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Chapter 5

Angular momentum and rotationally symmetric problems

In this chapter, we will consider a special and still very important type of problems: Ones that are rotationally symmetric. In quantum theory, one frequently encounters such problems. The most prominent example is the Hydrogen atom, which will also form our most elaborate example at the end of the chapter. We will see that the concept of angular momentum plays an important role, which is why we also start with that.

5.1 Angular momentum

5.1.1 Definition

Let us consider the spatial degree of freedom of particles in $\mathbb{R}^3$. So the position X and the momentum operator P have three components, as usual labeled X_1, X_2, X_3 and P_1, P_2, P_3. We now define the angular momentum operator:

Angular momentum operator: This operator is defined as

$$L = X \times P. \tag{5.1}$$

This is of course exactly the same definition as angular momentum is defined classically. In components, we have

$$L_i = \sum_{j,k} \epsilon_{i,j,k} X_j P_k, \tag{5.2}$$

where ϵ is the completely antisymmetric tensor, with

$$\epsilon_{i,j,k} = \begin{cases} 1 & \text{for even permutations of } (1,2,3), \\ -1 & \text{for odd permutations of } (1,2,3), \\ 0 & \text{otherwise.} \end{cases} \tag{5.3}$$

The angular momentum operator satisfies the following commutation relations:

$$[L_i, L_j] = i\hbar \sum_k \epsilon_{i,j,k} L_k, \tag{5.4}$$

$$[L_i, X_j] = i\hbar \sum_k \epsilon_{i,j,k} X_k, \tag{5.5}$$

$$[L_i, P_j] = i\hbar \sum_k \epsilon_{i,j,k} P_k. \tag{5.6}$$

I hope the overloading of i is not confusing here: In one instance, it is of course an index, in the other the complex unit.

5.1.2 Angular momentum operator as generator of rotations

Let us first discuss that the angular momentum operator is the generator of rotations. This will not be used later, so if this should not be entirely clear, do not worry. Let us denote with $R(n,\theta)$ the rotation operator, one that rotates around the axis defined by $n \in \mathbb{R}^3$ by the angle $\theta \in [0, 2\pi)$. For example if n is the unit vector along the z axis, then, this is just a rotation around the z axis. Such a rotation $R(n,\theta)$ acts as follows

$$|\psi\rangle \mapsto R(n,\theta)|\psi\rangle, \tag{5.7}$$

where $R(n,\theta)|\psi\rangle$ is the rotated state vector. A rotation is now reflected as the following transformation on wave functions,

$$(R(n,\theta)\psi)(x) = \psi(\mathcal{R}(n,\theta)^{-1}x). \tag{5.8}$$

Here, $\mathcal{R}$ is the rotation matrix actually acting in $\mathbb{R}^3$. Is this confusing? I hope not. R is the rotation operator actually acting in the Hilbert space. $\mathcal{R}$ is the rotation operator in $\mathbb{R}^3$. Mathematically, such a construction is called a representation. Intuitively, we turn the coordinates by $\mathcal{R}^{-1}$, and this is reflected by applying R in Hilbert space. Why the inverse? Well, this is actually a matter of definition. It makes a lot of sense for some reasons, but let us for the moment being just call it a convention. The angular momentum operator being the generator of rotations means the following:

Angular momentum as generator of rotations: For every $n \in \mathbb{R}^3$ and every angle $\theta \in [0, 2\pi)$, we have that

$$R(n,\theta) = \exp\left(-\frac{i}{\hbar}\theta n \cdot L\right). \tag{5.9}$$

In just the same way, it should be mentioned, the momentum operator is the generator of translations.

