Introduction to Quantum Physics

Rainer F. Hauser
rainer.hauser@gmail.com

January 17, 2025

Abstract

The video channel with the title "Professor M does Science" in YouTube offers a simple step-by-step but all the same very valuable and rigorous introduction into the world of quantum physics. This script covers the angular momentum and helps to digest the topic covered by a group of those videos but is not meant as a replacement for them.

4 Angular Momentum and Central Potentials

4.1 Angular Momentum

Angular momentum is a key concept in classical mechanics and in quantum mechanics. It is needed to describe the motion of particles in central potentials such as the hydrogen atom, but also the spin of a particle is a type of angular momentum.

In classical mechanics the angular momentum $\underline{L}$ is defined by $\underline{L} = \underline{x} \times \underline{p}$ where $\underline{x} = (x_1, x_2, x_3)$ is the position of the moving point mass from a reference point and $\underline{p}$ is the momentum of the point mass. In quantum mechanics angular momentum $\hat{\underline{L}} = (\hat{L}_1, \hat{L}_2, \hat{L}_3)$ is defined as

$$\hat{L}_1 = \hat{x}_2\hat{p}_3 - \hat{x}_3\hat{p}_2 \qquad \hat{L}_2 = \hat{x}_3\hat{p}_1 - \hat{x}_1\hat{p}_3 \qquad \hat{L}_3 = \hat{x}_1\hat{p}_2 - \hat{x}_2\hat{p}_1$$

using the usual quantization rules. The components of $\hat{\underline{L}}$ are Hermitian as

$$\hat{L}_1^\dagger = (\hat{x}_2\hat{p}_3 - \hat{x}_3\hat{p}_2)^\dagger = (\hat{x}_2\hat{p}_3)^\dagger - (\hat{x}_3\hat{p}_2)^\dagger = \hat{p}_3^\dagger\hat{x}_2^\dagger - \hat{p}_2^\dagger\hat{x}_3^\dagger = \hat{p}_3\hat{x}_2 - \hat{p}_2\hat{x}_3 = \hat{x}_2\hat{p}_3 - \hat{x}_3\hat{p}_2 = \hat{L}_1$$

shows just for one of the components using $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$ plus the facts that $\hat{x}_j$ and $\hat{p}_k$ are Hermitian and commute for $j \neq k$.

The commutation relations for the components of $\hat{\underline{L}}$ are

$$\begin{aligned}
\big[\hat{L}_1, \hat{L}_2\big] &= \big[\hat{x}_2\hat{p}_3 - \hat{x}_3\hat{p}_2, \hat{x}_3\hat{p}_1 - \hat{x}_1\hat{p}_3\big] = \big[\hat{x}_2\hat{p}_3, \hat{x}_3\hat{p}_1\big] - \big[\hat{x}_2\hat{p}_3, \hat{x}_1\hat{p}_3\big] - \big[\hat{x}_3\hat{p}_2, \hat{x}_3\hat{p}_1\big] + \big[\hat{x}_3\hat{p}_2, \hat{x}_1\hat{p}_3\big] \\
&= \big[\hat{x}_2\hat{p}_3, \hat{x}_3\hat{p}_1\big] + \big[\hat{x}_3\hat{p}_2, \hat{x}_1\hat{p}_3\big] = \hat{x}_3\big[\hat{x}_2\hat{p}_3, \hat{p}_1\big] + \big[\hat{x}_2\hat{p}_3, \hat{x}_3\big]\hat{p}_1 + \hat{x}_1\big[\hat{x}_3\hat{p}_2, \hat{p}_3\big] + \big[\hat{x}_3\hat{p}_2, \hat{x}_1\big]\hat{p}_3 \\
&= \big[\hat{x}_2\hat{p}_3, \hat{x}_3\big]\hat{p}_1 + \hat{x}_1\big[\hat{x}_3\hat{p}_2, \hat{p}_3\big] = \hat{x}_2\big[\hat{p}_3, \hat{x}_3\big]\hat{p}_1 + \big[\hat{x}_2, \hat{x}_3\big]\hat{p}_3\hat{p}_1 + \hat{x}_1\hat{x}_3\big[\hat{p}_2, \hat{p}_3\big] + \hat{x}_1\big[\hat{x}_3, \hat{p}_3\big]\hat{p}_2 \\
&= \hat{x}_2\big[\hat{p}_3, \hat{x}_3\big]\hat{p}_1 + \hat{x}_1\big[\hat{x}_3, \hat{p}_3\big]\hat{p}_2 = \hat{x}_2(-i\hbar)\hat{p}_1 + \hat{x}_1(i\hbar)\hat{p}_2 = i\hbar(\hat{x}_1\hat{p}_2 - \hat{x}_2\hat{p}_1) = i\hbar\,\hat{L}_3
\end{aligned}$$

using $[\hat{x}_j, \hat{x}_k] = [\hat{p}_j, \hat{p}_k] = 0$, $[\hat{x}_j, \hat{p}_k] = i\hbar\,\delta_{jk}$ and $[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}$. Thus, the commutation relations for the components of angular momentum are

$$\big[\hat{L}_1, \hat{L}_2\big] = i\hbar\,\hat{L}_3 \qquad \big[\hat{L}_2, \hat{L}_3\big] = i\hbar\,\hat{L}_1 \qquad \big[\hat{L}_3, \hat{L}_1\big] = i\hbar\,\hat{L}_2$$

or in a more compact form

$$\big[\hat{L}_j, \hat{L}_k\big] = i\hbar\sum_\ell \varepsilon_{jk\ell}\,\hat{L}_\ell \qquad \big[\hat{L}_j, \hat{L}_k\big] = i\hbar\,\varepsilon_{jk\ell}\,\hat{L}_\ell \tag{4.1}$$

using the Levi-Civita symbol $\varepsilon_{jk\ell}$ defined as $\varepsilon_{123} = \varepsilon_{231} = \varepsilon_{312} = 1$, $\varepsilon_{132} = \varepsilon_{213} = \varepsilon_{321} = -1$ and $\varepsilon_{jk\ell} = 0$ if two or three indices are equal. The left form is with explicit summation and the right form uses Einstein's summation convention.

Commutation relations allow to work with quantities in an abstract manner. In quantum mechanics there is an observable called spin that obeys the exact same commutation relations but has no classical counterpart. The spin can be understood in similar terms, and it is also called an angular momentum. Thus, one defines a general angular momentum $\underline{\hat{J}} = (\hat{J}_1, \hat{J}_2, \hat{J}_3)$ in quantum mechanics that obeys the commutation relations $\left[\hat{J}_j, \hat{J}_k\right] = i\hbar\,\varepsilon_{jk\ell}\,\hat{J}_\ell$. This includes the so-called orbital angular momentum $\underline{\hat{L}}$ as well as the spin angular momentum denoted by $\underline{\hat{S}}$.

As angular momentum has three components one can assign a magnitude $\underline{\hat{J}}^2$. It is defined as

$$\underline{\hat{J}}^2 = \hat{J}_1^2 + \hat{J}_2^2 + \hat{J}_3^2$$

and it is an observable because with $(\underline{\hat{J}}^2)^\dagger = \underline{\hat{J}}^2$ it is Hermitian. Its commutator with a component of the angular momentum is

$$\begin{aligned}\left[\underline{\hat{J}}^2, \hat{J}_1\right] &= \left[\hat{J}_1^2, \hat{J}_1\right] + \left[\hat{J}_2^2, \hat{J}_1\right] + \left[\hat{J}_3^2, \hat{J}_1\right] = \left[\hat{J}_2^2, \hat{J}_1\right] + \left[\hat{J}_3^2, \hat{J}_1\right] \\ &= \hat{J}_2\left[\hat{J}_2, \hat{J}_1\right] + \left[\hat{J}_2, \hat{J}_1\right]\hat{J}_2 + \hat{J}_3\left[\hat{J}_3, \hat{J}_1\right] + \left[\hat{J}_3, \hat{J}_1\right]\hat{J}_3 \\ &= \hat{J}_2(-i\hbar\hat{J}_3) + (-i\hbar\hat{J}_3)\hat{J}_2 + \hat{J}_3(i\hbar\hat{J}_2) + (i\hbar\hat{J}_2)\hat{J}_3 = 0\end{aligned}$$

shown just for the first one.

Because $[\hat{J}_j, \hat{J}_k] \neq 0$ for $j \neq k$ two different components of the angular momentum have no common set of eigenstates, cannot be measured simultaneously and are subject to an uncertainty principle. Other than the case of $[\hat{x}, \hat{p}] \neq 0$ where two different observables cannot be measured simultaneously here two components of the same physical quantity cannot be measured simultaneously.

4.2 Ladder Operators in Angular Momentum

Ladder operators – as the name suggests – allow to change angular momentum by a discrete amount such that one can go up and down a ladder. Similar operators exist for the quantum harmonic oscillator and quantum fields. Because $[\underline{\hat{J}}^2, \hat{J}_j] = 0$ these two operators form a set of commuting operators where $\hat{J}_j = \hat{J}_3$ is usually chosen by convention. One can describe the physical observables of angular momentum through the two operators $\underline{\hat{J}}^2$ and $\hat{J}_3$.

