

Introduction to Quantum Mechanics
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Lecture - 06

Solution for the radial component of wavefunction for the hydrogen atom

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General Solution for Spherically
Symmetric Systems

$$-\frac{\hbar^2}{2m} u'' + \frac{l(l+1)\hbar^2}{2mr^2} u + V(r)u = Eu$$
$$\frac{u}{r} = R(r) \quad \psi = R(r) Y_{lm}(\theta, \phi)$$
$$u \rightarrow r^{l+1} \text{ as } r \rightarrow 0$$

HYDROGEN ATOM / HYDROGEN-LIKE IONS

In the previous lecture we looked at the general solution for spherically symmetric systems, where we looked at the Schrodinger equation minus \hbar^2 over $2m$ u'' plus $\frac{l(l+1)\hbar^2}{2mr^2} u$ plus $V(r)u$ equals Eu ; where u/r gives me the radial component of the wave function and the wave function ψ itself is R as the function of r times Y_{lm} theta and phi. And found that u goes to r^{l+1} as r tends to 0.

In this lecture we want to focus on a specific problem of the hydrogen atom or hydrogen-like ions.

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$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$
$$-\frac{\hbar^2}{2m} u'' + \frac{l(l+1)\hbar^2}{2mr^2} u - \frac{Ze^2}{4\pi\epsilon_0 r} u = Eu$$

(1) We want to solve for bound states
 $E < 0$ $E = -|E|$

$$-\frac{\hbar^2}{2m} u'' + \frac{l(l+1)\hbar^2}{2mr^2} u - \frac{Ze^2}{4\pi\epsilon_0 r} u = -|E|u$$

$u(r \rightarrow \infty) ??$ ignore $\frac{1}{r^2}$ & $\frac{1}{r}$ terms

In such cases the potential energy $v r$ of the electron is given as minus $Z e$ square over 4π epsilon $0 r$. And therefore, the equation for u is going to be minus h cross square over $2 m$ u double prime plus $l l$ plus 1 h cross square over $2 m r$ square where m is the mass of the electron minus $Z e$ square over 4π epsilon $0 r$ u equals $E u$; I missed a u here. And this is the equation we want to solve.

What I am going to do in this lecture is not give you very rigorous solutions, I will give solutions for one or two values of l . And enable you enough to follow this in books if you wish too, because this is the first course so I do not really give a many details here.

So, now first thing we notice is we want to solve for bound states, and therefore E is less than 0 I am going to write E as minus modulus of E . And therefore, my equation now becomes minus h cross square over $2 m$ u double dash plus $l l$ plus 1 h cross square over $2 m r$ square u minus $Z e$ square over 4π epsilon $0 r$ u equals minus modulus of $E u$. So, first thing as we did in harmonic oscillators and all that we wish to see how u behaves as r tends to infinity; behaviour of u as r tends to infinity. In such cases I can ignore 1 over r square and 1 over r terms because they will become nearly 0 .

And therefore, I can write the equation as.

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In the limit of $r \rightarrow \infty$

$$-\frac{\hbar^2}{2m} u'' = -|E| u$$
$$u'' - \frac{2m|E|}{\hbar^2} u = 0$$

~~$u(r) = e^{\sqrt{\frac{2m|E|}{\hbar^2}} r} \quad \text{or} \quad e^{-\sqrt{\frac{2m|E|}{\hbar^2}} r}$~~

$$R(r \rightarrow \infty) \rightarrow 0 \Rightarrow u \rightarrow 0 \text{ as } r \rightarrow \infty$$
$$u(r) \sim e^{-\sqrt{\frac{2m|E|}{\hbar^2}} r} \sim e^{-\alpha r}$$
$$\alpha = \sqrt{\frac{2m|E|}{\hbar^2}}$$

So, in the limit of r tending to infinity I can write my equation as minus \hbar cross square over $2m$ u double prime is equal to minus $|E| u$ or u double prime minus $2m|E|$ over \hbar cross square u equals 0 . This has immediate solutions u equals either e raise to square root of $2m|E|$ over \hbar cross square r or e raise to minus square root of $2m|E|$ over \hbar cross square r .

Now, we would like the solution R r tending to infinity to go to 0 , which implies u also should go to 0 as r tends to infinity. So, the first solution this one is out. So, what we have is that u goes as e raise to minus square root of $2m|E|$ over \hbar cross square r which I will write as e raise to minus αr ; α is square root of $2m|E|$ over \hbar cross square.

