we use the relationship (4.21) to express

$$\psi(k) = \mathcal{F}\left[\psi(x)\right] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x \, \frac{1}{\left(2\pi\sigma_x^2\right)^4} \exp\left[-\frac{(x-\mu)^2}{4\sigma_x^2}\right] \mathrm{e}^{-\mathrm{i}kx}$$

$$= \left(\frac{2\sigma_x^2}{\pi}\right)^{\frac{1}{4}} \mathrm{e}^{-k^2\sigma_x^2} \, \mathrm{e}^{-\mathrm{i}k\mu} \, . \quad (4.28)$$

This further implies

$$|\psi(k)|^2 = \sqrt{\frac{2\sigma_x^2}{\pi}} \, \mathrm{e}^{-2k^2\sigma_x^2} \, . \quad (4.29)$$

By identifying

$$\sigma_k^2 = \frac{1}{4\sigma_x^2} \, , \quad (4.30)$$

Eq. (4.29) can be rewritten as

$$|\psi(k)|^2 = \frac{1}{\sqrt{2\pi\sigma_k^2}} \exp\left(-\frac{k^2}{2\sigma_k^2}\right) \, . \quad (4.31)$$

This is now another normal distribution but now in the k-representation, see Fig. 4.2.

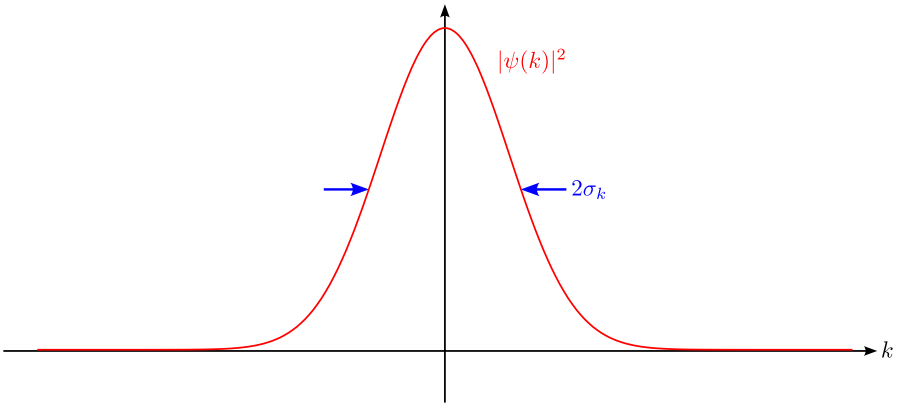

Figure 4.2: Normal distribution in the k-representation.

Note (again) that $\langle\psi|\psi\rangle = 1$, which we can check by employing the formula (B.6) once more, but it must be true since it stands for the same state $|\psi\rangle$, just expressed in a different basis. What is important here – we can modify Eq. (4.30) to write $\sigma_x\sigma_p = 1/2$, and since $p = \hbar k$, $\sigma_k = \sigma_p/\hbar$ (prove this yourself), we get

$$\sigma_x\sigma_p = \frac{\hbar}{2} \, . \quad (4.32)$$

Therefore, by all of this we actually proved that the normal distribution reaches the lower limit given by the Heisenberg uncertainty principle, see Eq. (2.88). How nice!

So far, we have inspected the operators $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$. Finally, we will focus on the most important one: the Hamilton operator. Technically, we could directly solve the eigenvalue problem $\hat{\mathbf{H}}\,|\psi\rangle = E\,|\psi\rangle$ in the x-representation. But we will adopt a different approach here. Recall that if we have two operators that commute, then they must share the eigenvectors (see the section about Heisenberg uncertainty principle). For the free particle, we have

$$\hat{\mathbf{H}} = \frac{\hat{\mathbf{p}}^2}{2m} \tag{4.33}$$

(a free particle has $V(x) = 0$). Hence, we immediately get

$$\left[\hat{\mathbf{p}}, \hat{\mathbf{H}}\right] = 0\,. \tag{4.34}$$

Therefore, $|k\rangle$ must also be an eigenvector of $\hat{\mathbf{H}}$, which we write as

$$\hat{\mathbf{H}}\,|k\rangle = E\,|k\rangle\ . \tag{4.35}$$

Now let's find out what are the allowed (measurable) values of E. We proceed as follows

$$\hat{\mathbf{H}}\,|k\rangle \to -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(\frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}kx}\right) = \frac{\hbar^2 k^2}{2m}\left(\frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}kx}\right) \leftarrow \frac{\hbar^2 k^2}{2m}\,|k\rangle\ , \tag{4.36}$$

i.e.,

$$\boxed{E(k) = \frac{\hbar^2 k^2}{2m}}\,. \tag{4.37}$$

We can see that

$$E \geq 0\,. \tag{4.38}$$

Now we have everything we need to be able to fully determine the time evolution of the free particle. We already know that each energy eigenstate evolves as

$$|E(t)\rangle = \exp\left(-\mathrm{i}\frac{E}{\hbar}t\right)|E\rangle\ . \tag{4.39}$$

In our case, that is

$$|k(t)\rangle = \frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}(kx-\omega t)}\,, \tag{4.40}$$

where we have identified

$$\omega(k) = \frac{\hbar k^2}{2m}\,. \tag{4.41}$$

We have just shown that a free particle with energy E is represented by a simple plane wave with phase velocity

$$v_{\mathrm{p}} = \frac{\omega(k)}{k} = \frac{\hbar k}{2m} = \frac{p}{2m} \tag{4.42}$$

(for more details, see Appendix A). Now that is a bit weird. From the classical mechanics, we know that the velocity of a particle expressed by it's momentum should be $v = p/m$. Why is then the phase velocity just half of that? Well, recall two important points. First, the phase velocity has nothing to do with a transport of energy. Moreover, the single state $|k\rangle$ is not physically realizable. So we do not need to care much about this result. Instead, we inspect a state that actually can exist in nature, i.e.,

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k\, A(k)\, \mathrm{e}^{\mathrm{i}(kx-\omega t)}\,, \tag{4.43}$$

where in this case $A(k) = \langle k|\psi_0\rangle$ represents a spectrum of amplitudes of the respective plane waves. If we further assume the spectrum to be tightly localized around some k_0 (corresponding to $p_0 = \hbar k_0$), the resulting wave-packet would then propagate with group velocity

$$v_\mathrm{g} = \left.\frac{\mathrm{d}\omega(k)}{\mathrm{d}k}\right|_{k=k_0} = \frac{p_0}{m}\,. \tag{4.44}$$

Now this is exactly the expression that we are used to from the classical mechanics.

Like I said, the free particle is not actually as simple to solve as in the classical case. Nevertheless, I hope that this rather long section helped you to get some valuable insight into how do we approach QM problems.

4.3 Particle in a Box (Infinite Quantum Well)

The next 1D example that is actually sometimes in the QM textbooks listed as the first example, since it is truly the simplest one, is the so called *infinite quantum well*, or simply the *particle in a box* (I prefer the latter). Basically, what this means is that we have a free (1D) particle whose movement is strictly restricted to the interval $x \in [0, L]$. Physically, this can be formulated by the potential energy given by the formula

$$V(x) = \begin{cases} 0\,, & x \in [0,L] \\ \infty\,, & \text{otherwise} \end{cases}\,, \tag{4.45}$$

see Fig. 4.3. Of course, this is not a realistic scenario, since it is impossible to create a box whose walls cannot be penetrated, but it can serve as a quite useful approximation. Our task now – and despite what we did with the free particle, this is the most typical task in QM – is to find the corresponding energy spectrum of the Hamilton operator, i.e., solving

$$\hat{\mathbf{H}}\,|\psi\rangle = E\,|\psi\rangle\,, \tag{4.46}$$

where

$$\hat{\mathbf{H}} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{x}})\,. \tag{4.47}$$

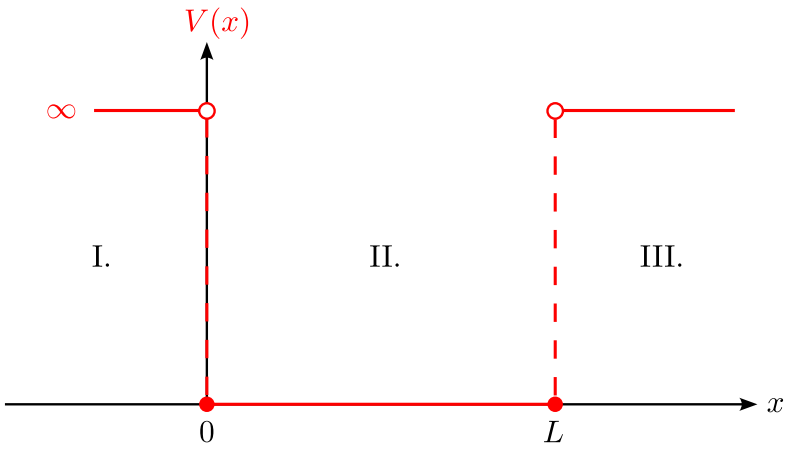

Figure 4.3: Potential energy of a particle in a box.

In the x-representation, this becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi\,. \tag{4.48}$$

As depicted in the figure, we separate our domain into three regions I., II. and III., and in each one of those, we denote the resulting wavefunction as $\psi_{\mathrm{I}}(x)$, ψ_{II} and $\psi_{\mathrm{III}}(x)$, respectively. But since we assume the particle not to be able to penetrate the walls of the box, we can immediately write the following:

$$\psi_{\mathrm{I}}(x) = \psi_{\mathrm{III}}(x) = 0\,. \tag{4.49}$$

Hence, our Eq. (4.48) reduces to

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_{\mathrm{II}}}{\mathrm{d}x^2} = E\psi_{\mathrm{II}} \quad \text{for} \quad x \in [0, d]\,, \tag{4.50}$$

where we used the fact that $V(x) = 0$ in the respective interval. The solution to this is simply

$$\psi_{\mathrm{II}}(x) = C_1\mathrm{e}^{\mathrm{i}kx} + C_2\mathrm{e}^{-\mathrm{i}kx}\,, \tag{4.51}$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}\,. \tag{4.52}$$

But this should not surprise us, as this is exactly the superposition of a right and left going particle with the corresponding momenta $p = \pm\hbar k$, which we derived in the preceding section, and since we assume the particle to be able to move freely inside the box, we could have simply written this directly. But now comes the key difference between the two cases. We stress out once again that this solution holds only inside the interval $x \in [0, d]$. So now that we have the general form of a solution in the three distinct parts, we have to somehow sew those together. And for such purpose, we must

formulate the appropriate boundary conditions. Due to the fact that we are dealing with a second order differential equation, we must specify how does the wavefunction and it's first derivative behave at the boundaries. Nevertheless, in this example, it turns out that we need only the condition on the first one of those. And it is very simple:

$$\boxed{\text{The wavefunction } \psi \text{ is continuous everywhere.}} \tag{4.53}$$

Why? Because if there is a discontinuity in the wavefunction, then the first derivative would become Dirac distribution (at that point) and the second derivative would be undefined. It is as simple as that. So in our case, we must have

$$\psi_{\mathrm{I}}(0^-) = \psi_{\mathrm{II}}(0)\,, \quad \psi_{\mathrm{II}}(L) = \psi_{\mathrm{III}}(L^+)\,. \tag{4.54}$$

(The 0^- and L^+ are there due to the fact that – based on our original definition – the region I. does not contain 0 and the region III. does not contain L. To satisfy those, it is convenient to express the solution (4.51) in a form

$$\psi_{\mathrm{II}}(x) = A\cos kx + B\sin kx\,, \tag{4.55}$$

which can be done by setting

$$C_1 = \frac{A - \mathrm{i}B}{2}\,, \quad C_2 = \frac{A + \mathrm{i}B}{2}\,, \tag{4.56}$$

whereas from the first condition we immediately get

$$B = 0\,. \tag{4.57}$$

The second condition then reads

$$A\cos kL = 0\,, \tag{4.58}$$

which has two solutions, the first being

$$A = 0\,, \tag{4.59}$$

but this does not make any sense, as in that case we would have $\psi = 0$ everywhere, and therefore there will not be any particle at all, so we discard it, and the second (physically sensible) one being

$$kL = n\pi\,, \quad n \in \mathbb{N}. \tag{4.60}$$

You might ask why did we keep only the positive values of n. First, due to the fact that the $\cos kl$ is an even function, the negative values of n would give exactly the same results as the positive ones. Second, $n = 0$ would result in (once again) the uninteresting solution $\psi = 0$ everywhere, so we drop it. Moving on, by combining the above with the definition (4.52), the only possible values of energy are

$$\boxed{E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2\,, \quad n = 1, 2, 3, \dots}\,. \tag{4.61}$$

This is now a very interesting result that we should comment on. First, as we can see, the spectrum of energies is discrete. This will turn out to be quite typical behavior of QM systems. Second, there is a lowest possible energy level of the particle being

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} \tag{4.62}$$

which is nonzero. How is that possible? It is simply the consequence of the Heisenberg uncertainty principle. If the particle would have zero energy, then it would also have zero momentum. But zero momentum corresponds to a specific eigenstate of $\hat{\mathbf{p}}$ with $\sigma_p = 0$. The Heisenberg uncertainty principle then dictates $\sigma_x = \infty$, but that is a contradiction with the assumption that the particle is strictly confined to the region $x \in [0, L]$. Moving on, let us now express the solution inside the box satisfying the boundary conditions as

$$\psi_n(x) = A \sin \frac{n\pi}{L} x \,. \tag{4.63}$$

To determine the value of the integration constant A, we further impose the normalization condition

$$\langle \psi_n | \psi_n \rangle = \int_0^L \mathrm{d}x \, |A|^2 \sin^2 \frac{n\pi}{L} x = 1 \,, \tag{4.64}$$

from which we get

$$A = \sqrt{\frac{2}{L}} \,. \tag{4.65}$$

Hence, the general solution of the energy eigenvalue equation inside the box becomes

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \,, \quad n = 1, 2, 3, \dots} \,, \tag{4.66}$$

see Fig. 4.4. Finally, to express the solution in the whole domain, we can write

$$\psi_n(x) = \begin{cases} 0 \,, & x < 0 \\ \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \,, & x \in [0, L] \\ 0 \,, & x > L \end{cases} \quad , \quad n = 1, 2, 3, \dots \tag{4.67}$$

Before moving on, let us once again revisit the Heisenberg uncertainty principle and rewrite the solution inside the box as

$$\psi_n(x) = -\mathrm{i} \sqrt{\frac{1}{2L}} \left(\mathrm{e}^{\mathrm{i} \frac{n\pi}{L} x} - \mathrm{e}^{-\mathrm{i} \frac{n\pi}{L} x} \right) \,, \tag{4.68}$$

which can be expressed by a superposition of the two momentum eigenstates as

$$|\psi_n\rangle = -\frac{\mathrm{i}}{\sqrt{2}} \left| p_n^+ \right\rangle + \frac{\mathrm{i}}{\sqrt{2}} \left| p_n^- \right\rangle \,, \tag{4.69}$$

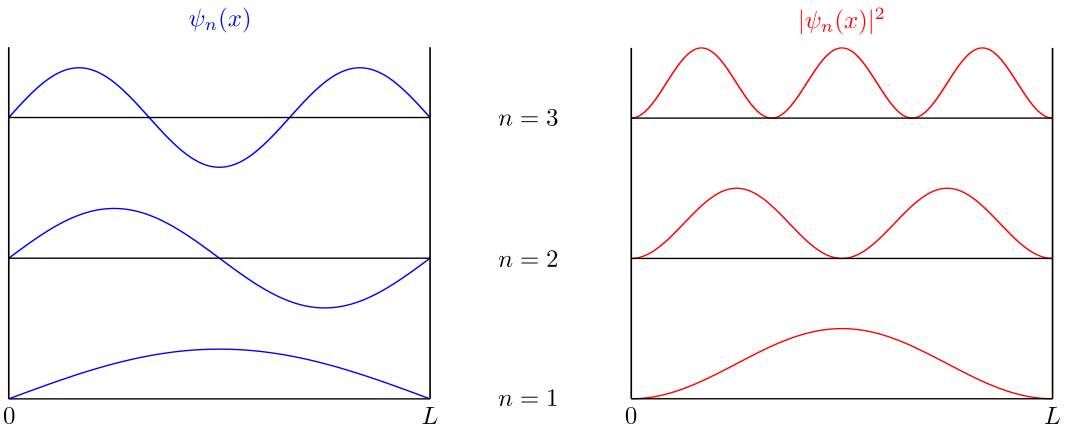

Figure 4.4: Wavefunction of the particle in a box.

where

$$p_n^{\pm} = \pm\hbar\frac{n\pi}{L}\,. \tag{4.70}$$

As en exercise, the reader is encouraged to check that those are truly the correct coefficients of the expansion, however, since the magnitudes squared of those must add up to unity, then – except for the phase factors represented by the $\mp$i in the numerators – there is basically no other choice. (Note that the individual momentum eigenstates cannot meet the required boundary conditions by themselves and therefore are unphysical.) In such case, we have

$$\bar{p}_n = 0\,, \quad \sigma_{p,n} = \frac{n\pi}{L}\hbar\,. \tag{4.71}$$

Next, it can be shown that

$$\begin{aligned} \bar{x}_n &= \int_0^L \mathrm{d}x\, x|\psi_n(x)|^2 = \frac{L}{2}\,, \\ \sigma_{x,n} &= \sqrt{\int_0^L \mathrm{d}x\, \left(x - \frac{L}{2}\right)^2 |\psi_n(x)|^2} = \frac{L}{n\pi}\sqrt{\frac{\pi^2 n^2 - 6}{12}}\,. \end{aligned} \tag{4.72}$$

By combining the above results, we express

$$\sigma_{x,n}\sigma_{p,n} = \hbar\sqrt{\frac{\pi^2 n^2 - 6}{12}}\,. \tag{4.73}$$

As we can see, the RHS is a monotonically increasing sequence of n. If we then choose the lowest possible $n = 1$, we get

$$\sigma_{x,1}\sigma_{p,1} \approx 0.57\hbar > \frac{\hbar}{2}\,, \tag{4.74}$$

and so

$$\boxed{\sigma_{x,n}\sigma_{p,n} > \frac{\hbar}{2}} \tag{4.75}$$

for all the energy eigenstates.

4.4 Particle in a Realistic Box (Finite Quantum Well)

It would be naive to assume that there exists something like the ideal box with $V \to \infty$ on the outside as presented above. Hence, here we make things a bit more realistic and consider the box to be defined by

$$V(x) = \begin{cases} 0\,, & x \in [-L/2, L/2] \\ V_0\,, & \text{otherwise} \end{cases}\,, \tag{4.76}$$

see Fig. 4.5

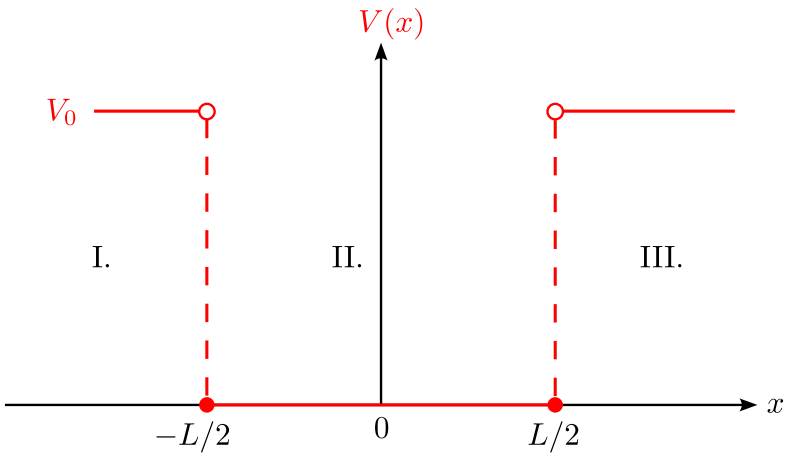

Figure 4.5: Finite Box.

