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Arjun Berera , Luigi Del Debbio
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1 Stories and Thoughts about Quantum Mechanics

Quantum mechanics emerged as a natural extension of classical mechanics. As physics probed into the microscopic realm, it could be argued it would be almost impossible not to discover quantum mechanics. The spectra of atoms, the blackbody spectra, the photoelectric effect and the behaviour of particles through an array of slits had characteristically non-classical features. These phenomena were waiting their time for a theory to explain them. That does not diminish from the huge scientific insights of the founders of the subject. In physics, the great accomplishments come more often than not from insight rather than foresight. Knowing what will be the right physics 50 years into the future is a game of speculation. Recognising what is the important physics in the present and being able to explain it is the work of scientific insight. Thus, whereas we might say Democritus had great foresight millennia ago to envision the discrete nature of particles, it was Albert Einstein, Max Planck, Niels Bohr, Erwin Schrödinger, Werner Heisenberg, Paul Dirac, Max Born and Wolfgang Pauli who had the insights to develop quantum mechanics. And since their foundational work, our understanding of the physical world grew dramatically like never before.

The ideas leading to quantum mechanics started with the realisation that phenomena which up to then were considered wave-like in nature, could also have particle properties and vice versa. In the classical picture, particle properties mean the phenomena have energy and momentum that are localised in space, whereas wave properties mean the energy and momentum are coherently distributed over space. Radiation, which classically was considered to be wave-like, was the first phenomenon to be found to also have a particle nature. This was first noticed in blackbody radiation. In the classical theory, based on a wave description of radiation, the theoretical expectation near the end of the nineteenth century was that at low wavelength, the power per unit area radiated by a blackbody became infinite, the Rayleigh–Jeans law. This was in contradiction to experiment, which found the power spectrum to go to zero. In what might be the most significant curve fit in the history of physics, in 1900 Planck observed that he could arrive at a function that explained the observed blackbody spectrum, but it required the energy of the radiation to take discrete values. In particular, at a given wavelength λ, the energy needed to take values $E_\lambda = 0, \epsilon, 2\epsilon, \ldots, n\epsilon, \ldots$, where $\epsilon = hc/\lambda$. Planck introduced the proportionality constant h between energy ϵ and wavelength λ, thus necessarily the dimensions of angular momentum, which is now known as Planck's constant. The value of **Planck's constant**,

$$h = 6.626196 \times 10^{-27} \text{ erg s},$$

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sets the typical scale of quantum phenomena. The **rationalised Planck's constant** is defined as

$$\hbar = h/(2\pi)\,.$$

Planck attempted to reconcile this strange functional form that he had obtained with classical physics but achieved limited success.

The full realisation that light possesses a dual particle-like property came in 1905 by Einstein. It was known from experiments by then that when light strikes a clean metal surface, electrons get emitted. Increasing the intensity of the light increased in proportion the number of electrons emitted, but the kinetic energy of the electrons would remain the same, contrary to classical expectation. Einstein applied the Planck blackbody results to assert that quantisation of light was an inherent property. His picture was that light was made up of discrete quanta of energy, using Planck's expression, $E = hc/\lambda$. The idea that radiation was composed of particles was further confirmed in 1923 by Arthur Compton in studies of electrons scattered by radiation, where he concluded that the scattering process could easily be explained as a scattering between the electron with another particle of energy $h\nu$, where ν is the frequency of the radiation. In other words, as if the radiation has particles of this quanta of energy.

