

Week 10

PHY 303 Quantum Mechanics

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The angular momentum eigenfunctions for the part describing the coordinates θ and φ in spherical polar coordinates that we discussed so far are valid for an arbitrary spherically symmetric potential, and besides the symmetry do not depend on the detailed form $V(r)$ of that potential. What remains to be done to find all 3D solutions of the TISE is to specify a radial potential $V(r)$ and then solve the radial Schrödinger equation (4.41).

4.6 Hydrogen atom

We shall do this now for the specific example of the Hydrogen atom. However, recall that our entire discussion so far was for a single particle, while a Hydrogen atom consists of two particles, the electron and the proton.

4.6.1 Separation of centre-of-mass motion [Bonus]

Luckily the problem simplifies to an effective single particle problem. The reasoning is the same as in classical mechanics, hence I shall not repeat it here fully, but instead refer you to the solution of the Kepler planetary problem in classical mechanics PHY305. Note that the coulomb potential and the gravitational potential have the exact same mathematical form, depending like $1/|\mathbf{r}_1 - \mathbf{r}_2|$ on the separation between the two bodies. Let the proton be at \mathbf{r}_p with mass M_p and the electron at \mathbf{r}_e with mass m_e . We then define the centre of mass coordinate \mathbf{R} , the relative coordinate \mathbf{r} the total mass M and the reduced mass μ through the relations:

$$\begin{aligned} M &= m_e + M_p, & \mu &= \frac{m_e M_p}{m_e + M_p}, \\ \mathbf{R} &= \frac{M_p \mathbf{r}_p + m_e \mathbf{r}_e}{M}, & \mathbf{r} &= \mathbf{r}_e - \mathbf{r}_p. \end{aligned} \quad (4.70)$$

Note, that since $M_p \approx 2000m_e$, we have $\mathbf{R} \approx \mathbf{r}_p$, $M \approx M_p$ and $\mu \approx m_e$.

The Hamiltonian (operator) for a proton and electron starts off as (see e.g. (4.28))

$$\hat{H} = -\frac{\hbar^2}{2m_p} \Delta_{\mathbf{r}_p} - \frac{\hbar^2}{2m_e} \Delta_{\mathbf{r}_e} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_e - \mathbf{r}_p|}. \quad (4.71)$$

It turns out that using the definitions (4.70), we can transform (4.71) into a Hamiltonian expressed in terms of centre of mass and relative coordinates.

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M}\Delta_{\mathbf{R}}}_{\hat{H}_{CM}} - \underbrace{\frac{\hbar^2}{2\mu}\Delta_{\mathbf{r}} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}}_{=\hat{H}_{rel}}. \quad (4.72)$$

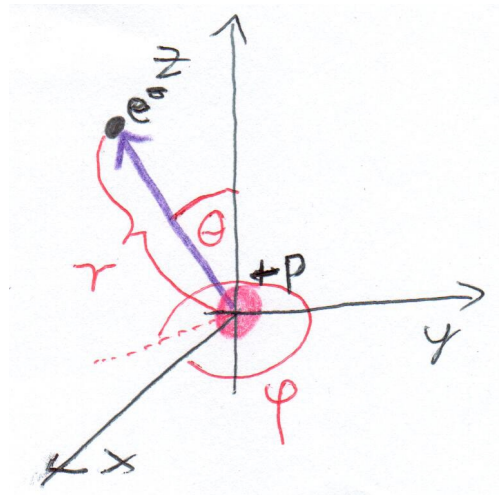
As we had seen in section 4.1.3, for the two-particles, the wavefunction now becomes six-dimensional: $\phi_{p+e}(\mathbf{R}, \mathbf{r})$. As we had seen in section 4.1.1 whenever the Hamiltonian is a sum of Hamiltonians for the two different coordinates, as is the case in (4.72), we can write the wavefunction as a product

$$\phi_{p+e}(\mathbf{R}, \mathbf{r}) = \phi_{CM}(\mathbf{R})\phi_{rel}(\mathbf{r}). \quad (4.73)$$

and then do a separation of variables (see section 1.6.5) to split the TISE or TDSE following from (4.72) into two separated ones for the centre-of-mass wavefunction $\phi_{CM}(\mathbf{R})$ and the relative wavefunction $\phi_{rel}(\mathbf{r})$. The centre-of-mass wavefunction $\phi_{CM}(\mathbf{R})$ will just behave like that for a free particle as discussed in section 2.4. The relative wavefunction is affected by the Coulomb potential as evident from (4.72) and thus will describe binding of the electron to the proton.

