Quantum Mechanical Solution for the Hydrogen Atom

The Coulomb potential is given by:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

The 3DTISWE is then given by:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

Here, clearly the coordinate system of choice is going to be spherical coordinates: You might want to refer to the useful page linked on our website.

$$x = r\sin(\theta)\cos(\varphi)$$
$$y = r\sin(\theta)\sin(\varphi)$$
$$z = r\cos(\theta)$$

In this coordinate system, the Laplacian is given by:

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

One of the first things to do is to replace the mass in the SWE by the reduced mass defined by:

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_n}$$

which reflects the fact that the center of mass of the system is actually not at the nucleus.

With this, the 3DTISWE for the hydrogen atom becomes:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{2\mu}{\hbar^2}(E-V)\psi = 0$$

We do exactly what we have done before now … we assume a solution of the form:

$$\psi(r,\theta,\varphi) = R(r)f(\theta)g(\varphi)$$

If you substitute into the SWE this solution then gives (after a bit of algebra):

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta[E-V] - \frac{\sin\theta}{f}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) = \frac{1}{g}\frac{\partial^2 g}{\partial\varphi^2}$$

We now can separate out the g portion:

$$\frac{1}{g}\frac{\partial^2 g}{\partial\varphi^2} = -m_\ell^2 \Rightarrow \frac{d^2 g}{d\varphi^2} + m_\ell^2\varphi = 0$$

Why we chose this particular separation constant is because from having solved the problem, we know it's much more convenient.

The g solutions are of the form:

$$g(\varphi) = e^{im_\ell\varphi}$$

We require that the solution be the same after a phase shift of 2π. Thus:

$$e^{im_\ell\varphi} = e^{im_\ell(\varphi+2\pi)} \Rightarrow m_\ell \in \{0,\pm1,\pm2,\ldots\}$$

This is often called the azimuthal equation

Now what remains of the SWE?

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=\frac{m_\ell^2}{\sin^2\theta}-\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)$$

This is again a separation of variables: r is on one side and the angle is on the other side. This means that each side is again equal to a constant, which with foresight we will say is:

$$\ell(\ell+1)$$

So the separated two equations are:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V-\frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]R=0 \text{ (Radial Equation)}$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell^2}{\sin^2\theta}\right]f=0 \text{ (Angular Equation)}$$

We are not actually going to present the solution of the angular equation here. However, solution of these gives the following conditions on the quantum numbers:

$$\ell=0,1,2,3,...$$

$$m_\ell=-\ell,-\ell+1,-\ell+2,...,-2,-1,0,+1,+2,...,\ell-1,\ell$$

Solution of the Radial equation

Let's look first at the case l=0. Then

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}[E-V]R=0$$

The Coulomb potential energy is given by:

$$V(r)=-\frac{e^2}{4\pi\varepsilon_0 r}$$

This allows the Radial equation to take the form:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_0 r}\right]R=0$$

The solutions of this are going to be exponentials:

$$R=Ae^{-\frac{r}{a_o}}$$

I can show this:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)=\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}=\frac{R}{a_o^2}-\frac{2R}{a_o r}$$

If you use this in the radial equation, you find:

$$\frac{R}{a_o^2}-\frac{2R}{a_o r}+\frac{2\mu}{\hbar^2}\left[E+\frac{e^2}{4\pi\varepsilon_0 r}\right]R=0\Rightarrow\left[\frac{1}{a_o^2}+\frac{2\mu}{\hbar^2}E\right]+\left[\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2}-\frac{2}{a_0}\right]\frac{1}{r}=0$$

This provides the condition upon the constant a_o: it needs to be such that the 1/r term multiplies zero. This then gives:

$$a_o=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

In fact, this is exactly the Bohr radius (see eq. 4.24). To find the energy, we then have:

$$E=-\frac{\hbar^2}{2\mu a_o^2}=-E_o$$

This is again equal to the lowest Bohr energy with the value of 13.6 eV.

Although we won't show it here, application of the same procedure will provide us with the result:

$$E_n=-\frac{E_o}{n^2};n=1,2,3,...$$

With the restriction placed upon the other quantum numbers which is:

$$\ell < n; |m_\ell| \leq \ell$$

The hydrogen radial wave functions are given by: (table 7.1)

n	l	$R_{n,l}$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2-\frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27-18\frac{r}{a_o}+2\frac{r^2}{a_o^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6-\frac{r}{a_o}\right)\frac{r}{a_o}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_o^2}e^{-r/3a_0}$

Solution of the Angular and Azimuthal Equaiton

It is customary to link the two angular solutions together into one solution which is an example of spherical harmonics:

$$Y(\theta,\varphi)=f(\theta)g(\varphi)$$

The f portion is always a polynomial of sin and cosines of order ℓ.

