Chapter 6

The 3–dimensional Schrödinger Equation

6.1 Angular Momentum

To study how angular momentum is represented in quantum mechanics we start by re-viewing the classical vector of orbital angular momentum

$$\vec{L} = \vec{x} \times \vec{p},\tag{6.1}$$

or in components

$$L_i = \epsilon_{ijk} \, x_j \, p_k \,.\tag{6.2}$$

To make the transition to quantum mechanics we replace the classical position and momentum variables with their quantum mechanical operator counterparts[1]

$$x_i \rightarrow X_i \equiv \hat{x}_i \equiv x_i \quad , \quad p_i \rightarrow P_i \equiv \hat{p}_i \equiv p_i = -i\hbar \, \nabla_i \,.\tag{6.3}$$

Then the **commutation relations** for angular momentum follow directly

$$[\, L_i \,,\, L_j \,] = i\hbar \, \epsilon_{ijk} \, L_k \tag{6.4}$$

$$[\, L_i \,,\, x_j \,] = i\hbar \, \epsilon_{ijk} \, x_k \tag{6.5}$$

$$[\, L_i \,,\, p_j \,] = i\hbar \, \epsilon_{ijk} \, p_k \,,\tag{6.6}$$

where Eq. (6.4) is known as the *Lie algebra*, in this case of the group $SO(3)$, the rotation group in three dimensions.

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[1]The notations to distinguish between operators and coordinates (or functions) are numerous, often capital letters, e.g. P instead of p, or hats, e.g. $\hat{x}$ instead of x, are used. Some authors however do not make a notational difference at all, but leave the distinction to the context of application. To simplify the notation we will follow this last rule from now on.

Theorem 6.1 *The orbital angular momentum is the generator of rotations in Hilbert space, i.e. $\exists$ unitary operator U, such that*

$$U(\varphi) \;=\; e^{\frac{i}{\hbar}\vec{\varphi}\vec{L}} \;\doteq\; \mathbb{1} \;+\; \tfrac{i}{\hbar}\,\vec{\varphi}\,\vec{L}$$

is generating infinitesimal rotations for small φ.

This means that the unitary operator $U(\varphi)$ rotates a given state vector $\psi(\vec{x})$, which we can easily calculate using our definitions

$$U(\vec{\varphi})\,\psi(\vec{x}) \;=\; \left(\mathbb{1} \,+\, \tfrac{i}{\hbar}\,\vec{\varphi}\,\vec{L} \right)\psi(\vec{x}) \;=\; \left(\mathbb{1} \,+\, \tfrac{i}{\hbar}\,\vec{\varphi}\,(\vec{x}\times\tfrac{\hbar}{i}\vec{\nabla}) \right)\psi(\vec{x})\,. \qquad (6.7)$$

By rearranging the triple product (remember $\vec{a}\cdot(\vec{b}\times\vec{c}) = (\vec{a}\times\vec{b})\cdot\vec{c}$) we then get

$$U(\vec{\varphi})\,\psi(\vec{x}) \;=\; \left(\mathbb{1} \,+\, (\vec{\varphi}\times\vec{x})\,\vec{\nabla} \right)\psi(\vec{x})\,, \qquad (6.8)$$

which basically is the Taylor expansion at the rotated vector $\vec{x}' = \vec{x} + (\vec{\varphi}\times\vec{x})$, visualized in Fig. 6.1

$$U(\vec{\varphi})\,\psi(\vec{x}) \;=\; \psi(\vec{x} + (\vec{\varphi}\times\vec{x})) \;=\; \psi(\vec{x}')\,. \qquad (6.9)$$
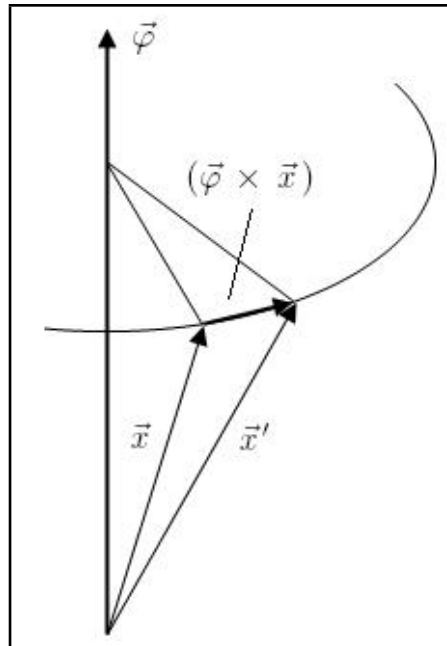

Figure 6.1: Rotation around the axis $\vec{\varphi}$ by an angle $|\vec{\varphi}|$. The vector $\vec{x}$ is rotated into $\vec{x}' = \vec{x} + (\vec{\varphi}\times\vec{x})$ by addition of the vector $(\vec{\varphi}\times\vec{x})$.

