Hydrogen atom

Heisenberg and his collaborators came up with a correct theory of quantum mechanics called "matrix mechanics" in 1925. The next year Schrödinger came up with "wave mechanics" also a correct theory of quantum mechanics, equivalent to matrix mechanics, but with a different approach. Schrödinger showed that his wave mechanics was correct by solving his Schrödinger equation for hydrogen atom and showing that the result coincides with experiments. This is what we will do in this article.

First, note that in 3d, Schrödinger equation can be expressed as follows:

$$\frac{\hbar^2}{2m}\nabla^2\psi + V(x,y,z)\psi = E\psi \tag{1}$$

where Laplacian "∇^2" is defined as follows:

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

In the spherical coordinate, it can be shown that Laplacian can be expressed as follows:

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \tag{3}$$

For a derivation, see M. Boas, *Mathematical Methods in the Physical Sciences*, Chapter 10, section 9. Therefore, Schrödinger equation seems to become:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + V(r)\psi = E\psi \tag{4}$$

where we assumed that the potential only depends on r. Actually, this is the whole point of solving problems in spherical coordinate. If V depends on θ, ϕ, there is no advantage in using spherical coordinate as we will see. Given this, let's look for solutions of following form:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{5}$$

Plugging this, we obtain:

$$\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = \frac{2m}{\hbar^2}(V(r) - E)RY \tag{6}$$

Dividing the both-hand sides by RY/r^2 and rearranging, we obtain:

$$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)=\frac{2mr^2}{\hbar^2}(V(r)-E)-\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)$$
(7)

Notice that the left-hand side is the function of θ and ϕ only, while the right-hand side is the function of r only. As the left-hand side is equal to the right-hand side we conclude that the both-hand sides should be merely a constant, which never depends on θ, ϕ and r. Therefore, we can separately solve the differential equations for the left-hand side and the right-hand side.

Given this, notice that the left-hand side of (7) is exactly negative one times the angular momentum squared operator we encountered in our earlier article "Spherical harmonics." So, Y is actually spherical harmonics.

Thus, the left-hand side becomes $-l(l+1)$. Plugging this back in, with $V(r)=-ke^2/r$, we obtain

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2(rR(r))}{\partial r^2}\right)+\left(\frac{\hbar^2\ell(\ell+1)}{2mr^2}-\frac{ke^2}{r}\right)R(r)=ER(r)\qquad(8)$$

Before solving this Schrödinger equation, we will think about its physical interpretation. To this end, we will heuristically drive the above Schrödinger equation by considering its classical analog.

Recall that in our earlier article "Planet's motion around the Sun," we changed the three-dimensional problem to one-dimensional problem by using the fact that angular momentum is conserved. We reproduce our earlier formula here for convenience:

$$E=\frac{1}{2}m\dot{r}^2+\frac{L^2}{2mr^2}-\frac{GMm}{r}\qquad(9)$$

The energy of hydrogen atom, which consists of a proton and an electron, is very similar to the system composed by the Sun and a planet, since both Coulomb force and gravitational force are inversely proportional to the square of distance. Replacing the gravitational potential energy to the Coulomb analog, the 1-dimensional effective Hamiltonian of hydrogen atom is given as follows:

$$H=\frac{p_r^2}{2m}+\frac{L^2}{2mr^2}-\frac{ke^2}{r}\qquad(10)$$

where p_r is the radial momentum, and m is the mass of the electron (precisely speaking, the reduced mass of the electron and the proton.) Considering that L^2 is quantized as $\hbar^2\ell(\ell+1)$, Schrödinger equation becomes:

$$\left[\frac{p_r^2}{2m}+\frac{\hbar^2\ell(\ell+1)}{2mr^2}-\frac{ke^2}{r}\right]\psi=E\psi\qquad(11)$$

As we had $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, we may just want to write

$$\left[\frac{p_r^2}{2m} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{ke^2}{r} \right] R(r) = ER(r) \tag{12}$$

as there is no θ and ϕ dependence in (11)

Anyhow, to heuristically derive the correct Schrödinger equation, we need to know how p_r can be expressed. Since we know that p_x is given by $-i\hbar \frac{\partial}{\partial x}$, we can guess $p_r = -i\hbar \frac{\partial}{\partial r}$. However, this turns out not to be the case, as p_r can be shown not to be Hermitian. To explain this point, let me digress into the wave function in 3d space.