Note that for the sake of the upcoming calculations, we have shifted the coordinates for the box to be placed symmetric around $x = 0$. Our aim is to solve the same equation as in the preceding section, i.e.,

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi\,. \tag{4.77}$$

The main difference is that, in this situation, the wavefunction $\psi(x)$ no longer vanishes outside the box. First, we focus on the region I., i.e., $x \in (-\infty, -L/2)$, where Eq. (4.77) takes the form

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_\mathrm{I}}{\mathrm{d}x^2} + V_0\psi_\mathrm{I} = E\psi_\mathrm{I}\,. \tag{4.78}$$

We will further assume $E < V_0$ for the particle to be bounded inside the box. In such case, we can rewrite the above as

$$\frac{\mathrm{d}^2\psi_\mathrm{I}}{\mathrm{d}x^2} - \varkappa^2\psi_\mathrm{I} = 0\,, \tag{4.79}$$

where

$$\varkappa \equiv \frac{\sqrt{2m(V_0 - E)}}{\hbar} > 0\,. \tag{4.80}$$

The solution to this is then

$$\psi_\mathrm{I}(x) = A\,\mathrm{e}^{\varkappa x} + B\,\mathrm{e}^{-\varkappa x}\,. \tag{4.81}$$

As the second term is diverging towards $x \to -\infty$ and we need the resulting wavefunction to be normalizable, we drop it, leaving us with

$$\psi_\mathrm{I}(x) = A\,\mathrm{e}^{\varkappa x}\,. \tag{4.82}$$

By following the same procedure once again just for the region III., we further obtain

$$\psi_\mathrm{III}(x) = B\,\mathrm{e}^{-\varkappa x}\,. \tag{4.83}$$

The solution inside the box is then the same as in the case of the infinite box, i.e.,

$$\psi_\mathrm{II}(x) = C\cos kx + D\sin kx \tag{4.84}$$

with

$$k \equiv \frac{\sqrt{2mE}}{\hbar}\,. \tag{4.85}$$

Now we need to sew everything together. We already know that the resulting wavefunction must be continuous. But generally, Eq. (4.77) is a second order differential equation, and we also need the appropriate condition on the first derivative of ψ. (The infinite box is an exception that can be solved without this knowledge.) We proceed with the following argumentation. If the wavefunction has a discontinuity in the first derivative at $x = x_0$, then the second derivative would diverge at that point. But since we have $|V(x)| < \infty$ everywhere, Eq. (4.77) would not be satisfied at x_0. Hence, we can state that

$$\boxed{\text{For } |V(x)| < \infty\text{, the first derivative of the wavefunction } \psi \text{ is continuous.}} \tag{4.86}$$

Based on this result, we can formulate all the required boundary conditions as

$$\begin{aligned}
\psi_\mathrm{II}(-L/2) &= \psi_\mathrm{I}(-L/2^-)\,,\\
\psi_\mathrm{II}(L/2) &= \psi_\mathrm{III}(L/2^+)\,,\\
\psi'_\mathrm{II}(-L/2) &= \psi'_\mathrm{I}(-L/2^-)\,,\\
\psi'_\mathrm{II}(L/2) &= \psi'_\mathrm{III}(L/2^+)\,.
\end{aligned} \tag{4.87}$$

By employing the expressions (4.82), (4.83) and (4.84), this becomes

$$\begin{aligned} C\cos(kL/2) - D\sin(kL/2) &= A\,\mathrm{e}^{-\varkappa L/2}\,, \\ C\cos(kL/2) + D\sin(kL/2) &= B\,\mathrm{e}^{-\varkappa L/2}\,, \\ kC\sin(kL/2) + kD\cos(kL/2) &= \varkappa A\,\mathrm{e}^{-\varkappa L/2}\,, \\ -kC\sin(kL/2) + kD\cos(kL/2) &= -\varkappa B\,\mathrm{e}^{-\varkappa L/2}\,, \end{aligned} \tag{4.88}$$

where we used the even/odd property of the cos/sin functions. Before moving on, let us analyze this system of equations qualitatively. At first sight, it might seem that we have four equations for six unknowns $A, B, C, D, k, \varkappa$. But $k = k(E)$ and $\varkappa = \varkappa(E)$, so actually, we have only five unknowns A, B, C, D, E. Still weird. How are we supposed to solve a system with more unknowns than equations? Remember, that there is one additional condition that must be satisfied, being

$$\int_{-\infty}^{\infty} \mathrm{d}x\,|\psi(x)|^2 = 1\,. \tag{4.89}$$

By combining all of this, we get exactly the same number of equations as unknowns. Despite all of this, we have one more problem to deal with. Our system of equations does not possess an analytical form of solution. Fortunately, there is a nice trick that allows us to find the solution graphically. By adding and subtracting the equations in the first and second pair, we get

$$\begin{aligned} 2C\cos(kL/2) &= (B + A)\,\mathrm{e}^{-\varkappa L/2}\,, \\ 2D\sin(kL/2) &= (B - A)\,\mathrm{e}^{-\varkappa L/2}\,, \\ 2kD\cos(kL/2) &= -(B - A)\varkappa\,\mathrm{e}^{-\varkappa L/2}\,, \\ 2kC\sin(kL/2) &= (B + A)\varkappa\,\mathrm{e}^{-\varkappa L/2}\,. \end{aligned} \tag{4.90}$$

We now consider four distinct cases.

1. $C = 0$, $D = 0$. Here the only possible solution is $A = 0$, $B = 0$. But then we would have $\psi = 0$, meaning that there is no particle at all. Hence, we drop this case.

2. $C \neq 0$, $D = 0$. By dividing the fourth equation by the first, we get

   $$k\tan(kL/2) = \varkappa\,. \tag{4.91}$$

   The remaining two equations then dictate $B = A$, and the resulting wavefunction will be symmetric w.r.t. $x = 0$.

3. $C = 0$, $D \neq 0$. By dividing the third equation by the second, we get

   $$k\cot(kL/2) = -\varkappa\,. \tag{4.92}$$

   The remaining equations then dictate $B = -A$, and the resulting wavefunction will be antisymmetric w.r.t. $x = 0$.

4. $C \neq 0$, $D \neq 0$. Here we would get both the conditions (4.91), (4.92). Multiplying those two together yields $k^2 + \varkappa^2 = 0$, but at the same time, Eqs. (4.80), (4.85) give $k^2 + \varkappa^2 = 2mV_0/\hbar^2 > 0$. This is a contradiction and the original system of equations does not possess a solution in this case.

To proceed further, we treat both the symmetric and the antisymmetric case at the same time, but keep in mind that they only work separately. By introducing

$$\xi = \frac{kL}{2}\,, \quad \eta = \frac{\varkappa L}{2}\,, \tag{4.93}$$

Eqs. (4.91) and (4.92) can be rewritten as

$$\begin{aligned} &\eta = \xi \tan\xi \quad \text{(symmetric)}\,, \\ &\eta = -\xi \cot\xi \quad \text{(antisymmetric)}\,. \end{aligned} \tag{4.94}$$

At the same time,

$$\xi^2 + \eta^2 = \frac{mV_0L^2}{2\hbar^2} \equiv R_0^2\,, \tag{4.95}$$

which is an equation of a circle of radius R_0 in the (ξ-η) plane. We can now plot everything together, see Fig. 4.6.

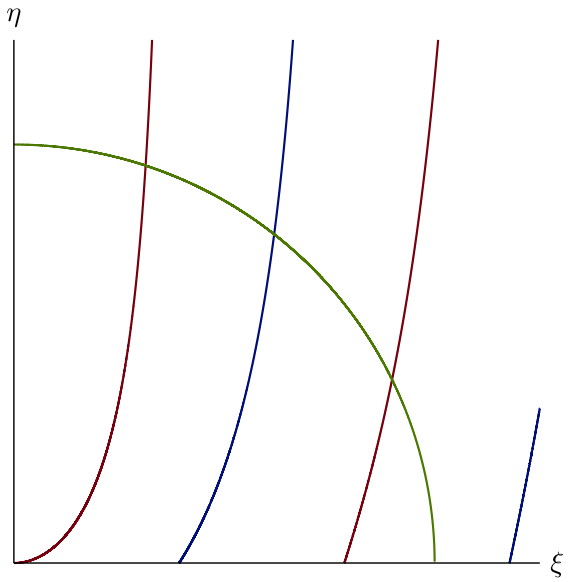

Figure 4.6: Graphical Solution.

The red curves represent the symmetric case, the blue ones the antisymmetric case, and in green is the circle determined by R_0. The corresponding eigenvalues of energy can now be extracted graphically (or numerically) from the above plot. As we can see, since $R_0 \propto V_0$, the higher the potential outside the box, the more energy values (and hence

the corresponding wavefunctions) we are going to get.

At this point, the reader is encouraged to use an appropriate computer algebra system to determine the profiles of the resulting wavefunctions and probability densities. The three solutions corresponding to Fig. 4.6 are plotted below.

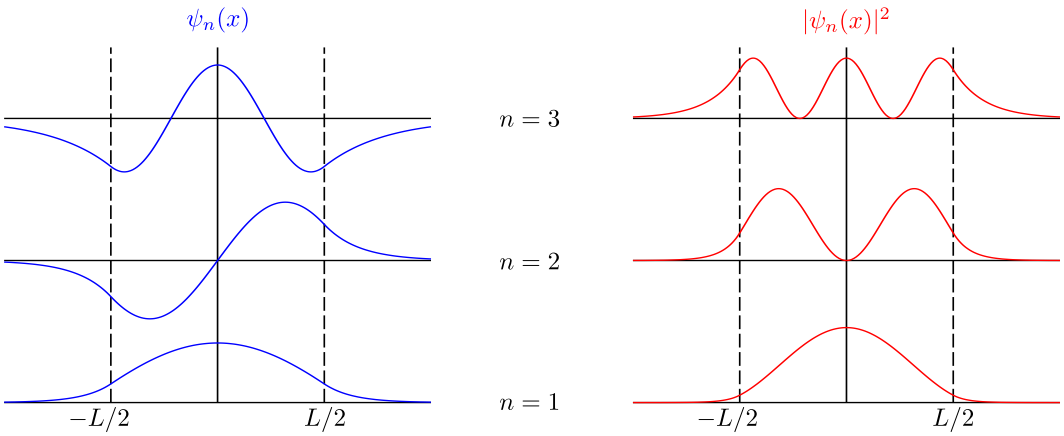

Figure 4.7: Wavefunction of the particle in a realistic box.

As we can see, regardless of the particle having energy $E < V_0$, there is a non-zero probability of finding the particle outside the box, which is something we would not encounter in the classical world.

4.5 Harmonic Oscillator

Probably the most important 1D problem in QM is the harmonic oscillator. Hence, this section is devoted to solving the energy eigenvalue problem

$$\hat{\mathbf{H}}\,|\psi\rangle = E\,|\psi\rangle \tag{4.96}$$

for the potential energy given by

$$V(x) = \frac{1}{2}m\omega^2 x^2\,, \tag{4.97}$$

where

$$k = m\omega^2 \tag{4.98}$$

stands for the oscillator stiffness. Hence,

$$\hat{\mathbf{H}} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{1}{2}m\omega^2\hat{\mathbf{x}}^2\,, \tag{4.99}$$

and the corresponding x-representation of Eq. (4.96) becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega x^2\psi = E\psi\,. \tag{4.100}$$

First, we rewrite it as

$$\frac{\mathrm{d}^2\psi}{\frac{m\omega}{\hbar}\mathrm{d}x^2} - \frac{m\omega}{\hbar}x^2\psi + \frac{2E}{m\omega}\psi = 0\,, \tag{4.101}$$

and by introducing the new dimensionless variable

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x\,, \tag{4.102}$$

further transform it into

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} - \xi^2\psi + K\psi = 0\,, \tag{4.103}$$

where we denoted

$$K = \frac{2E}{\hbar\omega}\,. \tag{4.104}$$

Now we investigate how does the solution behave in the limit $\xi \to \infty$, in which case the equation reduces to

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} - \xi^2\psi = 0\,. \tag{4.105}$$

The approximate asymptotic solution to this is

$$\psi(\xi) \approx A\,\mathrm{e}^{\frac{\xi^2}{2}} + B\,\mathrm{e}^{-\frac{\xi^2}{2}}\,, \tag{4.106}$$

where we must drop the first term due to the requirement for the resulting wavefunction to be normalizable. Based on this result, we substitute the following ansatz:

$$\psi(\xi) = u(\xi)\,\mathrm{e}^{-\frac{\xi^2}{2}} \tag{4.107}$$

with

$$\begin{aligned}\frac{\mathrm{d}\psi}{\mathrm{d}\xi} &= \mathrm{e}^{-\frac{\xi^2}{2}}\left[\frac{\mathrm{d}u}{\mathrm{d}\xi} - \xi u\right]\,,\\ \frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} &= \mathrm{e}^{-\frac{\xi^2}{2}}\left[\frac{\mathrm{d}^2u}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}u}{\mathrm{d}\xi} + (\xi^2-1)u\right]\,,\end{aligned} \tag{4.108}$$

into (4.103), resulting in

$$\frac{\mathrm{d}^2u}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}u}{\mathrm{d}\xi} + (K-1)u = 0\,. \tag{4.109}$$

This now represents the associated Hermite equation (see Appendix). To proceed further, we look for the solution in a form of the power series

$$u(\xi) = \sum_{j=0}^{\infty} c_j\xi^j\,, \tag{4.110}$$

with

$$\begin{aligned}\frac{\mathrm{d}u}{\mathrm{d}\xi} &= \sum_{j=0}^{\infty} j c_j \xi^{j-1}\,, \\ \frac{\mathrm{d}^2 u}{\mathrm{d}\xi^2} &= \sum_{j=0}^{\infty} j(j-1) c_j \xi^{j-2} = \sum_{j=0}^{\infty} (j+2)(j+1) c_{j+2} \xi^{j}\,.\end{aligned} \tag{4.111}$$

By inserting those into (4.109), we arrive at

$$\sum_{j=0}^{\infty} (j+2)(j+1) c_{j+2} \xi^j - 2\sum_{j=0}^{\infty} j c_j \xi^j + (K-1)\sum_{j=0}^{\infty} c_j \xi^j = 0\,, \tag{4.112}$$

where we can further factor out the ξ^j to get

$$\sum_{j=0}^{\infty} \left[(j+2)(j+1) c_{j+2} - (2j+1-K) c_j\right] \xi^j = 0\,. \tag{4.113}$$

By setting each term before the corresponding power of ξ equal to zero, we get the following recurrence relation:

$$c_{j+2} = \frac{2j+1-K}{(j+2)(j+1)} c_j\,. \tag{4.114}$$

Note that this expression relates only c_{j+2} and c_j, so to fully specify the solution, one must define c_0 and c_1 which basically play the role of the integration constants here. To ensure the resulting wavefunction to be normalizable, the power series must terminate for some chosen

$$0 \leq j_{\max} < 0\,, \tag{4.115}$$

or in other words,

$$c_j = 0 \quad \text{for} \quad j > j_{\max}\,. \tag{4.116}$$

Conventionally, we further relabel

$$j_{\max} \equiv n\,. \tag{4.117}$$

Now there are two distinct possibilities to satisfy this condition, being

$$c_0 \neq 0\,, c_1 = 0 \quad \text{or} \quad c_0 = 0\,, c_1 \neq 0\,, \tag{4.118}$$

(or being the exclusive or here), since we cannot terminate the series simultaneously for even and odd values of j. According to Eq. (4.114), we must then have

$$2n + 1 - K = 0\,. \tag{4.119}$$

The reader is encouraged to check that the combination of (4.123) and (4.119) truly satisfies the condition (4.116). By substituting for K from (4.104), we get the allowed values of the energy of the harmonic oscillator:

$$\boxed{E_n = \left(\frac{1}{2} + n\right)\hbar\omega \quad \text{with} \quad n = 0, 1, 2, \ldots}\,. \tag{4.120}$$

Similarly as in the case of a particle in a box, we can see that there is a nonzero lowest possible energy level

$$E_0 = \frac{\hbar\omega}{2} \tag{4.121}$$

dictated by the Heisenberg uncertainty principle. This is sometimes referred to as the *null oscillations*. Moving on, the solutions corresponding to those energy levels can then be written as

$$u_n(\xi) = \alpha_n H_n(\xi)\,, \tag{4.122}$$

where $H_n(\xi)$ stands for the associated Hermite polynomial (defined also in the Appendix), and α_n is the normalization constant. Using the conventional choice for the integration constants

$$c_0 = 1\,, c_1 = 0 \quad \text{or} \quad c_0 = 0\,, c_1 = 1\,, \tag{4.123}$$

and further employing the recurrence relation (4.114), we can calculate the first few Hermite polynomials:

$$\begin{aligned} H_0(\xi) &= 1\,, \\ H_1(\xi) &= \xi\,, \\ H_2(\xi) &= 1 - 2\xi^2\,, \\ H_3(\xi) &= \xi - \frac{2}{3}\xi^3\,, \\ H_4(\xi) &= 1 - 4\xi^2 + \frac{4}{3}\xi^4\,, \\ H_5(\xi) &= \xi - \frac{4}{3}\xi^3 + \frac{4}{15}\xi^5\,. \end{aligned} \tag{4.124}$$

As you can see, each of those truly contains only even or odd powers of ξ but not both. Finally, by inserting (4.122) into (4.107), we get the final form of our originally sought energy eigenstates

$$\boxed{\psi_n(\xi) = \alpha_n H_n(\xi)\,\mathrm{e}^{-\frac{\xi^2}{2}}}\,, \tag{4.125}$$

where α_n must be chosen to satisfy

$$\int_{-\infty}^{\infty} \mathrm{d}x\,|\psi_n(x)|^2 = 1\,. \tag{4.126}$$

We recall that Eq. (4.125) refers just to the continuous representation of the energy eigenstates, while the true eigenstates are then

$$|n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\,\psi_n(x)\,|x\rangle\ . \tag{4.127}$$

Now is the time to show the correspondence of all of this with the classical case. In any textbook on classical dynamics, you can find the formula for the classical probability

density of finding the oscillator at x to be

$$w_{\text{classical}}(x) = \frac{1}{\pi\sqrt{A^2 - x^2}}\,, \tag{4.128}$$

where

$$A = \sqrt{\frac{2E}{m\omega^2}} \tag{4.129}$$

represents the amplitude. So let's compare it with the obtained quantum result

$$w_n(x) = |\psi_n(x)|^2 = |\alpha_n|^2 H_n^2(\xi)\,\mathrm{e}^{-\xi^2}\,. \tag{4.130}$$

The comparison is depicted in Fig. 4.8.

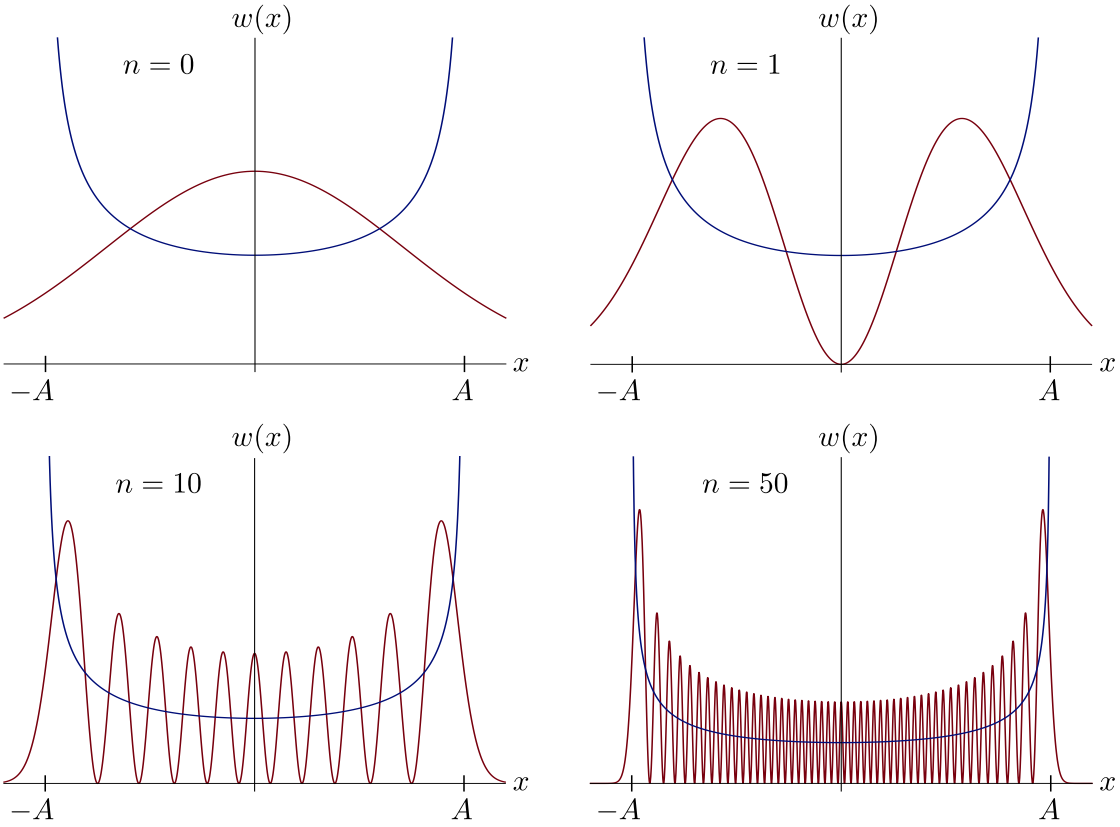

Figure 4.8: Harmonic oscillator.

As we can see, the probability density tends to replicate the classical shape in the case of large n. But note that the total energy is proportional to $\hbar \sim 10^{-34}$, so even, e.g., the $n = 50$ still corresponds to extremely low energy that we would not be able to measure by standard measurement procedures!

