Quantum Mechanics 2

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2 Chapter 4: Quantum Mechanics in Three Dimensions

Learning Goals

- To formulate and solve the Schroedinger equation in three dimensions.
- To identify and represent graphically the main features of the radial and angular components of the wave function of the hydrogen atom.
- To determine the conditions that lead to the quantisation of the energies and the wave functions in the three dimensional case.
- To apply the formalism of quantum mechanics to the cases of the extrinsic and intrinsic angular momentum.
- To understand the concept of the spin of elementary particles and its description in quantum theory, in particular for spin-1/2 particles.

In this section of the lecture notes we present the main concepts discussed in **Chapter 4 ("Quantum Mechanics in Three Dimensions")** of the course textbook. The goal of these lecture notes is to provide a self-consistent study resource for the students, which is then complemented by the live lectures (and their recordings), the tutorial sessions, as well as their own study of the textbook. The relevant textbook sections are indicated below, material from other sections not listed there will not be required for the examination.

Textbook sections

- **4.1**: The Schroedinger Equation.
- **4.2**: The Hydrogen Atom.
- **4.3**: Angular Momentum.
- **4.4**: Spin

Up to now, we have considered quantum systems composed by particles that move in **one spatial dimension**, such as the free particle, the quantum harmonic oscillator, and the particle in a well (remember that the dimensions of the Hilbert space are unrelated to the physical spatial dimensions of the system). While these systems are extremely useful to illustrate the basic concepts of quantum theory, to describe many realistic situations we need to apply the same quantum formalism to the cases of particles that move in **three spatial dimensions**, such as the electron in the hydrogen atom. In doing so, we will have to deal with the quantum version of *angular momentum* (which is obviously irrelevant for the one-dimensional case), and discuss new quantum phenomena that do not have a classical counterpart, such as the *spin* (intrinsic angular momentum) of elementary particles.

2.1 The Schroedinger equation in three dimensions

The starting point of our discussion will be the Schroedinger equation in three dimensions. Given the operator representation of the Hamiltonian, $\hat{H}$, one can write

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\Psi(\mathbf{r},t) = \left(-\frac{\hbar^2}{2m}(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2)+V(\mathbf{r})\right)\Psi(\mathbf{r},t)\,, \tag{2.1}$$

where[4] $\mathbf{r}=(x,y,z)$. By using the operator presentation of the linear momentum associated to the spatial coordinate r_i, namely $\hat{p}_{r_i} = -i\hbar(\partial/\partial r_i)$, we find that the Schroedinger equation reads

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right)\Psi(\mathbf{r},t)\,, \tag{2.2}$$

in terms of the **Laplacian** expressed in Cartesian coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\,. \tag{2.3}$$

The main difference as compared to the usual one-dimensional systems is that now the wave function (and the potential energy) depends on $\mathbf{r}$, so we need three coordinates to specify a point in space. In the following, we will focus on **stationary** solutions that satisfy the time-independent Schroedinger equation,

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})\,. \tag{2.4}$$

By deploying the formalism derived in the previous chapter, you can extend some of its key results to the case of three spatial dimensions, for example the commutation relations between coordinates and linear momenta:

$$[\hat{r}_i,\hat{p}_j] = i\hbar\delta_{ij}\,,\quad [\hat{r}_i,\hat{r}_j] = [\hat{p}_i,\hat{p}_j] = 0\,,\quad i=1,2,3\,. \tag{2.5}$$

In this chapter, we will deal with quantum systems with a very important characteristic: **spherically symmetric** (also known as **central**) potentials. These are potential that depend *exclusively* on the magnitude of $\mathbf{r}$ but not on its direction, that is

$$V(\mathbf{r}) = V(x,y,z) = V\left(\sqrt{x^2+y^2+z^2}\right) = V(r)\,,\quad r=\sqrt{x^2+y^2+z^2}=|\mathbf{r}|\,. \tag{2.6}$$

For this reason, it is convenient to switch from Cartesian coordinates to *spherical coordinates*, since these

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[4] In the following, we will denote two- and three-dimensional vectors in bold font.

make explicit the symmetries that characterise the potential of the problem, in particular the fact that $V(r)$ depends only on the radial coordinate but not on the angular ones.

Examples of important *central potentials* are the Coulomb potential between two electric charges,

$$V(r) \propto \frac{Q_1 Q_2}{r}\,, \tag{2.7}$$

the Yukawa potential that describes interactions mediated by a massive (rather than a massless, as is the case of electromagnetism) particle,

$$V(r) \propto \frac{Q_1 Q_2 \exp\left(-Br\right)}{r}\,, \tag{2.8}$$

the spherical harmonic oscillator

$$V(r) \propto kr^2\,, \tag{2.9}$$

and the *infinite spherical well*, which is defined by $V(r) = 0$ inside a sphere of radius a $(r < a)$ and then $V(r) = \infty$ outside the sphere (for $r > a$), which is the three-dimensional analog of the infinite square well.

Spherical coordinates. Spherical coordinates (r, θ, ϕ) (where θ and ϕ are called the *polar* and *azimuthal* angles respectively) are related to Cartesian coordinates by the following transformation:

$$\begin{aligned} x &= r\sin\theta\cos\phi\,, \\ y &= r\sin\theta\sin\phi\,, \\ z &= r\cos\theta\,, \end{aligned} \tag{2.10}$$

where $r^2 = x^2 + y^2 + z^2$. Spherical coordinates span the following ranges:

$$0 \le r \le \infty\,, \qquad 0 \le \theta \le \pi\,, \qquad 0 \le \phi \le 2\pi\,. \tag{2.11}$$

The inverse transformation, from Cartesian coordinates to spherical coordinates, takes the form

$$\begin{aligned} r &= \sqrt{x^2 + y^2 + z^2}\,, \\ \theta &= \arccos\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right) = \arccos\left(\frac{z}{r}\right)\,, \\ \phi &= \arctan\left(\frac{y}{x}\right)\,. \end{aligned} \tag{2.12}$$

Separation of variables. We can now express the time-independent Schroedinger equation in three-dimensions, Eq. (2.4) in spherical coordinates using the known expression of the Laplacian in this coordinate system, and we find

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V(r)\psi = E\psi\,. \tag{2.13}$$

This equation appears rather more complex than those you have seen up to know, so we need to do some preparatory work. The most efficient method to solve this equation is to use the method of **separation of variables**. The starting point is an *ansatz* where we post that the dependence of the wave function on the radial coordinate factorises with respect to the angular one, that is,

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)\,. \tag{2.14}$$

Note that this is a hypothesis that might or might not work, and one needs to verify explicitely if this is indeed the case. Inserting the ansatz Eq. (2.14) and multiplying the time-independent Schroedinger equation, Eq. (2.13), by $-2mr^2/(YR\hbar^2)$, we end up with the following expression:

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)-\frac{2mr^2}{\hbar^2}\left(V(r)-E\right)\right]=-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right)\right] \tag{2.15}$$

where we have made explicit that we assume a central potential $V(r)$. Our separation of variables strategy appears to have been successful, since we see that the LHS of the equation depends *only* on the radial coordinate r while the RHS *only* on the angular coordinates θ and ϕ.

The next step is based on the observation that the only way that two functions of different variables are equal to each other is if they are both *equal to some numerical constant.* If we denote this constant as $\ell(\ell+1)$, for reasons that will become clear soon, we end up with two separate second order differential equations

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)-\frac{2mr^2}{\hbar^2}\left(V(r)-E\right)\right]=\ell(\ell+1)\,, \tag{2.16}$$

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right)\right]=-\ell(\ell+1)\,, \tag{2.17}$$

which we can solve sequentially. These equations are known as the *radial equation* and the *angular equation* respectively.

Note that separation of variables has lead to a very significant reduction of the complexity of the differential equations to solve, and that in particular the angular equation is **independent of the potential** and thus its solution will apply to any quantum system characterised by a central potential $V(r)$. While here we are mostly interested in applying the quantum formalism to the Coulomb potential that describes the hydrogen atom, the angular part of the solution will be the same for any other central potential, and therefore we will not need to reinvent the wheel in those cases.

2.1.1 The angular equation

Let us start by solving the angular equation, Eq. (2.17). Again, we will try the method of separation of variables, so we will posit an ansatz of the form $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$. Inserting this ansatz and multiplying the equation by $\sin^2\theta$ we find that

$$\left[\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\ell(\ell+1)\sin^2\theta\right]=-\frac{1}{\Phi}\frac{d^2\Phi(\phi)}{d\phi^2}\,, \tag{2.18}$$

where again we see that the separation of variables strategy has worked successfully, since the LHS depends only in θ while the RHS only on ϕ, and hence they must be equal to some constant, which we will call it without loss of generality m^2 (which for the time being denotes an arbitrary complex number). So at this point the radial equation involves two complex numbers, ℓ and m are complex numbers. As we will show next, there are boundary conditions that the wave function must satisfy that restrict in a significant manner the possible values that ℓ and m are allowed to take.

The differential equation in ϕ is particularly easy, and it is a good strategy in this life to start with the easy things and then move from there on to the most challenging tasks. The most general solution of the second order homogeneous differential equation

$$\frac{d^2\Phi(\phi)}{d\phi^2}=-m^2\Phi(\phi)\,, \tag{2.19}$$

will be given by

$$\Phi(\phi) = Ae^{im\phi} + Be^{-im\phi} \,, \tag{2.20}$$

with A and B being some integration constants.

Now we should use the fact that, from the definition of the spherical coordinates, it follows that the azimuthal angle ϕ is restricted to lie in the range Eq. (2.11). This property implies that ϕ and $\phi + 2\pi$ correspond to the same physical angle, and for example Eq. (2.20) must be the same wave function as

$$\Phi(\phi + 2\pi) = Ae^{im(\phi+2\pi)} + Be^{-im(\phi+2\pi)} \,. \tag{2.21}$$

(An attentive reader might have noticed a loophole here: wave functions are not observables, and what needs to be invariant under the $\phi \to \phi + 2\pi$ transformation is instead the *square* of the wave function, which is the physical observable given its probabilistic interpretation. Now, the square of Eq. (2.20) reads

$$|\Phi(\phi)|^2 = |A|^2 + |B|^2 + A^* B e^{-2im\phi} + AB^* e^{2im\phi} \,, \tag{2.22}$$

so the same argument as before applies, now in a more robust manner.)

The requirement that the wave function (and its square) must be invariant under the $\phi \to \phi + 2\pi$ transformation is what is known as a **periodic boundary conditions**, that is, a boundary condition applied to a periodic function (which is typical for wavefunctions that involve angles). This periodic boundary condition enforces the requirement

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad \text{implying} \quad e^{\pm i 2\pi m} = 1 \quad \text{thus} \quad m = 0, \pm 1, \pm 2, \ldots \tag{2.23}$$

hence m must be an *integer number*. In other words, the solutions of Eq. (2.19) are **quantized** (discrete) with m being an *integer quantum number* that labels them. In summary, we can write the solution of Eq. (2.19) as

$$\Phi(\phi) = Ae^{im(\phi)} \,, \quad m = 0, \pm 1, \pm 2, \ldots \,, \tag{2.24}$$

which A some overall normalisation constant which will be fixed afterwards.