Recall that in 1d, the inner product between two vectors $|\psi_1\rangle$ and $|\psi_2\rangle$ is given as follows:

$$\langle \psi_2 | \psi_1 \rangle = \int dx \langle \psi_2 | x \rangle \langle x | \psi_1 \rangle = \int dx\, \psi_2^*(x) \psi_1(x) \tag{13}$$

By analogy, it is easy to see that the following must be satisfied in 3d:

$$\langle \psi_2 | \psi_1 \rangle = \int \int \int dx\, dy\, dz\, \psi_2^*(x, y, z) \psi_1(x, y, z) \tag{14}$$

In spherical coordinate, $dx\, dy\, dz$ the volume form for 3d Cartesian coordinate must be appropriately replaced by the spherical coordinate analog, as follows:

$$\langle \psi_2 | \psi_1 \rangle = \int \int \int r^2 \sin\theta dr\, d\theta\, d\phi\, \psi_2^*(r, \theta, \phi) \psi_1(r, \theta, \psi) \tag{15}$$

Now, let's check whether $p_{r0} = -i\hbar \frac{\partial}{\partial r}$ is Hermitian. If we use the notation $\psi_1(r, \theta, \phi) = R_1(r) Y_l^m(\theta, \phi)$ and $\psi_2(r, \theta, \phi) = R_2(r) Y_l^m(\theta, \phi)$ with the following fact,

$$\int \int Y_l^{m*}(\theta, \phi) Y_l^m(\theta, \phi) \sin\theta d\theta d\phi = 1 \tag{16}$$

we have

$$\langle \psi_2 | \psi_1 \rangle = \int r^2 dr\, R^*(r_2) R(r_1) \tag{17}$$

which implies

$$\langle \psi_2 | p_{r0} | \psi_1 \rangle = -i\hbar \int dr \left(r^2 R_2^* \frac{\partial R_1}{\partial r} \right) \tag{18}$$

$$\langle \psi_2 | p_{r0}^\dagger | \psi_1 \rangle = i\hbar \int dr \left(r^2 R_1 \frac{\partial R_2^*}{\partial r} \right)$$

$$= -i\hbar \int dr \left(\frac{\partial (r^2 R_1)}{\partial r} R_2^* \right)$$

$$= -i\hbar \int dr \left(\left(r^2 \frac{\partial R_1}{\partial r} + 2r R_1 \right) R_2^* \right)$$

$$= -i\hbar \int dr \left(r^2 \left(\frac{\partial R_1}{\partial r} + \frac{2}{r} R_1 \right) R_2^* \right) \tag{19}$$

3

Therefore, we see that $-i\hbar\frac{\partial}{\partial r}$ is not Hermitian as (18) is not equal to (19). So, $-i\hbar\frac{\partial}{\partial r}$ can't be p_r. Moreover, if p_r were indeed $-i\hbar\frac{\partial}{\partial r}$, (11) would have been

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial r^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{ke^2}{r}\right]R(r) = ER(r) \tag{20}$$

which *doesn't* coincide with (8).

So, why is $-i\hbar\frac{\partial}{\partial r}$ not Hermitian, while $p_x = -i\hbar\frac{\partial}{\partial x}$ is Hermitian? If you think about it, it's because r^2 factor in the inner product (17). In case of p_x, such factor is not present in the definition of the inner product in the Hilbert space of wave functions living in the 1-dimensional Cartesian coordinate.