4.6 Creation and Annihilation Operators

Here we provide another point of view on the harmonic oscillator based purely on algebraic manipulations without any specific choice of the representation. We start by rewriting the Hamilton operator (4.99) as

$$\frac{\hat{\mathbf{H}}}{\hbar\omega} = \frac{m\omega}{2\hbar}\hat{\mathbf{x}}^2 + \frac{1}{2m\hbar\omega}\hat{\mathbf{p}}^2 \,. \tag{4.131}$$

Next, we define

$$\hat{\mathbf{a}}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{\mathbf{x}} + \mathrm{i}\sqrt{\frac{1}{2m\hbar\omega}}\hat{\mathbf{p}} \,, \quad \hat{\mathbf{a}} = \sqrt{\frac{m\omega}{2\hbar}}\hat{\mathbf{x}} - \mathrm{i}\sqrt{\frac{1}{2m\hbar\omega}}\hat{\mathbf{p}} \,, \tag{4.132}$$

where $\hat{\mathbf{a}}^\dagger, \hat{\mathbf{a}}$ stand for the *creation* and the *annihilation* operator, respectively. Note that as the creation operator is the hermitian conjugate to the annihilation one, neither of those is hermitian and therefore they do not represent an observable quantity. For the purpose of upcoming calculations, we will need the following commutation relations:

$$\left[\hat{\mathbf{H}}, \hat{\mathbf{a}}^\dagger\right] = +\hbar\omega\hat{\mathbf{a}}^\dagger \,, \tag{4.133}$$

$$\left[\hat{\mathbf{H}}, \hat{\mathbf{a}}\right] = -\hbar\omega\hat{\mathbf{a}} \,, \tag{4.134}$$

which can both be derived simply by using the definitions (4.132) together with the canonical quantization formula (try it). Further,

$$\hat{\mathbf{a}}^\dagger\hat{\mathbf{a}} = \frac{\hat{\mathbf{H}}}{\hbar\omega} - \frac{1}{2} \,, \tag{4.135}$$

$$\hat{\mathbf{a}}\hat{\mathbf{a}}^\dagger = \frac{\hat{\mathbf{H}}}{\hbar\omega} + \frac{1}{2} \,. \tag{4.136}$$

which will come in handy. Now we will show that the creation operator, when acting on the n-th energy eigenstate, produces an eigenstate one energy level higher. First, assume the energy eigenstates to obey

$$\hat{\mathbf{H}}\left|n\right\rangle = E_n\left|n\right\rangle \,. \tag{4.137}$$

Then, we calculate

$$\hat{\mathbf{H}}\left(\hat{\mathbf{a}}^\dagger\left|n\right\rangle\right) = \hat{\mathbf{H}}\hat{\mathbf{a}}^\dagger\left|n\right\rangle = \left(\hat{\mathbf{a}}^\dagger\hat{\mathbf{H}} + \hbar\omega\hat{\mathbf{a}}^\dagger\right)\left|n\right\rangle = \left(E_n + \hbar\omega\right)\left(\hat{\mathbf{a}}^\dagger\left|n\right\rangle\right) \,, \tag{4.138}$$

where in the second equality we used (4.133). But

$$E_n + \hbar\omega = E_{n+1} \,, \tag{4.139}$$

and therefore

$$\hat{\mathbf{a}}^\dagger\left|n\right\rangle \propto \left|n+1\right\rangle \,. \tag{4.140}$$

Next, we repeat the above calculation but now with the annihilation operator, i.e.,

$$\hat{\mathbf{H}}\left(\hat{\mathbf{a}}\left|n\right\rangle\right) = \hat{\mathbf{H}}\hat{\mathbf{a}}\left|n\right\rangle = \left(\hat{\mathbf{a}}\hat{\mathbf{H}} - \hbar\omega\hat{\mathbf{a}}\right)\left|n\right\rangle = \left(E_n - \hbar\omega\right)\left(\hat{\mathbf{a}}\left|n\right\rangle\right) , \tag{4.141}$$

but since

$$E_n - \hbar\omega = E_{n-1} , \tag{4.142}$$

we get

$$\hat{\mathbf{a}}\left|n\right\rangle \propto \left|n-1\right\rangle . \tag{4.143}$$

So the annihilation operator, when acting on the n-th energy eigenstate, produces an eigenstate one energy level lower. Moving on, we know that there must be a state with lowest possible energy denoted as $|0\rangle$. Then, when acting on this by $\hat{\mathbf{a}}$, we must have

$$\hat{\mathbf{a}}\left|0\right\rangle = \left|o\right\rangle , \tag{4.144}$$

as there is no such thing as $|-1\rangle$. By taking the inner product of the above equation with itself, we obtain

$$\langle\hat{\mathbf{a}}\,0|\hat{\mathbf{a}}\,0\rangle = \left\langle 0\middle|\hat{\mathbf{a}}^\dagger\hat{\mathbf{a}}\middle|0\right\rangle = \left\langle 0\middle|\frac{\hat{\mathbf{H}}}{\hbar\omega} - \frac{1}{2}\middle|0\right\rangle = \left(\frac{E_0}{\hbar\omega} - \frac{1}{2}\right)\langle 0|0\rangle = \left(\frac{E_0}{\hbar\omega} - \frac{1}{2}\right) = 0 , \tag{4.145}$$

where in the second equality we used (4.135), in the fourth we assumed $\langle 0|0\rangle = 1$ (as always), and the zero after the last equality is here due to the presence of a zero vector $|o\rangle$ on the RHS of Eq. (4.144) with the property $\langle o|o\rangle = 0$. Also from the last equality, it follows that

$$E_0 = \frac{\hbar\omega}{2} . \tag{4.146}$$

By combining this result with the property of the creation operator, we can write

$$\left|n\right\rangle \propto \hat{\mathbf{a}}^n\left|0\right\rangle \tag{4.147}$$

with the corresponding energy

$$E_n = \left(\frac{1}{2} + n\right)\hbar\omega , \tag{4.148}$$

which is exactly the result obtained in the previous section. At this point, one might thing that we just determined the allowed energy spectrum of the harmonic oscillator based purely on the algebraic properties of the creation and annihilation operators. But we must realize that it would not be able to identify (4.139) and (4.142) without the knowledge resulting from the preceding analysis in the x-representation. So be careful here.

Next, let us find the proportionality constants of (4.140) and (4.143). First, we rewrite those as

$$\hat{\mathbf{a}}^\dagger\left|n\right\rangle = \alpha_n^{(+)}\left|n+1\right\rangle , \quad \hat{\mathbf{a}}\left|n\right\rangle = \alpha_n^{(-)}\left|n-1\right\rangle . \tag{4.149}$$

Then, by taking the inner products of the above equations with themselves, we get

$$\left\langle n\middle|\hat{\mathbf{a}}\hat{\mathbf{a}}^\dagger\middle|n\right\rangle = \left|\alpha_n^{(+)}\right|^2 ; \quad \left\langle n\middle|\hat{\mathbf{a}}^\dagger\hat{\mathbf{a}}\middle|n\right\rangle = \left|\alpha_n^{(-)}\right|^2 , \tag{4.150}$$

where all the energy eigenstates are (again) assumed to be normalized to unity. By employing Eqs. (4.135) and (4.136), the above can be further rewritten as

$$\left\langle n\middle|\frac{\hat{\mathbf{H}}}{\hbar\omega}+\frac{1}{2}\middle|n\right\rangle = \left|\alpha_n^{(+)}\right|^2 ; \quad \left\langle n\middle|\frac{\hat{\mathbf{H}}}{\hbar\omega}-\frac{1}{2}\middle|n\right\rangle = \left|\alpha_n^{(-)}\right|^2 , \tag{4.151}$$

from which we obtain

$$\frac{E_n}{\hbar\omega}+\frac{1}{2} = \left|\alpha_n^{(+)}\right|^2 ; \quad \frac{E_n}{\hbar\omega}-\frac{1}{2} = \left|\alpha_n^{(-)}\right|^2 . \tag{4.152}$$

Finally, using the expression for the energy spectrum (4.148), we arrive at

$$\alpha_n^{(+)} = \sqrt{n+1}\,; \quad \alpha_n^{(-)} = \sqrt{n}\,, \tag{4.153}$$

i.e.,

$$\hat{\mathbf{a}}^\dagger\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle , \quad \hat{\mathbf{a}}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle . \tag{4.154}$$

Those values can be easily remembered, as the number under the square root always corresponds to the higher of the two in the respective Kets.

Lastly, let us define the operator

$$\hat{\mathbf{N}} = \hat{\mathbf{a}}^\dagger\hat{\mathbf{a}}\,. \tag{4.155}$$

We can easily show that this is a hermitian operator, as

$$\hat{\mathbf{N}}^\dagger = \left(\hat{\mathbf{a}}^\dagger\hat{\mathbf{a}}\right)^\dagger = \hat{\mathbf{a}}^\dagger\hat{\mathbf{a}} = \hat{\mathbf{N}}\,. \tag{4.156}$$

Hence, $\hat{\mathbf{N}}$ must correspond to an observable quantity. By calculating

$$\hat{\mathbf{N}}\left|n\right\rangle = \hat{\mathbf{a}}^\dagger\hat{\mathbf{a}}\left|n\right\rangle = \sqrt{n}\hat{\mathbf{a}}^\dagger\left|n-1\right\rangle = \sqrt{n}\sqrt{n}\left|n\right\rangle = n\left|n\right\rangle , \tag{4.157}$$

which for the sake of readability we restate once again as

$$\hat{\mathbf{N}}\left|n\right\rangle = n\left|n\right\rangle , \tag{4.158}$$

we immediately see that the observable values (eigenvalues) of $\hat{\mathbf{N}}$ correspond to the amount of energy quanta $\hbar\omega$ contained in our harmonic oscillator.

To conclude this section, let me tell you that the operators $\hat{\mathbf{a}}^\dagger, \hat{\mathbf{a}}$ play a key role in QFT, where they create and annihilate particles, while $\hat{\mathbf{N}}$ then gives the total amount of particles in our system. So another purpose of this was to let you taste something much more interesting (and complicated) that might come later in your studies.

4.7 Periodic Potential

This section is devoted to the qualitative study of a quantum particle inside of a periodic potential, which plays a key role in electronics, where conductors and semiconductors are typically crystalline at the atomic level, and therefore, the resulting potential – sourced by the atomic cores placed at the vertices of the respective crystal lattice – is periodic.

4.7.1 Floquet-Bloch Theory

Before we start our analysis, we briefly introduce the *Floquet-Bloch theory* which represents an elegant approach to solving linear differential equations with periodic coefficients. We start by assuming a second order equation of the form

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + q(x)y = 0\,, \tag{4.159}$$

where the coefficient $q(x)$ is periodic with the period d, i.e.,

$$q(x+d) = q(x)\,. \tag{4.160}$$

First, we assume the normalized solution satisfying the following property

$$\begin{aligned} u(0) &= 1\,, \quad u'(0) = 0\,, \\ v(0) &= 0\,, \quad v'(0) = 1\,. \end{aligned} \tag{4.161}$$

A general solution to Eq. (4.159) can then be written as

$$y(x) = y(0)u(x) + y'(0)v(x)\,. \tag{4.162}$$

Due to the periodic property of $q(x)$, we can shift $x \to x + d$, by which Eq. (4.159) becomes

$$\left.\frac{\mathrm{d}^2 y}{\mathrm{d}x^2}\right|_{x+d} + q(x)y(x+d) = 0\,, \tag{4.163}$$

and therefore, if $y(x)$ is the solution then so is the $y(x+d)$. We can use this fact together with (4.162) to express the shifted normalized solutions

$$\begin{aligned} u(x+d) &= u(d)u(x) + u'(d)v(x)\,, \\ v(x+d) &= v(d)u(x) + v'(d)v(x)\,. \end{aligned} \tag{4.164}$$

The Floquet-Bloch theory now assumes an existence of a general solution to the original equation with the property

$$F(x+d) = \lambda F(x)\,, \tag{4.165}$$

where $F(x)$ is called the *Bloch wave* and λ the *Floquet multiplier*. By expressing the Bloch wave by means of the normalized solution as

$$F(x) = C_1 u(x) + C_2 v(x)\,, \tag{4.166}$$

we can further employ (4.164) to rewrite (4.165) as

$$C_1\left[u(d)u(x)+u'(d)v(x)\right]+C_2\left[v(d)u(x)+v'(d)v(x)\right]=\lambda\left[C_1u(x)+C_2v(x)\right]\,. \quad (4.167)$$

Since the functions $u(x), v(x)$ must be linearly independent (as they represent a general solution to the second order differential equation), we can rearrange the above into

$$\begin{pmatrix} u(d) & v(d) \\ v'(d) & u'(d) \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}=\lambda\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}\,. \quad (4.168)$$

But this is nothing less than the eigenvalue problem of a matrix

$$\mathbb{A}=\begin{pmatrix} u(d) & v(d) \\ v'(d) & u'(d) \end{pmatrix} \quad (4.169)$$

, where the Floquet multiplier λ plays the role of the eigenvalue. Hence, we can determine the respective values of λ by solving

$$\det(\mathbb{A}-\lambda\mathbb{I})=0\,, \quad (4.170)$$

i.e., finding the roots of the characteristic polynomial

$$\lambda^2-\left[u(d)+v'(d)\right]\lambda+W(d)=0\,, \quad (4.171)$$

where

$$W(d)=u(d)v'(d)-u'(d)v(d) \quad (4.172)$$

is the Wronskian. To evaluate the Wronskian, we proceed as follows. First, since both $u(x), v(x)$ solve our equation, we can write

$$\begin{aligned} u''+q(x)u&=0\,,\\ v''+q(x)v&=0\,. \end{aligned} \quad (4.173)$$

By multiplying the first of the above equations by v, the second one by u and further subtracting the second from the first, we get

$$\frac{\mathrm{d}W}{\mathrm{d}x}=0\,. \quad (4.174)$$

The solution to this is then

$$W(x)=const.\,, \quad (4.175)$$

but since $W(0)=1$, then $W(d)=1$ and the characteristic polynomial (4.171) becomes

$$\lambda^2-\left[u(d)+v'(d)\right]\lambda+1=0\,. \quad (4.176)$$

Finally, the resulting Floquet multipliers are

$$\lambda_{1,2} = \xi \pm \sqrt{\xi^2 - 1}\,, \tag{4.177}$$

where

$$\xi \equiv \frac{u(d) + v'(d)}{2}\,. \tag{4.178}$$

Moreover, it is easy to show that

$$\lambda_1 \lambda_2 = 1\,. \tag{4.179}$$

There are now two possible cases that can happen.

1. If $|\xi| > 1$, then $\lambda_{1,2} \in \mathbb{R}$, and according to (4.179), either $|\lambda_1| > 1, |\lambda_2| < 1$, or $|\lambda_1| < 1, |\lambda_2| > 1$. This means that one of the corresponding Bloch waves would diverge towards $x \to -\infty$ and the second one towards $x \to \infty$. In QM where only the normalizable solutions are allowed, this type of solution must then be discarded.

2. If on the other hand $|\xi| < 1$, we can rewrite (4.177) as

   $$\lambda_{1,2} = \xi \pm \mathrm{i}\sqrt{1 - \xi^2}\,, \tag{4.180}$$

   while $|\lambda_1| = |\lambda_2| = 1$. In such case, we can define the *Bloch phase* $\mu \in \mathbb{R}$ such that

   $$\xi = \cos \mu d\,, \tag{4.181}$$

   (the period d is here just for convention), while the Floquet multipliers become

   $$\lambda_{1,2} = \mathrm{e}^{\pm \mathrm{i}\mu d}\,. \tag{4.182}$$

   The corresponding Bloch waves then possess the property

   $$F_1(x + d) = \mathrm{e}^{\mathrm{i}\mu d} F_1(x)\,, \quad F_2(x + d) = \mathrm{e}^{-\mathrm{i}\mu d} F_2(x)\,, \tag{4.183}$$

   which is the physically acceptable solution in QM.

After determining the values of $\lambda_{1,2}$, we can return back to the eigenvalue problem (4.168), insert those into, e.g., the first one of the equations (the first row), and arrive at

$$C_1 = 1\,, \quad C_2 = \frac{\mathrm{e}^{\pm \mathrm{i}\mu d} - u(d)}{v(d)}\,, \tag{4.184}$$

where $C_1 = 1$ is chosen for convenience. By combining this with (4.166), we express the two linearly independent Bloch waves in the first period as

$$F_\pm(x) = u(z) + \frac{\mathrm{e}^{\pm \mathrm{i}\mu d} - u(d)}{v(d)}\,. \tag{4.185}$$

Finally – and here comes the whole elegance of the Floquet-Bloch theory – by simply employing the ansatz (4.183), we can now extend those into the whole domain as

$$F_{\pm}^{(\mathrm{ext})}(x) = \mathrm{e}^{\pm \mathrm{i}\mu n d} F_{\pm}(x - nd)\,, \tag{4.186}$$

where

$$n = \lfloor x/d \rfloor \tag{4.187}$$

labels the respective intervals $[nd, (n+1)d)$. This means that in order to solve the original Eq. (4.159), we just need to find the solution in the first period, hereinafter referred to as the *unit cell*, and the Floquet-Bloch theory then immediately tells us how to extend it into the rest of the domain. Powerful, isn't it?

Now we are armed with all the required theory and can further proceed into solving the promised QM problem.

4.7.2 Kronig-Penney Model

Of course, there are infinitely many possibilities for the shapes of the periodic potential $V(x)$. But since we are interested just in the qualitative behaviour of such system, we choose the simplest possible one called the *Kronig-Penney model*, in which we assume Dirac pulses placed periodically along the x axis as

$$V(x) = V_0 \sum_n \delta\left[x - \left(n + \frac{1}{2}\right) d\right]\,, \tag{4.188}$$

see Fig. 4.9.

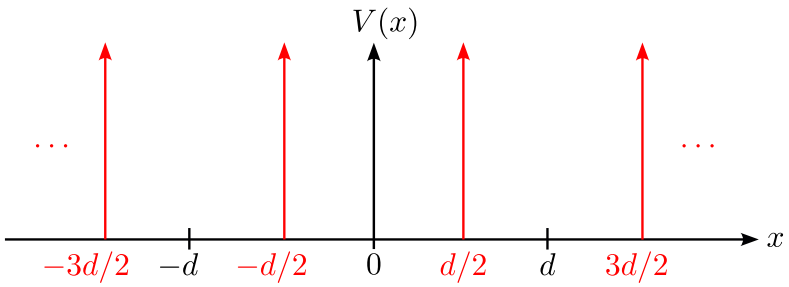

Figure 4.9: Kronig-Penney potential.

Our task now is to solve the energy eigenvalue problem

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi\,. \tag{4.189}$$

Due to the periodicity of $V(x)$, this equation represents exactly the type of model equation presented in the preceding section, and therefore we make use the Floquet-Bloch

theory. We start by determining the normalized solution in the first unit cell, i.e. the interval $x \in [0, d]$. But there is a slight problem due to the presence of the Dirac distribution at $x = d/2$. Hence, we separate the normalized solution into two parts as

$$u(x) = \begin{cases} u_1(x)\,, & x \in [0, d/2) \\ u_2(x)\,, & x \in (d/2, d] \end{cases}, \qquad v(x) = \begin{cases} v_1(x)\,, & x \in [0, d/2) \\ v_2(x)\,, & x \in (d/2, d] \end{cases}, \tag{4.190}$$

and later derive the appropriate boundary conditions to sew those two together. In the first part $x \in [0, d/2)$, Eq. (4.189) reduces to

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi\,, \tag{4.191}$$

which we have already solved several times. The normalized solution is

$$u_1(x) = \cos kx\,, \quad v_1(x) = \frac{\sin kx}{k} \tag{4.192}$$

with (as always)

$$k = \frac{\sqrt{2mE}}{\hbar}\,. \tag{4.193}$$

(Check it.) Then, we express the continuation to the $u_1(x), v_1(x)$ in the neighboring interval $x \in (d/2, d]$ as

$$\begin{aligned} u_2(x) &= U_1 \cos k(x - d/2) + U_2 \frac{\sin k(x - d/2)}{k}\,, \\ v_2(x) &= V_1 \cos k(x - d/2) + V_2 \frac{\sin k(x - d/2)}{k}\,. \end{aligned} \tag{4.194}$$

(The shifted argument and the division of the second term by k is chosen purely for convenience of the succeeding calculations but is by no means necessary.) Now we need to glue everything together at the problematic point $x = d/2$. We already discussed that the wavefunction must be continuous, i.e.,

$$u_1(d/2) = u_2(d/2)\,, \quad v_1(d/2) = v_2(d/2)\,. \tag{4.195}$$

From this requirement, we immediately get

$$U_1 = \cos\frac{kd}{2}\,, \quad V_1 = \frac{1}{k}\sin\frac{kd}{2}\,. \tag{4.196}$$

To deal with the "continuity" of the first derivative (actually, it will turn out to be a discontinuity), we rewrite Eq. (4.189) in the whole unit cell as

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V_0\delta\left(x - \frac{d}{2}\right)\psi = E\psi\,. \tag{4.197}$$

The trick now is to integrate the above over the interval $[d/2-\varepsilon, d/2+\varepsilon]$ and further take the limit $\varepsilon \to 0$ as

$$-\frac{\hbar^2}{2m}\lim_{\varepsilon\to 0}\int\limits_{d/2-\varepsilon}^{d/2+\varepsilon} \mathrm{d}x\,\psi''(x) + V_0 \lim_{\varepsilon\to 0}\int\limits_{d/2-\varepsilon}^{d/2+\varepsilon} \mathrm{d}x\,\delta\left(x-\frac{d}{2}\right)\psi(x) = E\lim_{\varepsilon\to 0}\int\limits_{d/2-\varepsilon}^{d/2+\varepsilon} \mathrm{d}x\,\psi(x)\,. \tag{4.198}$$

What happens is that the term on the RHS vanishes (we integrate a function over an interval of zero width), while the second term on the LHS spits out $\psi(d/2)$, resulting in

$$-\frac{\hbar^2}{2m}\left[\psi'(d/2_+) - \psi'(d/2_-)\right] + V_0\psi(d/2) = 0\,. \tag{4.199}$$