In the following we shall just assume that the proton is infinitely heavy, so that $\mu \rightarrow m_e$, and we work in the centre of mass frame (proton frame) of the atom. Then also the problem reduces to a single particle problem, that of the electron, using only $\phi_{rel}(\mathbf{r})$. However bear in mind, that to be precise, in all what follows we have to replace the mass of the electron m_e with the reduced mass of the electron-proton system μ .

4.6.2 Hydrogen wavefunctions



left: Assuming an infinitely heavy proton as discussed in the previous section, we use spherical polar coordinates to describe the location of the electron, with the proton at the origin of the coordinate system. The situation is sketched once more on the left, but really this is just the same diagram as that in section 4.2.

We know the electron mass is $m_e = 9.109 \times 10^{-31}$ kg, and the potential with which it interacts with the proton is the Coulomb potential (4.32), where $q = -e$ is the electron charge and $Q = +1$ that of the proton, while r is the distance between them. The potential in this section is thus

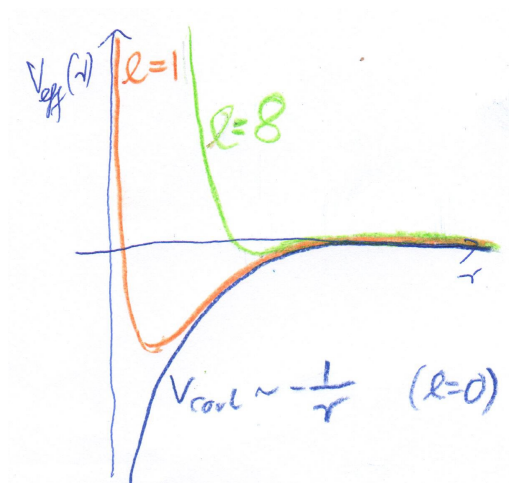
$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (4.74)$$

The situation clearly is spherically symmetric, so that that our discussion of section 4.2 so far fully applies. This means that 2/3 of the work are already done. We can write the 3D wavefunction of the electron as in Eq. (4.40):

$$\phi(r, \theta, \varphi) = R(r)Y(\theta, \varphi), \quad (4.75)$$

and already know the possible forms of Y depending on the angular momentum of the electron. What remains to be done is to solve the radial SE (4.41) to find $R(r)$. It turns out we can make the equation slightly simpler by the substitution $u(r) = rR(r)$, then, also using Eq. (4.74)

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dr^2} u(r) + \underbrace{\left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m_e} \frac{\ell(\ell+1)}{r^2} \right]}_{\equiv V_{\text{eff}}(r)} u(r) = Eu(r). \quad (4.76)$$



left: We are showing a drawing of the effective potential $V_{\text{eff}}(r)$ for a few values of ℓ on the left. Clearly, depending on the quantum number ℓ for the magnitude of angular momentum, see Eq. (4.52), there is an increasing centrifugal potential that pushes the electron outwards. This is what you also encountered in the solution of the Kepler problem of a planet orbiting the sun, only there classically. In contrast to classical mechanics, the centrifugal potential can only take certain shapes since angular momentum is quantised.

As we had seen in the case of the finite potential well in section 2.2.2, the TISE here admits two kinds of solutions, scattering states with $E > 0$ and bound states with $E < 0$. The former would describe the situation where an electron comes in with a positive energy from infinity, makes a fly-by past the proton (i.e. “scatters from it”) and then again escapes with conserved energy to infinity. In contrast, of course, in the bound state the electron is “stuck to the proton”. We will only consider bound states here, hence $E < 0$.