The classical picture of radiation also posed a problem for atoms. By 1913, experiments by Ernest Rutherford had established the structure of atoms as having a very tiny nucleus of positively charged particles. Niels Bohr, who had been working in the Rutherford laboratory at the time of his exciting discoveries, suggested the picture of the electrons as orbiting around this nucleus, bound to it by electrostatic attraction. In this classical picture, as the electrons are orbiting, as such accelerating, they are radiating energy. In such a picture the electron orbit should diminish as its energy goes into radiation, and within a fraction of a second the electron should spiral into the nucleus. Bohr showed in 1913 how this dilemma could be resolved by postulating that electrons only move in certain stable orbits of certain energy where they don't radiate, and in jumping between orbits they radiate energy equal to the difference between the energies of the two levels. Within this classical picture for an electron moving in a circular orbit at distance r from the nucleus acted on by a Coulomb field, since in that case the kinetic energy of the electron would equal half the magnitude of the potential energy, the total energy would be

$$E = -\frac{Ze^2}{2r}\,. \tag{1.1}$$

Thus the energy radiated by the atom as the electron moves from an orbit r_i to an orbit r_f under Bohr's assumption is

$$E_{\text{radiated}} = E_i - E_f = -\frac{Ze^2}{2}\left(\frac{1}{r_i} - \frac{1}{r_f}\right)\,. \tag{1.2}$$

Bohr argued his quantisation ideas in a few different ways, but perhaps the most far-reaching was his postulate that the angular momentum of the electron in the atom is quantised:

$$mvr = \frac{nh}{2\pi}\,, \tag{1.3}$$

where n is an integer and h is Planck's constant. From this expression was implied

$$E_{\text{radiated}} = \frac{2\pi^2 Z^2 m e^4}{c h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) . \tag{1.4}$$

A few years later, in 1916, Sommerfeld and Wilson developed a generalised quantisation rule that the integral of a dynamical variable over its conjugate variable around a cycle had to be equal to an integer of the Planck constant. This could be applied for example to angular momentum as the dynamical variable, leading to angular momentum quantisation or momentum and position, leading to energy quantisation. The work on radiation and the Bohr atom constituted what has come to be called the old quantum mechanics. This was an attempt at patching up experimental results within what was still believed to be an underlying classical picture of nature.

With the idea of radiation, which classically had been pictured as wave-like, successfully demonstrating particle-like properties, in 1924 Louis de Broglie suggested that perhaps matter, in particular electrons, which classically were pictured as particles, possess dual wave-like properties. He postulated that an electron of energy E and momentum p has a wavelength associated with it of

$$\lambda = \frac{h}{p} \tag{1.5}$$

and frequency

$$f = \frac{E}{h} . \tag{1.6}$$

A cursory examination of de Broglie's idea might suggest that it was a simple-minded guess and he just happened to be lucky enough to be right. This view might be further supported by the fact that de Broglie had completed his university studies in history with plans for a career in the civil service, to then go back and study science. This interpretation of de Broglie's work is in fact misleading. What is less well remembered is that Louis de Broglie had a physicist older brother, Maurice de Broglie, who was an experimental physicist studying X-rays, a research area at the cutting edge of the then developing quantum mechanics. Maurice helped initiate his brother's interest in physics, including sharing certain prevailing views advocated by W. H. Bragg, that X-rays display characteristics that are both wave- and particle-like. Louis had considerable knowledge of Maurice's views and had an in-depth understanding of the developments underway in physics at the time. Louis was by no means just an outsider who made a good guess. He had studied deeply the issues and views of his time, and it was more than a decade after he entered his studies in science that he came forth with his ideas on the wave nature of particles.

Verification of these properties was confirmed in 1927 in experiments on diffraction of electrons in crystals by Davisson and Germer and thin films by G. P. Thomson (Davisson and Thomson shared the 1937 Nobel Prize for discovering these wave properties of electrons). This was 31 years after J. J. Thomson, G. P.'s father, was awarded the Nobel Prize for discovering the electron as a particle. (An example from physics why children should not always listen to their parents!) This timeline may suggest a tidy picture of theoretical insight followed by experimental verification, but reality in physics is seldom so clean. In fact, experiments on electron beams through material had been done for many years previously, displaying evidence of their wave-like property. In particular, Davisson's experiments on electron scattering dated back before 1920, with results indicating patterns akin to diffraction. But these results needed proper interpretation, which seemed only to come once a compelling theoretical perspective was put forth.