The normalized spherical harmonics are shown in table 7.2 of your text:

ℓ	m_ℓ	Y_{ℓ,m_ℓ}
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\varphi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\cos^2\theta-1\right)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\varphi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}\left(5\cos^3\theta-3\cos\theta\right)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta\left(5\cos^2\theta-1\right)e^{\pm i\varphi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta e^{\pm 2i\varphi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta e^{\pm 3i\varphi}$

The probability density for the electron in the hydrogen atom is given by $\psi^*\psi$ where the wave function for the hydrogen atom is given by:

$$\Psi_{n,\ell,m_\ell} = R_{n,\ell}(r)\,Y_{\ell,m_\ell}(\theta,\varphi)$$

Section 7.3: Quantum Numbers

The three quantum numbers that we have obtained are:

n: the principal quantum number

l, : the orbital angular momentum quantum number

m_l: the magnetic quantum number

Example: What are the possible quantum numbers for a n=4 state in atomic hydrogen?

n	l	m_l
4	0	0
4	1	-1,0,1
4	2	-2,-1,0,1,2
4	3	-3,-2,-1,0,1,2,3

What is needed is a more physical interpretation of the meaning of these quantum numbers. The principle quantum number is the only quantum number that determines the energy states of hydrogen (ok, this is really not 100% true). This determines essentially the distance the wave function is going to be from the center, although this is not a completely correct description.

The orbital angular momentum quantum number *l* is associated only with the R and f functions of the wave function. Classically, we could find the angular momentum by:

$$\vec{L} = \vec{r} \times \vec{p}$$

The quantum number l is related to the magnitude of the orbital angular momentum L by:

$$L = \sqrt{\ell(\ell+1)}\hbar$$

This strange dependence must for now be accepted as a result of the quantum mechanics of the situation. Clearly, this angular momentum is at odds with Bohr's theory since, among other things, the possibility of L=0 is realized here. The energy levels are degenerate with regard to L. This most certainly was not in Bohr's theory.

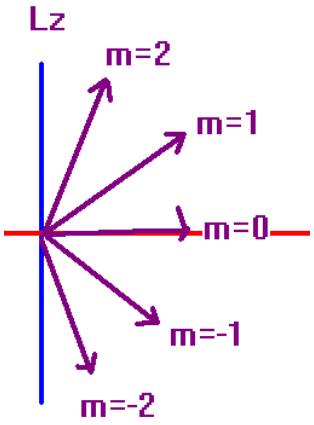
It is historically customary to associate letters with the values of angular momentum.

l	0	1	2	3	4
letter	s	p	d	f	g

which came originally from the spectroscopic names Sharp, Principal, Diffuse, and Fundamental. Higher letters follow the English alphabet. Note however that this is not spectroscopic notation and spectroscopic notation can be ambiguous and confusing.

Atomic states are normally referred to by the n number and the l number. Thus a state with n=2 and l=1 is called a 2p state.

The direction of the orbital angular momentum is determined actually by the magnetic quantum number, m_ℓ.



The values of the projection of the orbital angular momentum are given by:

$$L_z = m_\ell \hbar$$

We can also, for example, find out the angles shown in the above image.

How?

Consider the m=2 state above. Then the angle between L and the z axis is given by:

$$L_z = L\cos(\gamma) \Rightarrow \cos(\gamma) = \frac{L_z}{L} = \frac{2}{\sqrt{2(3)}} = \frac{2}{\sqrt{6}} \Rightarrow \gamma = 35^0, 65^0, 90^0, \ldots$$

now let me try to give you the argument for the unusual dependence of the angular momentum upon the quantum number.

There are a total of $2\ell+1$ allowed values of m_ℓ for a given value of L. Because there is nothing special about a particular direction of space, we expect:

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \langle L_z^2 \rangle$$

The average value of L^2 (Note the error in your text here) is then going to be given by:

$$\langle L^2 \rangle = 3\langle L_z^2 \rangle$$

To find the average value of L_z^2, we add up all the possible values and divide by the number of values. Thus:

$$\langle L_z^2 \rangle = \frac{\sum_{m_\ell=-\ell}^{m_\ell=+\ell} m_\ell^2 \hbar^2}{2\ell+1} = \frac{1}{3}\ell(\ell+1)\hbar^2$$

We thus have the result:

$$\langle L^2 \rangle = 3\langle L_z^2 \rangle = \ell(\ell+1)\hbar^2$$

This then tells us the values for the angular momentum:

$$L = \sqrt{\ell(\ell+1)}\hbar$$