To solve (4.76), we proceed with the same recipe as in section 2.3.2. We first make the equation dimensionless, to reduce the clutter in the notation. This is done by the redefinition $\rho = \kappa r$ with $\kappa = \sqrt{-2mE}/\hbar > 0 \in \mathbb{R}$ and the shorthand $\rho_0 = \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 \kappa}$ for which Griffith gives a bit of a motivation. We reach

$$\frac{d^2 u(\rho)}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u(\rho). \quad (4.77)$$

As in section 2.3.2 we try to first understand the asymptotic behaviour of $u(\rho)$. For $\rho \rightarrow \infty$, the only term in $[\dots]$ that remains is the 1, so we have $\frac{d^2 u(\rho)}{d\rho^2} = u(\rho)$, with the general solution $u(\rho) = Ae^{-\rho} + Be^{\rho}$. Clearly the second term would not be normalizable, so we settle with $u(\rho) = Ae^{-\rho}$ for large ρ (and large ρ implies large r).

At small $\rho \rightarrow 0$, the centrifugal term $\sim \ell$ in $[\dots]$ dominates, hence $\frac{d^2 u(\rho)}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u(\rho)$, with general solution $u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$ (check by back-substitution). But the second term blows up at $\rho \rightarrow 0$ so we set $D = 0$.

Most of the arguments above are not super rigorous (e.g. not valid for all values of ℓ), but they only serve to motivate one further re-definition of the function that we are solving for:

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho). \quad (4.78)$$

(we could have done even without any of the arguments above). Inserting (4.78) into (4.77) we reach

$$\rho \frac{d^2 v(\rho)}{d\rho^2} + 2(\ell + 1 - \rho) \frac{dv(\rho)}{d\rho} + [\rho_0 - 2(\ell + 1)]v(\rho) = 0. \quad (4.79)$$

Finally, again as in section 2.3.2 we take a power series Ansatz for $v(\rho)$

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j, \quad (4.80)$$

plug that into (4.79) and obtain a recursion relation for the coefficients:

$$a_{j+1} = \frac{2(j + \ell + 1) - \rho_0}{(j + 1)(j + 2\ell + 2)} a_j. \quad (4.81)$$

Of course we could have done the power series Ansatz for $u(\rho)$ directly and plugged that one into (4.77), but it turns out that that would be much more messy (see Griffith's footnote on page 136). We can again see that if the series would not terminate, the resultant function $u(\rho)$ would not be normalisable according to Eq. (4.49) (see technical arguments in Griffith). The termination must happen as in section 2.3.2, we require a maximum power j , let's say j_{\max} , for which the numerator of the fraction in (4.81) vanishes, such that $a_{j_{\max}+1}$ and all subsequent coefficients vanish. Hence

$$2(j_{\max} + \ell + 1) - \rho_0 = 0 \quad (4.82)$$

Let us define a new integer

$$n = j_{\max} + \ell + 1 \quad (4.83)$$

such that (4.84) becomes $2n = \rho_0$ and using the definition of ρ_0 , which contains the energy, we can finally write this termination condition as:

$$E = E_n = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2}. \quad (4.84)$$

Since n is an integer, we thus found a quantized energy yet again. Also note, that since $j_{\max} \geq 0$ we automatically have $n \geq \ell + 1$ or the other way round $\ell \leq n - 1$. It remains to find the wavefunction, for which we have to solve the recursion relation (4.81) for finding $v(\rho)$. Due to the termination condition (4.84) and (4.80) we already know that $v(\rho)$ is a polynomial of degree $j_{\max} = n - \ell - 1$. Mathematicians finally tell us that it is $v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho)$ in terms of the

Associated Laguerre polynomial: which is derived via

$$L_{q-p}^p(x) = (-1)^p \left(\frac{d}{dx} \right)^p L_q(x) \quad (4.85)$$

from the q 'th Laguerre polynomial:

$$L_q(x) = e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q). \quad (4.86)$$

For our later drawings of Hydrogen wavefunctions, we need the first few associated Laguerre polynomials:

$$L_0^0 = 1, \quad L_1^0 = -x + 1, \quad L_2^0 = x^2 - 4x + 2, \quad L_1^1 = 1 - 2x + 4, \quad L_2^1 = 3x^2 - 18x + 18. \quad (4.87)$$

More of them can be found in Griffith or the internet.