De Broglie's ideas that a wave is associated with a particle led to the expectation that there must be an equation that governs the wave. It was Schrödinger who arrived at the equation for such waves, which now is called the Schrödinger equation. There were other attempts at obtaining such a wave equation, notably by Peter Debye and separately Erwin Madelung, but they all failed in one way or another and are forgotten to the mainstream history on physics. Schrödinger was motivated by de Broglie's interpretation of the Sommerfeld quantisation condition that this can be viewed as the number of wavelengths which cover the exact orbit of the electron around the nucleus. To Schrödinger, this looked like an eigenvalue problem, which he was familiar with from his early work in continuous media. Schrödinger's key step was to replace in the Hamilton equation for classical mechanics

$$H\left(q, \frac{\partial S}{\partial q}\right) = E \tag{1.7}$$

S by $k \ln \psi$, with ψ the wave function. He imposed the conditions on this wave function that it must be real, single-valued and twice continuously differentiable. The reality condition he subsequently relinquished in deriving what now is called the time-dependent Schrödinger equation.

The question that perplexed physicists initially was what exactly does this wave function ψ represent. In particular, did this wave function represent a single particle or a beam of particles? If it were representing a beam of particles, then the resulting diffraction patterns that were observed could be argued as some kind of collective effect.

When just a single particle goes through a diffraction apparatus, such as an array of slits, and deposits its signature on the observation screen, in any single case the individual particle appears to leave the diffractive apparatus in a random fashion. However, when carried out many times, each time with a single particle through the diffraction apparatus, the result from all those cases is the screen showing an interference pattern. Such an experiment implies that the wave property attached to the particle applies to a single particle and that it has a probabilistic meaning. It was Max Born who, in 1926 (he was at Göttingen at the time but later became part of the faculty at Edinburgh), first put forth the probabilistic interpretation of the wave function. At that time, experiments to this level of sophistication were not available. In fact, even the wave nature of matter was not entirely on an experimental footing. Born was guided by his work on applying Schrödinger's wave function to the scattering of particles. He was trying to find an interpretation for his quantum scattering ideas. He liked the particle interpretation of scattering. The only way he could see to adhere to this picture and reconcile it with the Schrödinger wave function was to assert a probability interpretation of the wave function. Thus, he arrived at the conclusion that when particles scatter at the quantum level, one cannot ascribe a definite prediction where the particle will go but simply predict probabilities for the different occurrences.

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The Schrödinger approach to quantum mechanics is now the one most commonly used. But in fact a year before Schrödinger discovered his equation, it was Heisenberg who had formulated his matrix approach to quantum mechanics. It was from this line of development that the formal underlying mathematical structure of quantum mechanics started to be understood. Heisenberg's work led in 1926 to the paper by Born and Pascual Jordan and then the famous paper by Born, Heisenberg and Jordan, which were the first to set out a logical mathematical foundation for quantum mechanics based on the matrix approach. Subsequently Schrödinger, and separately Pauli, showed that the wave and matrix approaches were in fact equivalent. The final phase in the development of quantum mechanics was the formalisation of ideas. Up to even the end of the 1920s quantum mechanics was a collection of ideas with different equations seeming to work for different physical situations. What was missing was a formal understanding of the mathematical structure of the theory. It is in fact this work at the final phases that has since been the main point explained and studied in the many textbooks of quantum mechanics written from then to now. Several people were involved in this step of formalising the theory, including of course Schrödinger and Heisenberg but also Born, Pauli and Paul Dirac and most notably Jordan, David Hilbert and John von Neumann. The culmination of this work by the end of the 1920s was the formulation of quantum mechanics in Hilbert space with the concepts of representation and transformation.

Further Reading

Jammer, M. (1966). *The Conceptual Development of Quantum Mechanics*. McGraw-Hill, New York.

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Quantum States

Quantum mechanics describes the behaviour of matter and light at the atomic scale, where physical systems behave very differently from what we experience in everyday life – the laws of physics of the quantum world are different from the ones we have learned in classical mechanics. Despite this ‘unusual’ behaviour, the principles of scientific inquiry remain unchanged: the only way we can access natural phenomena is through experiment; therefore our task in these first chapters is to develop the tools that allow us to *compute predictions for the outcome of experiments starting from the postulates of the theory*. The new theory can then be *tested* by comparing theoretical predictions to experimental results. Even in the quantum world, *computing* and *testing* remain the workhorses of physics.