Quantisation from periodic boundary conditions

In previous courses, you saw how the quantisation of the wave function and of the allowed energies was often a consequence of the **boundary conditions** required on the wave function (and its derivative). For example, in the *particle in an infinite well* system, the quantisation of the energies followed from imposing that $\psi(x = 0) = \psi(x = L) = 0$, since the wave function must be continuous at the endpoints of the well (and the wavefunction vanished outside the well). Now we see that quantisation can also arise due to **periodic boundary conditions** in the case of angular variables.
In both cases, quantisation follows because the configuration of the quantum system imposes specific restrictions on the values that the wave function is allowed to take at certain points, and in turn by virtue of the Schroedinger equation this imposes restrictions on the allowed values for the energy E.

After having found the solutions for the azimuthal angle ϕ, we need to determine the dependence on the polar angle. The differential equation associated to the polar angle θ is a bit more involved:

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta(\theta)}{d\theta}\right) + \left(\ell(\ell+1)\sin^2\theta - m^2\right)\Theta = 0 \,. \tag{2.25}$$

Fortunately, there is no need to reinvent the wheel, since this differential equation is well known and has been extensively studied. In the case of the constant ℓ being a *positive integer*, this differential equation corresponds to the **associated Legendre equation** whose solutions are given by

$$\Theta(\theta) = BP_l^m(\cos\theta)\,, \quad l = 0, 1, 2, 3, \ldots\,, \quad m = 0, \pm 1, \pm 2\ \ldots, \pm l\,, \tag{2.26}$$

with $P_l^m(x)$ being a special type of functions called the *associated Legendre functions* and B some overall normalisation constant that will be fixed in a while. The mathematical aficionados can learn more about these special functions online or in the textbook: for the purpose of this course, we will consider them as given and provide their explicit expressions whenever they are required. Rather than on mathematical derivations, our focus here will be on the properties of these solutions and on their physical interpretation. Suffice here to say that the associated Legendre functions are *real functions* (rather than complex) of its argument.

Note that since Eq. (2.26) depends on the azimuthal angle θ via the cosinus, it automatically satisfies the relevant **periodic boundary conditions**, given that

$$\Theta(\theta + 2\pi) = BP_l^m(\cos(\theta + 2\pi)) = BP_l^m(\cos(\theta)) = \Theta(\theta)\,.$$

Furthermore, the solution of the associated Legendre equation imposes that m, which previously could take any integer value, should satisfy the restriction that $|m| < l$ (else there is no solution).

The integration constants B in Eq. (2.26) and A in Eq. (2.24) can be fixed at the same time by the requirement that the wave function must be normalised. For practical reasons, it is convenient to impose that the radial $R(r)$ and angular $Y(\theta, \phi)$ components of the three-dimensional wave function are *separately normalised*, although in principle only its product needs to be normalised. In spherical coordinates, the normalisation conditions boils down to

$$\int_0^\infty |R(r)|^2 r^2\, dr = 1\,, \tag{2.27}$$

$$\int_0^\pi \int_0^{2\pi} |Y(\theta, \phi)|^2 \sin\theta\, d\theta\, d\phi = 1\,, \tag{2.28}$$

where the extra factors of r^2 (in Eq. (2.27)) and $\sin\theta$ (in Eq. (2.28)) as compared to the usual normalisation conditions that one applies in Cartesian coordinates arise from the Jacobian of the change of variables.

Taking into account this normalisation requirement, and labeling the angular wave function by the quantum numbers l and m which can only take the values listed in Eq. (2.26), we end up with the following expression of the angular component of the wave function that solves the Schroedinger equation in three-dimensions:

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{(2\ell + 1)}{4\pi} \frac{(\ell - m)!}{(\ell + m)!}} e^{im\phi} P_\ell^m(\cos\theta)\,, \quad \ell = 0, 1, 2, 3, \ldots \quad m = 0, \pm 1, \pm 2, \ldots, \pm \ell\,, \tag{2.29}$$

which are known as the **spherical harmonics**. Their explicit expressions are not particularly informative, and you can find them in the textbook. However, what will be rather useful in the subsequent discussion of atomic orbitals will be the *symmetry properties* of the spherical harmonics. Furthermore, the spherical

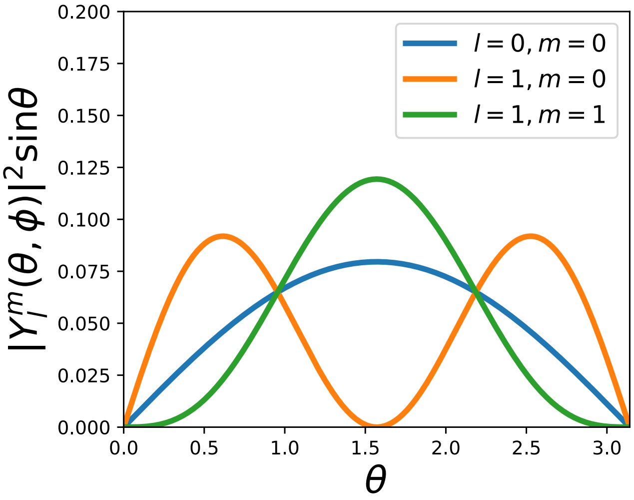

Figure 2.1: The probability densities in the polar angle θ associated to the first three spherical harmonics given in Eq. (2.32). The area under each curve integrates to one due to the normalisation condition Eq. (2.28).

harmonics defined this way are automatically orthonormal,

$$\int_0^{\pi}\int_0^{2\pi}\left[Y_{\ell'}^{m'}(\theta,\phi)\right]^*\left[Y_{\ell}^{m}(\theta,\phi)\right]^*\sin\theta\,d\theta\,d\phi=\delta_{\ell\ell'}\delta_{mm'}\,, \tag{2.30}$$

a property which will be important when assembling the wave functions of the hydrogen atom and related systems.

It is also interesting to work out what is the probability distribution associated to the angles θ and ϕ that one gets from the definition of the spherical harmonics. Taking into account the $P_l^m(x)$ are real functions, we can express the probability distribution in the angular variables as

$$P(\theta,\phi)=|Y_\ell^m(\theta,\phi)|^2\sin\theta=\left(\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}\right)\left(P_\ell^m(\cos\theta)\right)^2\sin\theta \tag{2.31}$$

The first thing we notice is that $P(\theta,\phi)$ does not depend on the azimuthal angle ϕ: this implies that all values of ϕ are *equally likely*. Then to determine the dependence on θ we need to indicate specific quantum numbers l and m. Below we provide some explicit examples:

$$\begin{aligned}
Y_0^0&=\left(\frac{1}{4\pi}\right)^{1/2} &&\rightarrow && P(\theta,\phi)=\frac{1}{4\pi}\sin\theta\,.\\
Y_1^0&=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta &&\rightarrow && P(\theta,\phi)=\left(\frac{3}{4\pi}\right)\cos^2\theta\sin\theta\,,\\
Y_1^{\pm1}&=\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi} &&\rightarrow && P(\theta,\phi)=\left(\frac{3}{8\pi}\right)\sin^3\theta\,.
\end{aligned} \tag{2.32}$$

These probability densities are shown in Fig. 2.1, where the area under each curve integrates to one due to the normalisation condition Eq. (2.28).

Before moving now to the radial equation, let us emphasize again that Eq. (2.29) will be the solution of any Schroedinger equation in three-dimensions with a radial potential. While for obvious reasons our main

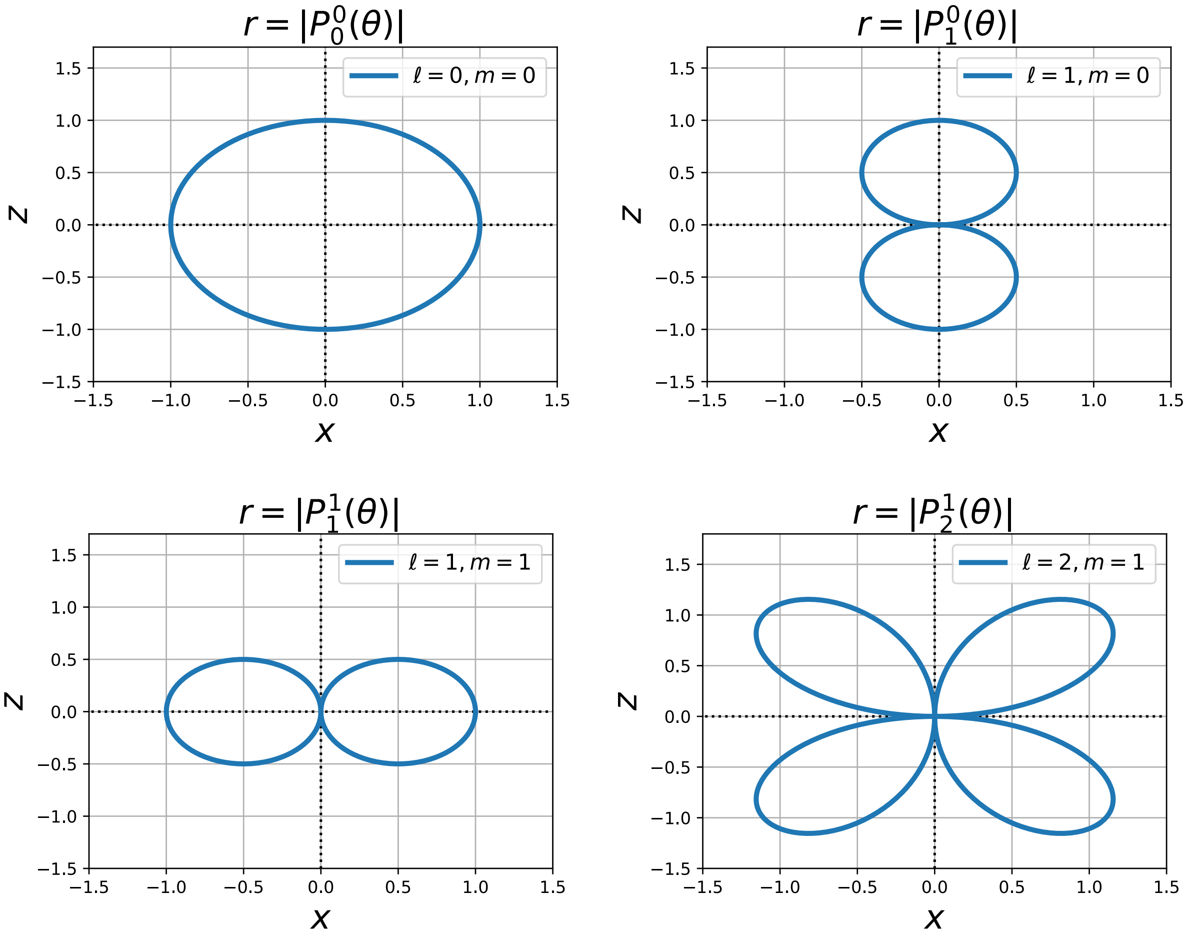

Figure 2.2: Graphical representation of the first few associated Legendre functions. The curves show the value of $r = |P_l^m(\theta)|$ as θ is varied from 0 to 2π.

interest is in the Coulomb potential, $V(r) \propto r^{-1}$, when we encounter other central potentials we can safely consider the angular part of the wave function as a done deal.