The ladder operators are defined using $\hat{J}_1$ and $\hat{J}_2$. The raising operator is $\hat{J}_+ = \hat{J}_1 + i\,\hat{J}_2$, and the lowering operator is $\hat{J}_- = \hat{J}_1 - i\,\hat{J}_2$. They are both not Hermitian and are therefore no observables. Actually, these two operators are each others adjoint such that $\hat{J}_+^\dagger = \hat{J}_-$ and $\hat{J}_-^\dagger = \hat{J}_+$ as

$$\hat{J}_+^\dagger = \left(\hat{J}_1 + i\,\hat{J}_2\right)^\dagger = \hat{J}_1^\dagger - i\,\hat{J}_2^\dagger = \hat{J}_1 - i\,\hat{J}_2 = \hat{J}_- \qquad \hat{J}_-^\dagger = \left(\hat{J}_1 - i\,\hat{J}_2\right)^\dagger = \hat{J}_1^\dagger + i\,\hat{J}_2^\dagger = \hat{J}_1 + i\,\hat{J}_2 = \hat{J}_+$$

proves.

Using these two newly defined operators $\hat{J}_+$ and $\hat{J}_-$ one can derive

$$\begin{aligned}\hat{J}_+\,\hat{J}_- &= \left(\hat{J}_1 + i\,\hat{J}_2\right)\left(\hat{J}_1 - i\,\hat{J}_2\right) = \hat{J}_1^2 + \hat{J}_2^2 + i\hat{J}_2\hat{J}_1 - i\hat{J}_1\hat{J}_2 = \hat{J}_1^2 + \hat{J}_2^2 - i\left[\hat{J}_1, \hat{J}_2\right] \\ &= \hat{J}_1^2 + \hat{J}_2^2 + \hbar\hat{J}_3 = \underline{\hat{J}}^2 - \hat{J}_3^2 + \hbar\hat{J}_3 \\ \hat{J}_-\,\hat{J}_+ &= \left(\hat{J}_1 - i\,\hat{J}_2\right)\left(\hat{J}_1 + i\,\hat{J}_2\right) = \underline{\hat{J}}^2 - \hat{J}_3^2 - \hbar\hat{J}_3\end{aligned}$$

and gets

$$\underline{\hat{J}}^2 = \frac{1}{2}\left(\hat{J}_+\,\hat{J}_- + \hat{J}_-\,\hat{J}_+\right) + \hat{J}_3^2$$

as an alternative definition for $\hat{\underline{J}}^2 = \hat{J}_1^2 + \hat{J}_2^2 + \hat{J}_3^2$. The commutation relations for the four operators $\hat{\underline{J}}^2$, $\hat{J}_3$ and $\hat{J}_\pm$ are

$$\big[\hat{\underline{J}}^2, \hat{J}_\pm\big] = 0 \qquad \big[\hat{J}_3, \hat{J}_+\big] = \hbar\,\hat{J}_+ \qquad \big[\hat{J}_3, \hat{J}_-\big] = -\hbar\,\hat{J}_- \qquad \big[\hat{J}_+, \hat{J}_-\big] = 2\hbar\,\hat{J}_3$$

and can be easily checked.

The eigenvalue equations are

$$\hat{\underline{J}}^2\,|\lambda,\mu\rangle = \lambda\,|\lambda,\mu\rangle \qquad\qquad \hat{J}_3\,|\lambda,\mu\rangle = \mu\,|\lambda,\mu\rangle$$

for the two compatible observables $\hat{\underline{J}}^2$ and $\hat{J}_3$. Because of the commutation relations one knows that if $|\lambda,\mu\rangle$ is an eigenstate of $\hat{\underline{J}}^2$ also $\hat{J}_\pm\,|\lambda,\mu\rangle$ is an eigenstate of $\hat{\underline{J}}^2$ as

$$\hat{\underline{J}}^2\big(\hat{J}_\pm\,|\lambda,\mu\rangle\big) = \hat{J}_\pm\big(\hat{\underline{J}}^2\,|\lambda,\mu\rangle\big) = \lambda\big(\hat{J}_\pm\,|\lambda,\mu\rangle\big)$$

proves, and that if $|\lambda,\mu\rangle$ is an eigenstate of $\hat{J}_3$ also $\hat{J}_+\,|\lambda,\mu\rangle$ is an eigenstate of $\hat{J}_3$ as

$$\hat{J}_3\big(\hat{J}_+\,|\lambda,\mu\rangle\big) = \hat{J}_+\hat{J}_3\,|\lambda,\mu\rangle + \hbar\hat{J}_+\,|\lambda,\mu\rangle = \mu\hat{J}_+\,|\lambda,\mu\rangle + \hbar\hat{J}_+\,|\lambda,\mu\rangle = (\mu+\hbar)\big(\hat{J}_+\,|\lambda,\mu\rangle\big)$$

shows using $[\hat{J}_3, \hat{J}_+] = \hbar\,\hat{J}_+ \Rightarrow \hat{J}_3\hat{J}_+ = \hat{J}_+\hat{J}_3 + \hbar\hat{J}_+$. Similarly, for $\hat{J}_-$ gives

$$\hat{J}_3\big(\hat{J}_+\,|\lambda,\mu\rangle\big) = (\mu+\hbar)\big(\hat{J}_+\,|\lambda,\mu\rangle\big) \qquad\qquad \hat{J}_3\big(\hat{J}_-\,|\lambda,\mu\rangle\big) = (\mu-\hbar)\big(\hat{J}_-\,|\lambda,\mu\rangle\big)$$

and this shows that $\hat{J}_\pm\,|\lambda,\mu\rangle$ are eigenstates of $\hat{J}_3$ but with eigenvalues $\mu \pm \hbar$.

To summarize, $\hat{J}_\pm\,|\lambda,\mu\rangle$ is an eigenstate of $\hat{\underline{J}}^2$ with eigenvalue λ and an eigenstate of $\hat{J}_3$ with eigenvalue $\mu \pm \hbar$ such that the action of $\hat{J}_\pm$ on an eigenstate $|\lambda,\mu\rangle$ can be written as

$$\hat{J}_+\,|\lambda,\mu\rangle = N_+\,|\lambda,\mu+\hbar\rangle \qquad\qquad \hat{J}_-\,|\lambda,\mu\rangle = N_-\,|\lambda,\mu-\hbar\rangle$$

and shows why $\hat{J}_+$ and $\hat{J}_-$ are called a raising and lowering operator, respectively. Because multiple applications of the raising or lowering operators allows to go up and down similarly to a ladder these operators are called ladder operators. With the norm

$$\begin{aligned}\Big\|\hat{J}_+\,|\lambda,\mu\rangle\Big\|^2 &= \langle\lambda,\mu|\hat{J}_+^\dagger\,\hat{J}_+|\lambda,\mu\rangle = \langle\lambda,\mu|\hat{J}_-\,\hat{J}_+|\lambda,\mu\rangle = \langle\lambda,\mu|\hat{\underline{J}}^2|\lambda,\mu\rangle - \langle\lambda,\mu|\hat{J}_3^2|\lambda,\mu\rangle - \langle\lambda,\mu|\hbar\hat{J}_3|\lambda,\mu\rangle \\ &= (\lambda - \mu^2 - \mu\hbar)\,\langle\lambda,\mu|\lambda,\mu\rangle = \lambda - \mu^2 - \mu\hbar = |N_+|^2\end{aligned}$$

using $\hat{J}_-\,\hat{J}_+ = \hat{\underline{J}}^2 - \hat{J}_3^2 - \hbar\hat{J}_3$ and similarly for $\Big\|\hat{J}_-\,|\lambda,\mu\rangle\Big\|^2$ one gets

$$\hat{J}_+\,|\lambda,\mu\rangle = \sqrt{\lambda - \mu^2 - \mu\hbar}\,|\lambda,\mu+\hbar\rangle \qquad\qquad \hat{J}_-\,|\lambda,\mu\rangle = \sqrt{\lambda - \mu^2 + \mu\hbar}\,|\lambda,\mu-\hbar\rangle \tag{4.2}$$

with the calculated factors $N_\pm = \sqrt{\lambda - \mu^2 \mp \mu\hbar}$.