Because quantum mechanics is so different from our intuitive, ‘classical’ description, the procedure we adopt for describing the quantum world needs to be defined carefully; the physical description of quantum phenomena must adhere very strictly to this procedure. In the first part of this book we will focus on presenting the basic postulates, and developing the mathematical tools needed for studying elementary systems. In time we want to be able to relate the mathematical constructs to actual physical processes. As we venture on this journey, we can only develop some intuition by practice; solving problems is an essential component for understanding quantum mechanics.

Experimental results at the beginning of the twentieth century first highlighted that the behaviour of physical systems at atomic scales is inconsistent with classical mechanics. As discussed in the previous chapter, the combined efforts of many eminent physicists led to a consistent picture of the new dynamics. Here we will not follow the historical route; unsurprisingly, the latter was rather tortuous. Instead we will start by stating the new principles, and then work towards deriving their consequences.

Despite its unintuitive aspects, quantum mechanics describes very concrete features of the world as we know it (e.g. the spectrum of the hydrogen atom). By now, many of its predictions have been tested to great accuracy, and have always been found in agreement with experiments. This book’s ambition is to set the foundations for developing a description of natural phenomena as observed in nature, i.e. to connect the abstract to the experiment. At every stage we will try to provide examples of physical systems described by the techniques that are being discussed.

It is useful to keep in mind the following disclaimer in Feynman’s lectures:[1]

> In this subject we have, of course, the difficulty that the quantum mechanical behavior of things is quite strange. Nobody has an everyday experience to lean on to get a rough,

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[1] R. P. Feynman, R. B. Leighton, M. Sands, *The Feynman Lectures on Physics – Quantum Mechanics*. Addison-Wesley, New York, 1965.

> intuitive idea of what will happen. So there are two ways of presenting the subject: We could either describe what can happen in a rather rough physical way, telling you more or less what happens without giving the precise laws of everything; or we could, on the other hand, give the precise laws in their abstract form. But, then because of the abstractions, you wouldn't know what they were all about, physically. The latter method is unsatisfactory because it is completely abstract, and the first way leaves an uncomfortable feeling because one doesn't know exactly what is true and what is false. [. . .] Here, we will try to find a happy medium between the two extremes.

Any first course in quantum mechanics suffers from the same problem, and this textbook makes no exception. We chose to start with an abstract definition of the laws, making use when possible of abstract mathematical notation. The explicit examples should allow the reader to appreciate the power of the mathematical tools, while making the mathematical notation more meaningful.

In order to start our journey into quantum mechanics, we need to introduce two main concepts:

1. the *state* of the system, and later in this book the dynamical laws that determine its time evolution;
2. the *observables* (i.e. the possible outcomes of experiments), which allow us to probe the state of the system.

This chapter is devoted to the introduction of the mathematical structure needed to characterise the state of a quantum system, while the study of observables is deferred to the following chapter in the book. Here we will see that physical states are associated with vectors in complex vector spaces, and we will define the main concepts that are going to be used to deal with physical states. These are the foundations of the theory and will be used throughout the book. Different physical systems will have states belonging to different vector spaces, but the general mathematical framework will remain the same for *all* quantum systems. The tools that we introduce in this chapter will then be used for all subsequent discussions. Examples and exercises should help you in building the skills needed to manipulate vectors in cases that are relevant for quantum mechanics.

2.1 States of a Quantum System

In classical mechanics, the state of a point-like system is described by the position and the momentum of its components. For an elementary particle in our usual three-dimensional space, the state of the system is defined by a six-dimensional **real** vector:

$$\left(\underline{x}, \underline{p}\right) . \tag{2.1}$$

Underlined letters indicate three-dimensional vectors, $\underline{x}$ and $\underline{p}$ being respectively the position and momentum of the particle. The knowledge of these two vectors at any moment in time allows us to compute all other properties of the system, for example its energy or its angular momentum. Moreover, once the dynamical laws are given, the state of the system at any other time can also be computed by solving the equations of motion.