As we will demonstrate in the next section, the properties of the spherical harmonics will determine the **shape of the electronic orbitals** of the hydrogen atom. Fig. 2.2 displays a graphical representation of the first few associated Legendre functions:

$$\begin{aligned} P_0^0\,(\theta) &= 1\,, \\ P_1^0\,(\theta) &= \cos\theta\,, \\ P_1^1\,(\theta) &= -\sin\theta\,, \\ P_2^1\,(\theta) &= 3\sin\theta\cos\theta\,, \end{aligned}$$

where the curves indicate the value of $r = |P_l^m(\theta)|$ as θ is varied from 0 to 2π (there is rotational invariance around the z axis). Clearly, different values of ℓ and m will lead to different shapes of the electronic orbitals: for example $(\ell, m) = (0, 0)$ is spherically symmetric, while $(\ell, m) = (2, 1)$ corresponds to orbitals which are tilted $\pi/4$ with respect to the z axis.

2.1.2 The radial equation

We can now go back to Eq. (2.16) and attempt to solve the differential equation associated to the radial component of the total wave function

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r)-E\right) = \ell(\ell+1)\,, \qquad (2.33)$$

with the added knowledge that ℓ is no longer an arbitrary complex number but that it must be a positive integer. This differential equation can be simplified quite a bit with a clever change of variables, $u(r) = rR(r)$, which after some algebra allows us to write Eq. (2.16) in a rather elegant way:

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u(r) = Eu(r)\,, \qquad (2.34)$$

which looks extremely similar to the standard one-dimensional Schroedinger equation for a wavefunction $u(r)$ if we define the **effective potential** as

$$V_{\rm eff}(r) \equiv V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\,, \qquad (2.35)$$

and hence we have that the radial component of the Schroedinger equation in three dimensions can be obtained by solving the following differential equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + V_{\rm eff}(r)u(r) = Eu(r)\,. \qquad (2.36)$$

If you think a bit, this is a quite interesting result: it means that the radial component of the Schroedinger equation in *three-dimensions* is the solution of a differential equation that is nothing else but the Schroedinger equation in *one-dimensions* corresponding to the potential Eq. (2.35). Furthermore, recall that the normalisation condition Eq. (2.27) implies that

$$\int_0^\infty |u(r)|^2 dr = 1\,. \qquad (2.37)$$

Without specifying Eq. (2.43) we cannot make any further progress. In the following we will solve the radial equation for two different potentials, first the *infinite spherical well* and then the *Coulomb potential* relevant for the description of the energy levels of the hydrogen atom.

The effective potential and angular momentum. Introducing the effective potential

$$V_{\rm eff}(r) \equiv V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\,, \qquad (2.38)$$

makes possible writing the differential equation for the radial component of the wave function as if it were that of a one-dimensional system. The second term in $V_{\rm eff}(r)$ is *positive definite*, that is, it tends to push the particle away from $r = 0$, and the larger the value of ℓ the more intense this contribution will be.

Of course this effect is not unfamiliar: it is qualitatively the same as the *centrifugal force* that one experiences in a classical rotating body. As we will see below, this correspondence can be made more accurate once we introduce the angular momentum representation in quantum mechanics, and there we will see that the piece proportional to $\ell(\ell+1)$ arises indeed from the total angular momentum of the particle.

In other words, Eq. (2.43) might appear to describe a one-dimensional system, but it retains some *memory* that actually the particle is moving in three dimensions by means of the contribution to $V_{\rm eff}$ coming from the total angular momentum (the centrifugal force).

2.2 The infinite spherical well

One of the systems that you discussed in your earlier study of quantum mechanics in one dimension was the **infinite square well**, whose potential was defined as

$$\begin{aligned} V(x) &= 0 \quad \text{for } -a \le x \le a \\ V(x) &= \infty \quad \text{for } |x| > a \end{aligned}$$

with $2a$ being the width of the well. This potential corresponds to a configuration where a particle is restricted to move in the region $|x| < a$ where it obeys the free-particle Schroedinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)\,. \tag{2.39}$$

The solution to this equation is the usual free particle solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx}\,, \quad k = \sqrt{2mE/\hbar^2} \tag{2.40}$$

subject to the continuity boundary conditions $\psi(x = -a) = \psi(x = a) = 0$. These boundary conditions implied that we can only have either *even* or *odd* solutions,

$$\psi(x) = A\cos(kx)\,, \quad \text{or} \quad \psi(x) = A\sin(kx)\,, \tag{2.41}$$

with the integration constant A now fixed by the normalisation condition of the wave function. Furthermore, for the *even solutions* the continuity boundary condition requires $\cos(ka) = 0$ so that $k = (\pi/2a)n$ with k being an odd integer ($n = 1, 3, 5, \ldots$). Hence we see that for the infinite quantum well, the **boundary conditions** on the wave function are the reason for the resulting **energy quantisation**:

$$E_n = \frac{\hbar^2\pi^2 n^2}{2m(2a)^2}\,, \quad n = 1, 3, 5, \ldots\,. \tag{2.42}$$

(the energy levels for $n = 2, 4, 6, \ldots$ are then obtained from imposing the continuity boundary conditions on the odd solutions).

We are now going to generalise this problem to the three dimensional case, which is known as the **infinite spherical well**, where now the corresponding potential is given by

$$\begin{aligned} V(r) &= 0 \quad \text{for } r \le a\,, \\ V(r) &= \infty \quad \text{for } r > a\,. \end{aligned}$$

In the same manner as for its one-dimensional counterpart, the wave function will vanish where the potential is infinite, $\psi(r, \theta, \phi) = 0$ for $r \ge a$, and hence we will also here have a *continuity boundary condition* demanding that $\psi(r = a, \theta, \phi) = 0$ for all values of the angular variables. This potential is clearly a *central potential*, since it depends only on r but not on the angular variables. Therefore, we can happily deploy all the machinery that we have developed in the previous sections concerning the solutions of the Schroedinger equation in three dimensions.

For the case of the infinite spherical well, the effective potential Eq. (2.35) is reduced to the term proportional to $\ell(\ell+1)$ (the centrifugal contribution) and hence the radial equation to be solved is:

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2}+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}u(r)=Eu(r)\,. \tag{2.43}$$

which if we define (by analogy to the one-dimensional case) $k=\sqrt{2mE/\hbar^2}$ can be rewritten as

$$\frac{d^2u(r)}{dr^2}=\left[\frac{\ell(\ell+1)}{r^2}-k^2\right]u(r)\,. \tag{2.44}$$

Note that for the specific case of $\ell=0$ this differential equation for $u(r)$ has exactly the same form as that of its associated one-dimensional counterpart Eq. (2.39), and hence it will share its same solution. Note however that this does not mean that the physical wave function will be the same, since recall that we have used the transformation $u(r)=rR(r)$ (and also this is only the radial component of the total wave function).

Therefore, in the case $\ell=0$, the most general solution for the radial wave function in the infinite spherical well potential will be given by

$$R(r)=\frac{u(r)}{r}=A\frac{\cos(kr)}{r}+B\frac{\sin(kr)}{r}\,. \tag{2.45}$$

However, we note that not all possible values of A and B will lead to **physical solutions** for the wave function. In particular, since the wave function must be **finite everywhere**, we must impose that $A=0$, else the term proportional to $\cos(kr)/r$ would diverge in the $r\to 0$ limit. Furthermore, the *continuity of the wave function* requires that $R(r=a)=0$ since the wave function vanishes outside the barrier, as for the one-dimensional case. This requirement implies

$$B\frac{\sin(ka)}{a}=0\,,\quad\rightarrow\quad E_{N,0}=\frac{N^2\pi^2\hbar^2}{2ma^2}\,,\quad N=1,2,3,\ldots\,, \tag{2.46}$$

which are the same solutions for the one-dimensional well, once one accounts for both odd and even solutions. Finally we can determine the normalisation constant B by means of the normalisation condition Eq. (2.37) and we end up with

$$u_{N,0}(r)=\sqrt{\frac{2}{a}}\sin\left(\frac{N\pi r}{a}\right)\,,\quad r\le a\,,\quad N=1,2,3,\ldots\,, \tag{2.47}$$

and vanishes for $r>a$. So for the specific case of $\ell=0$ the wave functions $u(r)$ as the same as in the case of the infinite square well. We also note that the solutions Eq. (2.47) are labelled by an integer quantum number N.

A new type of boundary condition

We have seen from this example that another option to fix the integration constants that arise in the solutions of the Schroedinger equation is to demand that **only physical solutions are kept** and the unphysical ones are discarded. Specifically, we know that for a physical quantum state its **wave function must be finite everywhere**, else probabilities would be bigger than one which does not make sense. This requirement is specially handy in three-dimensional problems.

The radial equation in the infinite spherical well system, Eq. (2.44), can also be solved for an arbitrary positive integer ℓ in terms of two families of special functions, the *spherical Bessel functions* of order ℓ, $j_\ell(x)$

and the *spherical Neumann function* of order ℓ, $n_\ell(x)$:

$$u(r) = Arj_\ell(kr) + Brn_\ell(kr)\,, \tag{2.48}$$

where again the properties of these special functions have been thoroughly studied. Since $n_\ell(kr)$, diverges for $r \to 0$ we need to impose $B = 0$, and hence our candidate solution looks like

$$R(r) = Aj_\ell(kr)\,. \tag{2.49}$$

As in the case $\ell = 0$, we now need to impose the continuity boundary condition of the wave function at $r = a$. This boundary condition, $j_l(ka) = 0$, can be solved in terms of the zeros of the spherical Bessel functions and allows us to compute the quantised energy values $E_{N,\ell}$ for $\ell > 0$ in analogy with Eq. (2.46). If we note by $\beta_{N\ell}$ the N-th zero of the ℓ-th spherical Bessel function we find that the allowed energies are given by

$$E_{N,\ell} = \frac{\hbar^2}{2ma^2}\beta_{N\ell}^2\,. \tag{2.50}$$

Finally, we can combine the solution to the radial equation with the angular components of the wavefunction, which we get for free since the spherical harmonics are the same for any central potential, and we get

$$\psi_{nlm}(r,\theta,\phi) = A_{n\ell}j_\ell\left(\beta_{N\ell}\frac{r}{a}\right)Y_l^m(\theta,\phi)\,, \tag{2.51}$$

where $A_{n\ell}$ is determined from the normalisation condition and we have introduced the **principal quantum number** n which orders the allowed energies starting with $n = 1$ for the ground state of the system. Since

$$j_0(x) = \frac{\sin(x)}{x} \tag{2.52}$$

we see that $\beta_{N0} = N\pi$ and thus we reproduce the results that we have obtained for $\ell = 0$.

2.3 The Coulomb potential and the hydrogen atom

After this warm up with the infinite spherical well, we can move to the main goal of this chapter which is solving the Schroedinger equation in three-dimensions for a physical system defined by a proton and an electron interacting by means of the Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\,, \tag{2.53}$$

which is required to construct the wavefunctions of the **hydrogen atom** and determine the spectrum of allowed energies. Therefore we now need to solve the radial equation for $u(r)$, Eq. (2.43), for the following effective potential

$$V_{\rm eff}(r) \equiv -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\,, \tag{2.54}$$

which is graphically represented in Fig. 2.3. for different values of the angular quantum number ℓ. Note how for ℓ there is no *centrifugal barrier* preventing the electron to become too close to $r = 0$, and indeed in this case as we will see $\psi(r = 0, \theta, \phi) \neq 0$. The larger the value of ℓ, the stronger the effect of this centrifugal barrier pushing the electron away from the origin.