This is now the correct sewing boundary condition, from which we can see that the resulting wavefunction has a discontinuity in the first derivative. By applying this to $u_1(x), u_2(x)$, we get

$$U_2 = -k\sin\frac{kd}{2} + \frac{2mV_0}{\hbar^2}\cos\frac{kd}{2}\,, \tag{4.200}$$

and further to $v_1(x), v_2(x)$,

$$V_2 = \cos\frac{kd}{2} + \frac{2mV_0}{\hbar^2}\frac{1}{k}\sin\frac{kd}{2}\,. \tag{4.201}$$

After some algebra, we get the following expressions for $u_2(x), v_2(x)$:

$$\begin{aligned} u_2(x) &= \cos kx + \frac{2mV_0}{\hbar^2 k}\cos\frac{kd}{2}\sin k\left(x-\frac{d}{2}\right)\,,\\ v_2(x) &= \frac{1}{k}\sin kx + \frac{2mV_0}{\hbar^2}\frac{1}{k^2}\sin\frac{kd}{2}\sin k\left(x-\frac{d}{2}\right)\,. \end{aligned} \tag{4.202}$$

Finally, we can combine everything together to express the normalized solution in the first unit cell as

$$u(x) = \begin{cases} \cos kx\,, & x\in[0,d/2) \\ \cos kx + \frac{2mV_0}{\hbar^2 k}\cos\frac{kd}{2}\sin k\left(x-\frac{d}{2}\right)\,, & x\in(d/2,d] \end{cases}\,, \tag{4.203}$$

$$v(x) = \begin{cases} \frac{\sin kx}{k}\,, & x\in[0,d/2) \\ \frac{1}{k}\sin kx + \frac{2mV_0}{\hbar^2}\frac{1}{k^2}\sin\frac{kd}{2}\sin k\left(x-\frac{d}{2}\right)\,, & x\in(d/2,d] \end{cases}\,. \tag{4.204}$$

Now to determine the values of k (i.e., the energy) for which the resulting solution would be physically acceptable, we determine

$$\xi = \frac{u_2(d)+v_2'(d)}{2} = \cos kd + \frac{mV_0 d}{\hbar^2}\frac{\sin kd}{kd}\,. \tag{4.205}$$

Further, by employing the definition of the Bloch phase, we write

$$\boxed{\cos\mu d = \cos kd + \frac{mV_0 d}{\hbar^2}\frac{\sin kd}{kd}}\,. \tag{4.206}$$

The above equation then has real solutions only if

$$\left|\cos kd + \frac{mV_0 d}{\hbar^2}\frac{\sin kd}{kd}\right| \leq 1\,. \tag{4.207}$$

The result obtained graphically is depicted in Fig. 4.10. As we can see, there are con-

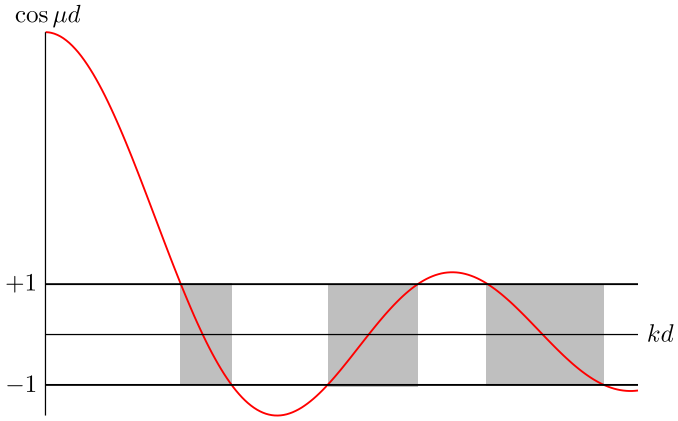

Figure 4.10: Kronig-Penney energy band spectrum.

tinuous intervals of k (colored gray), referred to as the *allowed energy bands*, that the particle can only take on. The white parts are then called the *forbidden energy bands* and the particle cannot exist within those.

A few words to conclude all of this: First, despite the fact that we derived the energy band structure only for the Kronig-Penney model consisting of a periodic Dirac potential, the same behavior would be observed for any type of periodic potential, even for (the more realistic) 3D problems. Second, of course no real periodic structure (e.g., a crystal) is infinite. However, in case of a finite structure, we would still get the same results, except instead of the allowed energy bands to be continuous, they would consist of discrete energy levels. But since the number of the levels in each allowed band is proportional to the number of unit cells, which would still be a very large number in a typical crystal where each unit cell is represented by an atom, the bands would appear as almost continuous. Third, the presented analysis including the rather detailed development of the Floquet-Bloch method can definitely be done much easier. But I personally consider this method so elegant and practical in all sort of scenarios that I wanted to present it here in all of it's glory, so hopefully it will prove itself useful for you in the future.

Chapter 5

Simple 3D Examples

The purpose of the previous chapter was to learn how do we approach solving QM problems and to build some intuition into how do QM systems behave in general. Nevertheless, we live in a 3D world (three spatial dimensions) and 1D systems mostly do not represent something that we can encounter in nature. Hence, this chapter is devoted to extending our 1D x-representation into three dimensions (3D formalism), and further solving some more realistic QM problems.

5.1 Generalization to 3D

The extension of the x-representation into 3D is pretty straightforward. First, we assume a quantum particle to which we assign a triplet of coordinates x_k ($k = 1, 2, 3$). According to the Postulate I., we then introduce the linear hermitian operators $\hat{\mathbf{x}}_k$ that obey the commutation relations

$$[\hat{\mathbf{x}}_k, \hat{\mathbf{x}}_l] = 0\,, \tag{5.1}$$

dictated by the canonical quantization formula. Now we construct the basis for the standard x-representation by formulating the eigenvalue problem

$$\hat{\mathbf{x}}_k \left|\boldsymbol{x}\right\rangle = x_k \left|\boldsymbol{x}\right\rangle\,, \tag{5.2}$$

where

$$\boldsymbol{x} = \begin{pmatrix} x_1 & x_2 & x_3 \end{pmatrix} \tag{5.3}$$

is the position vector of the particle and $|\boldsymbol{x}\rangle$ has the interpretation that the particle sits at $\boldsymbol{x}$. The fact that $\hat{\mathbf{x}}_k$ share the set of eigenvectors is justified by (5.1). Further, due to the $\hat{\mathbf{x}}_k$ being hermitian, the basis Ket-vectors $\{|\boldsymbol{x}\rangle\}$ satisfy the orthonormality condition

$$\langle \boldsymbol{x} | \boldsymbol{y} \rangle = \delta^3(\boldsymbol{x} - \boldsymbol{y})\,, \tag{5.4}$$

where

$$\delta^3(\boldsymbol{x} - \boldsymbol{y}) \equiv \delta(x_1 - y_1)\delta(x_2 - y_2)\delta(x_3 - y_3)\,. \tag{5.5}$$

One can easily show that

$$\int \mathrm{d}^3\boldsymbol{x}\,\delta^3(\boldsymbol{x}-\boldsymbol{y}) = 1\,, \tag{5.6}$$

where

$$\mathrm{d}^3\boldsymbol{x} \equiv \mathrm{d}x_1\,\mathrm{d}x_2\,\mathrm{d}x_3\,. \tag{5.7}$$

We can now express a general state of the particle as

$$|\psi\rangle = \int \mathrm{d}^3\boldsymbol{x}\,\psi(\boldsymbol{x})\,|\boldsymbol{x}\rangle\ . \tag{5.8}$$

As in the 1D case,

$$w(\boldsymbol{x}) = |\psi(\boldsymbol{x})|^2 \tag{5.9}$$

represents the probability density of finding the particle at $\boldsymbol{x}$. Meanwhile,

$$\langle\psi| = \int \mathrm{d}^3\boldsymbol{x}\,\psi^*(\boldsymbol{x})\,\langle\boldsymbol{x}|\ , \tag{5.10}$$

and the inner product of two states then gives

$$\langle\psi|\phi\rangle = \int \mathrm{d}^3\boldsymbol{x}\,\psi^*(\boldsymbol{x})\phi(\boldsymbol{x})\,. \tag{5.11}$$

Of course, we still need to keep our physical states normalized, resulting in the requirement

$$\boxed{\int \mathrm{d}^3\boldsymbol{x}\,|\psi(\boldsymbol{x})|^2 = 1}\,. \tag{5.12}$$

Moving on, we express the operators $\hat{\mathbf{x}}_k$ in the respective eigenbasis as

$$\boxed{\hat{\mathbf{x}}_k \to x_k}\,. \tag{5.13}$$

Based on Eq. (3.14), we further define the conjugate momenta operators as

$$\boxed{\hat{\mathbf{p}}_k \to -\mathrm{i}\hbar\frac{\partial}{\partial x_k}}\,. \tag{5.14}$$

It can be easily shown that such definition meets the required conditions given by the canonical quantization formulas, i.e.,

$$[\hat{\mathbf{x}}_k, \hat{\mathbf{p}}_l] = \mathrm{i}\hbar\delta_{kl}\,, \tag{5.15}$$

And this is basically all we need. E.g., the Hamiltonian in the 3D case can be written as

$$H = \frac{p_1^2 + p_2^2 + p_3^2}{2m} + V(x_1, x_2, x_3)\,. \tag{5.16}$$

According to the Postulate II., this translates into

$$\hat{\mathbf{H}} = \frac{\hat{\mathbf{p}}_1^2 + \hat{\mathbf{p}}_2^2 + \hat{\mathbf{p}}_3^2}{2m} + V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\,. \tag{5.17}$$

By employing the expressions (5.13) and (5.14), we get the corresponding 3D representation as

$$\hat{\mathbf{H}} \to -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\,, \tag{5.18}$$

where ∇^2 is the Laplace operator defined as

$$\nabla^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2}\,. \tag{5.19}$$

(Note that some authors prefer the notation $\nabla^2 \equiv \Delta$ which I do not like as Δ is frequently used for finite differences.) Thus, the equation for determining the eigenvalues of $\hat{\mathbf{H}}$ (the most important equation for majority of the QM problems) is

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right]\psi(\boldsymbol{x}) = E\psi(\boldsymbol{x})}\,. \tag{5.20}$$

Further, the Schrödinger equation then takes on the following form

$$\boxed{\mathrm{i}\hbar\frac{\partial\psi(t,\boldsymbol{x})}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right]\psi(t,\boldsymbol{x})}\,, \tag{5.21}$$

but we won't need it as we already know how to deal with the time evolution. By this procedure, it is then straightforward to extend all other operators into the 3D formalism.

5.2 Angular Momentum

Except for the Hamiltonian, there are two additional operators that play a key role in QM in 3D, and these are the k-th component of the angular momentum $\hat{\mathbf{L}}_k$, and the magnitude squared of the (total) angular momentum $\hat{\mathbf{L}}^2$. Let's start with the first one. In classical dynamics, we define the angular momentum as

$$\boldsymbol{L} = \boldsymbol{x} \times \boldsymbol{p}\,, \tag{5.22}$$

or in components

$$\begin{aligned} L_1 &= x_2 p_3 - x_3 p_2\,,\\ L_2 &= x_3 p_1 - x_1 p_3\,,\\ L_3 &= x_1 p_2 - x_2 p_1\,. \end{aligned} \tag{5.23}$$

This then translates into the language of QM as

$$\begin{aligned} \hat{\mathbf{L}}_1 &= \hat{\mathbf{x}}_2\hat{\mathbf{p}}_3 - \hat{\mathbf{x}}_3\hat{\mathbf{p}}_2\,,\\ \hat{\mathbf{L}}_2 &= \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1 - \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3\,,\\ \hat{\mathbf{L}}_3 &= \hat{\mathbf{x}}_1\hat{\mathbf{p}}_2 - \hat{\mathbf{x}}_2\hat{\mathbf{p}}_1\,. \end{aligned} \tag{5.24}$$

We will now focus on determining the commutation relation $\left[\hat{\mathbf{L}}_k, \hat{\mathbf{L}}_l\right]$. We proceed as follows:

$$\begin{aligned}
\left[\hat{\mathbf{L}}_1, \hat{\mathbf{L}}_2\right] &= [\hat{\mathbf{x}}_2\hat{\mathbf{p}}_3 - \hat{\mathbf{x}}_3\hat{\mathbf{p}}_2, \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1 - \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3] \\
&= [\hat{\mathbf{x}}_2\hat{\mathbf{p}}_3, \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1] - [\hat{\mathbf{x}}_2\hat{\mathbf{p}}_3, \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3] - [\hat{\mathbf{x}}_3\hat{\mathbf{p}}_2, \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1] + [\hat{\mathbf{x}}_3\hat{\mathbf{p}}_2, \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3] \\
&= \hat{\mathbf{x}}_2 [\hat{\mathbf{p}}_3, \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1] + [\hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1]\, \hat{\mathbf{p}}_3 - \hat{\mathbf{x}}_2 [\hat{\mathbf{p}}_3, \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3] - [\hat{\mathbf{x}}_2, \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3]\, \hat{\mathbf{p}}_3 \\
&\quad - \hat{\mathbf{x}}_3 [\hat{\mathbf{p}}_2, \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1] - [\hat{\mathbf{x}}_3, \hat{\mathbf{x}}_3\hat{\mathbf{p}}_1]\, \hat{\mathbf{p}}_2 + \hat{\mathbf{x}}_3 [\hat{\mathbf{p}}_2, \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3] + [\hat{\mathbf{x}}_3, \hat{\mathbf{x}}_1\hat{\mathbf{p}}_3]\, \hat{\mathbf{p}}_2 \\
&= \hat{\mathbf{x}}_2\hat{\mathbf{x}}_3 [\hat{\mathbf{p}}_3, \hat{\mathbf{p}}_1] + \hat{\mathbf{x}}_2 [\hat{\mathbf{p}}_3, \hat{\mathbf{x}}_3]\, \hat{\mathbf{p}}_1 + \hat{\mathbf{x}}_3 [\hat{\mathbf{x}}_2, \hat{\mathbf{p}}_1]\, \hat{\mathbf{p}}_3 + [\hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3]\, \hat{\mathbf{p}}_1\hat{\mathbf{p}}_3 \\
&\quad - \hat{\mathbf{x}}_2\hat{\mathbf{x}}_1 [\hat{\mathbf{p}}_3, \hat{\mathbf{p}}_3] - \hat{\mathbf{x}}_2 [\hat{\mathbf{p}}_3, \hat{\mathbf{x}}_1]\, \hat{\mathbf{p}}_3 - \hat{\mathbf{x}}_1 [\hat{\mathbf{x}}_2, \hat{\mathbf{p}}_3]\, \hat{\mathbf{p}}_3 - [\hat{\mathbf{x}}_2, \hat{\mathbf{x}}_1]\, \hat{\mathbf{p}}_3\hat{\mathbf{p}}_3 \\
&\quad - \hat{\mathbf{x}}_3\hat{\mathbf{x}}_3 [\hat{\mathbf{p}}_2, \hat{\mathbf{p}}_1] - \hat{\mathbf{x}}_3 [\hat{\mathbf{p}}_2, \hat{\mathbf{x}}_3]\, \hat{\mathbf{p}}_1 - \hat{\mathbf{x}}_3 [\hat{\mathbf{x}}_3, \hat{\mathbf{p}}_1]\, \hat{\mathbf{p}}_2 - [\hat{\mathbf{x}}_3, \hat{\mathbf{x}}_3]\, \hat{\mathbf{p}}_1\hat{\mathbf{p}}_2 \\
&\quad + \hat{\mathbf{x}}_3\hat{\mathbf{x}}_1 [\hat{\mathbf{p}}_2, \hat{\mathbf{p}}_3] + \hat{\mathbf{x}}_3 [\hat{\mathbf{p}}_2, \hat{\mathbf{x}}_1]\, \hat{\mathbf{p}}_3 + \hat{\mathbf{x}}_1 [\hat{\mathbf{x}}_3, \hat{\mathbf{p}}_3]\, \hat{\mathbf{p}}_2 + [\hat{\mathbf{x}}_3, \hat{\mathbf{x}}_1]\, \hat{\mathbf{p}}_3\hat{\mathbf{p}}_2 \\
&= 0 - \mathrm{i}\hbar\hat{\mathbf{x}}_2\hat{\mathbf{p}}_1 + 0 + 0 - 0 - 0 - 0 - 0 \\
&\quad - 0 - 0 - 0 - 0 + 0 + 0 + \mathrm{i}\hbar\hat{\mathbf{x}}_1\hat{\mathbf{p}}_2 + 0 \\
&= \mathrm{i}\hbar\,(\hat{\mathbf{x}}_1\hat{\mathbf{p}}_2 - \hat{\mathbf{x}}_2\hat{\mathbf{p}}_1) = \mathrm{i}\hbar\hat{\mathbf{L}}_3\,.
\end{aligned} \tag{5.25}$$

This was quite tiresome, but I think it is valuable to compute this type of commutation relation at least once by hand. By following exactly the same steps as above, it can be shown that in general the following commutation relations hold

$$\boxed{\left[\hat{\mathbf{L}}_1, \hat{\mathbf{L}}_2\right] = \mathrm{i}\hbar\hat{\mathbf{L}}_3\,, \quad \left[\hat{\mathbf{L}}_2, \hat{\mathbf{L}}_3\right] = \mathrm{i}\hbar\hat{\mathbf{L}}_1\,, \quad \left[\hat{\mathbf{L}}_3, \hat{\mathbf{L}}_1\right] = \mathrm{i}\hbar\hat{\mathbf{L}}_2}\,, \tag{5.26}$$

or in a more compact form

$$\left[\hat{\mathbf{L}}_k, \hat{\mathbf{L}}_l\right] = \mathrm{i}\hbar \sum_m \varepsilon_{klm}\hat{\mathbf{L}}_m\,, \tag{5.27}$$

where ε_{klm} stands for the Levi-Civita symbol. In the context of Heisenberg uncertainty principle, this means that a 3D particle can have only one component of the angular momentum, and usually this is chosen to be the $\hat{\mathbf{L}}_3$.

Next, we focus on the $\hat{\mathbf{L}}^2$. Classically, this would be defined as

$$L^2 = L_1^2 + L_2^2 + L_3^2\,. \tag{5.28}$$

Hence, in QM we have

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{L}}_1^2 + \hat{\mathbf{L}}_2^2 + \hat{\mathbf{L}}_3^2\,. \tag{5.29}$$

Now we compute the following commutation relation

$$\begin{aligned}
\left[\hat{\mathbf{L}}^2, \hat{\mathbf{L}}_3\right] &= \left[\hat{\mathbf{L}}_1^2 + \hat{\mathbf{L}}_2^2 + \hat{\mathbf{L}}_3^2, \hat{\mathbf{L}}_3\right] = \left[\hat{\mathbf{L}}_1^2, \hat{\mathbf{L}}_3\right] + \left[\hat{\mathbf{L}}_2^2, \hat{\mathbf{L}}_3\right] + \left[\hat{\mathbf{L}}_3^2, \hat{\mathbf{L}}_3\right] \\
&= \hat{\mathbf{L}}_1 \left[\hat{\mathbf{L}}_1, \hat{\mathbf{L}}_3\right] + \left[\hat{\mathbf{L}}_1, \hat{\mathbf{L}}_3\right] \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2 \left[\hat{\mathbf{L}}_2, \hat{\mathbf{L}}_3\right] + \left[\hat{\mathbf{L}}_2, \hat{\mathbf{L}}_3\right] \hat{\mathbf{L}}_2 + 0 \\
&= -\mathrm{i}\hbar\hat{\mathbf{L}}_1\hat{\mathbf{L}}_2 - \mathrm{i}\hbar\hat{\mathbf{L}}_2\hat{\mathbf{L}}_1 + \mathrm{i}\hbar\hat{\mathbf{L}}_2\hat{\mathbf{L}}_1 + \mathrm{i}\hbar\hat{\mathbf{L}}_1\hat{\mathbf{L}}_2 = 0\,,
\end{aligned} \tag{5.30}$$

where in the fourth equality we have used the previously obtained commutation relations (5.26). Generally then

$$\boxed{\left[\hat{\mathbf{L}}^2, \hat{\mathbf{L}}_k\right] = 0}\,. \tag{5.31}$$

This means that a particle can have simultaneously the magnitude and the k-th component of the angular momentum.