So, how can we fix this problem? If we "get rid of" the r^2 factor, we can do it. Let's define $u(r)$ by the following formula:

$$u(r) = rR(r) \tag{21}$$

Then, (17) is given by

$$\langle\psi_2|\psi_1\rangle = \int dr \, u^*(r_2)u(r_1) \tag{22}$$

where the r^2 factor is now absent. Given this, if we now say $p_r = -i\hbar\frac{\partial}{\partial r}$ acts on $u(r)$ instead of $R(r)$, we have

$$\langle\psi_2|p_{r0}|\psi_1\rangle = -i\hbar\int dr\left(u_2^*\frac{\partial u_1}{\partial r}\right) \tag{23}$$

$$\langle\psi_2|p_{r0}^\dagger|\psi_1\rangle = i\hbar\int dr\left(u_1\frac{\partial u_2^*}{\partial r}\right) \tag{24}$$

where we can see that $p_r = -i\hbar\frac{\partial}{\partial r}$ acts on $u(r)$ as a Hermitian operator. Therefore, as long as p_r acts on $u(r)$, $R(r)$ in (20) must be replaced by $u(r)$, which implies

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial r^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{ke^2}{r}\right]u(r) = Eu(r) \tag{25}$$

Actually, if you plug in $u(r) = rR(r)$, this equation coincides with (8).

Now, let's solve this equation. (25) implies,

$$\left(-\frac{\partial^2}{\partial r^2} + \frac{\ell(\ell+1)}{r^2} - \frac{2m}{\hbar^2}\frac{ke^2}{r} - \frac{2mE}{\hbar^2}\right)u = 0 \tag{26}$$

By being careful that E is negative since we are considering the case that electron is bound by the proton (i.e roughly speaking, orbiting around the proton), let's introduce the following notation:

$$\frac{\hbar^2\kappa^2}{2m} = -E, \qquad \rho = 2\kappa r \tag{27}$$

4

$$a_0 = \frac{\hbar^2}{mke^2}, \qquad \text{Ry} = \frac{\hbar^2}{2ma_0^2} \tag{28}$$

$$\lambda^2 = \left(\frac{1}{\kappa a_0}\right)^2 = \frac{\text{Ry}}{-E} \tag{29}$$

Here, Ry is called the Rydberg unit of energy and a_0 is called the Bohr radius. Then, the above equation is simplified as follows:

$$\frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u = 0 \tag{30}$$

For large ρ, this equation reduces to:

$$\frac{d^2u}{d\rho^2} - \frac{u}{4} = 0 \tag{31}$$

which implies

$$u \sim Ae^{-\rho/2} + Be^{\rho/2} \tag{32}$$

Given this, notice that u must not diverge for large ρ. Otherwise, it would imply that electrons orbiting inside hydrogen atom would be strongly distributed for the regions infinitely far away from the proton, the nucleus of hydrogen atom, which is non-sense. Therefore, we set $B = 0$, so

$$u \sim e^{-\rho/2} \qquad (\rho \to \infty) \tag{33}$$

when ρ is very small, (30) reduces to:

$$\frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u = 0 \tag{34}$$

To solve this equation, let's try a solution $u = \rho^q$, then we have:

$$q(q-1)\rho^{q-2} - \ell(\ell+1)\rho^{q-2} = 0 \tag{35}$$

which implies $q = -\ell, \ell+1$. Therefore, we have:

$$u \sim A\rho^{-\ell} + B\rho^{\ell+1} \tag{36}$$

As u cannot be infinity when $r = 0$, we must set $A = 0$. Therefore, we have

$$u \sim \rho^{\ell+1} \qquad (\rho \to 0) \tag{37}$$

With these two asymptotic forms, we are ready to solve (30) through a polynomial expansion as follows. Solution in the following form

$$u(\rho) = e^{-\rho/2}\rho^{\ell+1}F(\rho) \tag{38}$$

$$F(\rho) = \sum_{i=0}^{\infty} C_i \rho^i \tag{39}$$

with F growing more slowly than an exponential function satisfy (33) and (37). Plugging (38) to (30), we obtain (**Problem 1.**):

$$\left[\rho \frac{d^2}{d\rho^2} + (2\ell + 2 - \rho)\frac{d}{d\rho} - (\ell + 1 - \lambda) \right] F(\rho) = 0 \tag{40}$$