We note that the Schroedinger equation for the Coulomb potential admits two types of solutions:

- The **bound states** of the hydrogen atom with negative energies, $E < 0$. We can see from Fig. 2.3

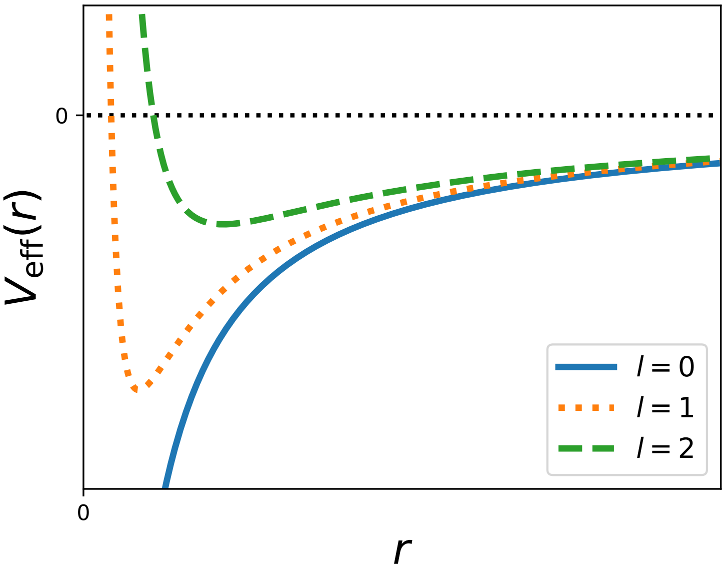

Figure 2.3: The effective potential $V_{\rm eff}(r)$ associated to the Coulomb potential for different values of the angular quantum number ℓ. Note how for ℓ there is no *centrifugal barrier* preventing the electron to become too close to $r = 0$, and indeed in this case as we will see $\psi(r = 0, \theta, \phi) \neq 0$.

that if $E < 0$ the wave function eventually becomes exponentially suppressed for $r \to \infty$ (since there $E < V_{\rm eff}(r)$, the classically forbidden region), which is the definition of a bound state (a wave function that vanishes asymptotically).

- The **scattering states** between an electron with positive energy, $E > 0$, and a proton. For $E > 0$, the wave function will displays for $r \to \infty$ the oscillatory behaviour characteristic of scattering states.

In the following we will focus on the bound states of the Coulomb potential, since these are the ones relevant for the description of the hydrogen atom. However, the eigenfunctions of the Schroedinger equation in three-dimensions will represent a complete basis only if one accounts both for the scattering and for the bound states.

The solution of the radial equation associated to the bound states of the Coulomb potential

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + \left(-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)u(r) = Eu(r)\,, \quad E < 0\,, \tag{2.55}$$

is quite elegant from the mathematical point of view but provides limited insight from the physics point of view, so we will assume it as a given and point the interested student to the derivation in the textbook.[5] Here we only mention that in this derivation, much as in the case of the infinite spherical well of the previous section, we need to make sure to **eliminate unphysical solutions**, in particular those that lead to a blow-up of the wave function at either $r = 0$ or $r \to \infty$. One can also show that demanding the vanishing of the radial wave function $R(r)$ in the $r \to \infty$ limits leads to a **quantisation of the energy** and hence to the associated radial wave functions.

---

[5] In principle we should define r as the distance between the electron and the center of mass of the electron-proton system, and replace the mass of the electron by the *reduced mass* μ. However this is numerically a very small effect so effectively in what follows we are taking the proton to be infinitely heavy and thus motionless.

The end result of the calculation is the radial wave function for the Coulomb potential:

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L^{2\ell+1}_{n-\ell-1}(2r/na)\right] \,, \quad n = 0,1,2,\ldots \quad \ell = 0,1,\ldots,n \tag{2.56}$$

where the overal prefactor ensures its appropriate normalisation:

$$\int_0^\infty r^2 R^2_{nl}(r)\, dr = 1\,. \tag{2.57}$$

A number of observations about this important result, Eq. (2.56), are required at this point:

- The radial wave function $R_{n\ell}(r)$ depends on two quantum numbers: the **principal quantum number** n and the **angular quantum number** l. The latter was expected since ℓ entered the definition of the effective potential Eq. (2.54), which *sensu strictu* should have been labelled as $V^{(\ell)}_{\rm eff}(r)$. The former is a consequence of the requirement imposed by the boundary condition that $u(r) \to 0$ for $r \to \infty$ to ensure physical, normalisable wave functions (Since $R = u/r$).

  However, as we discuss below, the energy E_n depends only on the principal quantum number n but not on the angular one ℓ.

- The solution for $R_{n\ell}(r)$ depends on a special family of functions $L^p_q(x)$ known as the *associate Laguerre polynomials*. You can easily find their tabulated expressions online. Here the only property that we need to know about them is that they are finite when $x = 0$ and grow at most as $\propto x^q$ at large x.

- The dependence on the radial coordinate r appears always divided by a parameter a which has length dimensions and that is known as the **Bohr radius**:

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.53 \times 10^{-10}\,\mathrm{m}\,, \tag{2.58}$$

  which in some loose sense can be interpreted as the radius of the orbit that an electron has in the ground state of the hydrogen atom.[6]

- The explicit expressions for the radial wave function $R_{nl}(r)$ with low values of the quantum numbers n and l can be found in the textbook, and the reader is encouraged to take a closer look and represent some of them with the graphical software of their choice.

  Here we only point out that for $r \gtrsim na$ these radial wave functions are exponentially suppressed as $e^{-r/na}$, while for $r \lesssim na$ they exhibit a polynomial behaviour in r/a with the highest order being $(r/a)^{n-1}$ from the properties of the associate Laguerre polynomials.

- Of particular interest in the present discussion are the solutions where $\ell = 0$, that is, where the effective potential is purely Coulomb and there is no centrifugal contribution. In this case, you can verify that the associate Laguerre polynomials $L^1_{n-1}(2r/na)$ goes to a finite constant at $r = 0$, and hence the radial wave function exhibits the remarkable property that

$$R_{n0}(r\to 0) \propto e^{-r/na}\,, \quad R_{n0}(r=0) = \text{constant}\,, \tag{2.59}$$

  and hence the radial wave function *does not vanish at the origin* $r = 0$.

---

[6] Needless to day, the classical concept of orbits is meaningless in quantum mechanics, so below we will specify rather more precisely the physical interpretation of the Bohr radius.

> This might seem an odd result, since $r = 0$ corresponds of course to the spatial location of the proton (the nucleus of the hydrogen atom) and surely the proton and the electron cannot occupy exactly the same position? Note that this is a clearly unphysical configuration, since the Coulomb potential is singular for $r = 0$. The way out of this conundrum is the observation that while $R_{n0}(r = 0) \neq 0$, the corresponding **radial probability density** $P_{n\ell}(r) \equiv r^2|R_{n\ell}(r)|^2$ does indeed vanish at $r = 0$.
>
> Therefore indeed we confirm that the electron has a vanishing probability to be found at $r = 0$, as could be expected from general physics arguments.

Putting everything together, we conclude that the complete wave function for the **bound states of the hydrogen atom** is given by the following expression:

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)\,, \tag{2.60}$$

in terms of the radial component Eq. (2.56) and the spherical harmonics Eq. (2.29). These wave functions are also known as the **atomic orbitals**. The allowed ranges for the three quantum numbers n, ℓ, and m which label these solutions are given by

$$n = 1, 2, 3, \ldots\,, \quad \ell = 0, 1, 2, \ldots, n-1\,, \quad m = -\ell, -\ell+1, \ldots, \ell-1, \ell\,. \tag{2.61}$$

The radial and angular components of the wave function are separately normalised. While the wave functions depend on *three quantum numbers*, the energies themselves are **quantised** but depend only on the principal quantum number n:

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2} = -\frac{13.6\,\text{eV}}{n^2}\,, \tag{2.62}$$

with $E_1 = -13.6\,\text{eV}$ representing the energy of the *ground state* ($n = 1$) of the hydrogen atom, also known as its **binding energy**: this is the energy that one needs to provide to remove an electron that occupies the ground state of the system.

The radius of the hydrogen atom. In Eq. (2.58) we introduced a numerical constant known as the *Bohr radius*, which we said had some relation with the size of a hydrogen atom. Let us make this connection more quantitative. We start with the radial wave function $R_{10}(r)$ corresponding to the *ground state of the hydrogen atom*:

$$R_{10}(r) = \frac{2}{a^{3/2}}\exp\left(-r/a\right)\,. \tag{2.63}$$

In quantum mechanics it makes no sense to ask a question such as *what is the radius of the electron orbit?*. Instead, questions that are meaningful to ask are:

- *What is the most likely value of radius of the electron orbit?*
- *What is the average value of the radius of the electron orbit?*

Note that in general the answer to these two questions, which superficially might appear to be the same, is different, so one has to be careful in checking what is being asked.

Let us answer these two questions in turn. We will need first to evaluate the corresponding radial probability density associated to this orbital:

$$P_{10}(r) = r^2|R_{10}(r)|^2 = \frac{4r^2}{a^3}\exp\left(-2r/a\right)\,. \tag{2.64}$$

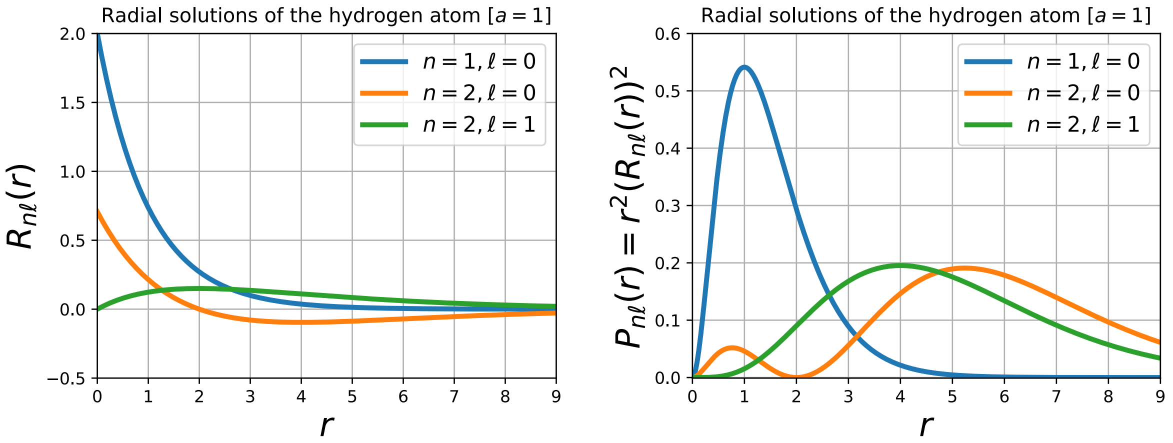

Figure 2.4: The radial wave functions $R_{n\ell}(r)$ and the associated probability distributions $P_{n\ell}(r)$ for the lowest three orbitals of the hydrogen atom (in units where $a = 1$). Note that while $R_{n0}(r = 0) \neq 0$, the associated probability densities vanish at the origin. Note also how the maximum of the probability distribution moves to the right (farther from the origin) as n increases; for $n = 1$ this maximum value is at $r^* = 1$, as we have derived in the text.