Next, we derive the commutation relation between the angular momentum and the Hamiltonian. First,

$$\left[\hat{\mathbf{L}}_3, \hat{\mathbf{p}}_k\right] = [\hat{\mathbf{x}}_1\hat{\mathbf{p}}_2 - \hat{\mathbf{x}}_2\hat{\mathbf{p}}_1, \hat{\mathbf{p}}_k] = \mathrm{i}\hbar\left(\hat{\mathbf{p}}_2\delta_{1k} - \hat{\mathbf{p}}_1\delta_{2k}\right)\,. \tag{5.32}$$

As the kinetic term of the Hamiltonian is proportional to p^2, we then follow by calculating

$$\begin{aligned}\left[\hat{\mathbf{L}}_3, \hat{\mathbf{p}}^2\right] &= \left[\hat{\mathbf{L}}_3, \hat{\mathbf{p}}_1^2 + \hat{\mathbf{p}}_2^2 + \hat{\mathbf{p}}_3^2\right] = \left[\hat{\mathbf{L}}_3, \hat{\mathbf{p}}_1^2\right] + \left[\hat{\mathbf{L}}_3, \hat{\mathbf{p}}_2^2\right] + \left[\hat{\mathbf{L}}_3, \hat{\mathbf{p}}_3^2\right] \\ &= \mathrm{i}\hbar\left(\hat{\mathbf{p}}_1\hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_2\hat{\mathbf{p}}_1\right) - \mathrm{i}\hbar\left(\hat{\mathbf{p}}_2\hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_1\hat{\mathbf{p}}_2\right) + 0 = 0\,.\end{aligned} \tag{5.33}$$

This can be further generalized to

$$\left[\hat{\mathbf{L}}_k, \hat{\mathbf{p}}^2\right] = 0\,, \tag{5.34}$$

from which it immediately follows that

$$\left[\hat{\mathbf{L}}^2, \hat{\mathbf{p}}^2\right] = 0 \tag{5.35}$$

Finally, we deal with the potential energy part of the Hamiltonian. To simplify the succeeding calculations, we switch to the (3D) x-representation and start by determining

$$[\hat{\mathbf{p}}_k, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)] \to -\mathrm{i}\hbar\frac{\partial V}{\partial x_k}\,. \tag{5.36}$$

This is basically just a 3D extension of the formula (2.40) derived in the context of the Ehrenfest theorems. Next, we calculate the following:

$$\begin{aligned}\left[\hat{\mathbf{L}}_3, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] &= [\hat{\mathbf{x}}_1\hat{\mathbf{p}}_2 - \hat{\mathbf{x}}_2\hat{\mathbf{p}}_1, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)] \\ &= \hat{\mathbf{x}}_1\left[\hat{\mathbf{p}}_2, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] - \hat{\mathbf{x}}_2\left[\hat{\mathbf{p}}_1, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] \\ &\to \mathrm{i}\hbar\left[x_2\frac{\partial V}{\partial x_1} - x_1\frac{\partial V}{\partial x_2}\right]\,.\end{aligned} \tag{5.37}$$

This then generalises to

$$\begin{aligned}\left[\hat{\mathbf{L}}_1, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] &\to \mathrm{i}\hbar\left[x_3\frac{\partial V}{\partial x_2} - x_2\frac{\partial V}{\partial x_3}\right]\,, \\ \left[\hat{\mathbf{L}}_2, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] &\to \mathrm{i}\hbar\left[x_1\frac{\partial V}{\partial x_3} - x_3\frac{\partial V}{\partial x_1}\right]\,, \\ \left[\hat{\mathbf{L}}_3, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] &\to \mathrm{i}\hbar\left[x_2\frac{\partial V}{\partial x_1} - x_1\frac{\partial V}{\partial x_2}\right]\,,\end{aligned} \tag{5.38}$$

or compactly

$$\left[\hat{\mathbf{L}}_k, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] \to -\mathrm{i}\hbar \sum_{l,m} \varepsilon_{klm} x_l \frac{\partial V}{\partial x_m} \,. \tag{5.39}$$

As we can see, the potential energy is the only problematic part, having a non-vanishing commutator with the angular momentum. At this rather sad point, one might thing that all is lost and that we simply cannot determine the energy and the angular momentum at the same time. But we will not give up our hope so easily, and in the next section, we show that we can get rid of all the nonzero terms on the RHS of the above expressions by assuming the potential energy to be spherically symmetric.

5.3 Spherically Symmetric Potential

We start by stating the transformation relations between the cartesian and spherical coordinate system:

$$\begin{aligned} x_1 &= r \sin\theta \cos\varphi \,, \\ x_2 &= r \sin\theta \sin\varphi \,, \\ x_3 &= r \cos\theta \,, \end{aligned} \tag{5.40}$$

with the inverse formulas

$$\begin{aligned} r &= \sqrt{x_1^2 + x_2^2 + x_3^2} \,, \\ \theta &= \arccos\left(\frac{x_3}{\sqrt{x_1^2 + x_2^2 + x_3^2}}\right) \,, \\ \varphi &= \arctan\left(\frac{x_2}{x_1}\right) \,. \end{aligned} \tag{5.41}$$

The following then applies:

$$\frac{\partial r}{\partial x_k} = \frac{x_k}{r} \,. \tag{5.42}$$

Assume now that the potential is spherically symmetric, i.e., $V = V(r)$. By applying the above result onto the third equation of (5.38), we get

$$\left[\hat{\mathbf{L}}_3, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] \to \mathrm{i}\hbar \left[x_2 \frac{\mathrm{d}V}{\mathrm{d}r} \frac{x_1}{r} - x_1 \frac{\mathrm{d}V}{\mathrm{d}r} \frac{x_2}{r}\right] = 0 \,. \tag{5.43}$$

The same then applies to the remaining two equations, and we can therefore write

$$\left[\hat{\mathbf{L}}_k, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] = 0 \,. \tag{5.44}$$

(The equality sign can be used here due to the presence of the zero on the RHS.) From this, we immediately get

$$\left[\hat{\mathbf{L}}^2, V(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{x}}_3)\right] = 0 \,. \tag{5.45}$$

So both of our operators $\hat{\mathbf{L}}_k$ and $\hat{\mathbf{L}}^2$ now commute with the kinetic and also the potential part of the Hamiltonian, so we can finally write

$$\left[\hat{\mathbf{L}}_k, \hat{\mathbf{H}}\right] = \left[\hat{\mathbf{L}}^2, \hat{\mathbf{H}}\right] = 0\,. \tag{5.46}$$

We did it! To summarize the results,

$$\boxed{\left[\hat{\mathbf{L}}_k, \hat{\mathbf{L}}^2\right] = \left[\hat{\mathbf{L}}_k, \hat{\mathbf{H}}\right] = \left[\hat{\mathbf{L}}^2, \hat{\mathbf{H}}\right] = 0 \quad \text{for} \quad V = V(r)}\,. \tag{5.47}$$

This means that in case of a spherically symmetric potential, we can simultaneously determine the total energy, the magnitude of the angular momentum and one of the components of the angular momentum. (Of course that assumes that the particle sits in one of the corresponding eigenstates and not in a general superposition of them.) Now the only thing remaining is to determine the respective eigenvalues and eigenvectors.

5.4 Eigenvalue Problem with Spherical Symmetry

Based on Eq. (5.47), we focus on solving the following eigenvalue problem:

$$\begin{aligned}
\hat{\mathbf{H}}\,|E,\lambda,\mu\rangle &= E\,|E,\lambda,\mu\rangle\ , \\
\hat{\mathbf{L}}^2\,|E,\lambda,\mu\rangle &= \lambda\,|E,\lambda,\mu\rangle\ , \\
\hat{\mathbf{L}}_3\,|E,\lambda,\mu\rangle &= \mu\,|E,\lambda,\mu\rangle\ ,
\end{aligned} \tag{5.48}$$

where E, λ, μ stand for the eigenvalues of energy, magnitude (squared) of the angular momentum and the z-component of the angular momentum, respectively. We will solve those in the x-representation but using the spherical coordinates (5.40). (We will refer to this as the spherical representation hereinafter.) We start with the third equation.

First, we take

$$\hat{\mathbf{L}}_3 = \hat{\mathbf{x}}_1\hat{\mathbf{p}}_2 - \hat{\mathbf{x}}_2\hat{\mathbf{p}_1} \to -\mathrm{i}\hbar x_1\frac{\partial}{\partial x_2} + \mathrm{i}\hbar x_2\frac{\partial}{\partial x_1} \tag{5.49}$$

and use the chain rule to express

$$\begin{aligned}
\frac{\partial}{\partial x_1} &= \frac{\partial r}{\partial x_1}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x_1}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x_1}\frac{\partial}{\partial \varphi} \\
&= \sin\theta\cos\varphi\frac{\partial}{\partial r} + \cos\theta\cos\varphi\frac{1}{r}\frac{\partial}{\partial \theta} - \frac{\sin\varphi}{\sin\theta}\frac{1}{r}\frac{\partial}{\partial \varphi}\,, \\
\frac{\partial}{\partial x_2} &= \frac{\partial r}{\partial x_2}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x_2}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x_2}\frac{\partial}{\partial \varphi} \\
&= \sin\theta\sin\varphi\frac{\partial}{\partial r} + \cos\theta\sin\varphi\frac{1}{r}\frac{\partial}{\partial \theta} + \frac{\cos\varphi}{\sin\theta}\frac{1}{r}\frac{\partial}{\partial \varphi}\,, \\
\frac{\partial}{\partial x_3} &= \frac{\partial r}{\partial x_3}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x_3}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x_3}\frac{\partial}{\partial \varphi} \\
&= \cos\theta\frac{\partial}{\partial r} - \sin\theta\frac{1}{r}\frac{\partial}{\partial \theta}\,,
\end{aligned} \tag{5.50}$$

resulting in

$$\hat{\mathbf{L}}_3 \to -\mathrm{i}\hbar\frac{\partial}{\partial\varphi}\,. \tag{5.51}$$

The corresponding eigenvalue problem then takes on the following form

$$-\mathrm{i}\hbar\frac{\partial\psi}{\partial\varphi} = \mu\psi\,, \tag{5.52}$$

with the solution being simply

$$\psi(r,\theta,\varphi) = \Phi(r,\theta)\,\mathrm{e}^{\mathrm{i}\frac{\mu}{\hbar}\varphi}\,, \tag{5.53}$$

where the function $\Phi(r,\theta)$ is to be determined later. Since this function must be periodic in the last argument with period 2π, we get the condition

$$\mathrm{e}^{\mathrm{i}\frac{2\pi\mu}{\hbar}} = 1\,, \tag{5.54}$$

i.e.,

$$\mu = m\hbar \quad \text{with} \quad m \in \mathbb{Z}\,. \tag{5.55}$$

The integer m is called the *magnetic quantum number*. Our wavefunction can now be rewritten as

$$\psi(r,\theta,\varphi) = \Phi(r,\theta)\,\mathrm{e}^{\mathrm{i}m\varphi}\,. \tag{5.56}$$

Hence, we can see that the only observable values of the z-component of the angular momentum are quantized with the elementary quantum being $\hbar$ (this is the physical interpretation of the Planck constant).

Next, we focus on the second of Eqs. (5.112). By the same procedure as presented above, we derive the representations

$$\begin{aligned}
\hat{\mathbf{L}}_1 &\to \mathrm{i}\hbar\left[\cot\theta\cos\varphi\frac{\partial}{\partial\varphi} + \sin\varphi\frac{\partial}{\partial\theta}\right]\,,\\
\hat{\mathbf{L}}_2 &\to \mathrm{i}\hbar\left[\cot\theta\sin\varphi\frac{\partial}{\partial\varphi} - \cos\varphi\frac{\partial}{\partial\theta}\right]\,,
\end{aligned} \tag{5.57}$$

which when combined with (5.51) results in

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{L}}_1^2 + \hat{\mathbf{L}}_2^2 + \hat{\mathbf{L}}_3^2 \to -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\varphi^2}\right] \equiv \hat{L}^2\,. \tag{5.58}$$

The $\hat{L}^2$ here denotes the spherical representation of $\hat{\mathbf{L}}^2$. Therefore, we arrive at the equation

$$-\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\varphi^2}\right]\psi = \lambda\psi\,, \tag{5.59}$$

which by substituting the formula (5.56) for the wavefunction $\psi(r,\theta,\varphi)$ becomes

$$-\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\theta}\right) - m^2\right]\Phi = \lambda\Phi\,, \tag{5.60}$$

Using the change of variable

$$\xi = \cos\theta \quad \text{with} \quad \frac{\partial}{\partial\theta} = -\sin\theta\frac{\partial}{\partial\xi}\,, \tag{5.61}$$

the equation becomes

$$\frac{\partial}{\partial\xi}\left[\left(1-\xi^2\right)\frac{\partial\Phi}{\partial\xi}\right] + \left(\frac{\lambda}{\hbar^2} - \frac{m^2}{1-\xi^2}\right)\Phi = 0\,. \tag{5.62}$$

This is the so called *associated Legendre equation* (see Appendix C), which supports nontrivial solution only if

$$\frac{\lambda}{\hbar^2} = \ell(\ell+1) \quad \text{with} \quad \ell \in \mathbb{N}_0\,, \tag{5.63}$$

and

$$|m| \leq \ell\,. \tag{5.64}$$

Since this now represents a more restrictive condition on m, we should rewrite Eq. (5.55) as

$$\boxed{\mu = m\hbar \quad \text{with} \quad m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell}\,. \tag{5.65}$$

The solution can then be written as

$$\Phi(r,\xi) = R(r)P_\ell^m(\xi)\,, \tag{5.66}$$

where $P_\ell^m(\xi)$ stand for the *associated Legendre polynomial*. Our wavefunction now becomes

$$\psi(r,\theta,\varphi) = R(r)\,Y_\ell^m(\theta,\varphi)\,, \tag{5.67}$$

where

$$Y_\ell^m(\theta,\varphi) = P_\ell^m\left(\cos\theta\right)\,\mathrm{e}^{\mathrm{i}m\varphi} \tag{5.68}$$

is called the *spherical harmonics*. A few profiles are depicted in Fig. 5.1. Let's get back to Eq. (5.63) which we restate as

$$\boxed{\lambda = \ell(\ell+1)\hbar^2 \quad \text{with} \quad \ell \geq 0}\,. \tag{5.69}$$

Such ℓ is then called the *azimuthal quantum number* and we see that the observable values of $\hat{\mathbf{L}}^2$ are (again) quantized. According to Eq. (5.65), for a given ℓ, there are $2l+1$ possible values for m, which implies the existence of a degeneracy factor

$$\boxed{g(l) = 2l+1}\,. \tag{5.70}$$

Before moving on, let us inspect the typically (but also randomly) selected case by setting $\ell = 2$, for which (according to Eq. (5.69)) the magnitude of the angular momentum becomes $L = \sqrt{\lambda} = \sqrt{6}\,\hbar$. Further, $m = -2, -1, 0, 1, 2$ with the allowed values of the z-components of the angular momentum being $L_3 = \mu = -2\hbar, -\hbar, 0, \hbar, 2\hbar$. Such a case is

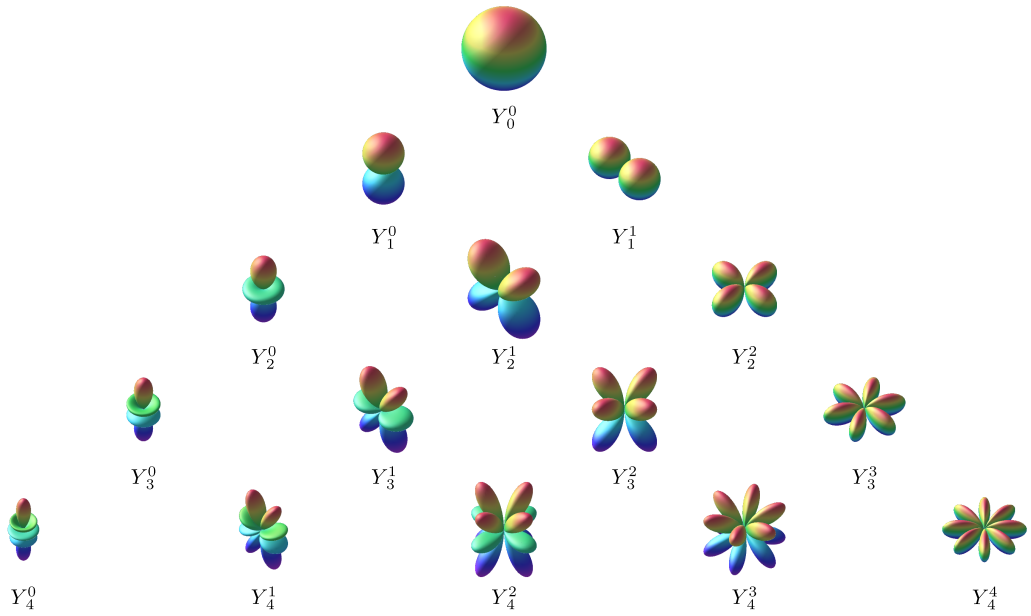

Figure 5.1: Spherical harmonics.

depicted in Fig. 5.2. Now an excellent question arises that almost seems like a paradox: We have derived those exact allowed values for L_3, but what if we just rotate our coordinate system? Shouldn't those values then change accordingly? The answer is provided by the Heisenberg uncertainty principle: No, this figure is wrong. As we saw previously, if we know the value of L_3, we cannot determine L_1 or L_2 anymore, and therefore, it does not make any sense to draw $\boldsymbol{L}$ as an arrow!

Last but not least, we focus on finding the energy spectrum of our spherically symmetric problem, i.e., solving the first one of Eqs. (5.112). Similarly as in both of the previous cases, we find the representation of the Hamilton operator in the spherical coordinates to be

$$\begin{aligned}\hat{\mathbf{H}} &= \frac{\hat{\mathbf{p}}_1^2+\hat{\mathbf{p}}_2^2+\hat{\mathbf{p}}_3^2}{2m} + V(\hat{\mathbf{x}}_1,\hat{\mathbf{x}}_2,\hat{\mathbf{x}}_3) \\ &\to -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]+V(r)\,.\end{aligned} \tag{5.71}$$

By comparing this with Eq. (5.58), we can immediately see that

$$\hat{\mathbf{H}} \to -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{L}^2}{2mr^2}+V(r)\,. \tag{5.72}$$

But we have already shown that

$$\hat{L}^2\psi = \ell(\ell+1)\hbar^2\psi\,, \tag{5.73}$$

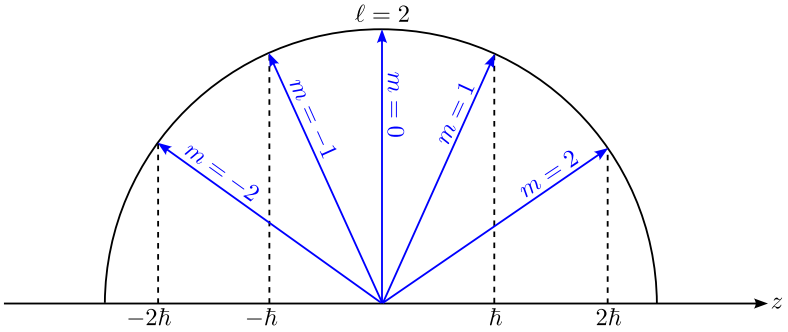

Figure 5.2: Allowed values of the z-component of the angular momentum for $\ell = 2$.

where $\psi(r, \theta, \varphi)$ is given by (5.67). Hence, our eigenvalue problem becomes

$$-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + V_{\mathrm{eff}}(r)R = ER\,, \tag{5.74}$$

where

$$\boxed{V_{\mathrm{eff}}(r) = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}} \tag{5.75}$$

is called the *effective potential energy*. One needs to be very careful here as in both the above equations, there is a symbol m present standing for the mass of our particle and this is not to be confused with the magnetic quantum number!

Up to this point, we have worked out everything with a general spherically symmetric potential $V(r)$, as it did not play any role either for $\hat{\mathbf{L}}_3$, or for $\hat{\mathbf{L}}^2$. But as you can see, that is not the case for $\hat{\mathbf{H}}$. Hence, our next step is to choose a specific expression for $V(r)$ and find the corresponding eigenvalues and eigenvectors specifically for the case.