Plugging (39) into the above equation and equating coefficients of equal powers in ρ yields (**Problem 2.**):

$$C_{i+1} = \frac{(i + \ell + 1) - \lambda}{(i+1)(i+2\ell+2)} C_i \tag{41}$$

In the limit that $i \to \infty$, this relation reduces to

$$C_{i+1} \sim \frac{C_i}{i} \tag{42}$$

Now, notice that this is also the ratio of coefficients obtained from the following expansion:

$$e^\rho = \sum C_i \rho^i = \sum \frac{\rho^i}{i!} \tag{43}$$

$$\frac{C_{i+1}}{C_i} = \frac{i!}{(i+1)!} = \frac{1}{i+1} \sim \frac{1}{i} \tag{44}$$

Therefore, for large ρ, we have $F(\rho) \sim e^\rho$ which implies:

$$u(\rho) \sim e^{-\rho/2}\rho^{\ell+1}e^\rho = e^{\rho/2}\rho^{\ell+1} \tag{45}$$

which diverges for large ρ, which doesn't make sense, as we mentioned earlier.

To make sense, the recursion relation (41) must terminate by vanishing at some finite value of i, which we denote i_{max}. By looking at the numerator of (41), we see that this is possible, if

$$i_{max} + \ell + 1 = \lambda \tag{46}$$

In other words, if this equation is satisfied F is finite since Taylor expansion terminates at i_{max} power of ρ, which in turn implies u is also finite. Since i_{max} and ℓ are integer, we see that λ is also an integer, which we call "principal quantum number" and denote by n as follows:

$$n = i_{max} + l + 1 \tag{47}$$

Given this, using (29) we conclude:

$$E_n = -\frac{\text{Ry}}{n^2} \tag{48}$$

This is exactly the formula found by Rydberg.

Now, let's think about what ℓ can be if the electron in an hydrogen atom is in state n. Let's look at state $n = 1$ first. (47) shows that the only way this can happen is when $\ell = 0$ since i_{max} can't be negative. Therefore when $n = 1$ there is no orbital angular momentum for the electron. This contradicts Bohr's model in which $n = 1$ state has angular momentum $\hbar$ which is nonzero. This shows that Bohr's derivation of Rydberg formula was a "fluke," even though it played an important role for the construction of correct quantum theory.

For other n as well, the possible values for l can be easily obtained from (47). The result is:

$$\ell = 0, \ 1, \ 2\ldots, \ n-2, \ n-1 \tag{49}$$

Furthermore, if you remember our earlier article "Angular momentum in quantum mechanics," we have:

$$m = -\ell, \ -\ell+1, \ldots, \ \ell-1, \ \ell \tag{50}$$

Also, we know that an electron can have spin up and spin down. Let's call this s. For example, $s = 1/2$ for spin up, and $s = -1/2$ spin down.

Summarizing, an arbitrary electron orbiting inside hydrogen atom can have certain n, ℓ, m, s. These numbers are called quantum numbers. You may be familiar with this if you learned what is called "orbital" in chemistry. The same structure of quantum numbers exists for atoms other than the hydrogen atom as well. However, what is different is that the energy of the electrons can be different if ℓ is different even if n is same. Remember that in our hydrogen atom case (48) only depends only on n and not ℓ. (However, even in hydrogen atom, the energy depends on l if one considers relativistic effect, but this effect is very tiny.) This is due to the fact that there are multiple numbers of electrons in non-hydrogenic atoms; notice that Schrödinger equation must contain extra terms for the Coulomb force between electrons, which change the eigenvalues for the energy matrix. Anyhow, we cannot solve Schrödinger equation for such atoms analytically; we can only do it numerically, with an aid of supercomputer. Many chemists use supercomputers to solve Schrödinger equation to find out the properties of atoms and molecules. Maybe more so than physicists.

At this moment, a comment on Pauli's exclusion principle is appropriate. If you remember our earlier article on bosons and fermions, you will know that two fermions cannot occupy the same state. This is true for electrons orbiting inside atoms as an electron is a fermion. In other words, two electrons cannot have all the same n, ℓ, m, s.

