

Lecture 2: Wavefunctions

Several experiments carried out around the beginning of last century, highlighted some fundamental limitations of classical mechanics. In particular, strong evidence was provided that small particles (i.e., the electron) might present, under certain conditions, a wave-like behaviour and, conversely, waves might behave as if they were particles (i.e., the photon) (see notes from PHY2081). This gave rise to the quantum treatment of matter. So, despite energy, momentum, and position of a particle are *still* important parameters also in quantum mechanics, it comes as a consequence that the state of a system does not correspond to simultaneous values of these quantities. In particular, it is impossible to determine simultaneously the position and the momentum of a particle. Without going into too much detail, this uncertainty in knowing the exact and simultaneous value of two conjugated variables can be expressed as:

$$\Delta q \Delta p \geq \hbar \quad (1)$$

(we recall here that $h = 6.62606957 \times 10^{-34} \text{ m}^2\text{kg/s}$ is the *Planck's constant*, and that $\hbar = h/2\pi$ is known as the *reduced Planck's constant*).

The natural question is then: how do we describe the state of a system?

Quantum Mechanics responds to this by introducing a complex function $\psi(\{r\}, t)$, which is a function of the position but not of the momentum. This function allows one to calculate, in any instant, the exact probabilities that a quantity of the system under study will acquire a certain value. In other words, classical mechanics claims that the values can be accurately determined, whereas quantum mechanics claims that the probabilities that a certain value is taken by a quantity can be accurately determined. For instance, the probability dP of finding a particle described by the wavefunction $\psi(\{r\}, t)$ in a position within the interval $[r, r + dr]$ is:

$$dP = |\psi(\{r\}, t)|^2 dr. \quad (2)$$

It is clear that the probability of finding a particle in any position in space must be 1. This translates into the condition:

$$\int_r |\psi(\{r\}, t)|^2 dr = 1. \quad (3)$$

An important consequence is that a wavefunction, in order to be called so, must be normalisable or, in other words, its integral must be finite. If this is the case, we can always find

a (generally complex) constant c_N so that the integral in Eq. 3 is equal to 1. The family of complex functions whose modulus square has a finite integral is called the *Hilbert space* (usually referred to as L^2). This space has many useful properties among which the most important probably is that it is a vectorial space. This means that given any two wavefunctions ψ_1 and ψ_2 and two any complex numbers c_1 and c_2 , the combination $\psi = c_1\psi_1 + c_2\psi_2$ is still a wavefunction. We can thus define a scalar product within this space, i.e. an operation between the elements of the space with the following characteristics:

- It gives as a result a complex scalar: $L^2 \cdot L^2 \rightarrow \mathbb{C}$
- It is a linear operator: $(\psi_1, a\psi_2 + b\psi_3) = a(\psi_1, \psi_2) + b(\psi_1, \psi_3), \forall a, b \in \mathbb{C} \psi_1, \psi_2, \psi_3 \in L^2$

The general definition of a scalar product implies that many different scalar products can be defined within a space. However, it is useful to define the following one:

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^* \psi_2 \, d r, \quad (4)$$

where the apex * indicates the complex conjugate and we have introduced the Dirac's notation. It is a useful notation since it allows to break the product into a *bra* $\langle \psi_1 |$ and a *ket* $|\psi_2\rangle$. A bra implies that the wavefunction comes from the left (and therefore it is complex conjugated) whereas a ket comes from the right side. The linear properties of the integral make the scalar product intrinsically linear. This product arises from the norm defined in L^2 :

$$\|\psi_1\|^2 = \langle \psi_1 | \psi_1 \rangle = \int |\psi_1|^2 \, d r. \quad (5)$$

2.a Example

The function $\psi = \exp(-r^2)$ belongs to L^2 and it can therefore describe a physical system, whereas the function $\psi = r$ does not. ■

Due to renormalisation, it follows immediately that the wavefunctions ψ and $c\psi$, being c any complex number, represent the same physical system. This has a very important meaning, since it shows one of the main differences between classical wave mechanics and quantum mechanics. In classical wave mechanics, these two waves are not interchangeable, since they have a different amplitude and they therefore represent two different physical systems. Another important property of ψ is that the total wavenfuction of a system T composed of two uncorrelated sub-systems A and B is given by the product of the two

wavefunctions ψ_A and ψ_B :

$$\psi_T = \psi_A \psi_B. \quad (6)$$

We will see later in the course that the concept of identical particles introduces a certain degree of correlation also among non-interacting particles.

We now proceed to see what is the value expected, and with what probability, for a dynamical variable (f) of the state described by the wavefunction ψ . The state ψ_n in which a dynamical variable f takes an exact value f_n is defined as:

$$f\psi_n = f_n\psi_n, \quad (7)$$

which means that ψ_n is an eigenfunction for the operator f with eigenvalue f_n . Let us assume that all these eigenfunctions are normalised:

$$\int_r |\psi_n|^2 dr = 1 \quad \forall n \quad (8)$$

A generic state will be described by a wavefunction which is a linear combination of those:

$$\psi = \sum_n a_n \psi_n. \quad (9)$$

Let us assume that we are to perform a measurement of the variable f of the state described by ψ . What is the probability P_n that the result will be f_n ?

This probability must be non negative, it must be a function of a_n , and it must obey the relation $P_n = \delta_{m,n}$ for $\psi = \psi_m$. we have used here the Kronecker symbol defined as $\delta_{m,n} = 1$ if $m = n$, zero otherwise. This last condition simply states that ψ_n will certainly give the value f_n and nothing else.

The fundamental postulate of Quantum Mechanics states that this probability is given by:

$$P_n = |a_n|^2 \quad (10)$$

We immediately see that all the eigenfunctions of any given dynamical variable are orthogonal (i.e., linearly independent):

$$\langle \psi_m | \psi_n \rangle = \int \psi_m^* \psi_n dr = \delta_{m,n}, \quad (11)$$

Without demonstrating it, we will only state that the family of functions ψ_n , eigenfunctions of a generic dynamical variable, represent an **orthonormal** (i.e. **with all members orthogonal**

to each other and with modulus 1) and complete set of functions (in other words, they form an orthonormal base). As an immediate consequence, any wavefunction can be expressed as a linear combination of those.

$$\psi = \sum_n a_n \psi_n. \quad (12)$$

This allows us to have a practical way to calculate the coefficients a_n :

$$a_n = \int \psi_n^* \psi \, d r. \quad (13)$$

In other words, the coefficient a_n is the projection of the state ψ over the eigenfunction ψ_n .