4.3 Eigenvalue Equation for the Angular Momentum Operators

The eigenvalues λ for $\hat{\underline{J}}^2$ satisfying $\hat{\underline{J}}^2\,|\lambda,\mu\rangle = \lambda\,|\lambda,\mu\rangle$ are positive or zero because

$$\begin{aligned}\langle\psi|\hat{\underline{J}}^2|\psi\rangle &= \langle\psi|\hat{J}_1^2|\psi\rangle + \langle\psi|\hat{J}_2^2|\psi\rangle + \langle\psi|\hat{J}_3^2|\psi\rangle = \langle\psi|\hat{J}_1^\dagger\hat{J}_1|\psi\rangle + \langle\psi|\hat{J}_2^\dagger\hat{J}_2|\psi\rangle + \langle\psi|\hat{J}_3^\dagger\hat{J}_3|\psi\rangle \\ &= \Big\|\hat{J}_1\,|\psi\rangle\Big\|^2 + \Big\|\hat{J}_2\,|\psi\rangle\Big\|^2 + \Big\|\hat{J}_3\,|\psi\rangle\Big\|^2 \geq 0\end{aligned}$$

and this especially means $\langle\lambda,\mu|\hat{\underline{J}}^2|\lambda,\mu\rangle = \lambda\,\langle\lambda,\mu|\lambda,\mu\rangle \geq 0$ proving $\lambda \geq 0$ since eigenstates are normalized. Further using

$$\begin{aligned}&\hat{\underline{J}}^2 - \hat{J}_3^2 = \frac{1}{2}\big(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\big) = \frac{1}{2}\big(\hat{J}_-^\dagger\hat{J}_- + \hat{J}_+^\dagger\hat{J}_+\big) \\ &\langle\lambda,\mu|\frac{1}{2}\big(\hat{J}_-^\dagger\hat{J}_- + \hat{J}_+^\dagger\hat{J}_+\big)|\lambda,\mu\rangle = \frac{1}{2}\big(\,\langle\lambda,\mu|\hat{J}_-^\dagger\hat{J}_-|\lambda,\mu\rangle + \langle\lambda,\mu|\hat{J}_+^\dagger\hat{J}_+|\lambda,\mu\rangle\,\big) \\ &= \frac{1}{2}\left(\Big\|\hat{J}_-\,|\lambda,\mu\rangle\Big\|^2 + \Big\|\hat{J}_+\,|\lambda,\mu\rangle\Big\|^2\right) \geq 0\end{aligned}$$

and

$$\langle\lambda,\mu|\hat{\underline{J}}^2 - \hat{J}_3^2|\lambda,\mu\rangle = \langle\lambda,\mu|\hat{\underline{J}}^2|\lambda,\mu\rangle - \langle\lambda,\mu|\hat{J}_3^2|\lambda,\mu\rangle = (\lambda-\mu^2)\,\langle\lambda,\mu|\lambda,\mu\rangle \geq 0$$

proves that $\mu^2 \leq \lambda$. Combined these two results show $\lambda \geq \mu^2 \geq 0$.

The raising operator $\hat{J}_+$ acts as $\hat{J}_+\,|\lambda,\mu\rangle = \sqrt{\lambda-\mu^2-\mu\hbar}\,|\lambda,\mu+\hbar\rangle$ on $|\lambda,\mu\rangle$ according to (4.2), and λ and μ must satisfy $-\sqrt{\lambda} \leq \mu \leq +\sqrt{\lambda}$ because of $\mu^2 \leq \lambda$. If one takes an arbitrary value μ between $-\sqrt{\lambda}$ and $+\sqrt{\lambda}$ one can apply $\hat{J}_+$ until $\mu > \sqrt{\lambda} - \hbar$. If one applies $\hat{J}_+$ one jumps over $\sqrt{\lambda}$, and this is not allowed. Thus, $\mu \leq \sqrt{\lambda}$ implies that μ has a maximum value $\mu_{\max}$ and the additional rule

$$\lambda = \mu^2 + \mu\hbar \Rightarrow \hat{J}_+\,|\lambda,\mu\rangle = 0$$

ensures that the state is killed and the ladder terminates. There is a maximum value to be reached and this must be the μ for which $\mu_{\max}^2 + \mu_{\max}\hbar = \lambda$ must hold. Applying $(\hat{J}_+)^p$ to $|\lambda,\mu\rangle$ must give $|\lambda,\mu+p\hbar\rangle = |\lambda,\mu_{\max}\rangle$ for some integer p. Further, the eigenvalues must be quantized because the lowering operator leads from $|\lambda,\mu_{\max}\rangle$ to $|\lambda,\mu_{\max}-\hbar\rangle$ and so on. Similarly, there must be a $\mu_{\min}$. The two conditions

$$\mu_{\max}^2 + \mu_{\max}\hbar = \lambda \qquad\qquad \mu_{\min}^2 - \mu_{\min}\hbar = \lambda$$

lead to $\mu_{\max}^2 + \mu_{\max}\hbar = \mu_{\min}^2 - \mu_{\min}\hbar$ and $\mu_{\min} = -\mu_{\max}$. Because from any μ one must reach $\mu_{\max}$ and $\mu_{\min}$ in integer steps of $\hbar$, $\mu_{\max} = \mu_{\min} + n\hbar$ for an integer n. From $\mu_{\max} = \mu_{\min} + n\hbar = -\mu_{\min} + n\hbar$ follows $\mu_{\min} = -\frac{n}{2}\hbar$ and $\mu_{\max} = +\frac{n}{2}\hbar$ and

$$\lambda = \mu_{\max}^2 + \mu_{\max}\hbar = \left(\frac{n}{2}\hbar\right)^2 + \frac{n}{2}\hbar^2 = \frac{n}{2}\left(\frac{n}{2}+1\right)\hbar^2$$

such that λ and μ can only assume values

$$\lambda = \frac{n}{2}\left(\frac{n}{2}+1\right)\hbar^2 \qquad\qquad \mu = -\frac{n}{2}\hbar, \left(-\frac{n}{2}+1\right), \left(-\frac{n}{2}+2\right), ..., \left(\frac{n}{2}-1\right), \frac{n}{2}\hbar$$

for $n = 0, 1, 2, ...$ where μ can assume $n+1$ values. Calling $j = \frac{n}{2}$ as usual in quantum mechanics then j can assume values $j = 0, \frac{1}{2}, 1, \frac{3}{2}, ...$ in steps of $\frac{1}{2}$. Thus, λ has values $\lambda = j(j+1)\hbar^2$ and μ has values $\mu = m\hbar$ where $m = -j, -j+1, ..., j-1, j$. Thus, the angular momentum eigenvalue equation can be written as

$$\hat{\underline{J}}^2\,|j,m\rangle = j(j+1)\hbar^2\,|j,m\rangle \qquad\qquad \hat{J}_3\,|j,m\rangle = m\hbar\,|j,m\rangle$$

with m one of the $2j+1$ values $-j, -j+1, ..., j-1, j$, and the action of the raising and lowering operators can be written as

$$\hat{J}_+\,|j,m\rangle = \hbar\sqrt{j(j+1)-m(m+1)}\,|j,m+1\rangle \quad \hat{J}_-\,|j,m\rangle = \hbar\sqrt{j(j+1)-m(m-1)}\,|j,m-1\rangle \quad (4.3)$$

using the quantum numbers j and m.

The two versions of the Planck constant $h = 6.62607015 \cdot 10^{-34}\,\mathrm{J\,s}$ and $\hbar = \frac{h}{2\pi}$ have units of angular momentum. Thus, the eigenvalues $\lambda = j(j+1)\hbar^2$ and $\mu = m\hbar$ of $\hat{J}_3$ are both consistent in terms of units. Some values for the eigenvalues and eigenvectors:

j	$j(j+1)\hbar^2$	m	$m\hbar$	$\lvert j,m\rangle$
0	0	0	0	$\lvert 0,0\rangle$
$\frac{1}{2}$	$\frac{3}{4}\hbar^2$	$-\frac{1}{2}$	$-\frac{1}{2}\hbar$	$\lvert\frac{1}{2},-\frac{1}{2}\rangle$
		$+\frac{1}{2}$	$+\frac{1}{2}\hbar$	$\lvert\frac{1}{2},+\frac{1}{2}\rangle$
1	$2\hbar^2$	-1	$-h$	$\lvert 1,-1\rangle$
		0	0	$\lvert 1,0\rangle$
		$+1$	$+h$	$\lvert 1,+1\rangle$

Conventions for the different types of angular momentum use $\hat{\underline{J}}$, j, m for general angular momentum, $\hat{\underline{L}}$, ℓ, m_ℓ for orbital angular momentum, and $\hat{\underline{S}}$, s, m_s for spin angular momentum. If it is clear from the context then m can be used instead of m_ℓ and m_s. Mathematically allowed values for j are $0, \frac{1}{2}, 1, \frac{3}{2}, ...$ theoretically. However, for orbital angular momentum only integer values for ℓ are possible, but for spin orbital angular momentum s can assume integer or half-integer values.

4.4 Orbital Angular Momentum

In classical physics angular momentum is the rotational equivalent of linear momentum and it is therefore found everywhere in systems with rotational motion. The corresponding quantity in quantum mechanics is orbital angular momentum and it is found in many system such as in the hydrogen atom.

Orbital angular momentum $\underline{\hat{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ is defined as

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \qquad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \qquad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

in quantum mechanics. Since orbital angular momentum describes motion in the three-dimensional space the most useful representation for it is in the position representation. Position and momentum operators are

$$\underline{\hat{r}} = (\hat{x}, \hat{y}, \hat{z}) = (x, y, z) \qquad \underline{\hat{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

in this representation and this means that

$$\hat{L}_x = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \qquad \hat{L}_y = -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \qquad \hat{L}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$

are the components of the orbital angular momentum operator in the position representation.