Due to the form $v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho)$, we see that the wavefunction depends on n and ℓ , as we would have expected since the differential equation (4.76) contains E (related to n through (4.84)) and separately also ℓ . Undoing all our substitutions further above, adding the angular momentum part, and inserting quantum numbers, we have found the wavefunction

$$\begin{aligned} \phi_{n\ell m}(r, \theta, \varphi) &= R_{n\ell}(r)Y_\ell^m(\theta, \varphi), \\ R_{n\ell}(r) &= \frac{1}{r}\rho^{\ell+1}e^{-\rho}v_{n\ell}(\rho), \end{aligned} \quad (4.88)$$

with dimensionless coordinate $\rho = r/(a_0n)$, where we used the

Bohr radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 5.29 \times 10^{-11} \text{m}. \quad (4.89)$$

We have purposefully held off the red boxes until now, to collect the complete

Electronic states and energies of the Hydrogen atom The energy of the electron in the Hydrogen atom is

$$E_n = - \underbrace{\frac{m}{2\hbar^2} \left(\frac{m_e e^2}{8\epsilon_0^2 \hbar^2} \right)}_{=R^*} \frac{1}{n^2}. \quad (4.90)$$

where the Rydberg constant is $R^* = 13.6 \text{ eV}$.

The corresponding complete and normalised wavefunctions are

$$\phi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r)Y_\ell^m(\theta, \varphi), \quad (4.91)$$

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-r/(na_0)} \left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right), \quad (4.92)$$

with spherical harmonics $Y_\ell^m(\theta, \varphi)$ given in (4.51).

- The hydrogen states depend on three quantum-numbers n , ℓ and m .
 - The principal quantum number¹² n is the only one that affects the energy of the electron, it describes the quantisation of energy. Its range is $n = 1, 2, \dots$ the positive integers.

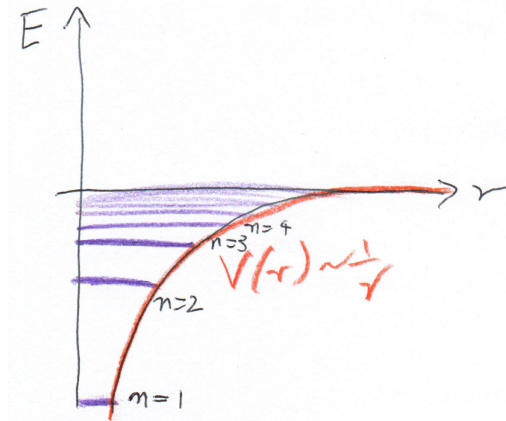
¹²Not principle quantum number

There is no maximal value. We can infer this range from the definition (4.83), with $j_{\max}, \ell \geq 0$ (see below). This quantum number affects the radial part $R_{n\ell}(r)$ of the wavefunction in (4.91), but not the angular one $Y_\ell^m(\theta, \varphi)$.

- The orbital quantum number ℓ describes the quantisation of the magnitude of (orbital) angular momentum, as seen in (4.52). It is the only quantum number that affects both parts of the wavefunction, the radial one and the angular one. It can take the values $0 \leq \ell \leq n - 1$. That ℓ is a positive integer we had seen in section 4.3, while the requirement $\ell \leq n - 1$ again follows from (4.83).
- The magnetic quantum number m describes the quantisation of the z-component of (orbital) angular momentum, as seen in (4.53). It is an integer that can take the range $-\ell \leq m \leq +\ell$, as we had seen in section 4.3.