Operators in the rotated system: Since we now know how the states themselves are affected by rotations, we need to consider how the operators are changed by such operations. Let us therefore consider some (linear) operator A acting on our state $\psi(\vec{x})$ and then apply a unitary (rotation) operator U

$$A\,\psi(\vec{x}) = \phi(\vec{x}) \quad \rightarrow \quad U\,A\,\psi(\vec{x}) = U\,\phi(\vec{x})\,. \tag{6.10}$$

We already know from Eq. (6.9) how the state vector is rotated. By further using the unitarity property $U^\dagger U = \mathbb{1}$ we get

$$U\,A\,\mathbb{1}\,\psi(\vec{x}) = U\,A\,U^\dagger\,\underbrace{U\,\psi(\vec{x})}_{\psi(\vec{x}')} = U\,\phi(\vec{x}) = \phi(\vec{x}')\,, \tag{6.11}$$

and we can at last define the operator in the rotated system as

$$A' = U\,A\,U^\dagger\,, \tag{6.12}$$

which, by using Theorem 6.1, we can rewrite for infinitesimal rotations as

$$A' \doteq A + \tfrac{i}{\hbar}\,\vec{\varphi}\left[\vec{L}\,,\,A\right]\,. \tag{6.13}$$

Examples: Let us next study two special cases of operators that take on a simple form under rotations.

I) Let A be a scalar, rotation invariant operator, then the commutator with the angular momentum operator vanishes and the operator remains unchanged

$$\left[\vec{L}\,,\,A\right] = 0 \quad \rightarrow \quad A = A'\,. \tag{6.14}$$

Examples for such operators are $\vec{p}\,^2$, $\vec{L}^2$ and H.

II) Let A be a vector-valued operator, then the commutator with the angular momentum operator is given by the commutation relations of Eq. (6.4) - Eq. (6.6) and the operator is rotated exactly like a vector in 3 dimensions, see Fig. 6.1,

$$A_i' = A_i + \tfrac{i}{\hbar}\,\varphi_j\,[L_j\,,\,A_i] = A_i + \tfrac{i}{\hbar}\,\varphi_j\,i\hbar\,\epsilon_{jik}\,A_k = A_i + \epsilon_{ijk}\,\varphi_j\,A_k\,, \tag{6.15}$$

resulting in

$$\vec{A}' = \vec{A} + \vec{\varphi} \times \vec{A}\,. \tag{6.16}$$

Examples for this class of operators are $\vec{L}$, $\vec{x}$ and $\vec{p}$.

6.2   Angular Momentum Eigenvalues

Studying again the **Lie algebra of the rotation group SO(3)**

$$[L_i, L_j] = i\hbar \, \epsilon_{ijk} \, L_k, \tag{6.17}$$

we can conclude that different components of the angular momentum operator, e.g. L_x and L_y, do not commute with each other, i.e. they are incompatible. By remembering the general uncertainty relation for operators A and B from Theorem 2.4, we can immediately deduce the uncertainty relation for angular momentum

$$\Delta L_\mathrm{x} \cdot \Delta L_\mathrm{y} \geq \tfrac{\hbar}{2} |\langle L_\mathrm{z} \rangle|. \tag{6.18}$$

In the context of an experiment this translates to the statement that different components of angular momentum observables can not be measured "simultaneously". In a theoretical framework this is expressed in the fact that these operators do not have common eigenfunctions.

We therefore need to find operators, that do have common eigenfunctions, i.e. which commute with each other. This requirement is fulfilled for $\vec{L}^2$ and any angular momentum component L_i, since

$$\left[\vec{L}^2, L_i \right] = 0 \quad \text{where} \quad i = 1, 2, 3. \tag{6.19}$$

The next task will be to find the eigenfunctions and eigenvalues of $\vec{L}^2$ and one of the components, w.l.o.g. L_z. We start with the ansatz

$$\vec{L}^2 f = \lambda f \quad, \quad L_\mathrm{z} f = \mu f, \tag{6.20}$$

and use the technique of ladder operators which we define as:

Definition 6.1   *The angular momentum **ladder operators** $L_\pm$ are defined by*

$$L_\pm := L_\mathrm{x} \pm i \, L_\mathrm{y}$$

where L_+ *is called the raising operator, and*
                 L_- *is called the lowering operator.*

With this definition and help of Eq. (6.17) one can easily rewrite the **Lie algebra of the angular momentum operators**

$$[L_\mathrm{z}, L_\pm] = \pm \hbar L_\pm \tag{6.21}$$

$$[\vec{L}^2, L_\pm] = 0 \tag{6.22}$$

$$[L_+, L_-] = 2\hbar L_\mathrm{z}. \tag{6.23}$$

Lemma 6.1   *If f is an eigenfunction of $\vec{L}^2$ and L_z then the function $L_\pm f$ is as well.*

Proof: We do the proof in two steps, first proving that $L_\pm f$ is an eigenfunction of $\vec{L}^2$ followed by the proof to be an eigenfunction of L_z :

$$\vec{L}^2 \, L_\pm \, f \ \overset{\text{Eq. (6.22)}}{=} \ L_\pm \, \vec{L}^2 \, f \ = \ \lambda \, L_\pm \, f \, , \tag{6.24}$$

$$\begin{aligned}
L_z \, L_\pm \, f \ &= \ L_z \, L_\pm \, f \ - \ L_\pm \, L_z \, f \ + \ L_\pm \, L_z \, f \ = \\
&= \ [\, L_z \, , \, L_\pm \,]\, f \ + \ L_\pm \, L_z \, f \ \overset{\text{Eq. (6.21)}}{=} \\
&= \ (\mu \pm \hbar)\, L_\pm \, f \, . \quad \text{q.e.d}
\end{aligned} \tag{6.25}$$