Let's examine its consequences. How many states are there given n? When $n = 1$, we call it "K shell." There are two states in K shell. $n = 1$, $\ell = 0$, $m = 0$, $s = 1/2$ and $n = 1$, $\ell = 0$, $m = 0$, $s = -1/2$. Therefore, there

can be no more than two electrons in K shell because of Pauli's exclusion principle. How many electrons can be in $n = 2$ called "L shell?" 8 electrons. You can check this yourself. (**Problem 3.**)

So, a total of 8 states. It actually turns out atoms are more chemically less reactive if shells they have are completely filled. For example, Helium, which has two electrons, can fill K shell. Neon, which has ten electrons, can fill both K shell and L shell. It is really amazing that all the properties of atoms and molecules can be reduced to a simple law called "quantum mechanics." (Remember our first article "A short introduction to the history of physics, and string theory as a 'Theory of Everything' ")

Pauli received the Nobel Prize in Physics 1945 for Pauli's exclusion priniciple, which he deserved it. Before coming up with Pauli's exclusion principle, he first introduced the fourth quantum number s. He showed that two-foldedness (Zweifachheit) of an electron, which is not classically explainable, can explain the atomic spectra. Others before him introduced their own fourth quantum numbers to explain the atomic spectra, but they didn't perfectly fit, as Pauli's one did.

Problem 4. Find the relation between the Rydberg unit of energy and the Rydberg constant introduced in our earlier article "Rydberg formula."

Problem 5. Find the normalized wave function for the ground state (i.e. $n = 1$) and calculate the probability that an electron in the ground state will be found at position $r < a_0$. (Hint[1])

Now, let's switch gear and ask a question. Why was the wave function of the form (5) the solution to the Schrödinger equation? Was it a coincidence? No. Let me explain the reason why. To this end, remember that the angular momentum is preserved in our case, as there is rotational symmetry. Upon rotation, the Coulomb potential doesn't change, as the distance to the center doesn't change upon rotation. This should ring a bell regarding our earlier claim that the whole point of using the spherical coordinate is that the potential doesn't depend on the angular direction θ and ϕ. Also, upon the rotation, the kinetic energy doesn't change either, as the kinetic energy is same whether one measures it in a system S or in a system S' rotated from the system S.

Actually, we can say the same thing a little bit more mathematically; the angular momentum commutes with the Hamiltonian. Let's check the potential term first. The Coulomb potential is given by $-ke^2/r$. Then, one can easily check

$$[L_x, -\frac{ke^2}{r}] = [L_y, -\frac{ke^2}{r}] = [L_z, -\frac{ke^2}{r}] = 0 \qquad (51)$$

as the Coulomb potential doesn't depend on θ and ϕ. Remember that L_x, L_y and L_z can be expressed only in terms of θ and ϕ completely without r.

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[1]When $l = 0$ $L_x Y = L_y Y = L_z Y = 0$ which implies Y is a constant that doesn't depend on θ and ϕ.

8

Now, let's check the kinetic term. We can easily check (**Problem 6.**)

$$[L_x, P_x^2 + P_y^2 + P_z^2] = 0 \tag{52}$$

Similarly, $[L_y, P_x^2 + P_y^2 + P_z^2] = [L_z, P_x^2 + P_y^2 + P_z^2] = 0$. Thus, we get

$$[L_x, H] = [L_y, H] = [L_z, H] = 0 \tag{53}$$

where

$$H = \frac{P_x^2 + P_y^2 + P_z^2}{2m} - \frac{ke^2}{r} \tag{54}$$

From (53), we conclude

$$[L^2, H] = [L_x^2 + L_y^2 + L_z^2, H] = 0 \tag{55}$$

Therefore, L^2 and H are simultaneously diagonizable. Thus, we can express the eigenfunction of Hamiltonian in the form of (5), as $Y(\theta, \phi)$ as well as $R(r)Y(\theta, \phi)$ are the eigenfunctions of L^2.