Often, however, these operators are needed in spherical coordinates (r, ϑ, φ) where r is the distance of the point from the origin, ϑ is the angle of the vector with the z-axis called the polar angle, and φ is the angle of the vector with the x-axis when projected into the xy-plane called the azimuthal angle. Spherical coordinates are restricted to $r \in [0, \infty)$, $\vartheta \in [0, \pi]$, $\varphi \in [0, 2\pi)$, and the mathematical relations between Cartesian and spherical coordinates are

$$x = r\,\sin\vartheta\,\cos\varphi \qquad y = r\,\sin\vartheta\,\sin\varphi \qquad z = r\,\cos\vartheta$$

$$r = \sqrt{x^2 + y^2 + z^2} \qquad \vartheta = \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}} \right) \qquad \varphi = \tan^{-1}\left(\frac{y}{x} \right)$$

in both directions. Note that here the so-called physics conventions are used while the mathematicians usually use conventions where ϑ and φ are exchanged.

To demonstrate how operators in quantum mechanics look like in spherical coordinates only the z-component of orbital angular momentum in position representation is shown. In $\hat{L}_z$ the factors x and y can simply be replaced but the derivatives become

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \vartheta}{\partial y}\frac{\partial}{\partial \vartheta} + \frac{\partial \varphi}{\partial y}\frac{\partial}{\partial \varphi}$$

using the chain rule. One can use

$$r^2 = (x^2 + y^2 + z^2) \quad \overset{\frac{\partial}{\partial y}}{\Rightarrow} \quad 2r\frac{\partial}{\partial r} = 2y \qquad \frac{\partial r}{\partial y} = \frac{y}{r} = \frac{r\,\sin\vartheta\,\sin\varphi}{r} = \sin\vartheta\,\sin\varphi$$

for the first term. Similarly, one can use

$$\cos\vartheta = \frac{z}{r} \quad \overset{\frac{\partial}{\partial y}}{\Rightarrow} \quad -\sin\vartheta\frac{\partial \vartheta}{\partial y} = z\frac{\partial}{\partial y}\left(\frac{1}{r}\right) \qquad \frac{\partial \vartheta}{\partial y} = \frac{z\,y}{r^3\sin\vartheta} = \frac{r\,\cos\vartheta\,r\,\sin\vartheta\,\sin\varphi}{r^3\,\sin\vartheta} = \frac{\cos\vartheta\,\sin\varphi}{r}$$

with

$$\frac{\partial}{\partial y}\left(\frac{1}{r}\right) = \frac{\partial}{\partial y}\left((x^2 + y^2 + z^2)^{-1/2}\right) = -\frac{1}{2}(x^2 + y^2 + z^2)^{-3/2}\,2y = -\frac{y}{r^3}$$

for the second term. Finally, one can use

$$\tan\varphi = \frac{y}{x} \qquad \overset{\frac{\partial}{\partial y}}{\Rightarrow} \qquad \frac{1}{\cos^2\varphi}\frac{\partial \varphi}{\partial y} = \frac{1}{x} \qquad \frac{\partial \varphi}{\partial y} = \frac{\cos^2\varphi}{x} = \frac{\cos^2\varphi}{r\,\sin\vartheta\,\cos\varphi} = \frac{\cos\varphi}{r\,\sin\vartheta}$$

for the third term. Putting this together gives

$$\frac{\partial}{\partial y} = \sin\vartheta\,\sin\varphi\,\frac{\partial}{\partial r} + \frac{\cos\vartheta\,\sin\varphi}{r}\,\frac{\partial}{\partial\vartheta} + \frac{\cos\varphi}{r\,\sin\vartheta}\,\frac{\partial}{\partial\varphi}$$
$$\frac{\partial}{\partial x} = \sin\vartheta\,\cos\varphi\,\frac{\partial}{\partial r} + \frac{\cos\vartheta\,\cos\varphi}{r}\,\frac{\partial}{\partial\vartheta} - \frac{\sin\varphi}{r\,\sin\vartheta}\,\frac{\partial}{\partial\varphi}$$

after a similar calculation for $\frac{\partial}{\partial x}$. Inserting $x = r\,\sin\vartheta\,\cos\varphi$ and $y = r\,\sin\vartheta\,\sin\varphi$ into $\hat{L}_z$ together with these result into $\hat{L}_z$ gives a very simple expression for $\hat{L}_z$ because many terms cancel. The results for all relevant orbital angular moment operators in spherical coordinates are

$$\hat{L}_x = i\hbar\left(\sin\varphi\,\frac{\partial}{\partial\vartheta} + \frac{\cos\varphi}{\tan\vartheta}\,\frac{\partial}{\partial\varphi}\right) \qquad \hat{L}_y = i\hbar\left(-\cos\varphi\,\frac{\partial}{\partial\vartheta} + \frac{\sin\varphi}{\tan\vartheta}\,\frac{\partial}{\partial\varphi}\right) \qquad \hat{L}_z = -i\hbar\,\frac{\partial}{\partial\varphi}$$

and

$$\underline{\hat{J}}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\vartheta^2} + \frac{1}{\tan\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)$$
$$\hat{L}_+ = \hbar\,e^{i\,\varphi}\left(\frac{\partial}{\partial\vartheta} + \frac{i}{\tan\vartheta}\,\frac{\partial}{\partial\varphi}\right) \qquad \hat{L}_- = \hbar\,e^{-i\,\varphi}\left(-\frac{\partial}{\partial\vartheta} + \frac{i}{\tan\vartheta}\,\frac{\partial}{\partial\varphi}\right)$$

listed without the derivation of these results.

4.5 Eigenvalues and Eigenfunctions of Orbital Angular Momentum

As shown above $\underline{\hat{J}}^2$ and $\hat{J}_3$ form a compatible set of observables, and the eigenvalue equations for the general angular momentum operators are

$$\underline{\hat{J}}^2\,|j,m\rangle = j(j+1)\hbar^2\,|j,m\rangle \qquad \hat{J}_3\,|j,m\rangle = m\hbar\,|j,m\rangle$$

with $j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, ...$ and $m = -j, -j+1, ..., j-1, j$. For orbital angular momentum these equations are written as

$$\underline{\hat{L}}^2\,|\ell,m\rangle = \ell(\ell+1)\hbar^2\,|\ell,m\rangle \qquad \hat{L}_z\,|\ell,m\rangle = m\hbar\,|\ell,m\rangle$$

with the wave functions $\langle\underline{r}|\ell,m\rangle = \psi_{\ell m}(x,y,z) = \psi_{\ell m}(r,\vartheta,\varphi)$ of the system. The eigenvalue equations

$$-\hbar^2\left(\frac{\partial^2}{\partial\vartheta^2} + \frac{1}{\tan\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)\psi_{\ell m}(r,\vartheta,\varphi) = \ell(\ell+1)\hbar^2\,\psi_{\ell m}(r,\vartheta,\varphi)$$
$$-i\hbar\,\frac{\partial}{\partial\varphi}\,\psi_{\ell m}(r,\vartheta,\varphi) = m\hbar\,\psi_{\ell m}(r,\vartheta,\varphi)$$

in spherical coordinates are written in terms of the so-called eigenfunction $\psi_{\ell m}(r,\vartheta,\varphi)$. Therefore the goal is to solve these two differential equations to determine the eigenvalues and eigenfunctions, and as one sees they only depend on ϑ and φ such that one can set $\psi_{\ell m}(r,\vartheta,\varphi) = f(r)\,Y_\ell^m(\vartheta,\varphi)$. The above two differential equations only determine $Y_\ell^m(\vartheta,\varphi)$ but not $f(r)$ such that $\underline{\hat{L}}^2$ and $\hat{L}_z$ build a set of commuting observables but not a complete set of commuting observables. This only becomes an issue when solving specific problems such as the hydrogen atom where the Hamiltonian is the additional observable.

To determine the allowed eigenvalues for the orbital angular momentum only the equation for $\hat{L}_z$ with $\frac{\partial}{\partial\varphi}$ is needed and one can $Y_\ell^m(\vartheta,\varphi) = F_\ell^m(\vartheta)\,G_\ell^m(\varphi)$. The remaining eigenvalue equation for $\hat{L}_z$ becomes

$$\frac{\partial}{\partial\varphi}G_\ell^m(\varphi) = i\,m\,G_\ell^m(\varphi)$$

and can be solved according to

$$\frac{df(x)}{dx} = \alpha\,f(x) \quad \Rightarrow \quad \frac{1}{f(x)}\frac{df(x)}{dx} = \alpha \quad \Rightarrow \quad \int\frac{1}{f(x)}\frac{df(x)}{dx}\,dx = \int\alpha\,dx$$
$$\Rightarrow \quad \ln\big(f(x)\big) = \alpha x + c \quad \Rightarrow \quad f(x) = A\,e^{\alpha\,x} \text{ with } A = e^c$$

using separation of variables. This gives

$$G_\ell^m(\varphi) = A\, e^{i\,m\,\varphi} \qquad\qquad Y_\ell^m(\vartheta,\varphi) = F_\ell^m(\vartheta)\, e^{i\,m\,\varphi}$$

where the constant A has been absorbed into $F_\ell^m(\vartheta)$. Because $\varphi \in [0, 2\pi)$ the condition $Y_\ell^m(\vartheta, 0) = Y_\ell^m(\vartheta, 2\pi)$ must be satisfied giving $F_\ell^m(\vartheta)e^0 = F_\ell^m(\vartheta)e^{i2\pi m}$ or $1 = e^{i2\pi m}$. Thus, m must be an integer and also ℓ must be an integer because $m = -\ell, -\ell+1, ..., \ell-1, \ell$. The eigenvalues ℓ and m for orbital angular momentum must therefore be integer and cannot be half-integers as found for the general angular momentum. Only the eigenvalues for spin angular momentum can assume half-integer values.