5.5 Hydrogen Atom

For the purpose of this text, we choose the most typical (and also practical) example, which is an electron in the Coulomb field

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\,, \tag{5.76}$$

where e stands for the elementary charge and ε_0 is the vacuum permittivity. Such a system then essentially represents the hydrogen atom consisting of one proton in the atomic core and one electron in the shell. In the following part, we will focus only on the case in which

$$E < 0\,, \tag{5.77}$$

for the electron to be bounded. Eq. (5.74) now becomes

$$-\frac{\hbar^2}{2m_e r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2}\right]R = ER\,. \tag{5.78}$$

Note that the mas of the electron was denoted as m_e to resolve the confusion with the magnetic quantum number m. By defining

$$u(r) = rR(r)\,, \tag{5.79}$$

we can further simplify this to

$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2u}{\mathrm{d}r^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2}\right] u = Eu\,. \tag{5.80}$$

Another useful substitution is

$$\varkappa = \frac{\sqrt{-8m_eE}}{\hbar}\,, \qquad \rho = \varkappa r\,, \quad \text{and} \quad \rho_0 = \frac{m_e e^2}{2\pi\varepsilon_0\hbar^2\varkappa}\,. \tag{5.81}$$

By dividing Eq. (5.80) by $4E$, we then get

$$\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2} = \left[\frac{1}{4} - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u\,. \tag{5.82}$$

First, we investigate how does the solution behave in the limit $\rho \to \infty$. In such case, the above equation simplifies to

$$\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2} = \frac{u}{4}\,. \tag{5.83}$$

The respective solution is

$$u(r) = A\,\mathrm{e}^{-\frac{\rho}{2}} + B\,\mathrm{e}^{\frac{\rho}{2}}\,, \tag{5.84}$$

where the second (diverging) term must be dropped due to the necessary condition for the resulting wavefunction to be normalizable. Next, we focus on the limit $r \to 0$. Now Eq. (5.82) becomes

$$\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u\,. \tag{5.85}$$

It is easy to check that the sought solution takes on the following form

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}\,, \tag{5.86}$$

where we drop the second diverging term. Since we now know the behaviour of the sought wavefunction in both the limit cases, we substitute the ansatz

$$u(\rho) = \rho^{\ell+1}\,\mathrm{e}^{-\frac{\rho}{2}}\,v(\rho) \tag{5.87}$$

into the original Eq. (5.82). The first and second derivatives of the above expression yield

$$\begin{aligned}
\frac{\mathrm{d}u}{\mathrm{d}\rho} &= \rho^{\ell}\,\mathrm{e}^{-\frac{\rho}{2}}\left[\left(\ell+1-\frac{\rho}{2}\right)v + \rho\frac{\mathrm{d}v}{\mathrm{d}\rho}\right]\,,\\
\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2} &= \rho^{\ell}\,\mathrm{e}^{-\frac{\rho}{2}}\left\{\left[-\ell-1+\frac{\rho}{4}+\frac{\ell(\ell+1)}{\rho}\right]v + (2\ell+2-\rho)\frac{\mathrm{d}v}{\mathrm{d}\rho} + \rho\frac{\mathrm{d}^2v}{\mathrm{d}\rho^2}\right\}\,,
\end{aligned} \tag{5.88}$$

which then results in the following equation for $v(\rho)$:

$$\rho\frac{\mathrm{d}^2 v}{\mathrm{d}\rho^2} + (2\ell + 2 - \rho)\frac{\mathrm{d}v}{\mathrm{d}\rho} + [\rho_0 - (\ell + 1)]\, v = 0\,. \tag{5.89}$$

This is the associated Laguerre equation with $\nu = 2\ell + 1$, see Appendix C. We proceed further by following exactly the same steps as when dealing with the 1D harmonic oscillator. Hence, we express $v(\rho)$ by the power series

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \tag{5.90}$$

with

$$\begin{aligned} \frac{\mathrm{d}v}{\mathrm{d}\rho} &= \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j\,, \\ \frac{\mathrm{d}^2 v}{\mathrm{d}\rho^2} &= \sum_{j=0}^{\infty} j(j-1) c_j \rho^{j-2} = \sum_{j=0}^{\infty} (j+1) j c_{j+1} \rho^{j-1}\,. \end{aligned} \tag{5.91}$$

By substituting the above formulas into (5.89), we arrive at

$$\begin{aligned} \sum_{j=0}^{\infty} (j+1) j c_{j+1} \rho^j + 2(\ell+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j \\ - \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - (\ell+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0\,, \end{aligned} \tag{5.92}$$

or by factoring out the ρ^j and collecting the sums

$$\sum_{j=0}^{\infty} \left\{ (j+1) j c_{j+1} + 2(\ell+1)(j+1) c_{j+1} - j c_j + [\rho_0 - (\ell+1)]\, c_j \right\} \rho^j = 0\,. \tag{5.93}$$

Now we just set each term before the respective powers of ρ^j equal to zero, resulting in the recursion formula for the coefficients c_j

$$c_{j+1} = \frac{(j + \ell + 1) - \rho_0}{(j+1)(j + 2\ell + 2)} c_j\,. \tag{5.94}$$

To be able to normalize the resulting wavefunction, we need the power series to be finite, so we choose $j_{\max}$ such that

$$c_j = 0 \quad \text{for} \quad j > j_{\max}\,, \tag{5.95}$$

i.e., $c_{j_{\max}}$ is the last nonzero coefficient of (5.90). The following then must hold true

$$(j_{\max} + \ell + 1) - \rho_0 = 0\,. \tag{5.96}$$

By defining the *principal quantum number*

$$\boxed{n = j_{\max} + \ell + 1 \quad \text{with} \quad n \geq 1}, \tag{5.97}$$

where the statement to the right follows from the facts that $j_{\max} \geq 0$ and $\ell \geq 0$, the condition (5.96) gives

$$\rho_0 = n\,, \tag{5.98}$$

and by further employing the relationship (5.81), we get the formula for the allowed energy levels of our Hydrogen atom as

$$\boxed{E_n = -\frac{m_e e^4}{2\hbar^2(4\pi\varepsilon_0)^2}\frac{1}{n^2} = \frac{E_1}{n^2}}, \tag{5.99}$$

where

$$E_1 = -\frac{m_e e^4 -}{2\hbar^2(4\pi\varepsilon_0)^2} \approx -13.6\,\mathrm{eV}\,. \tag{5.100}$$

This is the famous formula that Niels Bohr (1885 - 1962) "derived" without any knowledge of the modern quantum mechanics. The polynomial solution corresponding to the n-th energy level is then

$$v_n(\rho) = \alpha_{n,\ell,m} L^{2l+1}_{n-\ell-1}(\rho)\,, \tag{5.101}$$

where $\alpha_{n,\ell,m}$ is the normalization constant and $L^{\nu}_n(\rho)$ stand for the associated Laguerre polynomial. The complete wavefunction then becomes

$$\boxed{\psi_{n,\ell,m}(r,\theta,\varphi) = \frac{\alpha_{n,\ell,m}}{r}(\varkappa r)^{\ell+1}\,\mathrm{e}^{-\frac{\varkappa r}{2}}\,L^{2l+1}_{n-\ell-1}(\varkappa r)\,Y^m_\ell(\theta,\varphi)}\,. \tag{5.102}$$

The integration constant $\alpha_{n,\ell,m}$ must then be chosen to satisfy the normalization condition (5.12) which in the spherical coordinates reads

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} |\psi_{n,\ell,m}(r,\theta,\varphi)|^2\, r^2 \sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi = 1\,. \tag{5.103}$$

Last but not least, let us focus on the total degeneracy factor of the n-th energy level. From Eq. (5.97), we can see that for fixed n we have

$$0 \leq \ell < n\,, \tag{5.104}$$

i.e., n possible values of ℓ. But each ℓ has itself a degeneracy $g(\ell) = 2\ell + 1$. That means that in total we have

$$g(n) = \sum_{l=0}^{n-1} g(l) = \sum_{l=0}^{n-1} 2\ell + 1 = 2\frac{n-1}{2}n + n = n^2\,, \tag{5.105}$$

which we put in a box

$$\boxed{g(n) = n^2}\,. \tag{5.106}$$

All of this was by far the hardest problem we have dealt with so far and I strongly recommend you to walk through it once again to ensure you correctly understand all the steps.

5.6 Angular Momentum Revisited

In this section, we get back to our $\hat{\mathbf{L}}_3$ and $\hat{\mathbf{L}}^2$ operators and once again solve the corresponding eigenvalue problem, but this time without considering the Hamilton operator. First, we recall that

$$\left[\hat{\mathbf{L}}_1, \hat{\mathbf{L}}_2\right] = \mathrm{i}\hbar\hat{\mathbf{L}}_3\,, \quad \left[\hat{\mathbf{L}}_2, \hat{\mathbf{L}}_3\right] = \mathrm{i}\hbar\hat{\mathbf{L}}_1\,, \quad \left[\hat{\mathbf{L}}_3, \hat{\mathbf{L}}_1\right] = \mathrm{i}\hbar\hat{\mathbf{L}}_2 \quad \text{and} \quad \left[\hat{\mathbf{L}}_k, \hat{\mathbf{L}}^2\right]\,. \tag{5.107}$$

We now define the following two operators:

$$\begin{aligned} \hat{\mathbf{L}}_+ &= \hat{\mathbf{L}}_1 + \mathrm{i}\hat{\mathbf{L}}_2\,, \\ \hat{\mathbf{L}}_- &= \hat{\mathbf{L}}_1 - \mathrm{i}\hat{\mathbf{L}}_2\,. \end{aligned} \tag{5.108}$$

We will see that those operators play a similar role as the creation and annihilation operators in case of the harmonic oscillator. One can easily check that

$$\hat{\mathbf{L}}_\pm^\dagger = \hat{\mathbf{L}}_\mp\,. \tag{5.109}$$

For the sake of upcoming calculations, we will need the following commutation relations:

$$\left[\hat{\mathbf{L}}_3, \hat{\mathbf{L}}_\pm\right] = \pm\hbar\hat{\mathbf{L}}_\pm\,, \quad \left[\hat{\mathbf{L}}^2, \hat{\mathbf{L}}_\pm\right] = 0\,, \tag{5.110}$$

together with

$$\hat{\mathbf{L}}_+\hat{\mathbf{L}}_- = \hat{\mathbf{L}}^2 - \hat{\mathbf{L}}_3^2 + \hbar\hat{\mathbf{L}}_3\,, \quad \hat{\mathbf{L}}_-\hat{\mathbf{L}}_+ = \hat{\mathbf{L}}^2 - \hat{\mathbf{L}}_3^2 - \hbar\hat{\mathbf{L}}_3\,. \tag{5.111}$$

All of those can be derived simply by using the definitions (5.108) together with (5.107) and are left to the reader to prove.

Next, we focus on the eigenvalue problem

$$\begin{aligned} \hat{\mathbf{L}}^2\,|\lambda,\mu\rangle &= \lambda\,|E,\lambda,\mu\rangle\ , \\ \hat{\mathbf{L}}_3\,|\lambda,\mu\rangle &= \mu\,|E,\lambda,\mu\rangle\ . \end{aligned} \tag{5.112}$$

We now show that

$$\hat{\mathbf{L}}_+\,|\lambda,\mu\rangle \propto |\lambda,\mu+\hbar\rangle\ . \tag{5.113}$$

To do so, we calculate

$$\begin{aligned} \hat{\mathbf{L}}_3\left(\hat{\mathbf{L}}_+\,|\lambda,\mu\rangle\right) &= \hat{\mathbf{L}}_3\hat{\mathbf{L}}_+\,|\lambda,\mu\rangle = \left(\hat{\mathbf{L}}_+\hat{\mathbf{L}}_3 + \hbar\hat{\mathbf{L}}_+\right)|\lambda,\mu\rangle \\ &= (\mu+\hbar)\hat{\mathbf{L}}_+\,|\lambda,\mu\rangle = (\mu+\hbar)\left(\hat{\mathbf{L}}_+\,|\lambda,\mu\rangle\right)\ , \end{aligned} \tag{5.114}$$

where the second equality follows from (5.110). Similarly, one can then show that

$$\hat{\mathbf{L}}_-\,|\lambda,\mu\rangle \propto |\lambda,\mu-\hbar\rangle\ . \tag{5.115}$$

To check that the $\hat{\mathbf{L}}_\pm$ have no effect on the magnitude of the angular momentum, we simply express

$$\hat{\mathbf{L}}^2 \left(\hat{\mathbf{L}}_+ \left| \lambda, \mu \right\rangle \right) = \hat{\mathbf{L}}^2 \hat{\mathbf{L}}_+ \left| \lambda, \mu \right\rangle = \hat{\mathbf{L}}_+ \hat{\mathbf{L}}^2 \left| \lambda, \mu \right\rangle = \lambda \hat{\mathbf{L}}_+ \left| \lambda, \mu \right\rangle = \lambda \left(\hat{\mathbf{L}}_+ \left| \lambda, \mu \right\rangle \right) . \quad (5.116)$$

The second equality (again) follows from (5.110).

Moving on, for fixed λ, the spectrum of $\hat{\mathbf{L}}_3$ must be bounded from both sides. Hence, we assume the existence of some maximum ($\mu_{\max}$) and minimum ($\mu_{\min}$) values of μ. We will now show that the respective spectrum is symmetric around 0. We proceed as follows. First, as $|\lambda, \mu_{\max}\rangle$ correspond to the state with maximum μ, we must have

$$\hat{\mathbf{L}}_+ \left| \lambda, \mu_{\max} \right\rangle = \left| o \right\rangle . \quad (5.117)$$

If we then take the norm of both sides, we get

$$\left\langle \lambda, \mu_{\max} \middle| \hat{\mathbf{L}}_- \hat{\mathbf{L}}_+ \middle| \lambda, \mu_{\max} \right\rangle = \left\langle \lambda, \mu_{\max} \middle| \hat{\mathbf{L}}^2 - \hat{\mathbf{L}}_3^2 - \hbar \hat{\mathbf{L}}_3 \middle| \lambda, \mu_{\max} \right\rangle = 0 , \quad (5.118)$$

where in the first equality we used the expression (5.111). This results in an equation

$$\lambda - \mu_{\max}^2 - \hbar \mu_{\max} = 0 . \quad (5.119)$$

Similarly, from the requirement

$$\hat{\mathbf{L}}_- \left| \lambda, \mu_{\min} \right\rangle = \left| o \right\rangle \quad (5.120)$$

we get

$$\lambda - \mu_{\min}^2 + \hbar \mu_{\min} = 0 . \quad (5.121)$$

By subtracting (5.121) from (5.119), we get the following quadratic equation

$$\mu_{\min}^2 + \hbar \mu_{\min} - (\mu_{\max}^2 + \hbar \mu_{\max}) = 0 \quad (5.122)$$

which we can solve for $\mu_{\min}$ to obtain

$$\mu_{\min}^{(1)} = -\mu_{\max} , \quad \mu_{\min}^{(2)} = \mu_{\max} + \hbar . \quad (5.123)$$

But the second solution is in a contradiction with $\mu_{\max}$ already being the maximum. Hence, we obtain

$$\mu_{\min} = -\mu_{\max} , \quad (5.124)$$

by which we have proven the symmetry. We can now write

$$\mu = -\mu_{\max}, -\mu_{\max} + \hbar, \ldots, \mu_{\max} - \hbar, \mu_{\max} . \quad (5.125)$$

By dividing both sides by $\hbar$ and further defining the magnetic quantum number

$$m = \frac{\mu}{\hbar} , \quad (5.126)$$

and the azimuthal quantum number

$$\ell = \frac{\mu_{\max}}{\hbar}\,, \tag{5.127}$$

we can rewrite the above statement as

$$\boxed{\mu = m\hbar \quad \text{with} \quad m = -\ell, -\ell+1, \ldots, \ell-1, \ell}\,. \tag{5.128}$$

We therefore have $2\ell + 1$ possible values of μ, which means that

$$\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots\,. \tag{5.129}$$

From Eq. (5.119), we can further express

$$\lambda = \mu_{\max}^2 + \hbar\mu_{\max}\,, \tag{5.130}$$

which by substituting from (5.127) becomes

$$\boxed{\lambda = \ell(\ell+1)\hbar^2}\,. \tag{5.131}$$

Notice one significant difference between those results and the ones obtained by solving the corresponding eigenvalue problems in the spherical representation. In the latter, we got $\ell \in \mathbb{N}_0$, but the current analysis indicates that also the half-integer values should permissible! What does this mean? The half integer values arise due to the general commutation relations of the angular momentum operators (5.107). The condition $\ell \in \mathbb{N}_0$ is then an additional constraint due to the necessity of the spherical wavefunction to be periodic with $\varphi \to \varphi + 2\pi$. This means that we should discard the half integer values as they do not represent a physical reality. But in the next section, we will discuss another form of the angular momentum called the *spin*, for which even the half integer values are physically correct.

5.7 Spin

In this section, we discuss the intrinsic angular momentum of a quantum particle called the *spin*. First, we make some rough analogies with the classical dynamics. Imagine we have a spinning planet of total mass m_{p} orbiting around, e.g., the Sun sitting in the center of our coordinate system. In such case, we can write the following expression for the total angular momentum of the planet:

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}\,, \tag{5.132}$$

where

$$\boldsymbol{L} = \mathbf{x}_{\mathrm{c}} \times m_{\mathrm{p}}\mathbf{v}_{\mathrm{c}} \tag{5.133}$$

is the angular momentum of the center of mass of the planet ($\boldsymbol{x}_\mathrm{c}$, $\boldsymbol{v}_\mathrm{c}$ being the position and the velocity vector of the center of mass, respectively), and

$$\boldsymbol{S} = \boldsymbol{\omega} I \,, \tag{5.134}$$

where $\boldsymbol{\omega}$ and I stand for the angular velocity vector and the moment of inertia of the planet w.r.t. the axis of rotation passing through the center of mass, is the intrinsic angular momentum of the planet, see Fig. 5.3. Something similar then happens for our

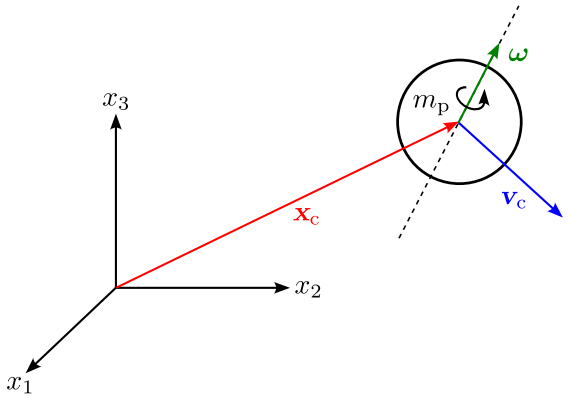

Figure 5.3: Planet orbiting around the Sun.

quantum particle, but with one crucial difference. In the classical case, we can imagine the planet to be consisting of infinitely many infinitesimal point masses $\mathrm{d}m$ orbiting around it's axis of rotation and the intrinsic angular momentum is then just the sum of the respective angular momenta of each such point mass w.r.t. the axis. For each of those point masses, we can then define the position vector $\boldsymbol{x}'$ in the center of mass coordinate system of the planet and further express the intrinsic angular momentum as

$$\boldsymbol{S} = \int\limits_{m_\mathrm{p}} \boldsymbol{x}' \times \boldsymbol{v}' \mathrm{d}m = \boldsymbol{\omega} \int\limits_{m_\mathrm{p}} \mathrm{d}m \, x_\perp^2 = \boldsymbol{\omega} I \,, \tag{5.135}$$

where $x'_\perp$ is the magnitude of the component of $\boldsymbol{x}'$ perpendicular to the axis, see Fig. 5.4.

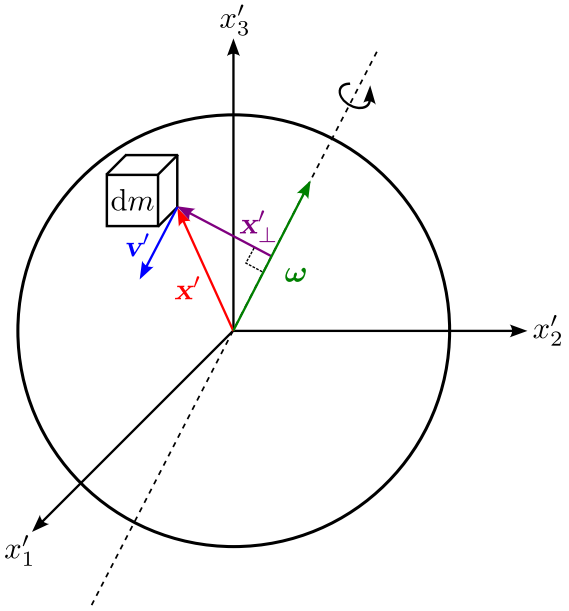

Figure 5.4: Intrinsic angular momentum of the planet.

But that is not the case in QM, where we assume the, e.g., electron to be a structureless point particle. This means that it does not make any sense to choose a center of mass coordinate system in which we would be able to decompose the particle into infinitesimal point masses and due to this we cannot define any spatially dependent wavefunction representing the spin at all! Hence, we shall now simply drop the proposed analogy with the planet and to reconcile with the fact that the spin of a quantum particle simply does not have a proper analogy with the classical world. I once saw a meme that greatly summarizes the above thoughts. It said: "The spin is like when a ball spins but it's not a ball. And it doesn't spin.".

To define the spin of a quantum particle, we postulate the same commutation relations as with the orbital angular momentum derived before, i.e.,

$$\left[\hat{\mathbf{S}}_1, \hat{\mathbf{S}}_2\right] = \mathrm{i}\hbar\hat{\mathbf{S}}_3\,, \quad \left[\hat{\mathbf{S}}_2, \hat{\mathbf{S}}_3\right] = \mathrm{i}\hbar\hat{\mathbf{S}}_1\,, \quad \left[\hat{\mathbf{S}}_3, \hat{\mathbf{S}}_1\right] = \mathrm{i}\hbar\hat{\mathbf{S}}_2 \quad \text{and} \quad \left[\hat{\mathbf{S}}_k, \hat{\mathbf{S}}^2\right]\,, \tag{5.136}$$

where $\hat{\mathbf{S}}_k$ and $\hat{\mathbf{S}}^2$ are the k-th component and the magnitude squared of the spin, respectively. We can then repeat the analysis presented in the above section, resulting in

$$\boxed{\mu_\mathrm{s} = m_\mathrm{s}\hbar \quad \text{with} \quad m_\mathrm{s} = -s, -s+1, \ldots, s-1, s}\,, \tag{5.137}$$

where m_s is the *magnetic spin number*, and

$$\boxed{\lambda_\mathrm{s} = s(s+1)\hbar^2 \quad \text{with} \quad s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots}\,, \tag{5.138}$$

where s stands for the *spin number*. Since we do not have any spatially dependent wavefunction, there is no additional condition on $m_{\rm s}$ and therefore we have no reason to discard the half-integer values of s. The spin of a quantum particle is an invariant quantity that characterizes the respective particle, similarly as, e.g., the electric charge or the mass (rest energy). The particles that carry half-integer spin are called the *fermions*, while integer spin particles are referred to as the *bosons*.