We see that $L_\pm f$ is an eigenfunction of L_z with eigenvalue $(\mu \pm \hbar)$. Thus, starting from some eigenvalue μ the ladder operators "switch" between all possible eigenvalues of L_z, "climbing" or "descending" the eigenvalue ladder of L_+ and L_- respectively. Since the eigenvalue λ of $\vec{L}^2$ is the same for all the eigenfunctions produced by the action of the ladder operators we know that for a given value λ of $\vec{L}^2$ the z-component L_z must be bounded by the square root of λ. Thus there exists some function f_{top}, corresponding to the highest possible value of L_z, such that

$$L_+ \, f_{\text{top}} \ = \ 0 \, . \tag{6.26}$$

Let us further assume the eigenvalue of L_z at f_{top} is $\hbar l$. We then have

$$L_z \, f_{\text{top}} \ = \ \hbar l \, f_{\text{top}} \ , \quad \vec{L}^2 \, f_{\text{top}} \ = \ \lambda \, f_{\text{top}} \, . \tag{6.27}$$

Before continuing we will establish an equality which will be useful in the following calculations

$$\begin{aligned}
L_\pm \, L_\mp \ &= \ (L_x \pm i\, L_y)(L_x \mp i\, L_y) \ = \ L_x^2 + L_y^2 \mp i \, \underbrace{[\, L_x \, , \, L_y \,]}_{i\hbar L_z} \ = \\
&= \ \underbrace{L_x^2 + L_y^2 + L_z^2}_{\vec{L}^2} - L_z^2 \pm \hbar \, L_z \\
\Rightarrow \ \vec{L}^2 \ &= \ L_\pm \, L_\mp \ + \ L_z^2 \mp \hbar \, L_z \, .
\end{aligned} \tag{6.28}$$

We can then use Eq. (6.28) to calculate the eigenvalue of $\vec{L}^2$ in terms of the z-component eigenvalue $\hbar l$

$$\vec{L}^2 \, f_{\text{top}} \ = \ (\, L_- \, L_+ \ + \ L_z^2 \ + \ \hbar \, L_z)\, f_{\text{top}} \ = \ \hbar^2 \, l(l+1)\, f_{\text{top}} \, , \tag{6.29}$$

where we used Eq. (6.26) and the left part of Eq. (6.27). Therefore we conclude that the angular momentum eigenvalue λ is given by

$$\lambda \ = \ \hbar^2 \, l(l+1) \, , \tag{6.30}$$

where $\hbar l$ is the highest possible value of L_z .

Before we analyze this result, let us do the analogue computation for the eigenfunction f_{bottom}, corresponding to the lowest possible eigenvalue of L_z (for a fixed value of λ), which we assume to be $\hbar \bar{l}$. Then the eigenvalue equations are

$$L_z\, f_{\text{bottom}} \;=\; \hbar \bar{l}\, f_{\text{bottom}} \quad , \quad \vec{L}^2\, f_{\text{bottom}} \;=\; \lambda\, f_{\text{bottom}} \,. \tag{6.31}$$

Using again Eq. (6.28) we apply $\vec{L}^2$ to f_{bottom}

$$\vec{L}^2\, f_{\text{bottom}} \;=\; (\, L_+\, L_- \,+\, L_z^2 \,-\, \hbar\, L_z)\, f_{\text{bottom}} \;=\; \hbar^2\, \bar{l}(\bar{l} - 1)\, f_{\text{bottom}} \,. \tag{6.32}$$

Since $\lambda = \hbar^2\, \bar{l}(\bar{l} - 1)$ we can equate this to the result of Eq. (6.30), which requires

$$\bar{l} \;=\; -\, l. \tag{6.33}$$

Result:　　The eigenvalues of L_z take on values between $-\hbar l$ and $+\hbar l$ in steps that are integer multiples of $\hbar$. Thus there is some integer N counting the steps from $-l$ to l such that

$$l \;=\; -l + N \quad \Leftrightarrow \quad l \;=\; \tfrac{N}{2} \,, \tag{6.34}$$

which implies for l to be either one of the integer values $0, 1, 2, \cdots$, or one of the half-integer values $\tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}, \cdots$. The number l appearing in the angular momentum eigenvalue equation (see Eq. (6.30)) is called the **azimuthal quantum number**. In order not to confuse it with the possible eigenvalues for the angular momentum z-component, one denotes the eigenvalue of L_z by $\mu = \hbar m$, where

$$m \;=\; -l, -l + 1, \cdots, 0, \cdots, l - 1, +l \tag{6.35}$$

is called the **magnetic quantum number**. For a given l there are $(2l + 1)$ values for m such that $|m| \le l$.

The eigenfunctions f turn out to be the so-called *spherical harmonics* Y_{lm}, where the index pair labels the corresponding eigenvalues of the angular momentum observables. Restating the eigenvalue equations in terms of the spherical harmonics we have

$$\vec{L}^2 Y_{lm} \;=\; \hbar^2\, l(l + 1)\, Y_{lm} \tag{6.36}$$

$$L_z Y_{lm} \;=\; \hbar\, m\, Y_{lm} \tag{6.37}$$

$$L_\pm Y_{lm} \;=\; \hbar\, \sqrt{l(l + 1) - m\,(m \pm 1))}\, Y_{l,m\pm 1} \,, \tag{6.38}$$

where the eigenvalue of $L_\pm$ is obtained from the normalization condition.