In order to determine the eigenfunctions the two differential equations

$$-\hbar^2\left(\frac{\partial^2}{\partial\vartheta^2} + \frac{1}{\tan\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right) Y_\ell^m(\vartheta,\varphi) = \ell(\ell+1)\hbar^2\, Y_\ell^m(\vartheta,\varphi)$$

$$-i\hbar\,\frac{\partial}{\partial\varphi}\, Y_\ell^m(\vartheta,\varphi) = m\hbar\, Y_\ell^m(\vartheta,\varphi)$$

have to be solved. The solutions are the spherical harmonics. Normalization defined as

$$\int |\psi_{\ell m}(x,y,z)|^2\, dx\, dy\, dz = 1 \qquad\qquad \int_0^\infty r^2\, dr \int_0^\pi \sin\vartheta\, d\vartheta \int |\psi_{\ell m}(r,\vartheta,\varphi)|^2\, d\varphi = 1$$

for $\psi_{\ell m}(r,\vartheta,\varphi) = f(r)\, Y_\ell^m(\vartheta,\varphi)$ is typically divided such that

$$\int_0^\infty r^2\, |f(r)|^2\, dr = 1 \qquad\qquad \int_0^\pi \sin\vartheta\, d\vartheta \int |Y_\ell^m(\vartheta,\varphi)|^2\, d\varphi = 1$$

is used.

As derived above the part of the eigenfunction without r is $Y_\ell^m(\vartheta,\varphi) = F_\ell^m(\vartheta)\, e^{i\,m\,\varphi}$. Because raising $|\ell, m\rangle$ with $m = \ell$ gives no state $\hat{L}_+\,|\ell,\ell\rangle = 0$ or

$$\hbar\, e^{i\,\ell\,\varphi}\left(\frac{\partial}{\partial\vartheta} + \frac{i}{\tan\vartheta}\,\frac{\partial}{\partial\varphi}\right) F_\ell^\ell(\vartheta)\, e^{i\,\ell\,\varphi} = 0 \qquad\qquad e^{i\,\ell\,\varphi}\frac{\partial}{\partial\vartheta}F_\ell^\ell(\vartheta) + \frac{i}{\tan\vartheta}F_\ell^\ell(\vartheta)\frac{\partial}{\partial\varphi}e^{i\,\ell\,\varphi} = 0$$

$$e^{i\,\ell\,\varphi}\frac{\partial}{\partial\vartheta}F_\ell^\ell(\vartheta) + \frac{i}{\tan\vartheta}F_\ell^\ell(\vartheta)\, i\,\ell\, e^{i\,\ell\,\varphi} = 0 \qquad\qquad \frac{\partial}{\partial\vartheta}F_\ell^\ell(\vartheta) - \frac{\ell}{\tan\vartheta}F_\ell^\ell(\vartheta) = 0$$

in spherical coordinates. Using separation of variables and integration again gives

$$\int \frac{1}{F_\ell^\ell(\vartheta)}\frac{\partial F_\ell^\ell(\vartheta)}{\partial\vartheta}\, d\vartheta = \int \ell\,\frac{\cos\vartheta}{\sin\vartheta} d\vartheta = \ell\int\frac{d(\sin\vartheta)}{\sin\vartheta}$$

with writing $d(\sin\vartheta) = \cos\vartheta\, d\vartheta$. The result becomes

$$\ln\left(F_\ell^\ell(\vartheta)\right) = \ell\,\ln(\sin\vartheta) + a_\ell = \ln\left((\sin\vartheta)^\ell\right) + a_\ell \qquad F_\ell^\ell(\vartheta) = c_\ell\,(\sin\vartheta)^\ell \qquad Y_\ell^\ell(\vartheta,\varphi) = c_\ell\,(\sin\vartheta)^\ell\, e^{i\,\ell\,\varphi}$$

with $c_\ell = e^{a_\ell}$. After some calculations one gets

$$c_\ell = \frac{(-1)^\ell}{2^\ell\,\ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}} \qquad\qquad Y_\ell^\ell(\vartheta,\varphi) = \frac{(-1)^\ell}{2^\ell\,\ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}\,(\sin\vartheta)^\ell\, e^{i\,\ell\,\varphi}$$

and this is the solution for $m = \ell$.

Using the lowering operator $\hat{L}_-\,|\ell,m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m-1)}\,|\ell, m-1\rangle$ successively

$$\hat{L}_- = \hbar\, e^{-i\,\varphi}\left(-\frac{\partial}{\partial\vartheta} + \frac{i}{\tan\vartheta}\,\frac{\partial}{\partial\varphi}\right) \qquad Y_\ell^\ell(\vartheta,\varphi) \xrightarrow{\hat{L}_-} Y_\ell^{\ell-1}(\vartheta,\varphi) \xrightarrow{\hat{L}_-} Y_\ell^{\ell-2}(\vartheta,\varphi) \xrightarrow{\hat{L}_-} ... \xrightarrow{\hat{L}_-} Y_\ell^{-\ell}(\vartheta,\varphi)$$

allows to get all the other solutions with the result

$$Y_\ell^m(\vartheta,\varphi) = \frac{(-1)^\ell}{2^\ell\,\ell!}\sqrt{\frac{(2\ell+1)(\ell+m)!}{4\pi(\ell-m)!}}\, e^{i\,m\,\varphi}\,(\sin\vartheta)^{-m}\,\frac{d^{\ell-m}}{d(\cos\vartheta)^{\ell-m}}\,(\sin\vartheta)^{2\ell} \tag{4.4}$$

after some tedious calculations. These functions are called the *spherical harmonics*.

4.6 The Angular Equations of Central Potentials

A central potential only depends on the distance from the origin. In other words, the potential looks in the center exactly the same in all directions. The reason why central potentials are so important is the hydrogen atom because if one has two particles whose interaction only depends on the distance between them then their relative motion can be described using a single fictitious particle that moves in a central potential.

A general potential in spherical coordinates $\underline{r} = (r, \vartheta, \varphi)$ is $V(\underline{r}) = V(r, \vartheta, \varphi)$ and a *central potential* is $V(\underline{r}) = V(r)$ such that it only depends on r. The Hamiltonian is

$$\hat{H} = \frac{\hat{\underline{p}}^2}{2m} + V(\hat{\underline{r}}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\hat{\underline{r}})$$

in the position representation on the right side. The Laplace operator in spherical coordinates is

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}\,r + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \vartheta^2} + \frac{1}{\tan\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)$$

such that the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}\,r + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \vartheta^2} + \frac{1}{\tan\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)\right] + V(r) \tag{4.5}$$

in spherical coordinates. Using $\hat{\underline{L}}^2$ the Hamiltonian can be written as

$$\hat{\underline{L}}^2 = -\hbar^2\left(\frac{\partial^2}{\partial \vartheta^2} + \frac{1}{\tan\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right) \qquad \hat{H} = -\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}\,r + \frac{1}{r^2}\left(-\frac{\hat{\underline{L}}^2}{\hbar^2}\right)\right] + V(r)$$

or with three terms

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}\,r + \frac{1}{2m\,r^2}\hat{\underline{L}}^2 + V(r)$$

where the first corresponds to the kinetic energy with respect to r, but the second term also corresponds to the kinetic energy and is proportional to $\hat{\underline{L}}^2$. This is rather nice because all the angular dependencies are contained in this second term, and the angular part of kinetic energy is already solved by the spherical harmonics (4.4).

