

Interpretation of the wavefunction

Proyecto de Innovación docente ID2022/163

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1. 1-dimensional particle without spin

The wave function corresponding to a particle in 1D without considering the spin coordinate is written as $\Psi(x)$, where x is the position of the particle in the one dimensional space. Its units are the inverse of the square root of the length, such as $L^{-1/2}$. The wave function is assumed to be normalised, i.e., its integral over the full space is equal to one:

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = \int_{-\infty}^{\infty} \Psi^*(x)\Psi(x)dx = 1 \quad (1)$$

According to M. Born, the square of the wave function ($|\Psi(x)|^2$) indicates the probability density (in this case, probability per unit length) of finding the particle along the x coordinate. The product $|\Psi(x)|^2 dx$ can be seen as the probability of finding the particle along an infinitesimally small length dx around the x value of the coordinate space. Finally, the probability of finding the particle in a region $-x_1 \leq x \leq x_2$ can be calculated using the integral

$$P = \int_{-x_1}^{x_2} |\Psi(x)|^2 dx = \int_{-x_1}^{x_2} \Psi^*(x)\Psi(x)dx \quad (2)$$

From the expression (1), it is deduced that the probability of finding the particle in the whole space available must be necessarily 1, since the particle must be found along this coordinate.

2. 3-dimensional particle without spin

The wave function corresponding to a particle in 3D without considering the spin coordinate is written as $\Psi(x, y, z)$, where (x, y, z) are the Cartesian coordinates which determine the position of the particle in the three-dimensional space. Its dimension is $L^{-3/2}$. The wave function is assumed to be normalised, i.e., it fulfills the following condition, equivalent to the 1D case:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(x, y, z)|^2 dx dy dz = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^*(x, y, z) \Psi(x, y, z) dx dy dz = 1 \quad (3)$$

The square of the wave function ($|\Psi(x, y, z)|^2$) is interpreted as the probability density (per unit volume) of finding the particle in a position given by (x, y, z) . The product $|\Psi(x, y, z)|^2 dx dy dz$ can be seen as the probability of finding the particle in a infinitesimal volume element $dx dy dz$ around the position (x, y, z) . Finally, the probability P of finding the particle in a space region V can be calculated using the triple integral

$$P = \int \int \int_V |\Psi(x, y, z)|^2 dx dy dz = \int \int \int_V \Psi^*(x, y, z) \Psi(x, y, z) dx dy dz \quad (4)$$

From the expression (3), it is deduced that the probability of finding the particle in the whole space available must necessarily be 1.

Let us consider now the effect of integrating over a single set of position coordinates. In the previous case, one could define, for example, the following function depending only on the z coordinate

$$D(z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(x, y, z)|^2 dx dy \quad (5)$$

whose dimension is L^{-1} and represents the probability density of finding the particle at a fixed value of z and any value of the coordinates x and y . The product $D(z) dz$, represents the probability of finding the particle in an interval dz around z (and again, any value of x and y).

The interpretation of the wave function does not depend on the coordinates used to describe the problem at hand. For example, we could work in spherical coordinates (r, θ, ϕ) . The dimension of the wave function corresponding to a three-dimensional spinless particle ($\Psi(r, \theta, \phi)$) would not change ($L^{-3/2}$) and its square represents the probability of finding the particle at a point of space defined by the coordinates (r, θ, ϕ) . The probability of finding the particle in a volume element centered around this point is obtained multiplying the square of the wave function by the volume element $r^2 \sin \theta dr d\theta d\phi$. The integration of this product over a definite region of the space V

$$P = \int \int \int_V |\Psi(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi = \int \int \int_V \Psi^*(r, \theta, \phi) \Psi(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi \quad (6)$$

gives the probability of finding the particle inside that region. Integrating the product $|\Psi(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$ over every angular coordinate except the radial distance r , one obtains the $P(r) dr$ radial probability

$$P(r) dr = \underbrace{\int_0^\pi \int_0^{2\pi} |\Psi(r, \theta, \phi)|^2 \sin \theta d\theta d\phi}_{P(r)} r^2 dr \quad (7)$$

of finding the particle in every angular direction and at a radial distance from the origin between r and $r+dr$. $P(r)$ would therefore be the probability density of finding the particle at a distance r from the origin and it is known as ‘radial distribution function’. In the case of the Hydrogen atom, where the Coulomb potential is central (it only depends on r), the wave function $\Psi(r, \theta, \phi)$ can be written as the product of a radial function $R_{nl}(r)$ and an angular function given by the $Y_{lm_l}(\theta, \phi)$ spherical harmonics. The probability density will be given as

$$\begin{aligned} P(r) &= \int_0^\pi \int_0^{2\pi} |\Psi(r, \theta, \phi)|^2 \sin \theta d\theta d\phi r^2 \\ &= \int_0^\pi \int_0^{2\pi} \underbrace{Y_{lm_l}^*(\theta, \phi) Y_{lm_l}(\theta, \phi)}_1 \sin \theta d\theta d\phi |R_{nl}(r)|^2 r^2 \\ &= |R_{nl}(r)|^2 r^2 \end{aligned} \quad (8)$$

3. N particles without spin in three dimensions

We will now generalize the previous cases to a N particle problem. The wave function of the system is written as $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ where \vec{r}_1 is the position vector of the first particle, \vec{r}_2 is the position vector of the second particle, etc. The dimension of this function is $L^{-3N/2}$ and the position vectors \vec{r} can be expressed in cartesian, spherical or any kind of coordinate system appropriated to tackle the problem. Here, it is important to clarify that in this case, the space where the studied physical system is settled is different from the space where the wave function is mathematically defined; the first is simply the space defined by the laboratory or the real space where the measurements are taking place, while the second is a $3N$ dimensional space defined by all the components of $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N$. Thus, the normalization condition for this wave function

$$\underbrace{\int \int \int \dots \int}_{\text{All space}} |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N = 1 \quad (9)$$

involves a multidimensional integral over the $3N$ dimensions ($x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N$ if we are working in Cartesian coordinates) of this second space.