Remark:　　If the system is in an eigenstate of L_z then the observables L_x and L_y have in general an uncertainty and the uncertainty relation can be easily computed since the expectation value of L_z is equal to its eigenvalue $\hbar m$

$$\Delta L_x \cdot \Delta L_y \;\ge\; \tfrac{\hbar}{2} \,|\langle\, L_z \,\rangle| \;=\; \tfrac{\hbar^2}{2}\, m \,. \tag{6.39}$$

6.3   Angular Momentum Eigenfunctions

In order to calculate the spherical harmonics, we will rewrite the angular momentum observable $\vec{L}$ in terms of spherical coordinates, see Fig. 6.2 ,

$$
\begin{aligned}
x &= r \sin \theta \cos \varphi \\
y &= r \sin \theta \sin \varphi \\
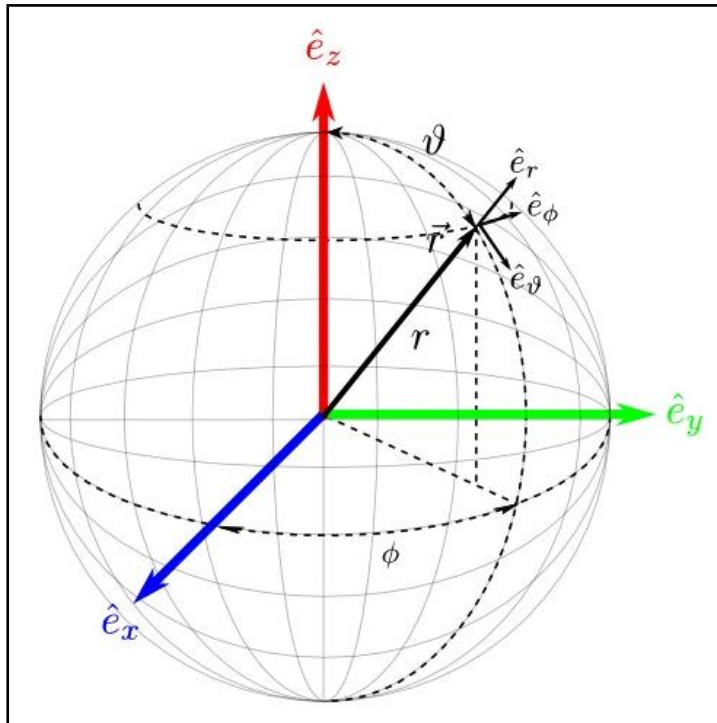z &= r \cos \theta \, .
\end{aligned}
\tag{6.40}
$$

Figure 6.2: Spherical coordinates: figure from:
http://de.wikipedia.org/w/index.php?title=Bild:Kugelkoordinaten_svg.png

To this end we will need to transform the nabla-operator

$$
\vec{\nabla} = \vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z}
\tag{6.41}
$$

by transforming its components, the partial derivatives, as well as the basis vectors $\vec{e}_i$ into spherical coordinates. The partial derivatives are easily transformed using

$$
\frac{\partial}{\partial x^i} = \frac{\partial y^j}{\partial x^i} \frac{\partial}{\partial y^j} \, ,
\tag{6.42}
$$

so that we have

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi} =$$

$$= \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{1}{r}\cos \theta \cos \varphi \frac{\partial}{\partial \theta} - \frac{1}{r}\frac{\sin \varphi}{\sin \theta}\frac{\partial}{\partial \varphi} \tag{6.43}$$

$$\frac{\partial}{\partial y} = \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{1}{r}\cos \theta \sin \varphi \frac{\partial}{\partial \theta} + \frac{1}{r}\frac{\cos \varphi}{\sin \theta}\frac{\partial}{\partial \varphi} \tag{6.44}$$

$$\frac{\partial}{\partial z} = \cos \theta \frac{\partial}{\partial r} - \frac{1}{r}\sin \theta \frac{\partial}{\partial \theta} \ . \tag{6.45}$$

For the transformation of the basis vectors, one first calculates the basis $\{\vec{e}_i'\}$ of the new coordinate system with respect to the old basis $\{\vec{e}_j\}$, e.g. $\vec{e}_1' = \vec{e}_r$,

$$\vec{e}_r = \left| \frac{\partial x^i}{\partial r} \right|^{-1} \vec{e}_j \frac{\partial x^j}{\partial r} = \frac{\vec{e}_x \frac{\partial x}{\partial r} + \vec{e}_y \frac{\partial y}{\partial r} + \vec{e}_z \frac{\partial z}{\partial r}}{\sqrt{(\frac{\partial x}{\partial r})^2 + (\frac{\partial y}{\partial r})^2 + (\frac{\partial z}{\partial r})^2}} \ , \tag{6.46}$$

and for the basis vectors of the spherical coordinate system with respect to the cartesian basis we get

$$\vec{e}_r = \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix} \quad , \quad \vec{e}_\theta = \begin{pmatrix} \cos \theta \cos \varphi \\ \cos \theta \sin \varphi \\ \sin \theta \end{pmatrix} \quad , \quad \vec{e}_\varphi = \begin{pmatrix} -\sin \varphi \\ \cos \varphi \\ 0 \end{pmatrix} \ . \tag{6.47}$$

From above expressions we can easily compute the cartesian basis vectors with respect to the basis of the spherical coordinate system, yielding

$$\vec{e}_x = \begin{pmatrix} \sin \theta \cos \varphi \\ \cos \theta \cos \varphi \\ -\sin \varphi \end{pmatrix} \quad , \quad \vec{e}_y = \begin{pmatrix} \sin \theta \sin \varphi \\ \cos \theta \sin \varphi \\ \cos \varphi \end{pmatrix} \quad , \quad \vec{e}_z = \begin{pmatrix} \cos \theta \\ -\sin \theta \\ 0 \end{pmatrix} \ . \tag{6.48}$$