This suggests that there is a close relation between central potentials and orbital angular momentum. In addition to the commutation relations

$$\left[\hat{\underline{L}}^2, \hat{L}_x\right] = \left[\hat{\underline{L}}^2, \hat{L}_y\right] = \left[\hat{\underline{L}}^2, \hat{L}_z\right] = 0$$

also

$$\left[\hat{H}, \hat{\underline{L}}^2\right] = 0 \qquad\qquad \left[\hat{H}, \hat{L}_x\right] = \left[\hat{H}, \hat{L}_y\right] = \left[\hat{H}, \hat{L}_z\right] = 0$$

are satisfied. This shows that angular momentum is a constant of motion for particles moving in central potentials. The set of compatible observables usually used is $\{\hat{H}, \hat{\underline{L}}^2, \hat{L}_z\}$. The eigenvalue equations are

$$\hat{H}\,\psi(\underline{r}) = E\,\psi(\underline{r}) \qquad \hat{\underline{L}}^2\,\psi(\underline{r}) = \ell(\ell+1)\hbar^2\,\psi(\underline{r}) \qquad \hat{L}_z\,\psi(\underline{r}) = m_\ell\hbar\,\psi(\underline{r}) \tag{4.6}$$

for these three observables. The solution of a particle moving in a central potential can be rewritten as the solution of these three simultaneous equations. The solution of two of them has been developed in the context of orbital angular momentum with $\ell = 0, 1, 2, ...$ and $m_\ell = -\ell, -\ell+1, ..., \ell$ such that only the first equation still has to be solved. As shown above $\psi(\underline{r})$ can be written as the product $R(r)\,Y_\ell^m(\vartheta, \varphi)$ where $Y_\ell^m(\vartheta, \varphi)$ are the spherical harmonics (4.4). They are the same for any central potential, and only the part $R(r)$ remains to be solved. However, $R(r)$ is different for different central potentials and has to be solved separately.

4.7 The Radial Equation of Central Potentials

Given the spherical harmonics for the angular solutions $Y_\ell^m(\vartheta,\varphi)$ the eigenfunctions of the Hamiltonian can be written as $\psi(\underline{r}) = R(r)\,Y_\ell^m(\vartheta,\varphi)$ and the eigenvalue equation becomes

$$\hat{H}\,R(r) = \left(-\frac{\hbar^2}{2m}\,\frac{1}{r}\,\frac{\partial^2}{\partial r^2}\,r + \frac{\ell(\ell+1)\hbar^2}{2m\,r^2} + V(r)\right) R(r) = E\,R(r) \tag{4.7}$$

because $\hat{H}$ is independent of ϑ and φ. This equation is called the radial equation, and it has to be solved for each $V(r)$ differently. However, the radial equation has general properties to be explored here. Because the Hamiltonian depends on the quantum number ℓ the notation $\hat{H}_\ell$ is used such that there is an infinite list of Hamiltonians for $\ell = 0, 1, 2, ...$ as possible values. The eigenvalue equation is

$$\hat{H}_\ell\,R_{k\ell}(r) = E_{k\ell}\,R_{k\ell}(r)$$

where k covers the energy spectrum. Because m_ℓ as the angular quantum number associated with the z-component of the orbital angular momentum does not feature in the eigenvalue equation, the eigenvalues $E_{k\ell}$ and the eigenfunctions $R_{k\ell}(r)$ do not depend on m_ℓ but $E_{k\ell}$ is at least $(2\ell+1)$-fold degenerate.

The eigenvalue equation can be rewritten as

$$\left(-\frac{\hbar^2}{2m}\,\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2m\,r^2} + V(r)\right) u_{k\ell}(r) = E_{k\ell}\,u_{k\ell}(r) \qquad \text{with } R_{k\ell}(r) = \frac{1}{r}\,u_{k\ell}(r)$$

in a first step. Next, it is assumed that the system is well-behaved for the limit $r \to 0$ such that

$$\lim_{r\to 0}\left(r^2\,V(r)\right) = 0$$

meaning that the potential does not approach zero faster than $V(r) \sim \frac{1}{r}$. With this assumption it seems that one looses some generality but in practice this is true for relevant potentials such as the Coulomb potential. The limit

$$\lim_{r\to 0}\left(\frac{\ell(\ell+1)\hbar^2}{2m\,r^2} + V(r) - E_{k\ell}\right) = \frac{\ell(\ell+1)\hbar^2}{2m\,r^2}$$

is therefore dominated by the $\frac{1}{r^2}$ and has to be satisfied for $\ell = 0$. The differential equation becomes

$$\left(-\frac{\hbar^2}{2m}\,\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2m\,r^2}\right) u_{k\ell}(r) = 0 \qquad \frac{d^2}{dr^2}\,u_{k\ell}(r) = \frac{\ell(\ell+1)}{r^2}\,u_{k\ell}(r)$$

for the limit $r \to 0$. With $u_{k\ell}(r) \propto r^\alpha$ the differential equation boils down to $\alpha(\alpha-1)r^{\alpha-2} = \ell(\ell+1)r^{\alpha-2}$ and $\alpha(\alpha-1) = \ell(\ell+1)$ with the two solutions $\alpha = \ell+1$ and $\alpha = -\ell$. This gives the two solutions

$$R_{k\ell}(r) \propto r^\ell \qquad\qquad R_{k\ell}(r) \propto r^{-\ell-1}$$

for the function $R_{k\ell}(r)$. The second solution is not possible because $\nabla^2\psi(\underline{r}) \sim \delta^{(\ell)}(\underline{r})$ cannot satisfy the original eigenvalue equation. The reason for this impossible second solution is the result of the fact that the Laplacian in spherical coordinates is only valid for $r \neq 0$. Thus, the only valid solution is $R_{k\ell}(r) \propto r^\ell$, and one can set up the constraint $u_{k\ell}(0) = 0$ to eliminate the other solution.

As discussed above the normalization of $\psi(\underline{r})$ has been separated into the normalization of the radial part and the angular part. Thus,

$$\int_0^\infty \left|u_{k\ell}(r)\right|^2 dr = 1$$

is the normalization of the radial part.

A single particle in one dimension can be described by a Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

consisting of kinetic energy and potential energy. The radial Hamiltonian for a particle moving in three dimensions is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2m\,r^2} + V(r) \qquad V_{\text{eff}}(r) = \frac{\ell(\ell+1)\hbar^2}{2m\,r^2} + V(r) \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V_{\text{eff}}(r) \tag{4.8}$$

and looks like the Hamiltonian of a particle moving in one dimensions in a so-called *effective potential* $V_{\text{eff}}(r)$. To make the analogy complete with the one-dimensional case one can imagine an infinite wall for negative values of r because of the constraint $r \in [0, \infty)$. This allows to apply all knowledge gained for the one-dimensional case to the case of the radial motion in three dimensions. Using the effective potential means forgetting that part of the potential energy is actually part of the kinetic energy.

Taking the Coulomb potential or other potentials with $V(r) \propto -\frac{1}{r}$ then the effective potential $V_{\text{eff}}(r)$ is $V(r)$ for $\ell = 0$ but is $V_{\text{eff}}(r) \propto -\frac{1}{r} + \frac{1}{r^2}$ for $\ell > 0$. The force due to the potential $V(r)$ is attractive for $[0, \infty)$ and the force due to $V_{\text{eff}}(r)$ is repulsive for small r where $\frac{1}{r^2}$ dominates over $\frac{1}{r}$ but gets more and more attractive for larger r. Very far away from the center of the potential is $V_{\text{eff}}(r) \approx V(r)$. This effective potential is called *centrifugal* for $\ell > 0$. Another name for the part of the effective potential coming from kinetic energy is the *angular momentum barrier* because it pushes the wave function away from the origin.

4.8 The Pauli Matrices

The *Pauli matrices* named after Wolfgang Pauli are three 2×2 matrices and their importance in quantum mechanics cannot be overestimated. They play a central role for spin $\frac{1}{2}$ particles, and they are the starting point to study any quantum system that can be described with a two-dimensional state space.

The Pauli matrices are defined as

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.9}$$

and are Hermitian because of $\sigma_k = \sigma_k^\dagger$ as well as involutory because of $\sigma_k = \sigma_k^{-1}$ (or, equivalently, $\sigma_k^2 = \mathbb{I}$). Thus, they are not only Hermitian but also unitary. The determinant of all three matrices is $\det \sigma_k = -1$, and their trace is $\text{tr}(\sigma_k) = 0$.

The eigenvalues of the first Pauli matrix calculated from $\det(\sigma_1 - \lambda\,\mathbb{I}) = 0$ are $\lambda = \pm 1$ as

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} \qquad \Rightarrow \det \begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} = (-\lambda)^2 - 1 = 0 \qquad \Rightarrow \lambda = \pm 1$$

shows. The eigenvalues for the other Pauli matrices are the same, and with the eigenvalue equation $\sigma_k\,\underline{v} = \lambda\,\underline{v}$ the eigenvalues and eigenvectors are

$$\begin{aligned}
\sigma_1: &\quad \lambda = +1 : \underline{v}_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \lambda = -1 : \underline{v}_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \\
\sigma_2: &\quad \lambda = +1 : \underline{v}_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} \qquad \lambda = -1 : \underline{v}_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix} \\
\sigma_3: &\quad \lambda = +1 : \underline{v}_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \lambda = -1 : \underline{v}_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\end{aligned} \tag{4.10}$$

for all three Pauli matrices.

The commutation relations demonstrated with the example for $[\sigma_1 \sigma_2] = \sigma_1\sigma_2 - \sigma_2\sigma_1$

$$[\sigma_1, \sigma_2] = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = 2i \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 2i\,\sigma_3$$

are

$$[\sigma_1\sigma_2] = 2i\,\sigma_3 \qquad [\sigma_2\sigma_3] = 2i\,\sigma_1 \qquad [\sigma_3\sigma_1] = 2i\,\sigma_2 \tag{4.11}$$

and all others vanish. Using the Levi-Civita symbol $\varepsilon_{jk\ell}$ the commutator relations can be written as

$$[\sigma_j\sigma_k] = 2i\sum_{\ell=1}^{3}\varepsilon_{jk\ell}\sigma_\ell \qquad\qquad j,k = 1,2,3$$

in compact form.