5.1.3 Spectrum of the angular momentum operator

The operator L^2 commutes with each component of L,

$$[L^2, L_j] = 0,\ j = 1, 2, 3. \tag{5.10}$$

The same is true, by the way, for any operator A for which

$$A = R(n,\theta) A R(n,\theta)^\dagger \tag{5.11}$$

for any $n \in \mathbb{R}^3$ and any $\theta \in [0, 2\pi)$, so any rotationally invariant operator. Therefore, the observables L^2 and L_3 are compatible, and they can be simultaneously diagonalized. Why L_3? This is just a convention, any direction would have done the job. Let us be specific and choose this z direction. Let us now identify the eigenvalues of L^2 and L_3. Let us for that purpose define

$$L_\pm = L_1 \pm i L_2. \tag{5.12}$$

These operators have the following properties:

$$\begin{aligned} L_\pm^\dagger &= L_\mp, && (5.13)\\ [L_3, L_\pm] &= i\hbar L_2 \pm L_1 = \pm\hbar L_\pm, && (5.14)\\ [L_+, L_-] &= -2i[L_1, L_2] = 2\hbar L_3, && (5.15)\\ [L^2, L_\pm] &= 0. && (5.16) \end{aligned}$$

It is not difficult to verify all of these commutation relations, use

$$L^2 = \frac{1}{2}(L_+L_- + L_-L_+) + L_3^2. \tag{5.17}$$

Let us denote with $|l, m\rangle$ the normalized eigenvectors of L^2 and L_3: We write

$$\begin{aligned} L^2|l,m\rangle &= \hbar l(l+1)|l,m\rangle, && (5.18)\\ L_3|l,m\rangle &= \hbar m|l,m\rangle, && (5.19) \end{aligned}$$

for reasons that will become clear in a second, where we will also specify what values l and m can take. We find

$$L_3 L_\pm |l,m\rangle \quad = \quad L_\pm L_3 |l,m\rangle \pm \hbar L_\pm |l,m\rangle, \tag{5.20}$$

that is to say,

$$L_3 (L_\pm |l,m\rangle) \quad = \quad \hbar(m \pm 1)\,(L_\pm |l,m\rangle)\,. \tag{5.21}$$

That means that unless $L_\pm |l,m\rangle$ is the zero vector, it is again an eigenvector of L_3, but with eigenvalue $\hbar(m\pm 1)$. What is more

$$L^2 (L_\pm |l,m\rangle) = L_\pm L^2 |l,m\rangle = \hbar^2 l(l+1)(L_\pm |l,m\rangle). \tag{5.22}$$

Therefore, $(L_\pm|l,m\rangle)$ is an eigenvector of L^2 with the same eigenvalue as $|l,m\rangle$.

We can go further than that. Consider the norm

$$\begin{aligned} \|L_\pm |l,m\rangle\|^2 \quad &= \quad \langle l,m| L_\mp L_\pm |l,m\rangle = \langle l,m|(L^2 - L_3^2 \mp \hbar L_3)|l,m\rangle \\ &= \quad \hbar^2 \left(l(l+1) - m^2 \mp m \right). \end{aligned} \tag{5.23}$$

Therefore, we can make use of normalization

$$L_\pm |l,m\rangle = \hbar\sqrt{l(l+1) - m(m\pm 1)}\,|l, m\pm 1\rangle. \tag{5.24}$$

Strictly speaking, the latter relation only follows up to a phase factor $e^{i\phi}$ with $\phi \in [0, 2\pi)$, but we have taken the standard convention where this phase factor vanishes. Since this norm is non-negative, we must have that

$$l(l+1) - m(m\pm 1) \geq 0. \tag{5.25}$$

From this it follows that

$$-l \leq m \leq l. \tag{5.26}$$

We also find that

$$L_+ |l,m\rangle = 0 \tag{5.27}$$

if and only if $m = l$ and

$$L_- |l,m\rangle = 0 \tag{5.28}$$

if and only if $m = -l$. One can recursively hence find all values of m: Starting from $|l,l\rangle$, one finds

$$L_- |l,l\rangle \quad \sim \quad |l, l-1\rangle, \tag{5.29}$$

$$(L_-)^2 |l,l\rangle \quad \sim \quad |l, l-2\rangle, \tag{5.30}$$

and so on. In order to to have this lead to the value $-l$, we have to have a $k \in \mathbb{N}$ such that $l - k = -l$. Hence, $l = k/2$. This argument is actually similar to the one when we algebraically solved the harmonic oscillator.