We shall now introduce the postulates that allow us to describe the state of a quantum system. It is useful here to focus on the peculiarities of the quantum description. We will try to highlight these peculiarities as we encounter them and to reinforce our understanding through examples and exercises. We should always be able to connect the abstract concepts that are going to be introduced to physics, i.e. use the mathematical tools to compute theoretical predictions for the outcome of experiments. This process needs to be carefully defined: we will need to specify exactly what quantities can be computed and how these calculations are performed.

The first postulate of quantum mechanics defines the **states** of a quantum system.

Postulate 1 Quantum states are identified by vectors in **complex** vector spaces.

It is important to emphasise that we deal with complex vector spaces, instead of the real vector spaces that are more familiar from classical mechanics. This entails some differences that will be discussed in this chapter. A first comment arises by comparing the state vector in classical and quantum mechanics. As we discussed in the example above, the state of a classical point-like system is described by its position and its momentum, a six-dimensional real vector. In this case the components of this six-dimensional vector are also observables: the position and the momentum of the particle can be measured in an experiment. In quantum mechanics the picture is more subtle. Experiments do not measure complex vectors and we will have to put in some more work to define what can be predicted about the outcome of experiments.

For now, let us begin by introducing the concepts from linear algebra that are needed to work with the elements of complex vector spaces. This is standard material to be found in linear algebra courses, which we summarise in order to have a consistent set of definitions and notations. The chapter is dotted with examples and simple exercises that will hopefully help the reader to check that they understand and are able to apply the concepts that are being introduced. Their connection to physics will be the subject of following chapters. As we introduce physical concepts later in this book, we will continuously refer to the material presented in this chapter.

2.1.1 Kets

Following Dirac's notation, vectors will be denoted by **kets**, so for example the elements of a vector space $\mathcal{H}$ are written as

$$|v\rangle \in \mathcal{H}. \tag{2.2}$$

More generally we will use the notation $|\ldots\rangle$, where $\ldots$ can be any combination of symbols used to identify the vector. Sometimes we will insert just one letter, e.g. $|\psi\rangle$, other times we will use one or more indices, e.g. $|n\rangle$, or $|n, m\rangle$, with n, m integers. Finally we will encounter instances where the kets are identified by a continuous index, e.g. $|\xi\rangle$ with $\xi \in \mathbb{R}$. We will use the words state, vector and ket interchangeably.

The defining property of a vector space is that linear combinations of vectors also belong to the vector space:

$$\forall |u\rangle, |v\rangle \in \mathcal{H}, \forall \alpha, \beta \in \mathbb{C}, \quad \alpha|u\rangle + \beta|v\rangle \in \mathcal{H}. \tag{2.3}$$

The fact that $\mathcal{H}$ is a complex vector space is reflected in the fact that the coefficients α and β are complex numbers. It is straightforward to generalise this result to the linear combination of a set of vectors indexed by some integer n:

$$\forall \{|u_n\rangle\} \subset \mathcal{H}, \forall \{\alpha_n\} \subset \mathbb{C}, \quad \sum_n \alpha_n |u_n\rangle \in \mathcal{H}. \tag{2.4}$$

In Eq. (2.4) we have deliberately not specified the range of values taken by the index n. Depending on the system under study we may deal with either finite or infinite sums. We will come back to this issue later in the chapter.

Mathematical Aside: Properties of Vector Spaces

Here are some useful rules for manipulating vectors. In the following formulae, kets indicate generic elements of $\mathcal{H}$ and coefficients are generic complex numbers. Some of these properties may look familiar to readers who have some experience with linear algebra.