The anticommutation relations demonstrated with the example for $\{\sigma_1\sigma_2\} = \sigma_1\sigma_2 + \sigma_2\sigma_1$

$$\{\sigma_1\sigma_2\} = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} + \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = \begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix}$$

are

$$\{\sigma_1\sigma_2\} = \{\sigma_2\sigma_3\} = \{\sigma_3\sigma_1\} = 0 \qquad \{\sigma_1\sigma_1\} = \{\sigma_2\sigma_2\} = \{\sigma_3\sigma_3\} = 2\mathbb{I} \tag{4.12}$$

or with the Kronecker delta symbol

$$\{\sigma_j\sigma_k\} = 2\delta_{jk}\,\mathbb{I} \qquad\qquad j,k = 1,2,3$$

in compact form.

Quantum operators associated with two-state systems can be written in terms of 2×2 matrices, and any 2×2 matrix can be written in terms of the identity matrix $\mathbb{I}$ and the three Pauli matrices. Thus, these four matrices build a basis for the complex 2×2 matrices. The identity matrix is usually called σ_0.

A given matrix

$$A = \begin{pmatrix}A_{11} & A_{12}\\ A_{21} & A_{22}\end{pmatrix} \qquad\qquad A_{jk}\in\mathbb{C}$$

can be written as $d_0\sigma_0 + d_1\sigma_1 + d_2\sigma_2 + d_3\sigma_3$ with $d_\mu \in \mathbb{C}$ such that

$$\begin{pmatrix}A_{11} & A_{12}\\ A_{21} & A_{22}\end{pmatrix} = d_0\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + d_1\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + d_2\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} + d_3\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \begin{pmatrix}d_0+d_3 & d_1-id_2\\ d_1+id_2 & d_0-d_3\end{pmatrix}$$

must be satisfied. To form a basis the σ_μ must be linearly independent, and any complex 2×2 matrix can be written as a linear combination of the σ_μ. For the linear independence one has to show that

$$d_0\sigma_0 + d_1\sigma_1 + d_2\sigma_2 + d_3\sigma_3 = 0 \qquad\qquad \Rightarrow d_\mu = 0$$

must be true. This follows from $d_0 + d_3 = d_1 - id_2 = d_1 + id_2 = d_0 - d_3 = 0$. With

$$A_{11} = d_0 + d_3 \qquad A_{12} = d_1 - id_2 \qquad A_{21} = d_1 + id_2 \qquad A_{22} = d_0 - d_3$$

the coefficients d_μ become

$$d_0 = \frac{1}{2}(A_{11} + A_{22}) \qquad d_1 = \frac{1}{2}(A_{12} + A_{21})$$
$$d_2 = \frac{i}{2}(A_{12} - A_{21}) \qquad d_3 = \frac{1}{2}(A_{11} - A_{22})$$

by adding and subtracting the above equations for A_{jk}. The coefficients d_μ are usually complex numbers. This is a very useful result as it turns out that the Pauli matrices are a convenient set of matrices to work with in many quantum problems involving a two-dimensional state space. The description of the spin angular momentum in spin $\frac{1}{2}$ particles such as the electron is an example.

The matrix elements must satisfy $A_{11}, A_{22} \in \mathbb{R}$ and $A_{21}^* = A_{12}$ for a Hermitian 2×2 matrix. This means

$$\begin{aligned} d_0 &= \frac{1}{2}(A_{11} + A_{22}) && \Rightarrow d_0 \in \mathbb{R} \\ d_1 &= \frac{1}{2}(A_{12} + A_{21}) = \frac{1}{2}(A_{21}^* + A_{21}) = \mathrm{Re}\{A_{21}\} && \Rightarrow d_1 \in \mathbb{R} \\ d_2 &= \frac{i}{2}(A_{12} - A_{21}) = \frac{i}{2}(A_{21}^* - A_{21}) = \mathrm{Im}\{A_{21}\} && \Rightarrow d_2 \in \mathbb{R} \\ d_3 &= \frac{1}{2}(A_{11} - A_{22}) && \Rightarrow d_3 \in \mathbb{R} \end{aligned}$$

and the coefficients d_μ are therefore all real for a Hermitian matrix.

4.9 Energy Eigenvalues of Two-State Quantum Systems

The Hamiltonian of a two-state quantum system is

$$\hat{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \qquad H_{11}, H_{22} \in \mathbb{R} \quad H_{21}^* = H_{12}$$

because $\hat{H}$ is Hermitian. The eigenvalue equation is $\hat{H}\,|\psi\rangle = \lambda\,|\psi\rangle$ and the characteristic equation to solve is $\det\Big(\hat{H} - \lambda\,\mathbb{I}\Big) = 0$

$$\begin{aligned} \det \begin{pmatrix} H_{11} - \lambda & H_{12} \\ H_{21} & H_{22} - \lambda \end{pmatrix} &= (H_{11} - \lambda)(H_{22} - \lambda) - H_{12}H_{21} = 0 \\ &= \lambda^2 - \lambda(H_{11} + H_{22}) + H_{11}H_{22} - H_{12}H_{21} = 0 \end{aligned}$$

in order to find the eigenvalues. Its solution is

$$\begin{aligned} \lambda &= \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\sqrt{(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - H_{12}H_{21})} \\ &= \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2} \end{aligned}$$

using $H_{12}H_{21} = |H_{12}|^2$ because of $H_{21}^* = H_{12}$.

The notation for the energy eigenvalues is usually E instead of λ, and they are

$$\begin{aligned} E_+ &= \frac{1}{2}(H_{11} + H_{22}) + \frac{1}{2}\sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2} \\ E_- &= \frac{1}{2}(H_{11} + H_{22}) - \frac{1}{2}\sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2} \end{aligned} \tag{4.13}$$

because a two-state quantum system can only have two eigenvalues. The eigenvalue equation is therefore $\hat{H}\,|\psi_\pm\rangle = E_\pm\,|\psi_\pm\rangle$ for such a quantum system which is often called a "2-level system".

The degenerated case $E_+ = E_-$ means that $(H_{11} - H_{22})^2 + 4|H_{12}|^2 = 0$ and therefore $(H_{11} - H_{22})^2 = 0$ and $4|H_{12}|^2 = 0$ because both terms are non-negative. Thus, the conditions $H_{11} = H_{22}$ and $H_{12} = H_{21} = 0$ must be satisfied if the spectrum is degenerate. In other words, the Hamiltonian must have the very simple form $\hat{H} = E\,\mathbb{I}$ if the system has only one eigenvalue E.

The Hamiltonian $\hat{H}$ can be written in the form $d_0\sigma_0 + d_1\sigma_1 + d_2\sigma_2 + d_3\sigma_3$ with real expansion coefficients d_μ as shown above. To simplify notations $\underline{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ and $\underline{d} = (d_1, d_2, d_3)$ are used, and the Hamiltonian can be written as $\hat{H} = d_0\sigma_0 + \underline{d} \cdot \underline{\sigma}$. The eigenvalue equation becomes

$$\det \begin{pmatrix} d_0 + d_3 - \lambda & d_1 - id_2 \\ d_1 + id_2 & d_0 - d_3 - \lambda \end{pmatrix} = [(d_0 - \lambda) + d_3][(d_0 - \lambda) - d_3] - (d_1 - id_2)(d_1 + id_2) = 0$$

arranged in a convenient way. Using $(a+b)(a-b) = a^2 - b^2$, this equation can be rewritten as

$$\begin{aligned}
&(d_0 - \lambda)^2 - d_3^2 - (d_1^2 - (id_2)^2) = (\lambda - d_0)^2 - d_1^2 - d_2^2 - d_3^2 = 0 \\
&(\lambda - d_0)^2 = d_1^2 + d_2^2 + d_3^2 \qquad\qquad \Rightarrow \lambda - d_0 = \pm\sqrt{d_1^2 + d_2^2 + d_3^2} \\
&\lambda = d_0 \pm \sqrt{d_1^2 + d_2^2 + d_3^2} = d_0 \pm |\underline{d}|
\end{aligned}$$

such that the two energy eigenvalues are

$$E_+ = d_0 + \sqrt{d_1^2 + d_2^2 + d_3^2} = d_0 + |\underline{d}| \qquad\qquad E_- = d_0 - \sqrt{d_1^2 + d_2^2 + d_3^2} = d_0 - |\underline{d}| \tag{4.14}$$

written in terms of the expansion coefficients for the Pauli matrices.