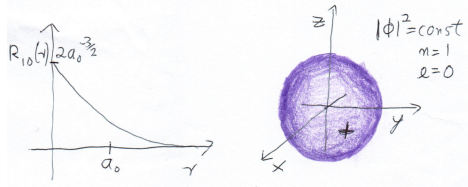
- For many, the Hydrogen atom will remain the most complex quantum problem for which you will see a complete analytical solution. That solution however is extremely important. With some slight modifications for larger atoms (PHY 402) it underpins our understanding of the periodic table, the existence of spectral lines (PHY 106) and atom-light interaction. With the latter, we can engineer many important tools for modern quantum experiments and technologies.
- A historic artefact that has remained useful due to avoiding cluttering notation with too many numbers is the spectroscopic notation, where we replace the orbital quantum number with a letter code $\ell = 0, 1, 2, 3, 4, \dots \rightarrow s, p, d, f, g, \dots$ (at \dots it continues alphabetically). We can then write e.g. the stat with quantum numbers $n = 2$ and $\ell = 1$ as $|2p\rangle$ and so forth. In PHY402 you shall see an extension of this notation that includes also the total angular momentum including spin, and its orientation.

Due to this widespread importance, and the lack of examples in section 4.2 let's see a few more examples and drawings here:



left: First let's sketch the Hydrogen energies as we did earlier inside of a drawing of the Coulomb potential $V(r)$ ((4.74)). Energy levels are not equidistant, with energy gaps decreasing between adjacent states of higher principal quantum number n . The classical turning point where $E = V(r)$ is moving further and further out. Mathematically, there is an infinite number of states as we approach $E \rightarrow 0$ from below. Practically, at some point these electrons are so weakly bound that such states would not be very relevant, except in outer space or very well shielded experiments.

Example 34, Lower quantum states of Hydrogen: Now let's revisit drawings of Hydrogen wavefunctions that we already saw in PHY106, but where now we know the (almost) complete derivation:



left: The simplest but also most important is the Hydrogen ground state $|1s\rangle$ (so $n = 1$, which forces $\ell = 0$ and hence $m = 0$). We draw the radial wavefunction

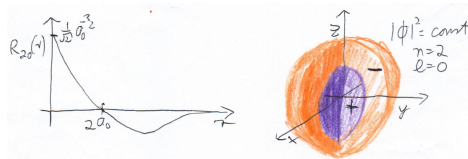
$$R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \quad (4.93)$$

on the left, it drops exponentially, with length-scale (=size of the atom), given by the Bohr radius a_0 .

In the right panel above, we draw an “equal probability surface” in 3D, e.g. the sphere where $|\phi(\mathbf{r})| = \text{const}$. It is a sphere, because

$$Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{4\pi}} \quad (4.94)$$

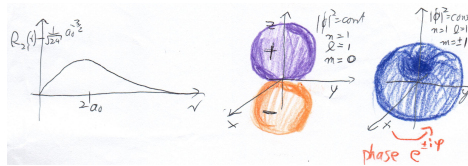
is spherically symmetric (since it simply does not depend on any angle).



left: The first excited state $n = 2$ allows several different angular momentum states. For $|2s\rangle$, i.e. $n = 2$, $\ell = 0$, $m = 0$, we again have a spherical symmetry using (4.94), but now we have one node in the radial wavefunction, see Eq. (4.87):

$$R_{20}(r) = \frac{1}{2\sqrt{6}a_0^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/(2a_0)} \quad (4.95)$$

The drawing is supposed to show a sphere, out of which we have cut out a quadrant to look inside and show the sign.



left: When angular momentum is nonzero $\ell = 1$, it can point in three different directions $m = +1, 0, -1$. Independent of that, the radial wavefunction looks as on the left,

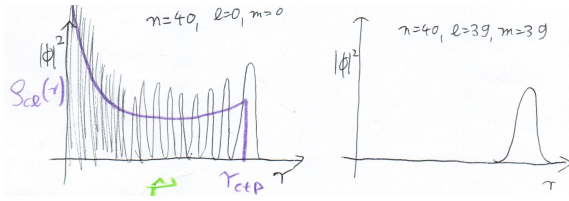
$$R_{21}(r) = \frac{1}{2\sqrt{6}a_0^{3/2}} \frac{r}{a_0} e^{-r/(2a_0)} \quad (4.96)$$

with reduced probability density at the proton. This is a consequence of the centrifugal barrier in V_{eff} , see Eq. (4.41).