- There exists a '+' operation between vectors:

$$\forall |\psi\rangle, |\phi\rangle \in \mathcal{H}, \quad |\psi\rangle + |\phi\rangle \in \mathcal{H}. \tag{2.5}$$

  We have already implicitly used this property in Eq. (2.3).
- The sum of vectors is associative and commutative:

$$|\psi\rangle + (|\phi\rangle + |\xi\rangle) = (|\psi\rangle + |\phi\rangle) + |\xi\rangle, \tag{2.6}$$
$$|\psi\rangle + |\phi\rangle = |\phi\rangle + |\psi\rangle. \tag{2.7}$$

  Therefore the brackets in the first line are superfluous, and one can write simply

$$|\psi\rangle + |\phi\rangle + |\xi\rangle. \tag{2.8}$$

- Multiplication of a vector by a complex number yields another vector:

$$\forall |\psi\rangle \in \mathcal{H}, \forall \alpha \in \mathbb{C}, \quad \alpha|\psi\rangle \in \mathcal{H}. \tag{2.9}$$

  We will typically write the complex coefficient to the left of the vector, but this is just a convention:

$$\alpha|\psi\rangle = |\psi\rangle\alpha. \tag{2.10}$$

- The multiplication by complex numbers is associative and distributive:

$$\alpha(\beta|\psi\rangle) = (\alpha\beta)|\psi\rangle, \tag{2.11}$$
$$\alpha(|\psi\rangle + |\phi\rangle) = \alpha|\psi\rangle + \alpha|\phi\rangle, \tag{2.12}$$
$$(\alpha + \beta)|\psi\rangle = \alpha|\psi\rangle + \beta|\psi\rangle. \tag{2.13}$$

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Let us examine in more detail the operations that are described in the first of these equations. Note that, on the left-hand side of Eq. (2.11), we first perform the multiplication of a vector, $|\psi\rangle$, by a complex number β. The result of this operation is a vector, which is then multiplied by the complex number α. The final result on the left-hand side is therefore a vector. On the right-hand side, we first multiply the two complex numbers α and β. The result of this operation is another complex number, $(\alpha\beta)$, which multiplies the vector $|\psi\rangle$. The result on the right-hand side is also a vector, as one would expect if the equality has to hold. As a consequence of Eq. (2.11), the expression $\alpha\beta|\psi\rangle$ can be used without ambiguities. It is useful to perform this kind of 'grammatical' analysis of the equations, until the reader feels completely familiar with the operations performed with vectors in complex vector spaces.

- Existence of a null vector $|0\rangle$, such that

$$|\psi\rangle + |0\rangle = |\psi\rangle, \tag{2.14}$$

$$0|\psi\rangle = |0\rangle, \tag{2.15}$$

$$\alpha|0\rangle = |0\rangle. \tag{2.16}$$

- For each vector $|\psi\rangle$, there exists an *inverse* vector with respect to the '+' operation, denoted $-|\psi\rangle$:

$$|\psi\rangle + (-|\psi\rangle) = |0\rangle\,. \tag{2.17}$$

Vector spaces are ubiquitous in physics. The most familiar examples being the real vector spaces used in classical mechanics. Despite the abstract definitions above, vector spaces encode familiar properties. It is worthwhile to discuss a simple example of a complex vector space, which allows us to illustrate the main concepts.

Example 2.1 Consider the set of complex column vectors of size 2, i.e. the set of column vectors that can be written as

$$|v\rangle \equiv \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}, \tag{2.18}$$

where v_1 and v_2 are complex numbers. This space is called $\mathbb{C}^2$. If we define the sum of vectors and the multiplication by a complex scalar λ respectively as

$$\begin{pmatrix} v_1 \\ v_2 \end{pmatrix} + \begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = \begin{pmatrix} v_1 + w_1 \\ v_2 + w_2 \end{pmatrix}, \tag{2.19}$$

$$\lambda \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} \lambda v_1 \\ \lambda v_2 \end{pmatrix}, \tag{2.20}$$

then $\mathbb{C}^2$ is a vector space. It is important to notice that the '+' sign on the left-hand side of Eq. (2.19) defines the sum of two column vectors. The '+' sign on the right-hand side