This is quite interesting. Purely from the algebraic structure, so using the commutation relations, we have found that l can take either the values

$$l = 0, 1, 2, \dots \tag{5.31}$$

or

$$l = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots. \tag{5.32}$$

The values for m are

$$m = -l, -l + 1, \dots, l - 1, l. \tag{5.33}$$

In other words, the following is true:

Spectrum of the angular momentum operator: The two operators L^2 and L_3 commute. Their eigenvectors are denoted as $\{|l, m\rangle\}$. Here, l can be either a positive integer or positive half-integer, with m taking integer-spaced values between $-l$ and l.

5.1.4 Angular momentum operator in the position representation

After all this algebraic beauty, let us get dirty again and compute the angular momentum operator in the position representation. Unsurprisingly, polar coordinates are a useful coordinate system for that. To start with, in the position representation, the angular momentum operator takes the form

$$L = \frac{\hbar}{i} X \times \nabla. \tag{5.34}$$

We remember that the momentum operator in the position representation is given by $(\hbar/i)\nabla$. We remind ourselves of the form of the ∇ differential operator in polar coordinates. This is

$$\nabla = e_r \frac{\partial}{\partial r} + e_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + e_\phi \frac{1}{r \sin\theta} \frac{\partial}{\partial \phi}. \tag{5.35}$$

We therefore get, with the first component being e_r,

$$\begin{aligned} L_1 &= \frac{\hbar}{i} \left(-\sin(\phi) \frac{\partial}{\partial \theta} - \cos(\phi) \mathrm{ctg}(\theta) \frac{\partial}{\partial \phi} \right), && (5.36) \\ L_2 &= \frac{\hbar}{i} \left(\cos(\phi) \frac{\partial}{\partial \theta} - \sin(\phi) \mathrm{ctg}(\theta) \frac{\partial}{\partial \phi} \right), && (5.37) \\ L_3 &= \frac{\hbar}{i} \frac{\partial}{\partial \phi}. && (5.38) \end{aligned}$$

This means that,

$$L_{\pm} = \hbar e^{\pm i\theta}\left(\pm\frac{\partial}{\partial\theta} + i\mathrm{ctg}(\theta)\frac{\partial}{\partial\phi}\right), \tag{5.39}$$

$$L^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right)\right). \tag{5.40}$$

We can hence write the eigenvalue equations as

$$\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right)\psi_{l,m}(\theta,\phi) = -l(l+1)\psi_{l,m}(\theta,\phi), \tag{5.41}$$

$$\frac{\partial}{\partial\phi}\psi_{l,m}(\theta,\phi) = im\psi_{l,m}(\theta,\phi). \tag{5.42}$$

We will write the wave function as

$$\psi_{l,m}(\theta,\phi)=\Phi_m(\phi)\Theta_{l,m}(\theta), \tag{5.43}$$

so that we immediately get

$$\Phi_m(\phi)=e^{im\phi}. \tag{5.44}$$

The continuity of the wave function implies

$$\Phi_m(\phi+2\pi)=\Phi_m(\phi), \tag{5.45}$$

and hence $m\in\mathbb{Z}$ and therefore also $l\in\mathbb{N}$, and again

$$l=0,1,2,\ldots,\quad m=-l,\ldots,l. \tag{5.46}$$

Inserting $\psi_{l,m}=\Phi_m\Theta_{l,m}$ we obtain the differential equation

$$\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}+l(l+1)\right)\Theta_{l,m}(\theta)=0. \tag{5.47}$$

The solutions of this differential equations are "known functions" in mathematical physics. This does not mean much: The fact that these functions are "known" is to my knowledge exactly their emergence in this very context. But if one thinks about it, other "known" functions are not very different in their status, after all. They are called *spherical harmonics*.