4.10 Energy Eigenstates of Two-State Quantum Systems

The eigenvalue equation for a two-state quantum system is $\hat{H}\,|\psi_\pm\rangle = E_\pm\,|\psi_\pm\rangle$ where $\hat{H}$ is the Hamiltonian and $E_\pm$ and $|\psi_\pm\rangle$ are the eigenvalues and eigenstates, respectively. The eigenvalues can either be written in terms of the matrix elements H_{jk} as in (4.13) or in terms of the expansion coefficients d_μ as in (4.14). The equation for the eigenstates $|\psi_\pm\rangle$ is

$$(d_0\sigma_0 + \underline{d}\cdot\underline{\sigma})\,|\psi_\pm\rangle = E_\pm\,|\psi_\pm\rangle \qquad\qquad \underline{d}\cdot\underline{\sigma}\,|\psi_\pm\rangle = E_\pm\,|\psi_\pm\rangle - d_0\sigma_0\,|\psi_\pm\rangle = E_\pm\,|\psi_\pm\rangle - d_0\,|\psi_\pm\rangle$$

because $\sigma_0 = \mathbb{I}$. Calling the scalar $E_\pm - d_0 = \lambda_\pm$ gives

$$\underline{d}\cdot\underline{\sigma}\,|\psi_\pm\rangle = \lambda_\pm\,|\psi_\pm\rangle$$

showing that the energy eigenstates $|\psi_\pm\rangle$ are also eigenstates of the operator $\underline{d}\cdot\underline{\sigma}$. This operator is

$$d_1\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + d_2\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} + d_3\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \begin{pmatrix}d_3 & d_1 - id_2\\ d_1 + id_2 & -d_3\end{pmatrix}$$

in matrix form. Changing coordinates from (d_1, d_2, d_3) to (d, ϑ, φ) with

$$d_1 = d\,\sin\vartheta\cos\varphi \qquad\qquad d_2 = d\,\sin\vartheta\sin\varphi \qquad\qquad d_3 = d\,\cos\vartheta$$

will turn out to be helpful. The operator $\underline{d}\cdot\underline{\sigma}$ becomes

$$\underline{d}\cdot\underline{\sigma} = \begin{pmatrix}d\,\cos\vartheta & d\,\sin\vartheta(\cos\varphi - i\,\sin\varphi)\\ d\,\sin\vartheta(\cos\varphi + i\,\sin\varphi) & -d\,\cos\vartheta\end{pmatrix} = \begin{pmatrix}d\,\cos\vartheta & d\,\sin\vartheta\,e^{-i\varphi}\\ d\,\sin\vartheta\,e^{i\varphi} & -d\,\cos\vartheta\end{pmatrix}$$

in the new coordinates, and

$$\begin{aligned}
\det(\underline{d}\cdot\underline{\sigma} - \lambda\,\mathbb{I}) &= \begin{pmatrix}d\,\cos\vartheta - \lambda & d\,\sin\vartheta\,e^{-i\varphi}\\ d\,\sin\vartheta\,e^{i\varphi} & -d\,\cos\vartheta - \lambda\end{pmatrix} \\
&= (d\,\cos\vartheta - \lambda)(-d\,\cos\vartheta - \lambda) - d\,\sin\vartheta\,e^{-i\varphi} d\,\sin\vartheta\,e^{i\varphi} \\
&= -(d\cos\vartheta - \lambda)(d\cos\vartheta + \lambda) - d^2\sin^2\vartheta \\
&= -d^2\cos^2\vartheta + \lambda^2 - d^2\sin^2\vartheta = 0 \\
\lambda^2 &= d^2(\cos^2\vartheta + \sin^2\vartheta) = d^2
\end{aligned}$$

has to be solved to find the eigenvalues of the operator $\underline{d}\cdot\underline{\sigma}$. The solution is simply $\lambda_\pm = \pm d = \pm|\underline{d}|$ because $d^2 = d_1^2 + d_2^2 + d_3^2$ and $\cos^2\vartheta + \sin^2\vartheta = 1$. The result could have been found more easily because $E_\pm = d_0 \pm |\underline{d}|$ has been determined above after setting $\lambda_\pm = E_\pm - d_0$. However, the detour with this result for the eigenvalues will turn out to be helpful in the following because the eigenstates can be determined from $\underline{d}\cdot\underline{\sigma}\,|\psi\rangle = d\,|\psi\rangle$ using the coordinates (d, ϑ, φ).

The equation for $\lambda_+ = +d$ is $\underline{d}\cdot\underline{\sigma}\,|\psi_+\rangle = d\,|\psi_+\rangle$ can be written as

$$\begin{pmatrix} d\cos\vartheta & d\sin\vartheta\, e^{-i\varphi} \\ d\sin\vartheta\, e^{i\varphi} & -d\cos\vartheta \end{pmatrix}\begin{pmatrix}\psi_{1+}\\ \psi_{2+}\end{pmatrix} = d\begin{pmatrix}\psi_{1+}\\ \psi_{2+}\end{pmatrix} \quad \Rightarrow \begin{pmatrix} d\cos\vartheta\,\psi_{1+} + d\sin\vartheta\, e^{-i\varphi}\,\psi_{2+} \\ d\sin\vartheta\, e^{i\varphi}\,\psi_{1+} - d\cos\vartheta\,\psi_{2+}\end{pmatrix} = d\begin{pmatrix}\psi_{1+}\\ \psi_{2+}\end{pmatrix}$$

leading to

$$d\cos\vartheta\,\psi_{1+} + d\sin\vartheta\, e^{-i\varphi}\,\psi_{2+} = d\,\psi_{1+} \qquad \Rightarrow (1-\cos\vartheta)\,\psi_{1+} = \sin\vartheta\, e^{-i\varphi}\,\psi_{2+}$$

where d can be canceled. Using $\cos(\alpha) = \cos^2(\frac{\alpha}{2}) - \sin^2(\frac{\alpha}{2})$ and $\sin(\alpha) = 2\,\sin(\frac{\alpha}{2})(\cos\frac{\alpha}{2})$ called double-angle formulae, one can write

$$1-\cos\vartheta = 1-\cos^2\left(\frac{\vartheta}{2}\right) + \sin^2\left(\frac{\vartheta}{2}\right) = 2\,\sin^2\left(\frac{\vartheta}{2}\right) \qquad \sin\vartheta = 2\,\sin\left(\frac{\vartheta}{2}\right)\cos\left(\frac{\vartheta}{2}\right)$$

and the equation becomes

$$2\,\sin^2\left(\frac{\vartheta}{2}\right)\,\psi_{1+} = 2\,\sin\left(\frac{\vartheta}{2}\right)\cos\left(\frac{\vartheta}{2}\right)\,e^{-i\varphi}\,\psi_{2+} \qquad \Rightarrow \sin\left(\frac{\vartheta}{2}\right)\,\psi_{1+} = \cos\left(\frac{\vartheta}{2}\right)\,e^{-i\varphi}\,\psi_{2+}$$

such that the two eigenstates of the operator $\underline{d}\cdot\underline{\sigma}$ and therefore also of the Hamiltonian $\hat{H}$ with the eigenvalues $E_\pm$ given in (4.14) are

$$\left.\begin{array}{l}\lambda_+ = d\\ E_+ = d_0 + |\underline{d}|\end{array}\right\}:\;\; |\psi_+\rangle = \begin{pmatrix}\cos\left(\frac{\vartheta}{2}\right)\,e^{-i\varphi}\\ \sin\left(\frac{\vartheta}{2}\right)\end{pmatrix} \qquad \left.\begin{array}{l}\lambda_- = -d\\ E_- = d_0 - |\underline{d}|\end{array}\right\}:\;\; |\psi_-\rangle = \begin{pmatrix}-\sin\left(\frac{\vartheta}{2}\right)\,e^{-i\varphi}\\ \cos\left(\frac{\vartheta}{2}\right)\end{pmatrix} \tag{4.15}$$

given here without the derivation for the eigenvalue λ_-.

To understand the usefulness of the change of variables from (d_1, d_2, d_3) to (d, ϑ, φ) note that the eigenstates are given in terms of trigonometric functions. In the original parameters the mathematical expressions would look very complicated. For most quantities of interest such as expectation values the answers depend on simple functions of ϑ and φ but not on $\frac{\vartheta}{2}$.

To check whether the two eigenstates $|\psi_\pm\rangle$ are orthonormal, the $\langle\psi_\pm|\psi_\pm\rangle$ have to be checked. With

$$\langle\psi_+|\psi_+\rangle = \begin{pmatrix}\cos\left(\frac{\vartheta}{2}\right)\,e^{i\varphi} & \sin\left(\frac{\vartheta}{2}\right)\end{pmatrix}\begin{pmatrix}\cos\left(\frac{\vartheta}{2}\right)\,e^{-i\varphi}\\ \sin\left(\frac{\vartheta}{2}\right)\end{pmatrix} = \cos\left(\frac{\vartheta}{2}\right)\,e^{i\varphi}\cos\left(\frac{\vartheta}{2}\right)\,e^{-i\varphi} + \sin^2\left(\frac{\vartheta}{2}\right) = 1$$

and similarly for $\langle\psi_-|\psi_-\rangle = 1$ and $\langle\psi_+|\psi_-\rangle = 0$ the two energy eigenstates build indeed an orthonormal basis for two-state systems.