To evaluate the most likely value of the electron radius, r^*, the need to determine the local maximum of $P_{10}(r)$ by imposing that the first derivative vanishes:

$$\left.\frac{d}{dr}P_{10}(r)\right|_{r=r^*} = 0 \quad \to \quad r^* = a\,, \tag{2.65}$$

and hence we see that the Bohr radius corresponds to the **most likely value of the radius** of the electron orbit in the ground state of hydrogen.

Next, we can evaluate the expectation value of the radius of the electron orbit:

$$\langle r\rangle = \int_0^\infty dr P_{10}(r) r = \frac{4}{a^3}\int_0^\infty dr\, r^3 \exp\left(-2r/a\right) = \frac{3}{2}a\,, \tag{2.66}$$

which is 50% higher than the Bohr radius, indicating that on average the electron orbits brings it farther away from the proton than the value indicated from the Bohr radius.

It is an interesting calculation to evaluate what is the dependence of both the most likely radius r^* and of its average value $\langle r\rangle$ of the electron's orbit as the quantum numbers n and ℓ are increased: you will evaluate some of them in the exercises of the tutorial session. Fig. 2.4 displays the radial wave functions $R_{n\ell}(r)$ and the associated probability distributions $P_{n\ell}(r)$ for the lowest three orbitals of the hydrogen atom (in units where the Bohr radius is $a = 1$). Note that while $R_{n0}(r = 0) \neq 0$, the associated probability densities vanish at the origin. Note also how the maximum of the probability distribution moves to the right (farther from the origin) as n increases; for $n = 1$ this maximum value is at $r^* = 1$, as we have derived above.

Electronic transitions. An electron occupying an atomic orbital $\psi_{n\ell m}$ finds itself in an *stationary state*. However, external perturbations can induce **electronic transitions** between orbitals with different energy. For example, an electron occupying an orbital with $n_i > n_f$ can decay into the orbital with principal quantum number n_f. Since $E_{n_i} > E_{n_f}$, this process can only take place while ensuring **energy conservation** if energy is emitted, typically in the form of a photon. Using energy conservation, we get can evaluate the energy of the emitted photon

$$E_i = E_f + E_\gamma \quad \to \quad E_\gamma = E_i - E_f = (-13.6\,\mathrm{eV}) \times \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) , \tag{2.67}$$

where I have used the expression for the orbital energy in terms of the ionisation energy of hydrogen, Eq. (2.62). Likewise, an electron in an orbital with principal quantum number $n_i < n_f$ can transition to a higher orbital n_f via the *absorption of a photon*, whose energy is now

$$E_i + E_\gamma = E_f \quad \to \quad E_\gamma = E_f - E_i = (-13.6\,\mathrm{eV}) \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) . \tag{2.68}$$

Photons with energies corresponding to Eqns. (2.67) and (2.68) define what is known as the **spectrum of hydrogen**; you can relate these energies to wavelengths or frequencies using the Planck formula for the photons,

$$E_\gamma = \frac{hc}{\lambda} = h\nu \, . \tag{2.69}$$

The prediction of the spectra lines of hydrogen was one of the first historical triumphs of quantum theory.

Hydrogen-like atoms. The previous results have been derived assuming a Coulomb potential representing the attraction between the proton and the electron that compose a hydrogen atom,

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \, . \tag{2.70}$$

However, it should be clear that the same discussion applies verbatim to the case of *hydrogen-like atoms*, systems defined as a single electron orbiting a nucleus composed by Z protons and $A - Z$ neutrons, with A being the atomic mass number (the neutrons are of course irrelevant in this context).

In this case, the Coulomb potential of this system is given by

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} \, , \tag{2.71}$$

so one can reuse all results obtained so far by doing the substitution $e^2 \to Ze^2$ in all formulae. For example, the bound state energy of a hydrogen-like atom will be given by

$$E_n(Z) = -\left[\frac{m_e}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{Z^2 E_1^H}{n^2} = -\frac{(13.6\,\mathrm{eV}) \times Z^2}{n^2} \, , \tag{2.72}$$

which are the same energies as for a hydrogen atom but now rescaled by a factor Z^2. In particular, the energy of the bound state of a hydrogen-like atom compares to that of the hydrogen atom by

$$E_1(Z) = E_1^H \times Z^2 \, , \tag{2.73}$$

which illustrates how the increase in the positive electric charge of the atomic nucleus leads to a stronger electronic bond in comparison with that of the hydrogen atom.

2.4 Angular momentum in quantum mechanics

Our main result in this Chapter so far has been Eq. (2.60), the complete wave function for the electron orbitals in the hydrogen atom, $\psi_{nlm}(r,\theta,\phi)$, which is labelled by three quantum numbers. The principal quantum number n determines the energy of the orbital via Eq. (2.62), while we know that l and m are somehow related to the *orbital angular momentum* (since they arise when considering the motion of the particle in the angular coordinates).

In order to formalize this connection in a more quantitative manner, our goal in this section is to present a quantum-mechanical theory of the **angular momentum**. Clearly, so far (in previous courses and in Chapter 3) we have limited ourselves to *one-dimensional problems* where angular momentum does not exist, so it is not surprising that it is only now, once we move to the three-dimensional configuration, that we need to worry about angular momentum in quantum mechanics.[7]

As you have learned in your study of classical mechanics, the angular momentum in three dimensions is defined as

$$\mathbf{L} = (L_x, L_y, L_x) = (yp_z - zp_y, zp_x - xp_z, xp_y - yp_x) = \mathbf{r} \times \mathbf{p}\,, \tag{2.74}$$

that is, the cross product between the position $\mathbf{r}$ of a particle (with respect to some reference point) and its linear momentum $\mathbf{p}$. The angular momentum is only non zero when the directions of $\mathbf{r}$ and $\mathbf{p}$ do not coincide (else the cross product vanishes).

What is the corresponding operator representation of the angular momentum $\widehat{\mathbf{L}}$ that one must deploy in the quantum-mechanical world? We just need to make the usual conversion between the position and linear momentum observables with their corresponding operators

$$\begin{gathered} x \to \hat{x} = x\,, \quad y \to \hat{y} = y\,, \quad z \to \hat{z} = z\,, \\ p_x \to \hat{p}_x = -i\hbar\frac{\partial}{\partial x}\,, \quad p_y \to \hat{p}_y = -i\hbar\frac{\partial}{\partial y}\,, \quad p_z \to \hat{p}_z = -i\hbar\frac{\partial}{\partial z}\,, \end{gathered} \tag{2.75}$$

and hence we find that the operator representation of the individual components of the angular momentum is given by

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\,, \tag{2.76}$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial x}\right)\,, \tag{2.77}$$

$$\hat{L}_x = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\,. \tag{2.78}$$

In the following, we will determine what are eigenvalues and the eigenvectors of $\widehat{\mathbf{L}}$ and demonstrate that these have a deep connection with the wave functions of the hydrogen atom that we have just derived.

First of all, one should derive the commutation relations for the angular momentum operator. In order to derive them, the only property that we need to use here is the commutation relations between the spatial coordinates and the linear momenta in the three-dimensional case

$$[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}\,, \quad [\hat{r}_i, \hat{r}_j] = [\hat{p}_i, \hat{p}_j] = 0\,, \tag{2.79}$$

---

[7] Actually, this statement is not quite true, since even for an electron moving in one dimension one needs to consider its spin, and thus a quantum theory of angular momentum is already necessary in that case.

and using these properties we find

$$\left[\hat{L}_x,\hat{L}_y\right] = [yp_z - zp_y, zp_x - xp_z] = [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \, . \quad (2.80)$$

Next we need to apply the commutation relations for r_i and p_j, for example $[zp_y, zp_x] = 0$ and

$$[yp_z, zp_x] = \hat{y}\hat{p}_z\hat{z}\hat{p}_x - \hat{z}\hat{p}_x\hat{y}\hat{p}_z = \hat{y}\hat{p}_x\hat{p}_z\hat{z} - \hat{y}\hat{p}_x\hat{z}\hat{p}_z = \hat{y}\hat{p}_x\left[\hat{p}_z,\hat{z}\right] = -i\hbar\hat{y}\hat{p}_x \, .$$

Using these relations and after some algebra we find

$$[L_x, L_y] = i\hbar\left(xp_y - yp_x\right) = i\hbar L_z \, , \quad (2.81)$$

and likewise for the other commutators. In summary we find that the commutation relations between the individual components of the angular momentum operator are given by:

$$[L_x, L_y] = i\hbar L_z \, , \quad [L_y, L_z] = i\hbar L_x \, , \quad [L_z, L_x] = i\hbar L_y \, . \quad (2.82)$$

That is, the commutator between two components of the angular momentum is proportional to the other component. Following the discussion about the formalism of quantum mechanics that we had in the previous chapter, we can derive some some important consequences from this result:

Commutation relations for angular momentum

Since the three components of the angular momentum do not commute, they will have associated a Heisenberg-type **uncertainty relation**. Furthermore, it will not the possible to find a **complete set of functions** which are simultaneously eigenfunctions of L_i and L_j for $i \neq j$. Using the terminology that we derived in the previous section, we say that L_x, L_y, and L_z are **incompatible observables** that cannot be measured simultaneously, at least in a general quantum state.

The fact that L_i and L_j for $i \neq j$ do not commute implies therefore an uncertainty relation of the form

$$\sigma_{L_i}\sigma_{L_j} \geq \frac{\hbar}{2}\Big|\left\langle L_k\right\rangle\Big| \, , \quad i \neq j \neq k \, . \quad (2.83)$$

Note however how in the specific case where we have a quantum state such that $\langle L_k\rangle = 0$ then L_i and L_j *do commute* and thus can be measured simultaneously. But in general, it will be impossible to find a set of functions which are simultaneously eigenfunctions of σ_{L_i} and σ_{L_j} for $i \neq j$.

Furthermore, although at first sight it might seem unintuitive, the **square of the angular momentum** L^2 does commute with its individual components. Indeed, if one defines

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2 \, , \quad (2.84)$$

it can be shown L^2 commutes with L_i. For example, let us evaluate the following commutator:

$$\left[L^2, L_x\right] = \left[L_x^2 + L_y^2 + L_z^2, L_x\right] = \left[L_y^2 + L_z^2, L_x\right] \quad (2.85)$$

since of course L_x commutes with itself. To simplify this expression, we can use a useful relation involving the commutators of three operators $\hat{A}, \hat{B}$ and $\hat{C}$,

$$\left[\hat{A}\hat{B}, \hat{C}\right] = \hat{A}\left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{C}\right]\hat{B}\,, \tag{2.86}$$

which as you can check follows from the definition of the commutator. Therefore, we have that

$$\begin{aligned} \left[L^2, L_x\right] &= L_y\left[L_y, L_x\right] + \left[L_y, L_x\right]L_y + L_z\left[L_z, L_x\right] + \left[L_z, L_x\right]L_z \\ &= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z(i\hbar L_y) + (i\hbar L_y)L_z \\ &= i\hbar\left(-L_yL_z - L_zL_y + L_zL_y + L_yL_z\right) = 0\,. \end{aligned} \tag{2.87}$$

Since the same derivation applies to the other components, we have demonstrated that the total angular momentum commutes with its individual components:

$$\left[L^2, L_x\right] = \left[L^2, L_y\right] = \left[L^2, L_z\right] = 0\,. \tag{2.88}$$

Note that this result has the important consequence that:

Angular momentum measurements

In a general quantum system, it will be possible to *simultaneously determine* its **total angular momentum** and **its component in one specific direction** (but not for more than one direction!). Hence, each individual component of **L** is **compatible** with L^2 and one can find a set of eigenfunctions that simultaneously diagonalises the two operators. Specifically, there exists a complete set of functions that are at the same time eigenfunctions of L^2 and of L_z. As we discuss below, it happens that these eigenfunctions will also be eigenfunctions of the Hamiltonian $\hat{H}$.