Before we discuss their properties, let us finally write out what we have so far,

$$\begin{aligned}\psi_{l,m}(\theta,\phi) &= Y_{l,m}(\theta,\phi)\\ &= (-1)^{(m+|m|)/2}P_{l,|m|}(\cos(\theta))e^{im\phi}\left(\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right)^{1/2}\end{aligned} \tag{5.48}$$

We have here made use of the so-called *associated Legendre functions*. They are defined as

$$P_{l,m}(x)=(1-x^2)^{m/2}\frac{d^m}{dx^m}P_l(x), \tag{5.49}$$

for $m>0$, $x=\cos(\theta)$. Here P_l are the *Legendre polynomials* defined as

$$P_l(x)=\frac{1}{2^l l!}\frac{d^l}{dx^l}. \tag{5.50}$$

These are polynomials of degree l in x and hence $P_{l,m}$ are polynomials of degree $l-m$, multiplied by $\sin^m(x)$. They have $l-m$ zeros in the interval $x \in [-1,1]$. The Legendre polynomials satisfy a recursion relation,

$$(l+1)P_{l+1} = (2l+1)xP_l - lP_{l-1}, \tag{5.51}$$

$$(1-x^2)\frac{d}{dx}P_l = l(P_{l-1} - xP_l). \tag{5.52}$$

Using these recursion relations, one can in fact construct the Legendre polynomials of the lowest orders and, for that matter, also the associated Legendre polynomials (which then define the solution of our problem at hand). The first Legendre polynomials are

$$P_0(x) = 1, \tag{5.53}$$

$$P_1(x) = x, \tag{5.54}$$

$$P_2(x) = \frac{1}{2}(3x^2-1), \tag{5.55}$$

$$P_3(x) = \frac{1}{2}(5x^3-3x). \tag{5.56}$$

The associated Legendre polynomials satisfy the differential equation

$$\left((1-x^2)\frac{d^2}{dx^2} - 2x\frac{d}{dx} + l(l+1) - \frac{m^2}{1-x^2}\right)P_{l,m}(x) = 0. \tag{5.57}$$

One also finds a number of useful relations for the spherical harmonics. One of them already by construction: This is the completeness relation. Why are spherical harmonics orthogonal for different values of m and l? Well, because they are position representations of eigenvectors of different eigenvalues, which are always orthogonal. It is a good sanity check, however, to confirm in the position representation that this really holds true. We find the orthogonality relation

$$\int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\phi Y_{l,m}(\theta,\phi)^* Y_{a,b}(\theta,\phi) = \delta_{l,a}\delta_{m,b}. \tag{5.58}$$

For different values of l and a as well as for different values of m and b, this expression simply vanishes. Again, let us be specific and name a few spherical harmonics:

$$\begin{aligned} Y_{0,0} &= \frac{1}{\sqrt{4\pi}}, && (5.59)\\ Y_{1,0} &= \frac{\sqrt{3}}{\sqrt{4\pi}}\cos(\theta), && (5.60)\\ Y_{1,1} &= -\frac{\sqrt{3}}{\sqrt{8\pi}}\sin(\theta)e^{i\phi}, && (5.61)\\ Y_{2,0} &= \frac{\sqrt{5}}{\sqrt{16\pi}}(3\cos^2(\theta)-1), && (5.62)\\ Y_{2,1} &= -\frac{\sqrt{15}}{\sqrt{8\pi}}\sin(\theta)\cos(\theta)e^{i\phi}, && (5.63)\\ Y_{2,2} &= \frac{\sqrt{15}}{\sqrt{32\pi}}\sin^2(\theta)e^{2i\phi}. && (5.64) \end{aligned}$$

For negative values of m one can make use of the useful relation

$$Y_{l,-m}(\theta,\phi) = (-1)^m Y^*_{l,m}(\theta,\phi). \tag{5.65}$$

The eigenfunctions associated with $l = 0$ are called "s-orbitals", those of $l = 1$ are "p-orbitals", of $l = 2$ "d-orbitals, $l = 3$ "f-orbitals", and so on. We have hence gone a long – and quite painful – way: We have understood the angular dependence of the problem. We now turn to the radial part.