Eqs. (6.43) - (6.45) together with Eq. (6.48) are then inserted into our definition of the nabla-operator (Eq. (6.41)) to finally find

$$\vec{\nabla} = \vec{e}_r \frac{\partial}{\partial r} + \vec{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \vec{e}_\varphi \frac{1}{r \sin \theta}\frac{\partial}{\partial \varphi} \ . \tag{6.49}$$

We now want to calculate the angular momentum operator components with respect to the cartesian basis, i.e. L_x, L_y and L_z, in terms of spherical coordinates. We recall that the angular momentum operator is defined as

$$\vec{L} = \vec{x} \times \vec{p} = \frac{\hbar}{i}\vec{x} \times \vec{\nabla} \ , \tag{6.50}$$

we use Eq. (6.49) and the cartesian representation of the r, θ, φ basis vectors (Eq. (6.47)), and additionally, by comparing Eq. (6.40) and the r-basis vector we note that the position

vector $\vec{x}$ can be written as $\vec{x} = r\,\vec{e}_r$. Finally[2] we find

$$L_x = \frac{\hbar}{i}\left(-\sin\varphi\,\frac{\partial}{\partial\theta} - \cos\varphi\,\cot\theta\,\frac{\partial}{\partial\varphi}\right) \tag{6.51}$$

$$L_y = \frac{\hbar}{i}\left(\cos\varphi\,\frac{\partial}{\partial\theta} - \sin\varphi\,\cot\theta\,\frac{\partial}{\partial\varphi}\right) \tag{6.52}$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\,. \tag{6.53}$$

For the ladder operators (Definition 6.1) follows then in spherical coordinates

$$L_\pm = \hbar\,e^{\pm i\varphi}\left(\pm\frac{\partial}{\partial\theta} + i\,\cot\theta\,\frac{\partial}{\partial\varphi}\right)\,, \tag{6.54}$$

for the angular momentum squared

$$\vec{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\,, \tag{6.55}$$

and for the eigenvalue equations (Eq. (6.36) and Eq. (6.37))

$$\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)Y_{lm} = -l(l+1)\,Y_{lm} \tag{6.56}$$

$$\frac{\partial}{\partial\varphi}Y_{lm} = i\,m\,Y_{lm}\,. \tag{6.57}$$

In order to solve this partial differential equations we use a **separation ansatz**, the same method as in Section 4.1, Eq. (4.2),

$$Y_{lm}\left(\theta,\varphi\right) = P(\theta)\,\Phi(\varphi)\,. \tag{6.58}$$

Inserting this ansatz into Eq. (6.57) we immediately find

$$\Phi(\varphi) = e^{i\,m\,\varphi}\,. \tag{6.59}$$

Furthermore, from the continuity of the wave function we conclude that $\Phi(\varphi + 2\pi) = \Phi(\varphi)$, which restricts the magnetic quantum number m (and thus also l) to be an integer number (eliminating the possibility for half-integer numbers), i.e.,

$$l = 0, 1, 2, \cdots \tag{6.60}$$

$$m = -l, -l+1, \cdots, 0, \cdots, l-1, +l\,. \tag{6.61}$$

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[2]We could have obtained this result much faster by just transforming the partial derivatives and expressing $\vec{x}$ by r, θ and φ, but we wanted to explicitly present the apparatus of spherical coordinates, especially the form of the nabla operator and how one can calculate it.

Thus the spherical harmonics we want to calculate from Eq. (6.56) are of the form

$$\Rightarrow \quad Y_{lm}(\theta, \varphi) = e^{im\varphi} P(\theta) . \tag{6.62}$$

Inserting expression (6.62) into Eq. (6.56) we get

$$\left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} - \frac{m^2}{\sin^2\theta} + l(l+1) \right) P(\theta) = 0 , \tag{6.63}$$

and with a change of variables

$$\xi = \cos\theta \quad \Rightarrow \quad \frac{\partial}{\partial\theta} = \frac{\partial\xi}{\partial\theta} \frac{\partial}{\partial\xi} = -\sin\theta \frac{\partial}{\partial\xi} , \tag{6.64}$$

Eq. (6.63) thereupon becomes

$$\left(\left(1 - \xi^2\right) \frac{d^2}{d\xi^2} - 2\xi \frac{d}{d\xi} + l(l+1) - \frac{m^2}{1-\xi^2} \right) P_{lm}(\xi) = 0 , \tag{6.65}$$

which is the **general Legendre equation**. It is solved by the *associated Legendre functions*, also called associated Legendre polynomials[3], which can be calculated from the (ordinary) Legendre polynomials P_l via the formula

$$P_{lm}(\xi) = \left(1 - \xi^2\right)^{\frac{m}{2}} \frac{d^m}{d\xi^m} P_l . \tag{6.66}$$

The Legendre polynomials P_l, on the other hand, can be calculated from **Rodrigues'**
formula

$$P_l(\xi) = \frac{1}{2^l \, l!} \frac{d^l}{d\xi^l} \left(\xi^2 - 1\right)^l . \tag{6.67}$$