The above property implies that it should be possible to find functions $f(\mathbf{x})$ that satisfy the corresponding eigenvalue equations:

$$L^2 f(\mathbf{x}) = \lambda f(\mathbf{x})\,, \quad L_z f(\mathbf{x}) = \mu f(\mathbf{x})\,, \tag{2.89}$$

or the equivalent relations with L_x or L_z. The allowed eigenvalues can be determined using a *ladder strategy*, similar as what you did with the harmonic oscillator. The derivation is mathematically elegant but not particularly enlightening from the physics point of view, so we refer the interested student to the textbook and here we just quote the final result:

$$L^2 f_\ell^m(\mathbf{x}) = \hbar^2\ell(\ell+1)f_\ell^m(\mathbf{x})\,, \quad L_z f_\ell^m(\mathbf{x}) = \hbar m f_\ell^m(\mathbf{x})\,, \tag{2.90}$$

with the quantised eigenfunctions being labelled by two quantum numbers ℓ and m which can take the following values:

$$\ell = 0, 1/2, 1, 3/2, \ldots\,; \quad m = -\ell, -\ell+1, \ldots, \ell-1, \ell\,. \tag{2.91}$$

This result should be familiar to you: it looks suspiciously close to the spherical harmonics that we defined in Eq. (2.29). Of course, this is no coincidence, and as we will discuss next the spherical harmonics are the sought-for **simultaneous eigenfunctions of L^2 and L_z**. The only difference appears to be that Eq. (2.91) allows for half-integer values of ℓ: these are *not* spurious solutions, but rather related to a new type of angular momentum which is unique to quantum mechanics: the **spin** of elementary particles, which will be discussed in Sect. 2.5.

On the relation between L^2 and L_z

From our discussion of the formalism of quantum mechanics, we know that the outcomes of a possible measurement of L^2 will be given by its eigenvectors, $\hbar^2\ell(\ell+1)$, and likewise the outcome of a given measurement of L_z will return $\hbar m$ subject to the constraint of Eq. (2.91). Interestingly, one notes that in all cases the outcome of the measurement of $\sqrt{L^2}$ will be **larger** that that of L_z since $\sqrt{\ell(\ell+1)} > \ell$ and $m_{\rm max} = \ell$. The reason for this result is that if a measurement of $\sqrt{L^2}$ returned the same outcome than that of L_z it would mean that $L_x = L_y = 0$. This would imply **absolute certainty** on the knowledge of all components of $\mathbf{L}$, which is incompatible with Heisenberg's uncertainty Eq. (2.83).

In order to determine the simultaneous eigenfunctions of L^2 and L_z that are defined by Eq. (2.90) it is convenient to switch to spherical coordinates, the reason being that the dependence on the radial coordinate drops out and the differential equations to be solved will depend only on the angular coordinates θ and ϕ. If you write the angular momentum $\mathbf{L} = -i\hbar\left(\mathbf{r}\times\nabla\right)$ and express the gradient in spherical coordinates after some algebra you find that the operator expression for the angular momentum in the z direction is given by

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}\,, \tag{2.92}$$

whose eigenfunctions are the same ones as those of Eq. (2.19). Indeed, if we solve the associated eigenvalue equations in Cartesian coordinates

$$\hat{L}_z f_\ell^m(r,\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}f_\ell^m(r,\theta,\phi) = \hbar m f_\ell^m(r,\theta,\phi)\,, \tag{2.93}$$

we easily see that the eigenfunctions are

$$f_\ell^m(r,\theta,\phi) = g(r,\theta)e^{im\phi}\,, \tag{2.94}$$

with the periodic boundary conditions in ϕ being ensured by the constraints in Eq. (2.91) (if we discard the half-integer solutions, which in this case are *not* compatible with the periodic boundary conditions.)

Next, we note that the squared angular momentum, given by

$$L^2 = \mathbf{L}\cdot\mathbf{L} = -\hbar^2\left(\mathbf{r}\times\nabla\right)\cdot\left(\mathbf{r}\times\nabla\right) \tag{2.95}$$

can also be expressed in spherical coordinates and is given by

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\,. \tag{2.96}$$

You can derive this result either by expressing $\left(\mathbf{r}\times\nabla\right)\cdot\left(\mathbf{r}\times\nabla\right)$ in terms of the Laplacian and then transforming to spherical coordinates, or by using the raising and lowering operator method. Now, we note that we have already encountered this equation! Indeed, when solving the angular equation for θ, Eq. (2.25), we had that the θ-dependent part of the angular wave function obeyed

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) + \left(\ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right)\Theta = 0\,. \tag{2.97}$$

Therefore, the solution of the eigenvalue equation for $\hat{L}^2$

$$\hat{L}^2 f_\ell^m(r,\theta,\phi) = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] f_\ell^m(r,\theta,\phi) = \hbar^2\ell(\ell+1) f_\ell^m(r,\theta,\phi)\,, \tag{2.98}$$

is nothing but the spherical harmonics $Y_l^m(\theta,\phi)$, given that we have demonstrated that:

$$f_\ell^m(r,\theta,\phi) = h(r)\Theta_l^m(\theta)e^{im\phi}\,, \tag{2.99}$$

Hence we can conclude that there spherical harmonics are the sought-for **simultaneous eigenfunctions of L^2 and L_z**, which makes possible achieving a deeper understanding of the properties of the electronic orbitals of the hydrogen atom.

Eigenvalues of the hydrogen atom orbitals

We have found that the solutions of the Schroedinger equation for the electronic orbitals of the hydrogen atom are simultaneous eigenfunctions of three operators: the Hamiltonian $\hat{H}$, the total angular momentum L^2 and its component in the z direction, L_z, with eigenvalues being given by

$$\begin{aligned}
\hat{H}\psi_{nlm}(r,\theta,\phi) &= E\psi_{nlm}(r,\theta,\phi)\,,\\
L^2\psi_{nlm}(r,\theta,\phi) &= \hbar^2\ell(\ell+1)\psi_{nlm}(r,\theta,\phi)\,,\\
L_z\psi_{nlm}(r,\theta,\phi) &= \hbar m\psi_{nlm}(r,\theta,\phi)\,.
\end{aligned}$$

This result implies that the can **simultaneously measure** E, L^2 and L_z of a given electronic orbital.

The property that $\hat{H}$, L^2, and L_z all commute between themselves (and hence a simultaneous eigenfunction basis exists) can be also noted by expressing the three-dimensional Schroedinger equation as

$$\hat{H}\psi_{nlm} = \frac{1}{2mr^2}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{L}^2\right]\psi_{nlm} + V(r)\psi_{nlm} = E\psi_{nlm} \tag{2.100}$$

and noting that $\hat{L}^2$ commutes with the Hamiltonian, $\left[\hat{H},\hat{L}^2\right]$, since it only acts on the angular variables while the non-$\hat{L}^2$ part of $\hat{H}$ acts only on the radial coordinate. Hence we can write

$$\left[\hat{H},\hat{L}^2\right] = \left[\hat{H},\hat{L}_z\right] = \left[\hat{L}_z,\hat{L}^2\right] = 0\,, \tag{2.101}$$

which is consistent with the existence of the simultaneous eigenvector basis that we have just derived.

2.5 Intrinsic angular momentum: Spin

When we determined the eigenvalues of the total angular momentum operator $\hat{L}^2$ in Eq. (2.90), we found that the angular quantum number ℓ could take both *integer* and *half-integer* values: $\ell = 0, 1/2, 1, 3/2, 2$, and so on. However, for the discussion of the solutions of the hydrogen atom, only the solutions with $\ell = 0, 1, 2, \ldots$ were relevant for the spherical harmonics, else the periodic boundary conditions would not be satisfied. For example, if $m = \pm 1/2$ then the spherical harmonics are not invariant under the $\phi \to \phi + 2\pi$ transformation. What about the half-integer solutions? Are they simply unphysical solutions to some differential equation and we can happily throw then away? As we will see, nothing would be more mistaken: these half-integer solutions play a crucial role in quantum mechanics and can be associated to one phenomenon that does not have a classical counterpart: the **spin** (or intrinsic angular momentum) of elementary particles.

Let us recall that in classical mechanics an object admits two types of angular momentum:

- **Orbital** or **extrinsic angular momentum**, associated to the motion of the center of mass of the object with respect to some external reference point: $\mathbf{L} = \mathbf{r} \times \mathbf{p}$.
- **Intrinsic angular momentum** or **spin**, associated with the rotation of the object with respect to some axis that passes through its center of mass, $\mathbf{L} = I\boldsymbol{\omega}$ where $\boldsymbol{\omega}$ represents the angular velocity and I the moment of inertia of the body with respect to the aforementioned axis.

  Note that this intrinsic angular momentum is not something conceptually different from the orbital one: it is only the sum of orbital angular momentum from all the constituents of the rigid body.

Hence, in classical mechanics the orbital (extrinsic) and the intrinsic (spin) angular momentum are essentially the same physical quantity, just evaluated in a different manner. However, in quantum mechanics it is essential to separate the extrinsic angular momentum $\mathbf{L}$ from the internal one, which we call spin and denote by the symbol $\mathbf{S}$.

Spin in quantum mechanics

The quantum mechanical spin $\mathbf{S}$ is a **fundamental property of elementary particles**, such as electron or the proton, with no counterpart in classical physics. In this respect, spin is on a similar footing to the charge or the mass of a particle: it is an intrinsic property that cannot be changed **without modifying the identity of the particle**. Also, do not push too far the analogy of imaging a tiny electron spinning around its axis, since one quickly finds unphysical results this way.

From the mathematical point of view, the distinction between orbital and intrinsic angular momentum remains as immaterial as in the classical case, and thus the **quantum theory of spin** follows readily from our previous discussion of angular momentum (it is essentially the same physical quantity, at the end of the day). In particular, given that we still live in three dimensions, we can define the components S_x, S_y, S_z of the spin of a particle (recall, its intrinsic angular momentum) whose associated operators $\hat{S}_x, \hat{S}_y, \hat{S}_z$ satisfy the usual commutation relations for angular momentum, recall Eq. (2.82),

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z\,, \quad \left[\hat{S}_y, \hat{S}_z\right] = i\hbar\hat{S}_x \quad \left[\hat{S}_z, \hat{S}_x\right] = i\hbar\hat{S}_y\,. \tag{2.102}$$

Likewise, if we denote by s the quantum number that labels the total spin and m that of its component of in the z direction[8], and we denote by $|s, m\rangle$ an eigenstate of both $\hat{S}^2$ and $\hat{S}_z$, we know from our previous discussion of angular momentum that their eigenvalues will be

$$\hat{S}^2|s, m\rangle = \hbar^2 s(s+1)|s, m\rangle\,, \quad \hat{S}_z|s, m\rangle = \hbar m|s, m\rangle\,. \tag{2.103}$$

Furthermore, we can define the *raising* and *lowering* spin operators whose action on those eigenstates is

$$\hat{S}_\pm|s, m\rangle = \hbar\sqrt{(s(s+1) - m(m\pm 1))}|s, m\pm 1\rangle\,, \quad \hat{S}_\pm \equiv \hat{S}_x \pm i\hat{S}_y\,, \tag{2.104}$$

a relation that can be verified by using the commutation relations of Eq. (2.102), in particular

$$\left[\hat{S}_z, \hat{S}_\pm\right] = \pm\hbar S_\pm\,, \quad \left[\hat{S}^2, \hat{S}_\pm\right] = 0\,. \tag{2.105}$$

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[8] In some textbooks one uses instead m_s, to separate it from m_l which is associated to the z component of the orbital spin. This distinction is not crucial here, but will become important in future chapters.