The square of the wave function $|\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2$ represents the probability density (probability per unit volume in the $3N$ dimensional space where the function Ψ is defined) of finding the particle 1 in \vec{r}_1 , the particle 2 in \vec{r}_2 , etc. If this square value is multiplied by the volume element $d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N$ of the $3N$ dimensional space, we obtain the probability of finding the particle 1 in a volume element $d\vec{r}_1$ centered in \vec{r}_1 , the particle 2 in a volume element $d\vec{r}_2$ centered in \vec{r}_2 , etc. The value of the integral of the square function over a given V volume gives the probability P ,

$$P = \int \int \int \dots \int_V |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N \quad (10)$$

3N integrals

of finding the particles inside this region.

However, if we integrate the probability density $|\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2$ over all the spatial coordinates except for those corresponding to two of the particles (for simplicity we chose

particle 1 and 2), we obtain the following function of probability density

$$D(\vec{r}_1, \vec{r}_2) = \underbrace{\int \int \int \dots \int}_{3N - 6 \text{ integrals}} |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_3 d\vec{r}_4 \dots d\vec{r}_N \quad (11)$$

for which the dimension is L^{-6} and represents the probability density (probability per unit volume in the 6 dimensional space defined by \vec{r}_1 y \vec{r}_2) of finding the particle 1 in \vec{r}_1 and the particle 2 in \vec{r}_2 when the rest of the particles (from 3 to N) are in any position of the space. As it was expected, if we multiply this function by $d\vec{r}_1 d\vec{r}_2$, we obtain the probability of finding the particle 1 in a volume element $d\vec{r}_1$ centered in \vec{r}_1 and the particle 2 in a volume element $d\vec{r}_2$ centered in \vec{r}_2 when the rest of the particles (from 3 to N) are in any position of the space.

If we integrate now the probability density $D(\vec{r}_1, \vec{r}_2)$ over the coordinates of the particle 2, we obtain a new probability density

$$D'(\vec{r}_1) = \int \int \int D(\vec{r}_1, \vec{r}_2) d\vec{r}_2 \quad (12)$$

which dimension is L^{-3} and represents the probability density (probability per unit volume in the space defined by the 3 coordinates of the particle 1) of finding the particle 1 in the position \vec{r}_1 when the rest of the particles (from 2 to N) are in any position of the space. Again, if we multiply $D'(\vec{r}_1)$ by the volume element $d\vec{r}_1$ we obtain the probability of finding the particle 1 in a volume element $d\vec{r}_1$ centered in \vec{r}_1 when the rest of the particles (from 2 to N) are in any position of the space.

4. N identical particles without spin in three dimensions: The electronic density

In this subject, we will be focused mainly on the wave function of systems with N electrons. In the quantum mechanical framework, the evolution of the particles cannot be followed in an individual manner, since we can not define trajectories due to the Heisenberg uncertainty

principle. For this reason, the identical particles (for instance, the electrons) are indistinguishable and every property of a system composed by identical particles must be independent of the particle index (1,2,...,N) used for label them.

This discussion implies that, when studying a system with N electrons, it is meaningless to look for a probability density of finding the i -th electron in a particular point of the space independently of where are the rest of them. It only makes sense to consider the probability density of finding any of the electrons in a given point of the space; this property is named as electronic density $\rho(r)$. The electronic density is of great importance since, in the case of molecules, it determines many of the molecular properties and their reactivity. Furthermore, it can be experimentally determined by X-ray diffraction.

If the total wave function of a system with N electrons is $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$, then the integral

$$\int \int \dots \int |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N \quad (13)$$

gives the probability density of finding the electron 1 in \vec{r}_1 independently of the position of the rest of the electrons of the system. Since they are indistinguishable particles, this probability density must be the same for the electron 1, the electron 2, etc, as long as it is calculated in the same spatial point. In other words, it has to be fulfilled that

$$\begin{aligned} \int \int \dots \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N &= \int \int \dots \int |\Psi(\vec{r}_1, \vec{r}, \vec{r}_3, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_3 \dots d\vec{r}_N \\ &= \int \int \dots \int |\Psi(\vec{r}_1, \vec{r}_2, \vec{r}, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_2 d\vec{r}_4 \dots d\vec{r}_N \\ &\dots \dots \\ &= \int \int \dots \int |\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r})|^2 d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_{N-1} \end{aligned}$$

where the first integral corresponds to the probability density of finding the electron 1 in \vec{r} independently of the position of the rest of the electrons, the second integral corresponds to the probability density of finding the electron 2 in \vec{r} independently of the position of the rest of the electrons, etc.

The electron density $\rho(r)$ is given by

$$\rho(\vec{r}) = N \int \int \dots \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N \quad (14)$$

and it represents the probability density of finding any electron in the point \vec{r} of the space. The electronic density always fulfills the following properties:

$$\begin{aligned} \rho(\vec{r}) &\geq 0 \\ \int \rho(\vec{r}) d\vec{r} &= N \end{aligned}$$

i.e., the electronic density is a positive function which integral over all the space equals the number of electrons in the system.

Though in this lecture we did not consider the electronic spin in the electronic density, its inclusion is straightforward, as we will see in the following chapters of the subject.