5.2 Rotationally invariant problems

Rotationally invariant problems are those for which the potential merely depends on the distance from the origin. In other words, the Hamiltonian commutes with rotations. Many important problems are of this form. First and foremost, the Hamiltonian of the hydrogen atoms takes this form.

5.2.1 General considerations

We hence consider Hamiltonians of the form, $R = |X|$,

$$H = \frac{P^2}{2m} + V(R). \tag{5.66}$$

We have that

$$L^2 = X^2P^2 - (X\cdot P)^2 + i\hbar X\cdot P. \tag{5.67}$$

To bring the above Hamiltonian into a more convenient form, notice that

$$P^2 = P_R^2 + \frac{L^2}{R^2}, \tag{5.68}$$

with the radial position operator R and the canonically conjugate quantity P_R. This operator P_R takes in the radial position representation the form

$$\frac{\hbar}{i}\left(\frac{\partial}{\partial r}+\frac{1}{r}\right). \tag{5.69}$$

In this form, we can write out the time-independent Schroedinger equation (the eigenvalue equation of the Hamiltonian). This is so important that it gets a box:

Eigenfunctions of the Hamiltonian of a rotationally invariant problem: For $\theta \in [0, \pi)$, $\phi \in [0, 2\pi)$, $r > 0$,

$$\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{1}{2mr^2}L^2+V(r)\right)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi). \tag{5.70}$$

These are the eigenvalue equations in the radial position representation. The time-independent Schroedinger equation of the hydrogen atom is of this form. What is more, we have almost completely solved it already! The only remaining piece is to understand the radial part. We already know the eigenfunctions of L^2, so we make a separation ansatz

$$\psi(r,\theta,\phi)=R(r)Y_{l,m}(\theta,\phi), \tag{5.71}$$

for $R : [0,\infty) \rightarrow \mathbb{C}$. Inserting this into Eq. (5.70), we get

$$\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{1}{2mr^2}l(l+1)+V(r)\right)R(r)=ER(r), \tag{5.72}$$

for $r > 0$.

Let us pause for a moment here. Why can we make this separation ansatz and not lose generality? Since H is invariant under rotations, we have that

$$[H,L]=[H,L^2]=0. \tag{5.73}$$

That is to say, H, L^2 and one component of L are simultaneously diagonalizable.

We have gone a long way, but are not quite there yet. The above equation is merely an equation of a single variable. But it does not have the form of a Schroedinger equation of a particle moving in a potential in one dimension. But this form we can easily achieve. We simply have to substitute

$$R(r)=u(r)/r, \tag{5.74}$$

for a function $u : (0,\infty) \rightarrow \mathbb{C}$. Using

$$\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)R(r)=\left(\frac{1}{r}\frac{\partial}{\partial r}r\right)^2\frac{u}{r}=\frac{1}{r}\frac{\partial^2}{\partial r^2}u, \tag{5.75}$$

we obtain

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right) u(r) = Eu(r). \tag{5.76}$$

This is exactly the form of a time-independent Schroedinger equation of a particle in a potential. The potential is no longer just V, however, but

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{5.77}$$

This is just like in classical physics, where the bare potential is modified by a centrifugal term $\sim 1/r^2$. This means, by the way, that there is not necessarily a bound state. From normalization one finds that V must be of the form

$$V(r) = o\left(\frac{1}{\sqrt{r}}\right), \tag{5.78}$$

in terms of the Landau notation, so V must "decay more rapidly" as $1/\sqrt{r}$ for large r.