For $m = 0$ the associated functions are just the Legendre polynomials themselves. The P_l are polynomials of the order l, while the P_{lm} are of order $(l-m)$ in ξ, multiplied with a factor $\sqrt{(1-\xi^2)^m} = \sin^m\theta$, and have $(l-m)$ roots in the interval $(-1,1)$. To give an impression about their form we will write down some examples for (associated) Legendre polynomials

$$P_0 = 1 , \quad P_1 = \cos\theta , \quad P_2 = \tfrac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$P_{1,0} = \cos\theta , \quad P_{1,1} = \sin\theta . \tag{6.68}$$

For the normalized (to 1) spherical harmonics in terms of θ and φ we then find the following expression

$$Y_{lm}(\theta, \varphi) = (-1)^{\frac{1}{2}(m+|m|)} \left[\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{\frac{1}{2}} e^{im\varphi} P_{l|m|}(\cos\theta) . \tag{6.69}$$

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[3]Technically, they are only polynomials if m is even, but the term became accustomed and is also used for odd values of m.

These are the eigenfunctions of $\vec{L}^2$ and L_z, which satisfy

$$Y_{l,-m} = (-1)^m Y_{lm}^*, \tag{6.70}$$

as well as

$$Y_{l0}(\theta, \varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta). \tag{6.71}$$

Some examples for spherical harmonics are

$$Y_{00} = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}, \quad Y_{10} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta, \quad Y_{1\pm1} = \mp\left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta\, e^{\pm i\varphi}. \tag{6.72}$$

The spherical harmonics as well as the (associated) Legendre polynomials form orthogonal[4] systems; the (associated) Legendre polynomials on the interval $[-1, +1]$ and the spherical harmonics on the unit sphere. This means that all (square integrable) functions can be expanded in terms of these special functions in the respective regions. The orthogonality relations are written as

$$\int_{4\pi} d\Omega\, Y_{lm}^*(\theta, \varphi)\, Y_{l'm'}(\theta, \varphi) = \delta_{ll'}\,\delta_{mm'}, \tag{6.73}$$

where the integration is carried out over the unit sphere, which is denoted by the value 4π of the full solid angle Ω, see also Eq. (6.91), and

$$\int_{-1}^{+1} d\xi\, P_{lm}(\xi)\, P_{l'm}(\xi) = \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!}\delta_{ll'}. \tag{6.74}$$

This last equation reduces to the orthogonality relation for the Legendre polynomials if we set $m = 0$

$$\int_{-1}^{+1} d\xi\, P_l(\xi)\, P_{l'}(\xi) = \frac{2}{2l+1}\delta_{ll'}. \tag{6.75}$$

The spherical harmonics additionally form a complete system with completeness relation

$$\sum_{m=-l}^{+l}\sum_{l=0}^{\infty} Y_{lm}^*(\theta, \varphi)\, Y_{lm}(\theta', \varphi') = \frac{1}{\sin\theta}\delta(\theta - \theta')\,\delta(\varphi - \varphi'). \tag{6.76}$$

6.4 The 3–dimensional Schrödinger Equation

With the knowledge about the (orbital) angular momentum operator $\vec{L}$ from the previous sections we now want to solve the time-independent Schrödinger equation in 3 dimensions for a potential V, which only depends on r, i.e. $V = V(r)$,

$$\left(-\frac{\hbar^2}{2m}\Delta + V(r)\right)\psi(\vec{x}) = E\,\psi(\vec{x}). \tag{6.77}$$

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[4]The spherical harmonics are also complete and normalized to one.

The operator Δ is the Laplacian (or Laplace-operator)

$$\Delta = \vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} , \tag{6.78}$$

which we transform into spherical coordinates by inserting Eqs. (6.43) - (6.45) into expression (6.78) and differentiating according to Leibniz's law. This leads us to

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} . \tag{6.79}$$

Comparing expression (6.79) to the squared angular momentum operator in spherical coordinates (Eq. (6.55)), we recognize that we can rewrite the kinetic part of the Hamiltonian of Eq. (6.77) as

$$- \frac{\hbar^2}{2m} \Delta = - \frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\vec{L}^2}{2mr^2} . \tag{6.80}$$

The Schrödinger equation is then of the form

$$\left(- \frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\vec{L}^2}{2mr^2} + V(r) \right) \psi(\vec{x}) = E \psi(\vec{x}) , \tag{6.81}$$

which we solve by a separation ansatz into a function only depending on the radius r, the so called *radial wave function* $R(r)$, and a function comprising of the angle- dependencies of the wave function

$$\psi(r, \theta, \varphi) = R(r) \, Y_{lm}(\theta, \varphi) . \tag{6.82}$$

Since the spherical harmonics are eigenfunctions of the squared angular momentum operator, see Eq. (6.36), we can rewrite the Schrödinger equation as an equation just for its radial component $R(r)$

$$\left(- \frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2 \, l(l+1)}{2mr^2} + V(r) \right) R_l(r) = E \, R_l(r) . \tag{6.83}$$

This equation does still depend on the azimuthal quantum number l therefore we assign a corresponding label to the radial wave function. To simplify the equation we follow three simple steps, the first one is to rewrite the differential operator on the left side

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} . \tag{6.84}$$

Next we replace the function $R(r)$ by the so-called **reduced wave function** $u(r)$, which is defined by:

Definition 6.2   *The **reduced wave function** $u_l(r)$ is given by*

$$u_l := r \, R_l(r) .$$

Differentiating the reduced wave function we get

$$u' \;=\; (r\,R)' \;=\; R \,+\, r\,R' \tag{6.85}$$

$$u'' \;=\; 2\,R' \,+\, r\,R'' \tag{6.86}$$

$$\frac{u''}{r} \;=\; R'' \,+\, \frac{2}{r}\,R' \,. \tag{6.87}$$

Comparing this result to the one of Eq. (6.84) the Schrödinger equation (6.83), when multiplied by r can be reformulated for the reduced wave function

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2\, l\,(l+1)}{2mr^2} + V(r) \right) u_l(r) \;=\; E\,u_l(r) \,. \tag{6.88}$$

The third step is to define an effective potential $V_{\text{eff.}}(r)$ to bring the equation to a more appealing form.