5.8 Hydrogen Atom Continued

Now let's get back to our electron bound in the Hydrogen atom. An electron is a particle characterized (among other parameters) by

$$\boxed{s = \frac{1}{2}\,, \quad m_s = \pm\frac{1}{2}}\,, \tag{5.139}$$

where the latter follows from (5.137). Hence, there are only two possible values of the projection of the spin into the x_3 axis, being

$$\mu_{\rm s} = \pm\frac{\hbar}{2}\,, \tag{5.140}$$

while the magnitude squared of the spin (5.138) is

$$\lambda_{\rm s} = \frac{3}{4}\hbar^2\,. \tag{5.141}$$

We denote the corresponding spin eigenstates $|s, m_{\rm s}\rangle$ as

$$\left|\frac{1}{2}, +\frac{1}{2}\right\rangle \equiv |\uparrow\rangle\ , \quad \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \equiv |\downarrow\rangle\ , \tag{5.142}$$

hereinafter referred to as the *spin eigenbasis*, obeying

$$\hat{\mathbf{S}}_3\,|\uparrow\rangle = \frac{\hbar}{2}\,|\uparrow\rangle\ , \quad \hat{\mathbf{S}}_3\,|\downarrow\rangle = -\frac{\hbar}{2}\,|\downarrow\rangle\ , \tag{5.143}$$

and

$$\hat{\mathbf{S}}^2\,|\uparrow\rangle = \frac{3}{4}\hbar^2\,|\uparrow\rangle\ , \quad \hat{\mathbf{S}}^2\,|\downarrow\rangle = \frac{3}{4}\hbar^2\,|\downarrow\rangle\ . \tag{5.144}$$

By employing Eq. (1.159), the representation of $\hat{\mathbf{S}}_3$ in the spin eigenbasis is

$$\hat{\mathbf{S}}_3 \to \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\ , \tag{5.145}$$

while

$$|\uparrow\rangle \to \begin{pmatrix} 1 \\ 0 \end{pmatrix}\ , \quad |\downarrow\rangle \to \begin{pmatrix} 0 \\ 1 \end{pmatrix}\ . \tag{5.146}$$

Further,

$$\hat{\mathbf{S}}^2 \to \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} . \tag{5.147}$$

The remaining two operators $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ then must satisfy (5.136), resulting in

$$\hat{\mathbf{S}}_1 \to \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \hat{\mathbf{S}}_2 \to \frac{\hbar}{2} \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} . \tag{5.148}$$

By defining the *Pauli matrices*

$$\boxed{\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} , \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}, \tag{5.149}$$

we can express the spin operators compactly as

$$\hat{\mathbf{S}}_k \to \frac{\hbar}{2}\sigma_k \, . \tag{5.150}$$

A general state of the spin can now be expressed as a superposition

$$|\psi\rangle = \alpha^{(\uparrow)} |\uparrow\rangle + \alpha^{(\downarrow)} |\downarrow\rangle \to \begin{pmatrix} \alpha^{(\uparrow)} \\ \alpha^{(\downarrow)} \end{pmatrix} , \tag{5.151}$$

while the normalization condition yields

$$\left(\alpha^{(\uparrow)}\right)^2 + \left(\alpha^{(\downarrow)}\right)^2 = 1 \, . \tag{5.152}$$

Previously, we derived the degeneracy factor of the n-th energy level of the electron (bound in the Hydrogen atom) to be $g(n) = n^2$. From the above analysis, however, we see that each of those energy levels has another degeneracy corresponding to the two possible values of m_s. Therefore, the total degeneracy factor including the spin is

$$\boxed{g(n) = 2n^2} . \tag{5.153}$$

By combining everything together, we can now define the most general representation for the n-th energy eigenstate of the electron as

$$\begin{aligned} \left| n, \ell, m, m_\mathrm{s} = +\frac{1}{2} \right\rangle &\to \begin{pmatrix} 1 \\ 0 \end{pmatrix} \psi_{n,\ell,m}(r, \theta, \varphi) \, , \\ \left| n, \ell, m, m_\mathrm{s} = -\frac{1}{2} \right\rangle &\to \begin{pmatrix} 0 \\ 1 \end{pmatrix} \psi_{n,\ell,m}(r, \theta, \varphi) \, . \end{aligned} \tag{5.154}$$

Note that there is no need to include the spin number $s = 1/2$ as this is always the case for an electron.

5.9 Quantum Numbers of Hydrogen Atom

To summarize the results of the preceding calculations, in Tab. 5.1 we provide all of the quantum numbers together with their allowed values.

Quantum Number	**Symbol**	**Allowed Values**
principal	n	$1, 2, 3, \ldots$
azimuthal	ℓ	$0, \ldots, n-1$
magnetic	m	$-\ell, -\ell+1, \ldots, \ell-1, \ell$
magnetic spin	m_s	$\pm\frac{1}{2}$

Table 5.1: Quantum numbers of an electron bound in the Hydrogen atom.

We stress out once again that those apply only in the case of an electron bound in the Hydrogen atom, i.e., with

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\,. \tag{5.155}$$

For a different type of potential energy that is still spherically symmetric, the only thing that would change is the principal quantum number, whereas to obtain the respective values one would need to conduct a similar type of analysis as presented in Sec. Hydrogen Atom. Moreover, if the potential energy is not spherically symmetric, the angular momentum operators will no longer commute with the Hamiltonian and we will not be able to determine those simultaneously. The only thing that will preserve in such case is the magnetic spin quantum number which always stays the same if we deal with an electron.

To conclude this chapter, it might seem that solving QM problems in 3D is significantly more complicated than in the 1D case. But one should (hopefully) realize that, in principle, there is no qualitative difference in the calculation procedure. The only part that actually gets harder is the technical one, e.g., the use of spherical coordinates instead of cartesian, etc.

Chapter 6

Two Particle System

Up to this point, everything we have done was assuming the studied system to be one particle with various forms of the potential energy. This chapter is devoted to extending the analysis onto a system of two particles, while our ultimate goal is the famous *Pauli's exclusion principle*.

6.1 Continuous Representation of Two Particle System

We start by assuming our studied system to contain two particles which we label as particle 1 and particle 2. Classically, to each one of those particles, we would assign a triplet of coordinates x_{kj}, where $k = 1, 2$ labels the particle and $j = 1, 2, 3$ the corresponding x, y, z coordinate, respectively. Then, according to the Postulate I., we introduce the linear hermitian operators $\hat{\mathbf{x}}_{kj}$ with the property

$$\left[\hat{\mathbf{x}}_{kj}, \hat{\mathbf{x}}_{k'j'}\right] = 0\,, \tag{6.1}$$

dictated by the canonical quantization formula. To construct the appropriate basis for the x-representation, we formulate the eigenvalue problem

$$\hat{\mathbf{x}}_{kj}\,|\boldsymbol{x}_1, \boldsymbol{x}_2\rangle = x_{kj}\,|\boldsymbol{x}_1, \boldsymbol{x}_2\rangle\ , \tag{6.2}$$

where

$$\boldsymbol{x}_k = \begin{pmatrix} x_{k1} & x_{k2} & x_{k3} \end{pmatrix} \tag{6.3}$$

stands for the position vector of the k-th particle, and $|\boldsymbol{x}_1, \boldsymbol{x}_2\rangle$ has the interpretation that the particle 1 sits at $\boldsymbol{x}_1$, while the particle 2 at $\boldsymbol{x}_2$. The fact that all of the $\hat{\mathbf{x}}_{kj}$ share the set of eigenvectors is justified by (6.1). Due to $\hat{\mathbf{x}}_{kj}$ being hermitian, such a basis then must obey the orthonormality condition

$$\langle \boldsymbol{x}_1, \boldsymbol{x}_2 | \boldsymbol{y}_1, \boldsymbol{y}_2\rangle = \delta^3(\boldsymbol{x}_1 - \boldsymbol{y}_1)\delta^3(\boldsymbol{x}_2 - \boldsymbol{y}_2)\,. \tag{6.4}$$

A general two particle state can now be expressed as

$$|\psi\rangle = \int \mathrm{d}^3\boldsymbol{x}_1 \mathrm{d}^3\boldsymbol{x}_2\, \psi(\boldsymbol{x}_1, \boldsymbol{x}_2)\,|\boldsymbol{x}_1, \boldsymbol{x}_2\rangle\ , \tag{6.5}$$

where

$$w(\boldsymbol{x}_1, \boldsymbol{x}_2) = |\psi(\boldsymbol{x}_1, \boldsymbol{x}_2)|^2 \tag{6.6}$$

represents the probability density of finding particle 1 at $\boldsymbol{x}_1$ and particle 2 at $\boldsymbol{x}_2$. Further,

$$\langle\psi| = \int \mathrm{d}^3\boldsymbol{x}_1 \mathrm{d}^3\boldsymbol{x}_2 \, \psi^*(\boldsymbol{x}_1, \boldsymbol{x}_2) \, \langle \boldsymbol{x}_1, \boldsymbol{x}_2| \; . \tag{6.7}$$

and the inner product of two Ket-vectors reads

$$\langle\psi|\phi\rangle = \int \mathrm{d}^3\boldsymbol{x}_1 \mathrm{d}^3\boldsymbol{x}_2 \, \psi^*(\boldsymbol{x}_1, \boldsymbol{x}_2)\phi(\boldsymbol{x}_1, \boldsymbol{x}_2) \, . \tag{6.8}$$

As always, we require each state to be normalized, resulting in the requirement

$$\langle\psi|\psi\rangle = \int \mathrm{d}^3\boldsymbol{x}_1 \mathrm{d}^3\boldsymbol{x}_2 \, |\psi(\boldsymbol{x}_1, \boldsymbol{x}_2)|^2 = 1 \, , \tag{6.9}$$

6.2 Particle Exchange Operator

Next, we define the operator $\hat{\mathbf{P}}$ by it's action on the two-particle wavefunction as

$$\hat{P}\psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \psi(\boldsymbol{x}_2, \boldsymbol{x}_1) \, , \tag{6.10}$$

where $\hat{\mathbf{P}} \to \hat{P}$. To decipher the physical meaning of $\hat{\mathbf{P}}$, assume the state where particle 1 sits at $\boldsymbol{x}_A$ and particle 2 at $\boldsymbol{x}_B$, i.e.,

$$|\psi\rangle = |\boldsymbol{x}_A, \boldsymbol{x}_B\rangle \; . \tag{6.11}$$

It is trivial to show that the corresponding wavefunction is

$$\psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \delta^3(\boldsymbol{x}_1 - \boldsymbol{x}_A)\delta^3(\boldsymbol{x}_2 - \boldsymbol{x}_B) \, . \tag{6.12}$$

Now lets act with $\hat{\mathbf{P}}$ onto $|\psi\rangle$ as

$$\hat{\mathbf{P}} \, |\psi\rangle \to \hat{P}\psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \delta^3(\boldsymbol{x}_2 - \boldsymbol{x}_A)\delta^3(\boldsymbol{x}_1 - \boldsymbol{x}_B) \, . \tag{6.13}$$

The resulting state is

$$\hat{\mathbf{P}} \, |\psi\rangle = \int \mathrm{d}^3\boldsymbol{x}_1 \mathrm{d}^3\boldsymbol{x}_2 \, \delta^3(\boldsymbol{x}_2 - \boldsymbol{x}_A)\delta^3(\boldsymbol{x}_1 - \boldsymbol{x}_B) \, |\boldsymbol{x}_1, \boldsymbol{x}_2\rangle = |\boldsymbol{x}_B, \boldsymbol{x}_A\rangle \; . \tag{6.14}$$

We can write this down as

$$\hat{\mathbf{P}} \, |\boldsymbol{x}_A, \boldsymbol{x}_B\rangle = |\boldsymbol{x}_B, \boldsymbol{x}_A\rangle \; , \tag{6.15}$$

which means that $\hat{\mathbf{P}}$ switches the positions of our two particles, and that's why it is usually called the *particle exchange operator*. It is apparent that

$$\hat{\mathbf{P}}^2 = \hat{\mathbf{1}} \, , \tag{6.16}$$

since exchanging the particles twice results in the original configuration, which also follows directly from (6.10). This means that

$$\hat{\mathbf{P}}^{-1} = \hat{\mathbf{P}} \,. \tag{6.17}$$

Now let's get back to a general state $|\psi\rangle$ and calculate

$$\left\langle \hat{\mathbf{P}}\psi \middle| \hat{\mathbf{P}}\psi \right\rangle = \int \mathrm{d}^3\boldsymbol{x}_1 \mathrm{d}^3\boldsymbol{x}_2 \, |\psi(\boldsymbol{x}_2, \boldsymbol{x}_1)|^2 = 1 \,, \tag{6.18}$$

which follows from the fact that $\boldsymbol{x}_1, \boldsymbol{x}_2$ are being the integration variables here and therefore can be relabeled as $\boldsymbol{x}_1 \leftrightarrow \boldsymbol{x}_2$, resulting in (6.9). This means that

$$\langle \psi | \psi \rangle = \left\langle \hat{\mathbf{P}}\psi \middle| \hat{\mathbf{P}}\psi \right\rangle \,, \tag{6.19}$$

and so $\hat{\mathbf{P}}$ is unitary, i.e.,

$$\hat{\mathbf{P}}^{\dagger} = \hat{\mathbf{P}}^{-1} \,. \tag{6.20}$$

By combining Eqs. (6.16) and (6.20), we get

$$\hat{\mathbf{P}}^{\dagger} = \hat{\mathbf{P}} \,, \tag{6.21}$$

i.e., $\hat{\mathbf{P}}$ is hermitian. Now we focus on the eigenvalue problem of $\hat{\mathbf{P}}$, which we state as

$$\hat{\mathbf{P}} \, |\lambda\rangle = \lambda \, |\lambda\rangle \,. \tag{6.22}$$

Since $\hat{\mathbf{P}}$ is unitary, we must have $|\lambda| = 1$, and further since $\hat{\mathbf{P}}$ is hermitian, $\lambda \in \mathbb{R}$. Hence, there are only two possible values of λ, being

$$\lambda = \pm 1 \,. \tag{6.23}$$

By denoting the corresponding eigenvectors as $|+\rangle, |-\rangle$, we can rewrite (6.22) as

$$\hat{\mathbf{P}} \, |+\rangle = |+\rangle \,, \quad \hat{\mathbf{P}} \, |-\rangle = - \, |-\rangle \,. \tag{6.24}$$

Before moving on, we write down the general form of the Hamiltonian for the two particle system in the x-representation as

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla^2_{\boldsymbol{x}_1} - \frac{\hbar^2}{2m_2} \nabla^2_{\boldsymbol{x}_2} + V(\boldsymbol{x}_1, \boldsymbol{x}_2) \,, \tag{6.25}$$

where $\nabla^2_{\boldsymbol{x}_1}$ stands for the Laplace operator w.r.t. the coordinates corresponding to the particle 1 and similarly then for $\nabla^2_{\boldsymbol{x}_2}$. Our next step is to determine the commutation relation between $\hat{\mathbf{P}}$ and $\hat{\mathbf{H}}$ in a special case where the particles 1 and 2 are identical.

6.3 Identical Particles

In case the two particles are being identical, we have $m_1 = m_2 \equiv m$, and further

$$V(\boldsymbol{x}_1, \boldsymbol{x}_2) = V(\boldsymbol{x}_2, \boldsymbol{x}_1)\,, \tag{6.26}$$

since by interchanging two identical particles we cannot change the total potential energy. In such case, we have

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{x}_1} - \frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{x}_2} + V(\boldsymbol{x}_1, \boldsymbol{x}_2)\,. \tag{6.27}$$

It is now straightforward and let up to the reader to check that

$$\hat{H}\psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \hat{P}\hat{H}\hat{P}\psi(\boldsymbol{x}_1, \boldsymbol{x}_2)\,, \tag{6.28}$$

which we can generalize to

$$\hat{\mathbf{H}} = \hat{\mathbf{P}}\hat{\mathbf{H}}\hat{\mathbf{P}}\,. \tag{6.29}$$

But since $\hat{\mathbf{P}}^{-1} = \hat{\mathbf{P}}$, this then immediately gives

$$\left[\hat{\mathbf{H}}, \hat{\mathbf{P}}\right] = 0\,, \tag{6.30}$$

and since the two operators commute, they are compatible, meaning that they share the set of eigenvectors, i.e.,

$$\begin{aligned} \hat{\mathbf{H}}\,|n, \pm\rangle &= E_n\,|n, \pm\rangle\ , \\ \hat{\mathbf{P}}\,|n, \pm\rangle &= \pm\,|n, \pm\rangle\ , \end{aligned} \tag{6.31}$$

where E_n stands for the total energy of the system. Of course there is no reason to assume the energy spectrum to be discrete, but this does not affect the upcoming analysis by any means.

For the sake of simplicity, we will now assume the particles to be mutually non-interacting. (Of course this is not a typical physical situation, as, e.g., in a general atom, if there are more than one electrons in the shell, they interact with each other. So consider this as an approximation.) In such case, the potential energy must be separable into

$$V(\boldsymbol{x}_1, \boldsymbol{x}_2) = V^{(\mathrm{s})}(\boldsymbol{x}_1) + V^{(\mathrm{s})}(\boldsymbol{x}_2)\,, \tag{6.32}$$

where $V^{(\mathrm{s})}(\boldsymbol{x})$ stands for the potential energy of a single particle, and since we are considering the particles to be identical, it must take on the same form for both of them. Our Hamiltonian can now be written

$$\hat{H} = \hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1} + \hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_2}\,, \tag{6.33}$$

where

$$\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1} = -\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{x}_1} + V^{(\mathrm{s})}(\boldsymbol{x}_1)\,, \quad \hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_2} = -\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{x}_2} + V^{(\mathrm{s})}(\boldsymbol{x}_2)\,, \tag{6.34}$$

As in the case of the potential energies, $\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1}$ and $\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_2}$ are the same. We will now search for the solution to the energy eigenvalue problem

$$\left(\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1} + \hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_2}\right)\psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = E\psi(\boldsymbol{x}_1, \boldsymbol{x}_2) \tag{6.35}$$

that can be separated as

$$\psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2)\,. \tag{6.36}$$

By inserting the above ansatz into (6.35) and dividing both sides by $\psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2)$, we get

$$\frac{\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1}\psi(\boldsymbol{x}_1)}{\psi(\boldsymbol{x}_1)} + \frac{\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_2}\psi(\boldsymbol{x}_2)}{\psi(\boldsymbol{x}_2)} = E\,. \tag{6.37}$$

Focusing on the first term on the LHS of the above equation, if we further apply $\boldsymbol{\nabla}_{\boldsymbol{x}_1}$ on both sides, we get

$$\boldsymbol{\nabla}_{\boldsymbol{x}_1}\left[\frac{\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1}\psi_1(\boldsymbol{x}_1)}{\psi_1(\boldsymbol{x}_1)}\right] = \boldsymbol{0}\,, \tag{6.38}$$

and hence

$$\frac{\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1}\psi_1(\boldsymbol{x}_1)}{\psi_1(\boldsymbol{x}_1)} = E_1\,, \tag{6.39}$$

where $E_1 = const.$ The same can then be done with the second term on the LHS of (6.37), i.e.,

$$\frac{\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_2}\psi_2(\boldsymbol{x}_2)}{\psi_2(\boldsymbol{x}_1)} = E_2\,. \tag{6.40}$$

Hence, we obtain the two independent equations

$$\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_1}\psi_1(\boldsymbol{x}_1) = E_1\psi_1(\boldsymbol{x}_1)\,, \quad \hat{H}^{(\mathrm{s})}_{\boldsymbol{x}_2}\psi_2(\boldsymbol{x}_2) = E_2\psi_2(\boldsymbol{x}_2)\,, \tag{6.41}$$

where

$$E_1 + E_2 = E\,. \tag{6.42}$$

The fact that we were able to separate the original problem into the two independent equations should not be surprising to us due to the fact that we assumed both the particles to be mutually non-interacting. We can see that both of the above equations are exactly the same, and hence so are the respective solutions and the corresponding energy eigenvalues. We can therefore drop all the unnecessary lower indices and solve either one of those to obtain the single-particle energy spectrum together with the corresponding wavefunctions, satisfying

$$\hat{H}^{(\mathrm{s})}_{\boldsymbol{x}}\psi_n(\boldsymbol{x}) = E_n\psi_n(\boldsymbol{x})\,. \tag{6.43}$$

The $\boldsymbol{x}$ is then replaced by $\boldsymbol{x}_1$ or $\boldsymbol{x}_2$ for the particle 1 or 2, respectively. (Note that there might be additional quantum numbers that determine the total energy, as, e.g., in the case of the Hydrogen atom. In such case, you might consider m, n as sets of the respective quantum numbers.) Finally, we can write our separable solution as

$$\psi_{mn}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \psi_m(\boldsymbol{x}_1)\psi_n(\boldsymbol{x}_2)\,, \tag{6.44}$$

where m, n labels the energy eigenstates of the two particles, while the total energy of the system is then

$$E_{mn} = E_m + E_n \,. \tag{6.45}$$

To proceed further, we now move on to the eigenvalue problem for $\hat{\mathbf{P}}$. We already know, that there are only two possibilities for the respective eigenvalues, being

$$\hat{P}\psi^{\pm}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \pm\psi^{\pm}(\boldsymbol{x}_1, \boldsymbol{x}_2) \,. \tag{6.46}$$

By employing the defining property of the particle exchange operator (6.10), this can be rewritten as

$$\begin{aligned} \psi^{+}(\boldsymbol{x}_2, \boldsymbol{x}_1) &= +\psi^{+}(\boldsymbol{x}_1, \boldsymbol{x}_2) \,, \\ \psi^{-}(\boldsymbol{x}_2, \boldsymbol{x}_1) &= -\psi^{-}(\boldsymbol{x}_1, \boldsymbol{x}_2) \,. \end{aligned} \tag{6.47}$$

We then say that ψ^+ is symmetric, while ψ^- is antisymmetric. By employing the result (6.44), the only possible way to satisfy the above conditions is

$$\boxed{\begin{aligned} \psi^{+}_{mn}(\boldsymbol{x}_1, \boldsymbol{x}_2) &= \alpha^{+}\left[\psi_m(\boldsymbol{x}_1)\psi_n(\boldsymbol{x}_2) + \psi_n(\boldsymbol{x}_1)\psi_m(\boldsymbol{x}_2)\right] \\ \psi^{-}_{mn}(\boldsymbol{x}_1, \boldsymbol{x}_2) &= \alpha^{-}\left[\psi_m(\boldsymbol{x}_1)\psi_n(\boldsymbol{x}_2) - \psi_n(\boldsymbol{x}_1)\psi_m(\boldsymbol{x}_2)\right] \end{aligned}}\,, \tag{6.48}$$

where $\alpha^{\pm}$ are the normalization constants. These are now the correct representations of the originally sought eigenvectors $|n, \pm\rangle$, just with the two indices m, n, i.e.,

$$|m, n, +\rangle \to \psi^{+}_{mn}(\boldsymbol{x}_1, \boldsymbol{x}_2) \,, \quad |m, n, -\rangle \to \psi^{-}_{mn}(\boldsymbol{x}_1, \boldsymbol{x}_2) \,. \tag{6.49}$$

Particles described by the $|m, n, +\rangle$ are called *bosons* (Satyendra Nath Bose, 1894 – 1974), while particles described by the $|m, n, -\rangle$ are called *fermions* (Enrico Fermi, 1901 - 1954). Based on the property of the antisymmetric wavefunction of the fermions, we can now observe one fascinating fact. Consider the case in which we have $m = n$. Then,

$$\boxed{\psi^{-}_{nn}(\boldsymbol{x}_1, \boldsymbol{x}_2) = 0}\,, \tag{6.50}$$

and that means that two fermions cannot exist at the same quantum state, they always have to differ in at least one of the respective quantum numbers. And this is the so called *Pauli's exclusion principle*. This has now some very interesting consequences. Imagine that we have a gas of electrons. Then, we somehow cool it to 0 K. As we know from the thermodynamics, a classical ideal gas obeys the equation of state

$$PV = nRT \,, \tag{6.51}$$

so at absolute zero, the gas would have zero pressure. This is due to the fact that each molecule of the gas reaches zero energy. However, that is not the case for the electron gas, as the Pauli's exclusion principle forbids two electrons to be at the same quantum state. Hence, the more electrons we have in the gas, the higher energy levels are occupied and therefore we have nonzero pressure. And this is, e.g., what keeps a white dwarf (one of the possible final states of a star) from collapsing.