5.2.2 Spectrum of the hydrogen atom

There is a lot to say about arbitrary potentials, and it is good to know how this procedure works. Essentially, we have to solve the radial problem separately. We will early on focus on the most important case, however, the one reflecting the potential of the hydrogen atom. To start with, it is more convenient not to think of r as a coordinate, but of

$$\xi = \kappa r, \tag{5.79}$$

with

$$\kappa = \frac{1}{\hbar}\sqrt{-2mE}. \tag{5.80}$$

Then Eq. (5.76) becomes

$$\left(\frac{d^2}{d\xi^2} - \frac{l(l+1)}{\xi^2} - \frac{V(\xi/\kappa)}{|E|} - 1\right) u(\xi) = 0. \tag{5.81}$$

We will now be more specific and concentrate on the Coulomb potential, so the one encountered when considering the motion of a charged electron in the presence of the field of an atomic nucleus. This potential goes like $1/r$, or, more precisely, we have

$$V(r) = -\frac{e_0^2}{r}, \tag{5.82}$$

where e_0 is the elementary unit of charge. We define

$$\xi_0 = \frac{\sqrt{2m}}{\sqrt{|E|}}\frac{e_0^2}{\hbar}, \tag{5.83}$$

then we get

$$\left(\frac{d^2}{d\xi^2}-\frac{l(l+1)}{\xi^2}-\frac{\xi_0}{\xi}-1\right)u(\xi)=0. \tag{5.84}$$

We will now substitute u for a different expression. We are perfectly free to do this, of course. The reason for this particular choice is that it respects the asymptotic behavior of u nicely. We define a new function $w:(0,\infty)\to\mathbb{C}$ as

$$u(\xi)=\xi^{l+1}e^{-\xi}w(\xi). \tag{5.85}$$

With this insertion, we get the differential equation

$$\left(\xi\frac{d^2}{d\xi^2}+2(l+1-\xi)\frac{d}{d\xi}+(\xi_0-2(l+1))\right)w(\xi)=0. \tag{5.86}$$

In the lack of a better idea, we write w as a sum

$$w(\xi)=\sum_{j=0}^{\infty}a_j\xi^j. \tag{5.87}$$

We therefore get

$$\sum_{j=0}^{\infty}a_j\left(j(j+1)\xi^{j-1}+2(l+1)j\xi^{j-1}-2j\xi^j+(\xi_0-2(l+1))\xi^j\right)=0. \tag{5.88}$$

The coefficients of each power of ξ have to vanish, and therefore

$$\left((j+1)j+2(l+1)(j+1)\right)a_{j+1}+\left(-2j+(\xi_0-2(l+1))\right)a_j=0. \tag{5.89}$$

This gives rise to a recursive relation for the coefficients,

$$a_{j+1}=\frac{2(j+l+1)-\xi_0}{(j+1)(j+2l+2)}a_j. \tag{5.90}$$

We can now make a fairly subtle observation. When considering the behavior for large j, we have to have

$$\frac{a_{j+1}}{a_j}\to\frac{2}{j},\ j\to\infty. \tag{5.91}$$

This means that

$$w(\xi)=\Theta(e^{2\xi}), \tag{5.92}$$

again in the Landau notation (it is helpful to familiarize with this notation). In order not to have $u(\xi)\sim e^{\kappa\xi}$ for large ξ, the sum has to be finite. Let us assume that the sum stops after the N-th term, so

$$a_{N+s}=0 \tag{5.93}$$

for $s = 1, 2, \ldots$. Then

$$\xi_0 = 2(N + l + 1), \tag{5.94}$$

$N = 0, 1, 2, \ldots$. n appeared here as a "computational trick" in this argument, but it is in fact a quite profound quantity. N is the "radial quantum number". We are in fact now done. The eigenvalues of the Hamiltonian are given by

$$E = -\frac{2me_0^4}{\xi_0^2 \hbar^2} = -\frac{me_0^4}{2\hbar^2 (n + l + 1)^2}. \tag{5.95}$$