These operators are denoted as raising and lowering operators because of the following property:

$$\hat{S}_z \left(\hat{S}_\pm |s,m\rangle \right) = \hbar(m \pm 1) \left(\hat{S}_\pm |s,m\rangle \right) \,, \tag{2.106}$$

and hence $\hat{S}_\pm |s,m\rangle$ is also an eigenfunction of $\hat{S}_z$ but now with eigenvalue $\hbar(m \pm 1)$ instead of $\hbar m$ as in the original state $|s,m\rangle$, hence justifying the property of Eq. (2.104).

A crucial difference in the discussion of spin as compared to that of the orbital angular momentum is that now the eigenfunctions *do not need to be* the spherical harmonics (actually, there is not even a reference to the angles θ and ϕ when discussing spin!). That is, the spherical harmonics $Y_l^m(\theta,\phi)$ are certainly eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ but they are not the only possible solutions of the angular momentum (recall that spin is just angular momentum) operator eigenvalue equations. Therefore, we should use the full set of values of s and m without excluding the half-integer values

$$s = 0, \frac{1}{2}, 1, \frac{3}{2} 2, \ldots \,, \qquad m = -s, -s+1, \ldots, s-1, s \,. \tag{2.107}$$

For each value of the spin s of a given particle, we can construct explicit matrix representations of the spin operators $\hat{S}_z$ and $\hat{S}^2$.

Now, you might ask, what determines the value of the total spin quantum number s of a given particle, and can s change as a consequence of some interactions? Actually it turns out that no, and that as mentioned above the spin s of a particle is one of its defining properties much in the same way as its mass m and its electric charge q:

The spin of elementary particles

According to their spin s, elementary particles can be divided into two groups: **fermions** with half-integer values of the spin, and **bosons** for integer spin values. For examples, electrons and quarks (and protons and neutrons) are fermions with spin $s = 1/2$, while photons are bosons with $s = 1$. The recently discovered Higgs boson is a spin-less particle with zero spin, $s = 0$. This classification is essential in that that the spin of a particle has a very significant impact on its properties and their interactions, as we will verify in the next Chapter.

The theory of spin-1/2. The above discussion holds for any value of the spin s associated to elementary particles. In this course, we will focus mostly on $s = 1/2$, which is the spin quantum number associated to electrons and protons, and hence of direct relevance to study quantum mechanics for electronic, atomic, and molecular physics. We will also consider spin $s = 1$, which is interesting both from the conceptual point of view as well as relevant to discuss the interactions of electromagnetic light (composed by photons, $s = 1$ particles) with matter.

With this motivation, let us now present the quantum theory of $s = 1/2$ particles. The eigenvalue equations from Eq. (2.103) in this case read

$$S^2 \Big| \frac{1}{2}, m \Big\rangle = \frac{3\hbar^2}{4} \Big| \frac{1}{2}, m \Big\rangle \,, \quad S_z \Big| \frac{1}{2}, m \Big\rangle = \hbar m \Big| \frac{1}{2}, m \Big\rangle \,, \tag{2.108}$$

with $m = +1/2$ or $m = -1/2$ being the only two allowed values of the quantum number associated to S_z. Since s is fixed and $m = \pm 1/2$, spin-1/2 particles live in a **two-dimensional Hilbert space** (for the spin-related part of the wave functions). In the literature one can find a large variety of options in the notation to refer to these two eigenstates of $\hat{S}_z$, including:

- **spin up**: $\left|\frac{1}{2},\frac{1}{2}\right\rangle$, $|+_z\rangle$, $|\uparrow_z\rangle$, χ_+, ...
- **spin down**: $\left|\frac{1}{2},-\frac{1}{2}\right\rangle$, $|-_z\rangle$, $|\downarrow_z\rangle$, χ_-, ...

In most cases, it is easy to deduce by context which notation is being used to denote these eigenstates of $\hat{S}_z$, but please be careful specially when other components of $\hat{\mathbf{S}}$ are also involved.

Given that the eigenvectors of $\hat{S}_z$ form a complete basis ($\hat{S}_z$ being an Hermitian operator), we can express the **most general spin state** of a spin-1/2 particle as an electron as follows

$$|\Psi\rangle = c_+|+\rangle + c_-|-\rangle = \begin{pmatrix} c_+ \\ c_- \end{pmatrix}, \quad |+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{2.109}$$

in terms of the eigenstates $|+\rangle$ and $|-\rangle$ expressed in their conventional (though by no means unique) column vector representation. We can work out the matrix representation of the operators $\hat{S}^2$ and $\hat{S}_z$ in this specific basis. Let us start with the total spin operator $\hat{S}^2$. The equations that its components must satisfy are

$$\hat{S}^2|+\rangle = \frac{3\hbar^2}{4}|+\rangle \quad \to \quad \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3\hbar^2}{4}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.110}$$

$$\hat{S}^2|-\rangle = \frac{3\hbar^2}{4}|-\rangle \quad \to \quad \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3\hbar^2}{4}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{2.111}$$

from where we see that

$$\hat{S}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{2.112}$$

Likewise, you can determine that the matrix representation of $\hat{S}_z$ in this basis is given by

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{2.113}$$

You can verify that the eigenvalue equation for $\hat{S}_z$ has eigenvalues $\pm\hbar/2$ with eigenvectors $|+\rangle$ and $|-\rangle$, as expected from Eq. (2.108).

You can also work out the matrix representation for $\hat{S}_x$ and $\hat{S}_y$, and verify that you can express them as $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$ in terms of the so-called Pauli matrices

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{2.114}$$

As they should, the three components of $\mathbf{S}$ are Hermitian and satisfy the defining commutation relations Eq. (2.102). You can check that $\hat{S}_x$ and $\hat{S}_y$ also have $\pm\hbar/2$ as eigenvalues.

From the discussions in Sect. 1.4, we know that, if our (normalised) quantum state is expressed in terms of the eigenvectors of $\hat{S}_z$,

$$|\Psi\rangle = c_+|+\rangle + c_-|-\rangle, \tag{2.115}$$

then the probability of measuring $S_z = +\hbar/2$ will be $|c_+|^2$ and that of $S_z = -\hbar/2$ will be $|c_-|^2$, with of course $|c_+|^2 + |c_-|^2 = 1$ given that there are the only two possible outcomes of the measurement. Furthermore, we can also evaluate the possible outcomes of a measurement of S_x or S_y in the same quantum state: to answer this question we need to solve the eigenvalue equations for $\hat{S}_x$ or $\hat{S}_y$. As mentioned above, in **any direction** the only two possible outcomes of a measurement of the spin are $\pm\hbar/2$ (as it could not be otherwise, given that the choice of z axis is ultimately arbitrary!).

For example, in the case of $\hat{S}_x$ we find that the normalised eigenvectors are

$$|+_x\rangle = \frac{1}{\sqrt{2}}\left(\begin{array}{c} 1 \\ 1 \end{array}\right) = \frac{1}{\sqrt{2}}\left(|+_z\rangle + |-_z\rangle\right) , \tag{2.116}$$

$$|-_x\rangle = \frac{1}{\sqrt{2}}\left(\begin{array}{c} 1 \\ -1 \end{array}\right) = \frac{1}{\sqrt{2}}\left(|+_z\rangle - |-_z\rangle\right) , \tag{2.117}$$

in terms of the eigenstates of $\hat{S}_z$. Note that we have added a subindex to indicate explicitely to which direction the various spin eigenstates refer to. By inverting this linear system we get

$$|+_z\rangle = \frac{1}{\sqrt{2}}\left(|+_x\rangle + |-_x\rangle\right) , \quad |-_z\rangle = \frac{1}{\sqrt{2}}\left(|+_x\rangle - |-_x\rangle\right) , \tag{2.118}$$

or also using the frequently used arrow notation

$$|\uparrow_z\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle + |\downarrow_x\rangle\right) , \quad |\downarrow_z\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle - |\downarrow_x\rangle\right) . \tag{2.119}$$

We can use these relations to express our original state vector $|\Psi\rangle$ in terms of the eigenstates of $\hat{S}_x$:

$$|\Psi\rangle = \left(c_+|+_z\rangle + c_-|-_z\rangle\right) = \left(\frac{c_+ + c_-}{\sqrt{2}}\right)|+_x\rangle + \left(\frac{c_+ - c_-}{\sqrt{2}}\right)|-_x\rangle . \tag{2.120}$$

and hence the probabilities of measuring S_x in the positive or negative directions will be, following the prescription of the generalised probability interpretation, given by

$$P(S_x = +\hbar/2) = \left|\left(\frac{c_+ + c_-}{\sqrt{2}}\right)\right|^2 \qquad P(S_x = -\hbar/2) = \left|\left(\frac{c_+ - c_-}{\sqrt{2}}\right)\right|^2 \tag{2.121}$$

which taking into account the normalisation of the state vector $|\Psi\rangle$ can be shown to satisfy $P(S_x = +\hbar/2) + P(S_x = -\hbar/2)/ = 1$, as it could not be otherwise.

The uncertainty principle for spin-1/2 particles

You may have noticed from the previous derivation an interesting particular case: if $|\Psi\rangle$ is a **determinate state** of S_z (meaning that either c_+ or c_i vanish) then $P(S_x = +\hbar/2) = P(S_x = -\hbar/2) = 1$: we have the same likelihood for the two possible outcomes of measuring S_x. In other words, our uncertainty about the outcome of a measurement of S_x in this state is maximal. Since S_x and S_z are incompatible observables, good knowledge of one of them implies a worsened knowledge about the other, recall that the generalised uncertainty principle applied to spin-1/2 gives

$$\sigma_{S_x}\sigma_{S_z} \geq \left|\frac{1}{2i}\left\langle -i\hbar\,\hat{S}_y\right\rangle\right| = \frac{\hbar}{2}\left|\left\langle \hat{S}_y\right\rangle\right| .$$

The addition of angular momenta. Of crucial relevance for many applications of quantum mechanics is the situation where we have a quantum system composed by **more than one particle** (as we will study in the next Chapter) and we need to evaluate the **total angular momentum** of the system. We must be careful here, since angular momentum is a *vector* and not a *scalar*, and a naive addition of angular momenta will in general yield the wrong result.