A few words to conclude this chapter. First, we derived everything just for a system consisting of two particles, but the whole analysis could be simply extended to arbitrarily many particles. By simply I mean that we will follow exactly the same steps, but the actual derivation would be much more tedious and laboring. Next, we have made a not very realistic assumption where the two particles do not mutually interact. The real systems of course usually do not behave like this, but the qualitative observation about the "repulsion" of fermions due to the Pauli's exclusion principle still holds. Lats but not least, we should note that in a world of particle physics, there is no law of particle conservation, and at high enough energies, particles can interact in many ways, resulting in a different amount of various different particles, so the whole statement about assuming N particles is itself just wrong. But in such case, the standard QM cannot be used anymore and one would need to visit the fascinating world of the QFT, which is a completely different story.

Appendix A

Fundamentals of Wave Theory

In this appendix, we provide a brief introduction into the topic of the theory of waves, which is going to be very handy when dealing with certain types of problems in QM. We start by assuming an equation of the form

$$\mathcal{L}\left[\psi(\boldsymbol{x},t)\right]=0\,, \tag{A.1}$$

where $\mathcal{L}$ is a linear differential operator and $\psi(\boldsymbol{x},t)$ represents the quantity that "sways", i.e., the *wave*. For convenience, we often use the complex representation

$$\psi(\boldsymbol{x},t)=A(\boldsymbol{x},t)\,\mathrm{e}^{\mathrm{i}\varphi(\boldsymbol{x},t)}\,, \tag{A.2}$$

where $A(\boldsymbol{x},t)$ is called the amplitude and $\varphi(\boldsymbol{x},t)$ the phase. Note that in some physical problems where $\psi(\boldsymbol{x},t)$ represents a directly measurable quantity (pressure, displacement, electric/magnetic field, etc.), we would then take only the real part of $\psi(\boldsymbol{x},t)$. Next, we define the angular frequency and the wave-vector as

$$\omega=-\frac{\partial\varphi(\boldsymbol{x},t)}{\partial t}\,,\quad \boldsymbol{k}=\boldsymbol{\nabla}\varphi(\boldsymbol{x},t)\,, \tag{A.3}$$

where the "-" sign at the RHS of the angular frequency is chosen for convenience. Now we seek some simplest form of the solution $\psi(\boldsymbol{x},t)$. Setting $A(\boldsymbol{x},t)=0$ does not make much sense as there would be no resulting wave. So let's set $A(\boldsymbol{x},t)=A=const.$ We cannot do the same with the phase $\varphi(\boldsymbol{x},t)$ as the resulting wave would be just constant everywhere, and that's not a proper wave. Hence, let's try the simplest combination of $\boldsymbol{x}$ and t: $\varphi(\boldsymbol{x},t)=ax+by+cz+dt$ (do not confuse the last term with a differential). The resulting expression for the wave is then

$$\psi(\boldsymbol{x},t)=A\,\mathrm{e}^{\mathrm{i}(ax+by+cz+dt)}\,. \tag{A.4}$$

By employing the formulae (A.3), the above expression can be rewritten as

$$\psi(\boldsymbol{x},t)=A\,\mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)}\,. \tag{A.5}$$

From now on, we will call this the *plane wave*. Why? Generally, we define the so called *wavefront* as the surface defined by $\varphi(\mathbf{x}, t) = const.$ In this case, the resulting equation is

$$\boldsymbol{k} \cdot \boldsymbol{x} = const. + \omega t \,, \tag{A.6}$$

which (for fixed t) represents an analytical equation of the plane with normal $\boldsymbol{k}$ (that is in fact one of the important properties of $\boldsymbol{k}$). Now assume a simplified case in which all (plane) waves travel only in one direction. In that case, we can rotate our coordinate system such that

$$\boldsymbol{k} = \begin{pmatrix} k \\ 0 \\ 0 \end{pmatrix} , \tag{A.7}$$

where $k = \|\boldsymbol{k}\|$ is called the *wavenumber*, while the plane wave would simplify to

$$\psi(x, t) = A \, \mathrm{e}^{\mathrm{i}(kx - \omega t)} \,. \tag{A.8}$$

Now we ask the following question: can the values of ω and k be arbitrary? The answer is simply no. If we take the 1D plane-wave and insert it into the original equation (A.1), we get an algebraic equation of the form

$$D(\omega, k) = 0 \tag{A.9}$$

which is called the *dispersion equation* and represents a direct relationship between ω and k. (Note that this works only in case where the plane wave actually does solve the equation.) From the dispersion equation, we can then derive the *dispersion relations* as either

$$\omega = \omega(k) \quad \text{or} \quad k = k(\omega) \,. \tag{A.10}$$

(We will use the first one). It might not be always possible to express the above relations analytically, but in principle such dependence always exists at least implicitly.

Next, we focus on how fast do the individual wave-fronts propagate along the (arbitrarily chosen) x axis. We start by employing (once again) the equation determining the wavefront:

$$kx - \omega(k)t = const. \tag{A.11}$$

Such an equation now defines a relationship between x and t as

$$x(t) = \frac{\omega(k)}{k} t + const. \tag{A.12}$$

(The $1/k$ in the second term of the RHS got absorbed by the *const.*) We then define the *phase velocity* of the plane wave as

$$v_\mathrm{p} = \frac{\mathrm{d}x(t)}{\mathrm{d}t} = \frac{\omega(k)}{k} \,. \tag{A.13}$$

Let's put the result in a box

$$\boxed{v_\mathrm{p} = \frac{\omega(k)}{k}}\,. \tag{A.14}$$

Note that the phase velocity has nothing to do with the actual transport of any form of energy, and hence there is no restriction that it cannot be greater than c.

The plane wave is nice and simple, but realistically, no such solution can exist. But since the original Eq. (A.1) is linear, we can assume (by the principle of superposition) that any general solution can be expressed as

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k\, A(k)\, \mathrm{e}^{\mathrm{i}(kx-\omega t)}\,, \tag{A.15}$$

where $A(k)$ represents the amplitude of the plane wave with wavenumber k (hereinafter referred to as the *spectrum* of $\psi(x,t)$, but don't confuse it with the spectrum of eigenvalues) and the factor $1/\sqrt{2\pi}$ is chosen for convenience. Now how do we determine $A(k)$? Assume that we are given the initial shape of the wave at $t = 0$ as $\psi(x,0) = \psi_0(x)$. Then, it must hold that

$$\psi_0(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k\, A(k)\, \mathrm{e}^{\mathrm{i}kx}\,. \tag{A.16}$$

But this is exactly the expression for the inverse Fourier transform of $A(k)$. Hence, we can write

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x\, \psi_0(x)\, \mathrm{e}^{-\mathrm{i}kx}\,. \tag{A.17}$$

We have already determined the phase velocity of a plane wave. Now another question arises: is there a way to somehow determine an actual velocity of a general wave given by Eq. (A.15)? The answer is yes, but only in case where the spectrum $A(k)$ is tightly localized around some central value k_0, see Fig. A.1.

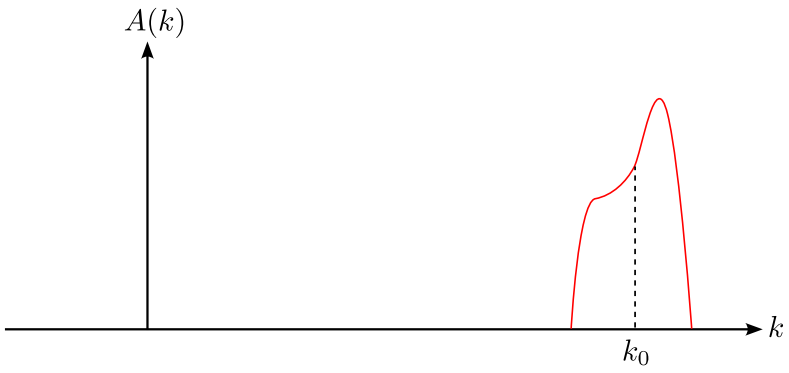

Figure A.1: Tightly localized spectrum.

Mathematically, this can be expressed as

$$A(k) \approx 0 \quad \text{outside of} \quad \frac{k - k_0}{k_0} \ll 1 \,. \tag{A.18}$$

We will call such a wave as the *wave packet* hereinafter. In such case, we can approximate $\omega(k)$ by the Taylor polynomial of the first order as

$$\omega(k) \approx \omega_0 + v_\mathrm{g}(k - k_0) \,, \tag{A.19}$$

where $\omega_0 = \omega(k_0)$, and

$$\boxed{v_\mathrm{g} = \left.\frac{\mathrm{d}\omega(k)}{\mathrm{d}k}\right|_{k=k_0}} \tag{A.20}$$

is the so called *group velocity* (we will see it's physical interpretation shortly). By inserting this approximation into (A.15), we get

$$\psi(x,t) \approx \mathrm{e}^{\mathrm{i}(k_0 x - \omega_0 t)} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k \, A(k) \, \mathrm{e}^{\mathrm{i}(k-k_0)(x - v_\mathrm{g} t)} \,. \tag{A.21}$$

We can now shift the integration variable $k \to k + k_0$, as this keeps both the differential and the integration limits unchanged, i.e.,

$$\psi(x,t) \approx \mathrm{e}^{\mathrm{i}(k_0 x - \omega_0 t)} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k \, A(k + k_0) \, \mathrm{e}^{\mathrm{i}k(x - v_\mathrm{g} t)} \,. \tag{A.22}$$

(If you are uncomfortable with this step, think of it as first substituting for $\varkappa = k - k_0$ and then relabeling $\varkappa \to k$). The $A(k + k_0)$ now represents the original spectrum $A(k)$ but shifted to the origin, as displayed in Fig. A.2

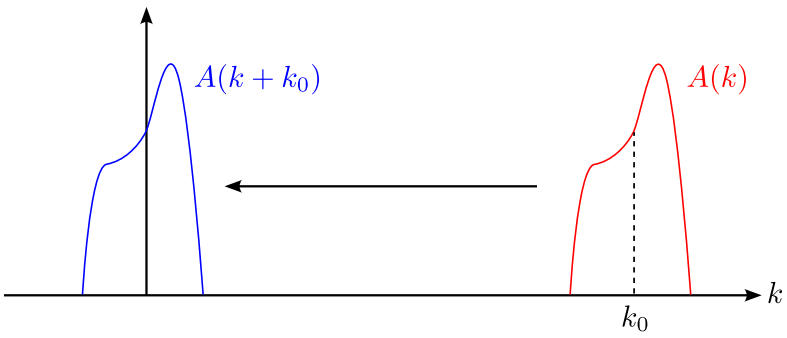

Figure A.2: Tightly localized spectrum shifted to the origin.

By further defining

$$\psi_0(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k \, A(k + k_0) \, \mathrm{e}^{\mathrm{i}kx} \,, \tag{A.23}$$

Eq. (A.22) becomes

$$\psi(x,t) \approx \psi_0(x - v_\mathrm{g} t)\, \mathrm{e}^{\mathrm{i}(k_0 x - \omega_0 t)}\,. \tag{A.24}$$

Finally, this now represent a base-band wave (that means that the spectrum is centered around $k_0 = 0$) $\psi_0(x)$ propagating along the x axis with the group velocity v_g (here you have the promised interpretation), modulated by the a plane wave with wavenumber k_0 and phase velocity $v_\mathrm{p} = \omega_0/k_0$, see Fig. A.3.

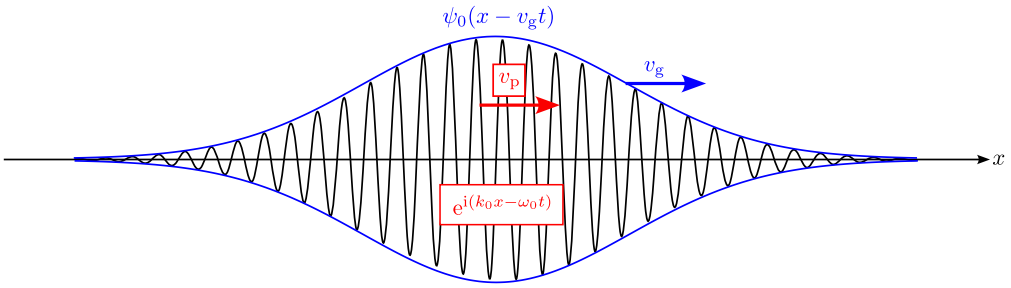

Figure A.3: Wave packet.

(If this reminds you of the historically used AM radio, then you are exactly correct.) Note that in (mostly rare) situations, a dispersion relation might arise such that $v_\mathrm{p} v_\mathrm{g} < 0$, in which case the phase velocity of the modulating plane wave has an opposite direction to the group velocity. We would then call this the *anomalous dispersion*. But mostly, we will have $v_\mathrm{p} v_\mathrm{g} > 0$, which is then called (unsurprisingly) the *normal dispersion*.

Appendix B

Gaussian Integral

Assume we would like to evaluate the Gaussian integral

$$I = \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2}\,\mathrm{d}x\,. \tag{B.1}$$

(As this is pure calculus, we write the differential after the integrand.) We start by writing

$$I^2 = \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2}\,\mathrm{d}x \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha y^2}\,\mathrm{d}y = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha\left(x^2+y^2\right)}\,\mathrm{d}x\,\mathrm{d}y\,. \tag{B.2}$$

Now we switch to the polar coordinates

$$x = r\cos(\varphi)\,, \quad y = r\sin(\varphi)\,, \tag{B.3}$$

which gives us

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha\left(x^2+y^2\right)}\,\mathrm{d}x\,\mathrm{d}y = \int_{0}^{2\pi}\int_{0}^{\infty} \mathrm{e}^{-\alpha r^2} r\,\mathrm{d}r\,\mathrm{d}\varphi = \frac{\pi}{\alpha}\int_{0}^{\infty} \mathrm{e}^{-\xi}\,\mathrm{d}\xi = \frac{\pi}{\alpha}\,, \tag{B.4}$$

where in the first equality we substituted for $\xi = -\alpha r^2$. Therefore,

$$I^2 = \frac{\pi}{\alpha} \tag{B.5}$$

and

$$\boxed{\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}}\,. \tag{B.6}$$

Now assume a slightly modified version of the above integral:

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2+\beta x}\,\mathrm{d}x\,. \tag{B.7}$$

By completing the square in the exponent as

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2+\beta x}\,\mathrm{d}x = \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha\left(x-\frac{\beta}{2\alpha}\right)^2+\frac{\beta^2}{4\alpha}}\,\mathrm{d}x \tag{B.8}$$

we get

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha\left(x-\frac{\beta}{2\alpha}\right)^2+\frac{\beta^2}{4\alpha}}\,\mathrm{d}x = \mathrm{e}^{\frac{\beta^2}{4\alpha}} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha\left(x-\frac{\beta}{2\alpha}\right)^2}\,\mathrm{d}x = \mathrm{e}^{\frac{\beta^2}{4\alpha}} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha\xi^2}\,\mathrm{d}\xi = \mathrm{e}^{\frac{\beta^2}{4\alpha}}\sqrt{\frac{\pi}{\alpha}}\,, \tag{B.9}$$

i.e.,

$$\boxed{\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2+\beta x}\,\mathrm{d}x = \mathrm{e}^{\frac{\beta^2}{4\alpha}}\sqrt{\frac{\pi}{\alpha}}}\,. \tag{B.10}$$

Last integral we will need for the purpose of this text is

$$\int_{-\infty}^{\infty} x^2\,\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x\,. \tag{B.11}$$

This can be done by differentiating Eq. (B.6) with respect to α, resulting in

$$\boxed{\int_{-\infty}^{\infty} x^2\,\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}}\,. \tag{B.12}$$

Appendix C

Special Differential Equations

Here we provide a list of various types of second-order differential equations that are relevant to the problems of QM.

C.1 Hermite Equation

The canonical form is

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}y}{\mathrm{d}x} + 2\lambda y = 0\,. \tag{C.1}$$

The polynomial solutions are called the *Hermite polynomials* and are denoted as

$$H_\lambda(x)\,, \tag{C.2}$$

while the following condition must hold:

$$\lambda \in \mathbb{N}_0\,. \tag{C.3}$$

The Hermite polynomials can be obtained by employing the formula

$$H_\lambda(x) = (-1)^\lambda\, \mathrm{e}^{x^2} \frac{\mathrm{d}^\lambda}{\mathrm{d}x^\lambda}\, \mathrm{e}^{-x^2}\,. \tag{C.4}$$

C.2 Associated Legendre Equation

The canonical form is

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[(1-x^2)\frac{\mathrm{d}y}{\mathrm{d}x}\right] + \left[\ell(\ell+1) - \frac{m^2}{1-x^2}\right] y = 0\,. \tag{C.5}$$

The polynomial solutions are called the *associated Legendre polynomials* and are denoted as

$$P_l^m(x)\,, \tag{C.6}$$

while the following conditions must hold:

$$\ell \in \mathbb{N}_0\,; \qquad m \in \mathbb{Z} \quad \wedge \quad |m| \leq \ell\,. \tag{C.7}$$

The associated Legendre polynomials can be obtained by employing the formula

$$P_\ell^m(x) = (-1)^m (1-x^2)^{\frac{|m|}{2}} \frac{\mathrm{d}^{|m|}}{\mathrm{d}x^{|m|}} P_\ell(x)\,, \tag{C.8}$$

where $P_\ell(x)$ stand for the Legendre polynomial given by

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \frac{\mathrm{d}^\ell}{\mathrm{d}x^\ell} (x^2-1)^\ell\,. \tag{C.9}$$

C.3 Associated Laguerre Equation

The canonical form is

$$x\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + (\nu + 1 - x)\frac{\mathrm{d}y}{\mathrm{d}x} + \lambda y = 0\,. \tag{C.10}$$

The polynomial solutions are called the *associated Laguerre polynomials* and are denoted as

$$L_\lambda^\nu(x)\,, \tag{C.11}$$

while the following condition must hold:

$$\lambda \in \mathbb{N}_0\,. \tag{C.12}$$

Typically, we also require

$$\nu \in \mathbb{R} \quad \wedge \quad \nu > -1\,, \tag{C.13}$$

but this is not a necessary condition.