Let us define

$$n = N + l + 1 \tag{5.96}$$

as the "main quantum number", then we get the following values:

Energy values of the hydrogen atom:

$$E_n = -\frac{me_0^4}{2\hbar^2} \frac{1}{n^2}, \; n = 1, 2, \ldots. \tag{5.97}$$

Indeed, the energy values – so the eigenvalues of the Hamiltonian – merely depend on the combination $n = N + l + 1$. For a given value of n, the values

$$l = 0, 1, \ldots, n - 1 \tag{5.98}$$

of the angular momentum quantum number are possible. Taking into account that on top of that, m takes the values

$$m = -l, -l + 1, \ldots, l - 1, l, \tag{5.99}$$

then one finds that the n-th level is

$$\sum_{j=0}^{n-1} (2j + 1) = 2\frac{n(n-1)}{2} + n = n^2 \tag{5.100}$$

fold degenerate. We hence know the spectrum of the Hamiltonian of the hydrogen atom.

5.2.3 Orbitals of the hydrogen atom

Now we are there for all practical purposes. It is still interesting to see how the radial part looks in the position representation. After all, we went through this ordeal also for the angular part of the orbitals. Let us hence get it over with. Unsurprisingly, we start from Eq. (5.86), and set $\xi_0 = 2n$, to get

$$\left(\frac{d^2}{d(2\xi)^2} + \left((2l + 1) + 1 - (2\xi) \frac{d}{d(2\xi)} + ((n + l) - (2l + 1)) \right) \right) w(\xi) = 0. \tag{5.101}$$

This differential equation is the *Laguerre differential equation*. Again this is a "known differential equation", and the solutions are "known". Again, there are Laguerre polynomials and associated Laguerre polynomials. The latter are written as L_a^b with non-negative integers a, b. So the radial solution is given by the following expression:

Radial solution: With $\xi = \kappa r$ and for a constant A,

$$w(\xi) = A L_{n+l}^{2l+1}. \tag{5.102}$$

It follows from properties of these associated Laguerre polynomials that the radial part has $N = n - l - 1$ positive zeros.

This is it! We are now done with the solution of the hydrogen atom, and we can write down all orbitals in the position representation. This is no new material, but rather a summary:

Eigenfunctions of the hydrogen atom: For $n = 0, 1, \dots$, $l = 0, \dots, n-1$, $m = -l, \dots, l$,

$$\begin{aligned} \psi_{n,l,m}(r,\theta,\phi) &= R_{n,l}(r) Y_{l,m}(\theta,\phi), & (5.103)\\ R_{n,l}(r) &= \frac{u(r)}{r} & (5.104)\\ &= \left(\frac{(n-l-1)!(2\kappa)^3}{2n((n+l)!)^3}\right)^{1/2} (2\kappa r)^l e^{-\kappa r} L_{n+l}^{2l+1}(2\kappa r), \end{aligned}$$

with

$$\kappa = \frac{\sqrt{2m|E|}}{\hbar} = \frac{m e_0^2}{\hbar^2 n}. \tag{5.105}$$

Obviously, these eigenfunctions are orthogonal. We can also write

$$\kappa = \frac{1}{na}, \tag{5.106}$$

where a denotes the so-called *Bohr radius*,

$$a = \frac{\hbar^2}{m e_0^2}. \tag{5.107}$$

Note also that the radial part does not depend on m at all. The position representation of these eigenfunctions are the orbitals. The ones for $l = 0$ are rotationally symmetric, the others are not. The "term schemes" known from spectroscopy are simply combinatorical consequences of the above energy levels:

Each difference between two energy eigenvalues gives rise to a line in a spectrum. The corresponding spectral series are called “Lyman series”, “Balmer series”, “Paschen series” and so on. This is today rather of historical importance.