For the sake of the argument, let us consider here a quantum system composed by two particles with well-defined spin states $|s_1, m_1\rangle$ and $|s_2, m_2\rangle$. We denote the composite state[9] of the system by $|s_1\ s_2, m_1\ m_2\rangle$, and the action of the corresponding spin operators on it is given by

$$\begin{aligned}
\hat{S}_1^2|s_1\ s_2, m_1\ m_2\rangle &= s_1(s_1+1)\hbar^2|s_1\ s_2, m_1\ m_2\rangle\,, \\
\hat{S}_2^2|s_1\ s_2, m_1\ m_2\rangle &= s_2(s_2+1)\hbar^2|s_1\ s_2, m_1\ m_2\rangle\,, \\
\hat{S}_{1,z}|s_1\ s_2, m_1\ m_2\rangle &= m_1\hbar\,|s_1\ s_2, m_1\ m_2\rangle\,, \\
\hat{S}_{2,z}|s_1\ s_2, m_1\ m_2\rangle &= m_1\hbar\,|s_1\ s_2, m_1\ m_2\rangle\,.
\end{aligned} \tag{2.122}$$

We would like to determine what is the total angular momentum of this state, defined as

$$\mathbf{S} \equiv \mathbf{S}_1 + \mathbf{S}_2\,. \tag{2.123}$$

Concerning the z component of the total angular momentum, one can see that

$$\hat{S}_z|s_1\ s_2, m_1\ m_2\rangle = \left(\hat{S}_{1,z} + \hat{S}_{2,z}\right)|s_1\ s_2, m_1\ m_2\rangle = (m_1\hbar + m_2\hbar)\,|s_1\ s_2, m_1\ m_2\rangle\,, \tag{2.124}$$

and hence $m = m_1 + m_2$ is the value of the total angular momentum in the z direction, S_z, associated to the quantum state $|s_1\ s_2, m_1\ m_2\rangle$.

Determining the values that S^2 can take in this composite system is rather more complicated, and here we will work out the explicit derivation in the case of $s_1 = s_2 = 1/2$, that is, for a system composed by two spin-1/2 particles. Since each particle's z-component of the spin can be positive or negative ($m_1 = \pm 1/2$ and $m_2 = \pm - 1/2$) we will have four possible combinations, each with a **well-defined value of** $m = m_1 + m_2$, constructed as

$$\begin{aligned}
|\uparrow\uparrow\rangle &\equiv \left|\frac{1}{2}\ \frac{1}{2}, \frac{1}{2}\ \frac{1}{2}\right\rangle \quad (m=1) \\
|\uparrow\downarrow\rangle &\equiv \left|\frac{1}{2}\ \frac{1}{2}, \frac{1}{2}\ \frac{-1}{2}\right\rangle \quad (m=0) \\
|\downarrow\uparrow\rangle &\equiv \left|\frac{1}{2}\ \frac{1}{2}, \frac{-1}{2}\ \frac{1}{2}\right\rangle \quad (m=0) \\
|\downarrow\downarrow\rangle &\equiv \left|\frac{1}{2}\ \frac{1}{2}, \frac{-1}{2}\ \frac{-1}{2}\right\rangle \quad (m=-1)\,.
\end{aligned} \tag{2.125}$$

where now we adopt a notation $|\uparrow\uparrow\rangle$ where the first entry in the ket indicates m_1 and the second m_2. Inspection of Eq. (2.125) reveals something peculiar. We see that m varies from $m = +1$ to $m = -1$, and this suggest that the composite states have total spin $s = 1$. But there are two different combinations that lead to $m = 0$, which appears to be inconsistent (since a quantum state with well-defined values of $\hat{S}^2$ and

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[9] Sensu strictu we should introduce here the **tensor product** to describe quantum systems consisting of multiple subsystems, each of which associated to a different Hilbert space. But we can come back to this subtlety on the subsequent chapters.

$\hat{S}_z$ is unique up to an overall normalisation). How to solve this problem?

The solution to this conundrum is subtle: only *three of the four combinations* defined in Eq. (2.125) actually correspond to $s = 1$ states, while the other combination instead has associated a total spin of $s = 0$, explaining why $m = 0$ was repeated (since for $s = 0$ the only option is $m = 0$). To identify which is the combination that has associated $s = 0$, we can use the spin lowering operator that we defined in Eq. (2.104). Recall that this operator exhibited the useful property that

$$\hat{S}_-|s,m\rangle = \hbar\sqrt{(s(s+1)-m(m-1))}\;|s,m-1\rangle\,, \tag{2.126}$$

so its action on a state with $s = m = 1$ will turn it into a $s = 1$ and $m = 0$ state:

$$\hat{S}_-|s=1,m=1\rangle = \sqrt{2}\hbar\;|s=1,m=0\rangle\,. \tag{2.127}$$

Certainly $|\uparrow\uparrow\rangle$ is a $s = m = 1$ state, so let me act on it with the lowering operator:

$$\begin{aligned}\hat{S}_-|\uparrow\uparrow\rangle &= \hat{S}_{1,-}\left|\frac{1}{2}\,\frac{1}{2},\;\frac{1}{2}\,\frac{1}{2}\right\rangle + \hat{S}_{2,-}\left|\frac{1}{2}\,\frac{1}{2},\;\frac{1}{2}\,\frac{1}{2}\right\rangle \\ &= \left|\frac{1}{2}\,\frac{1}{2},\;\frac{-1}{2}\,\frac{1}{2}\right\rangle + \left|\frac{1}{2}\,\frac{1}{2},\;\frac{1}{2}\,\frac{-1}{2}\right\rangle = |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\,.\end{aligned} \tag{2.128}$$

where we have used Eq. (2.126) for the $s_1 = m_1 = 1/2$ and $s_2 = m_2 = 1/2$ states. Hence we conclude that $\hat{S}_-|\uparrow\uparrow\rangle = |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle$ is the combination with $s = 1$ and $m = 0$, and then the linearly independent combination $|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle$ has instead $s = 0$ and hence $m = 0$.

Putting all this information together, we see that we have three states with total spin $s = 1$ (and $m = \pm 1, 0$, as required by the properties of angular momentum) which are known as the **triplet states**

$$\begin{aligned}|1\;1\rangle &\equiv |\uparrow\uparrow\rangle \quad (s=1, m=1)\,,\\ |1\;0\rangle &\equiv \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \quad (s=1, m=0)\,,\\ |1{-1}\rangle &\equiv |\downarrow\downarrow\rangle \quad (s=1, m=-1)\,.\end{aligned} \tag{2.129}$$

Note that we have normalised the combination with $m = 0$. Then, the combination associated to a total spin of $s = 0$ (which hence can only have $m = 0$) is denoted as the **singlet state** and is given by:

$$|0\;0\rangle \equiv \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)\,, \tag{2.130}$$

which again has been normalised. This derivation illustrates that a system composed by two spin-1/2 particles can carry either a total spin of $s = 1$ (for the triplet states) or of $s = 0$ (for the singlet state), depending on the configuration of the individual spins. As a further piece of evidence, we can demonstrate that the triplet states are eigenvectors of $\hat{S}^2$ with eigenvalues of $2\hbar^2$ while the application of $\hat{S}^2$ destroys the singlet state (since the eigenvalue is zero). That is, if we have that

$$S^2 = (\mathbf{S}_1 + \mathbf{S}_2)\cdot(\mathbf{S}_1 + \mathbf{S}_2) = S_1^2 + S_2^2 + 2\mathbf{S}_1\cdot\mathbf{S}_2\,, \tag{2.131}$$

then we will find

$$\hat{S}^2|1\;0\rangle = 2\hbar^2|1\;0\rangle\,,\quad \hat{S}^2|0\;0\rangle = 0\,. \tag{2.132}$$

where note that $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ commute between then since they act on *different Hilbert spaces* (more about this in the next chapters).

Towards the spin-statistics theorem

You might notice an interesting feature of the triplet combinations defined in Eq. (2.129): they are *invariant (symmetric) upon the* **exchange of the two particles**. However, the singlet state is instead *antisymmetric* upon the exchange of the two particles, since

$$|0\ 0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \quad \rightarrow \quad \frac{1}{\sqrt{2}}\left(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle\right) = -|0\ 0\rangle\,. \tag{2.133}$$

This observation will become crucial in the next Chapter, when we discuss how the spin of a particle determines which energy levels can be occupied and which ones cannot.

Generalisation to other spin combinations. The previous example represents the simplest possible example of spin combination, that involving two spin-1/2 particles. The general problem of combining a spin s_1 particle with a spin s_2 particle is rather more involved. The general answer is that the allowed combinations will have s between s_1+s_2 and $|s_1-s_2|$ in integer steps. We can give some examples:

- The case we have just discussed above corresponded to $s_1=1/2$ and $s_2=1/2$. In this case the general answer is that the allowed combinations range between $s=s_1+s_2=1$ and $s=|s_1-s_2|=0$ in integer steps, hence indeed $s=0,1$ as we just found.

- Assume you want to combine the spin of a photon ($s_1=1$) with that of a proton ($s_2=1/2$). The allowed combinations range between $s=s_1+s_2=3/2$ and $s=|s_2-s_1|=1/2$ with integer steps, hence $s=3/2$ and $s=1/2$.

- Likewise, if you were to combine the spin of a gravitino (a hypothetical spin-3/2 particle) with that of a graviton (the quantum of the gravitational force, a spin-2 particle), then the allowed combinations range between $s=s_1+s_2=7/2$ and $s=|s_2-s_1|=1/2$ with integer steps, hence $s=7/2,5/2,3/2,1/2$ will be possible values of the total spin of the system.

In general, it can be shown that the allowed state vectors representing two-particle systems with spins s_1 and s_2 will be given by:

$$|s\ m\rangle = \sum_{m_1+m_2=m} C^{s_1 s_2 m}_{m_1 m_2 m}|s_1\ s_2, m_1\ m_2\rangle\,, \tag{2.134}$$

with $C^{s_1 s_2 m}_{m_1 m_2 m}$ being known as the Clebsch-Gordan coefficients. The derivation of the Clebsch-Gordan coefficients is mathematically very interesting but not particularly relevant for the physics of this course, so we will not cover it further. The interested student is encouraged to read a bit about **group theory**, the mathematical theory of symmetries.

Finally, as repeatedly emphasized, from the mathematical point of view spin follows exactly the same rules as orbital angular momentum. Hence, the same rules that we have discussed for the combination of the spin states of two different particles will also apply to the **combination of spin with orbital angular momentum**. For instance, for an electron of the hydrogen atom with quantum numbers n,ℓ,m its total angular momentum (spin plus orbital) will be either $\ell-1/2$ or $\ell+1/2$, following the general prescription.

Summary

We can now recapitulate what have we learned in this chapter concerning the the quantum mechanics of three-dimensional systems.

I/ We can solve the Schroedinger equation in three dimensions by the method of separation of variables; in the case of central potentials the dependence on the angular coordinates decouples from that of the radial coordinate.

II/ The solutions of the Schroedinger equation in three dimensions for the Coulomb potential are simultaneous eigenfunctions of $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$, with quantum states labelled by the eigenvalues of these operators.

III/ The properties of the radial solution $R(r)$ and the spherical harmonics $Y_l^m(\theta, \phi)$ determine the properties of the electronic orbitals of the hydrogen atom, such as for example what are the most likely values of the radial coordinate r or the angular shape of the different orbitals.

IV/ The quantum theory of angular momentum can be applied to spin, the intrinsic angular momentum of elementary particles, and we can also determine the total spin content of two-particle systems.