The angular wavefunctions are now no longer spherically symmetric, with

$$Y_{10}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_{1\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\varphi}. \quad (4.97)$$

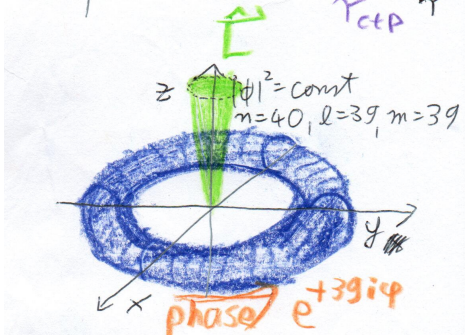
Example 35, Rydberg states of Hydrogen: We had seen many examples before, where low energy quantum states do not seem to have much in common with our classical physics intuition, but high lying ones do, see e.g. example [15](#). This is also the case for the Hydrogen atom, hence we take a look at its Rydberg states, which means large n (say $n > 10$).



left: Due to the structure of the Laguerre polynomials, the radial wave-function of Hydrogen has $j = n - l = 1$ nodes. For $n = 40$ and $l = 0$ the gives a highly oscillatory probability density as shown on the left.

If we smoothen the fast oscillations, we obtain a probability density that resembles that of a classical electron in a Coulomb potential $\rho_{cl}(r)$, shown in violet. As usual, the quantum results reaches farther than the classical turning point r_{ctp} , there showing exponential decay.

In contrast, for the maximum possible $l = 39$, there are no nodes and the radial wavefunction appears almost Gaussian, centered on large radii.



left: If we look into the 3D probability density we see why: This forms a torus/donut as shown left. Together with the radial phase $e^{39i\varphi}$ this implies the electron making an almost “circular orbit” around the proton, like a planet.

The angular momentum implied by this state is also shown in green. We see that the motion is almost constrained to a the $x - y$ plane, as it would be classically, also revisit example [33](#).

4.6.3 Meaning of the z -axis

Now that we are done with the Hydrogen atom, we should wonder about what is special about the z -axis¹³. The answer is of course “nothing”, the Coulomb potential [\(4.74\)](#) is perfectly symmetric. However changing the z -axis does change the meaning of all our Hydrogen eigenstates states $\phi_{nlm}(\mathbf{r})$ as you can see from e.g. the drawing in example [35](#). For the state shown, if we chose a different z -axis, we get a completely different torus orientation. How can this be reconciled?

Degeneracy of angular momentum states. We see in Eq. [\(4.90\)](#) that energy only depends on n . We see in [\(4.52\)](#) that the magnitude of angular momentum only depends on l . Together this means that all states with different azimuthal quantum numbers m are degenerate in both, energy and magnitude of angular momentum. As written in the (newly added, please read now) section [3.4.1](#), whenever that is the case we have some freedom to chose our eigen-basis within the

¹³In fact we should wonder that already at the end of week 9.

degenerate subspace. For the case here, that means that any function

$$\tilde{Y}_\ell^m(\theta, \varphi) = \sum_{m'} c_{m'}^{(\ell m)} Y_\ell^{m'}(\theta, \varphi), \quad (4.98)$$

will also be an eigenfunction of the Hamiltonian and the magnitude of angular momentum (but no longer of the z-component of the angular momentum). With this construction, it is possible to “rotate” the orbital shapes in example [34](#) into different “directions”, see video. This is done for example in the real spherical harmonics used in chemistry. So also the mathematics reproduces the features that the z-axis can be chosen arbitrarily.

Degeneracy of angular momentum states. In practice though, there typically is a smart choice of z-axis and lots of bad choices. This is because (except in this course), we never consider the Hydrogen atom in isolation. You are either concerned with its excitation by light or its interrogation by light. Usually this means that calculations get easier, if you choose your z-axis along a physically meaningful direction, e.g. that of the polarisation of the electric field in the light. Nevertheless, you are free to choose any other axis, at the expense of “requiring more states” in your calculation.