Let me conclude this article with a comment on the spherical harmonics. First, I will introduce the term "homogeneous polynomial of degree ℓ." It is defined by

$$p(c\vec{r}) = c^l p(\vec{r}) \tag{56}$$

Of course, if $\vec{r} = (x, y, z)$ then, such a polynomial can be expressed as

$$p(x, y, z) = \sum_{a+b+c=\ell} A_{abc} x^a y^b z^c \tag{57}$$

Now, I will show that $r^l Y_l^m$ is a homogeneous polynomial of degree ℓ. To this end, let's try to solve Laplace equation $\nabla^2 \psi = 0$, in spherical coordinate system (3). As before, if we write $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, we have

$$\frac{d}{dr}\left(r^2 \frac{dR(r)}{dr}\right) = \ell(\ell+1)R(r) \tag{58}$$

The solution is given by

$$R(r) = Ar^\ell + \frac{B}{r^{\ell+1}} \tag{59}$$

Let's now consider the solution which does not diverge at $r = 0$. So, $B = 0$. Thus, we can write

$$\nabla^2 \left(r^\ell Y_\ell^m(\theta, \phi)\right) = 0 \tag{60}$$

Now, notice that $r^\ell Y_\ell^m(\theta, \phi)$ satisfies the property (56).

Let's show that it also satisfies (57). This also means that a, b, c there are neither non-integers nor negative. Now, recall that $Y_l^0(\theta, \phi)$ is the degree ℓ

polynomial of $\cos\theta = z/r$. If ℓ is even, this polynomial has only even power. Thus, it can be written as something like

$$a_\ell z^\ell + a_{\ell-2} z^{\ell-2} r^2 + \cdots + a_0 r^\ell \tag{61}$$

as $r^2 = x^2 + y^2 + z^2$, the above polynomial can be expressed in the form of (57). A similar analysis can be performed for odd-ℓ.

Now, we can act L^+ and L^- on $r^\ell Y_\ell^0(\theta, \phi)$ to obtain other $r^\ell Y_\ell^m(\theta, \phi)$. As L^+ and L^- act by differentiating with respect to the positions such as x, y, z, and then multiplying the positions x, y, z, they cannot change the condition $\ell = a + b + c$. Nor can they introduce negative exponents or fractional exponents.

In conclusion, we see that $r^\ell Y_\ell^m$ is a homogeneous polynomial of degree ℓ and is harmonic (i.e., satisfies $\nabla^2 \psi = 0$). Actually, one can even show that there are exactly $2\ell + 1$ lineraly independent such polynomials, just like the number of possible m for Y_ℓ^m. We will not show the proof, except for $\ell = 2$. When $\ell = 2$, we have 5 following linearly independent polynomials:

$$xy, \quad yz, \quad zx, \quad x^2 - y^2, \quad x^2 - z^2 \tag{62}$$

They satisfy the Laplace equation $\nabla^2 \psi = 0$. $y^2 - z^2$ doesn't count as it is a linear combination of $x^2 - y^2$ and $x^2 - z^2$.

Summary

- If you solve the Schrödinger equation for hydrogen atom, the radial part and the angular part are completely separated. It's because the angular momentum commutes with the Hamiltonian.

- The energy of the hydrogen atom is given by $E_n = -\dfrac{\text{Ry}}{n^2}$. Ry is the Rydberg constant, and n is the principal quantum number, which is a positive integer.

- Given n, ℓ ranges from $0, 1, 2, \cdots, n-1$ where ℓ denotes the quantum number for the orbital angular momentum (i.e. the orbital angular momentum is given by $\sqrt{\ell(\ell+1)}\hbar$.)

- Given ℓ, m ranges from $-\ell, -\ell+1, \cdots, \ell-1, \ell$, where m denotes the quantum number for the L_z.

- An electron can have either spin up ($s = 1/2$) or spin down ($s = -1/2$).

- Pauli's exclusion principle says that two fermions cannot occupy the same state. Therefore, two electrons in a same hydrogen cannot have all the same n, ℓ, m, s.