Definition 6.3　　*The **effective Potential** $V_{\text{eff.}}(r)$ is given by*

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

The Schrödinger equation in 3 dimensions, a second order partial differential equation, has thus become a 1–dimensional ordinary differential equation for the reduced wave function, which is of the same form as the one-dimensional Schrödinger equation, except from the term $\hbar^2\, l\,(l+1)/2mr^2$ in the effective potential. This additional term is a repulsive potential, called *centrifugal term*, in analogy to the classical (pseudo) force

$$u_l''(r) \,+\, \frac{2m}{\hbar^2}\,(E_l - V_{\text{eff.}}(r))\,u_l(r) \;=\; 0 \,. \tag{6.89}$$

Normalization:　　Let us now study how the normalization condition of the total wave function influences the current situation. We can write the normalization condition as

$$\int_{4\pi} d\Omega \int_0^\infty dr\, r^2\, |\psi(r,\theta,\varphi)|^2 \;=\; 1 \,, \tag{6.90}$$

where again the integration over the whole solid angle has to be understood as

$$\int_{4\pi} d\Omega \;=\; \int_0^{2\pi} d\varphi \int_0^\pi d\theta\, \sin\theta \,. \tag{6.91}$$

Because the spherical harmonics are normalized, see Eq. (6.73), we can easily transform our normalization condition to

$$\int_0^\infty dr\, r^2\, |R_l(r)|^2 \;=\; 1\;, \tag{6.92}$$

which translates to the reduced wave function as

$$\int_0^\infty dr\, |u_l(r)|^2 \;=\; 1\;. \tag{6.93}$$

The normalizability of the radial wave function $R(r) = \frac{u(r)}{r}$ restricts it to be bounded at the origin, which subsequently requires the reduced wave function to vanish at the origin

$$u_l(r = 0) \;=\; 0\;. \tag{6.94}$$

This constraint imposes the character of an odd function, sketched in Fig. 6.3, on the reduced wave function. The ground state of the 3–dimensional problem thus corresponds to the first excited state of the 1–dimensional problem, and is therefore not available for potentials of arbitrary strength, as already mentioned in Section 4.5.1 (see also Fig. 4.5 and the corresponding remark).
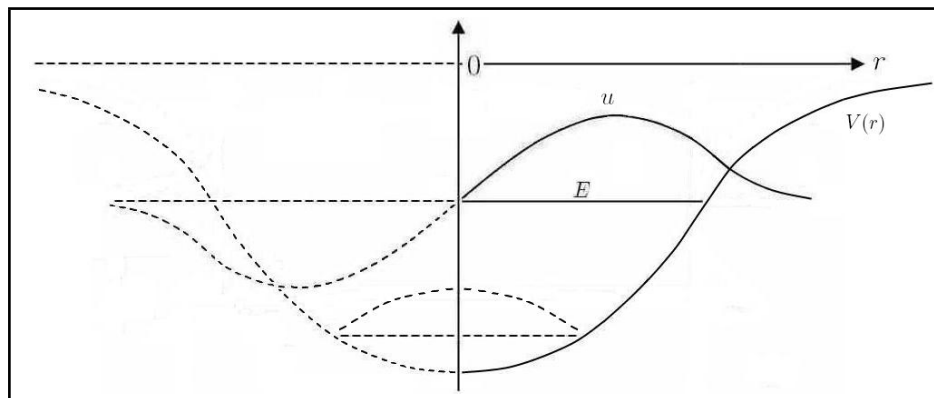

Figure 6.3: Bound states in 3 dimensions: The 3–dim. problem can be reduced to a 1–dim problem in r, but the reduced wave function u of the ground state then is an odd function, which does not allow for a bound state for arbitrarily weak potentials $V(r)$.

> **Theorem 6.2**   *In a 3–dimensional problem, the potential must exhibit a minimal strength for the ground state to exist. (without proof)*

Furthermore, if there is no ground state for azimuthal quantum number $l = 0$, then there won't be a ground state (in this problem) for any other $l \neq 0$ either.

6.5 Coulomb Potential and H–Atom

We now want to use the three–dimensional Schrödinger equation to calculate the energy levels of the simplest atomic system, the hydrogen atom, consisting only of an electron of mass m_e and a proton, which is considered as infinitely massive in this approximation (though to introduce a reduced mass would be straightforward). Furthermore, the spin of the particles is not considered. In order to proceed we simply insert for the attraction of the electron the **Coulomb potential** into the term $V(r)$

$$V(r) = -\frac{q^2}{4\pi\epsilon_0 r} = -\frac{e^2}{r} \ . \tag{6.95}$$

We then introduce constants that are typical characteristics of such a system to further simplify and analyze the problem at hand. The first of which will be the *fine structure constant* α

$$\alpha = \frac{e^2}{\hbar c} = \frac{q^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} \ . \tag{6.96}$$

The fine structure constant is a fundamental constant, whose numerical value does not depend on the choice of units, and which therefore can be displayed in numerous ways, e.g. in units of $\hbar = c = 1$, $\alpha = \frac{q^2}{4\pi\epsilon_0}$ and thus the Coulomb potential is $V(r) = -\alpha/r$. This is also the reason for its many different physical interpretations, the most common of which is as the coupling constant of the electromagnetic interaction, i.e. the strength at which photons couple to the electric charge. Another interpretation, relevant for our calculations, is that the fine structure constant can be seen as the ratio of the typical electron velocity in a bound state of the hydrogen atom to the speed of light. Viewing it that way, the smallness of α gives us the justification for neglecting effects predicted by the theory of special relativity.

The characteristic length unit of the hydrogen atom is the *Bohr radius* r_B

$$r_B = \frac{\hbar^2}{m_e e^2} = \frac{1}{\alpha}\frac{\hbar}{m_e c} = \frac{1}{\alpha}\lambda_C \approx 0,53\,\mathring{A}\ , \tag{6.97}$$

where λ_C is the Compton wavelength of the electron. Finally, we can construct a constant with dimension of energy out of the constants already used

$$E_I = \frac{m_e e^4}{2\hbar^2} = \tfrac{1}{2}\,m_e c^2 \alpha^2 \approx 13,6\,eV\ , \tag{6.98}$$

which is the *ionization energy* of the hydrogen atom. With this knowledge we now easily reformulate the Schrödinger equation in terms of dimensionless variables

$$\rho = \frac{r}{r_B}\ , \quad \epsilon = -\frac{E}{E_I}\ , \tag{6.99}$$

which yields the equation

$$\left(\frac{1}{\rho} \frac{d^2}{d\rho^2} \rho - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \epsilon \right) R_l(\rho) = 0 \ . \tag{6.100}$$

This differential equation can be solved by the ansatz

$$R_l(\rho) = e^{-\sqrt{\epsilon}\rho} \rho^{l+1} Q_{n',l}(\rho) \ . \tag{6.101}$$

It will provide us an equation for the yet unknown functions $Q_{n',l}(\rho)$, which we express as a power series. The series has to terminate at a finite degree for reasons of normalizability, resulting such in a polynomial of degree n', the *radial quantum number*. These polynomials are called the associated Laguerre polynomials. The normalizable solutions (Eq. (6.101)) correspond to particular values of ϵ

$$\epsilon = \frac{1}{(n'+l+1)^2} = \frac{1}{n^2} \ . \tag{6.102}$$

By changing the notation to a new label n, the *principal quantum number*, we find that ϵ_n is an eigenvalue for all radial equations where $l < n$. We thus find that the solutions of the 3–dimensional Schrödinger equation are labeled by three integer quantum numbers: n, l and m, such that

$$n = 1, 2, \cdots \quad , \quad l = 0, 1, \cdots, n-1 \quad , \quad m = -l, \cdots, +l \ . \tag{6.103}$$

The energy solutions depend only[5] on the principal quantum number

$$E_n = -\epsilon \, E_I = -\frac{E_I}{n^2} \ , \tag{6.104}$$

which, by reinserting our constant from Eq. (6.98), provides the so called *Bohr formula*

$$E_n = -\frac{m_e \, e^4}{2\hbar^2 n^2} \ . \tag{6.105}$$

To every energy level correspond different values of angular momentum, the degeneracy in terms of the principal quantum number is

$$\sum_{l=0}^{n-1} (2l+1) = n^2 \ , \tag{6.106}$$

since for a given n there are $(n-1)$ possible values of l, each one allows for $(2l+1)$ different values of m. Finally, the solutions of the Schrödinger equation can be written in terms of the characteristic constants of our problem and the quantum numbers as

$$\psi_{n,l,m}(r, \theta, \varphi) = Y_{lm}(\theta, \varphi) e^{-r/n r_B} \left(\frac{r}{r_B} \right)^l Q_{n-l-1}(\frac{r}{r_B}) \ . \tag{6.107}$$

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[5]This is, of course, only true in our approximation, where we neglected any special relativistic influences and spin.

Remark I: The fact that there is degeneracy with respect to the angular momentum is an interesting property of the $1/r$ potential. It hints at an additional symmetry other than the rotational invariance. This symmetry also has a counterpart in the classical theory, where it is the Lenz vector that is a constant of motion in this kind of potential.

Remark II: The treatment of the hydrogen atom has been totally nonrelativistic in this section. When we use the correct relativistic description, such as the relativistic energy–momentum relation and the spin, we find an additional splitting of the now degenerate levels. Such effects include the 2 possible spin levels for each set of quantum numbers n, l and m, as well as interactions of the magnetic moment, caused by the motion of the electron, which are called spin-orbit-interactions and that lead to the *fine structure* of the hydrogen atom. When we furthermore include the interaction of the electron with the spin of the proton, we get the so-called *hyperfine structure*. All these effects can be better understood in terms of the Dirac equation, which is the relativistic counterpart of the Schrödinger equation, though they can be treated with perturbative methods to get satisfying results (see Chapter 8). With such perturbative methods we can also treat the influences of exterior fields which cause the Zeeman–effect for magnetic and the Stark–effect for electric fields.