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General Solution $u(r) = \left[\sum_{i=1}^n (a_i r^i) \right] e^{-\alpha r}$

(1) The polynomial in r is finite
 (2) lowest power of r is 1
 $u \rightarrow 0$ as $r \rightarrow 0$

$l=0$ Case: $-\frac{\hbar^2}{2m} u'' - \frac{Ze^2}{4\pi\epsilon_0 r} u = E u$

$u = r e^{-\alpha r}$ $u' = e^{-\alpha r} - \alpha r e^{-\alpha r}$
 $u'' = -2\alpha e^{-\alpha r} + \alpha^2 r e^{-\alpha r}$

$-\frac{\hbar^2}{2m} (-2\alpha + \alpha^2 r) e^{-\alpha r} - \frac{Ze^2}{4\pi\epsilon_0} e^{-\alpha r} = E r e^{-\alpha r}$

Now the general solution therefore: $u(r)$ this will depend on l can be written as summation i equals 1 through whatever some polynomial n ; $a_i r^i$ times this is a polynomial e raise to minus αr . The polynomial is finite polynomial because you can show if n tends to infinity this blows up as e raise to plus αr and you do not want that to happen, because solution would not be going to 0 as r tends to infinity. So, you wanted to be a finite polynomial.

So, number one notice that the polynomial in r is finite. And number two that the lowest power of r is 1. Why is that because you want u to be go into 0 as r tends to 0. So, these are two things that we keep in mind. And now what I will do is instead of solving for this polynomial in general I will build up solution for certain cases.

So, let me consider l equals 0 case first. In that case my equation is u double prime minus h cross square over $2m$, minus $Z e$ square over $4 \pi \epsilon_0 r$ u equals $E u$. I am going to consider u equals $r e$ raise to minus αr which means that u prime is e raise to minus αr minus αr e raise to minus αr , and therefore u double prime is $-2 \alpha e$ raise to minus αr plus $\alpha^2 r e$ raise to minus αr .

Let us substitute this in the equation I get $-\frac{\hbar^2}{2m} (-2\alpha + \alpha^2 r) e$ raise to minus αr minus $\frac{Ze^2}{4\pi\epsilon_0} e$ raise to minus αr equals $E r e$ raise to minus αr ; e raise to minus αr term cancels throughout.

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$$-\frac{\hbar^2}{2m} (-2\alpha + \alpha^2 r) - \frac{Ze^2}{4\pi\epsilon_0} = Er$$

$$+\frac{\hbar^2\alpha}{m} - \frac{Ze^2}{4\pi\epsilon_0} = 0$$

$$-\frac{\hbar^2}{2m} \alpha^2 = E$$

$$\alpha^2 = \frac{2m|E|}{\hbar^2}$$

$$\Rightarrow E = -|E|$$

$$\frac{\hbar^2}{m} \sqrt{\frac{2m|E|}{\hbar^2}} = \left(\frac{Ze^2}{4\pi\epsilon_0}\right)$$

$$|E| = \frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2$$

$$E = -\frac{Z^2 e^4 m}{32\pi^2 \epsilon_0^2 \hbar^2} = -13.6 Z^2 \text{ eV}$$

So, I am left with minus \hbar^2 over $2m$ minus 2α plus $\alpha^2 r$ minus $Z e^2$ over $4\pi\epsilon_0$ is equal to E times r . Now terms of the same power should be the same and this immediately tells me that minus \hbar^2 over m plus $\alpha^2 r$ minus $Z e^2$ over $4\pi\epsilon_0$ is 0. And minus \hbar^2 over $2m$ alpha square is equal to E .

This is automatically satisfied because alpha square is $2m|E|$ over \hbar^2 and this therefore gives me that E is equal to minus $|E|$. This is something we have been working with, but this equation gives me the energy because this tells me that \hbar^2 over m square root of $2m|E|$ over \hbar^2 is equal to $Z e^2$ over $4\pi\epsilon_0$. And therefore, $|E|$ comes out to be $Z e^2$ over $4\pi\epsilon_0$ square times m over $2\hbar^2$. And therefore, the energy for this state is minus Z square e^4 m over $32\pi^2 \epsilon_0^2 \hbar^2$ which comes out to be minus $13.6 Z^2$ electron volts.

So, we found that this is the ground state energy.

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$$R(r) = C_n \frac{r e^{-\alpha r}}{r} Y_{00}(\theta, \phi)$$

$$= C_n e^{-\alpha r} Y_{00}$$

$e^{-\alpha r}$

$l=0$ $u(r) = (ar + br^2) e^{-\alpha r}$ Highest power of $r = 2$

$$u'(r) = (a + 2br) e^{-\alpha r} - \alpha (ar + br^2) e^{-\alpha r}$$

$$u''(r) = 2b e^{-\alpha r} - 2\alpha (a + 2br) e^{-\alpha r} + \alpha^2 (ar + br^2) e^{-\alpha r}$$

And the wave function $R(r)$ for the ground state energy is going to be $r e^{-\alpha r}$ divided by r times $Y_{00}(\theta, \phi)$ plus some normalization constant which can be calculated. So, this state is $e^{-\alpha r} Y_{00}$ which is also a constant C_n .

So, the ground state looks like finite at $r = 0$ and this decays exponentially it is $e^{-\alpha r}$ times a constant Y_{00} . Still working on $l = 0$; let us find out the solution which is a higher polynomial. So, I am going to take $u(r)$ to be $ar + br^2 e^{-\alpha r}$. So, this highest power of n in this is 2.

You again calculate $u'(r)$ which is $a + 2br e^{-\alpha r} - \alpha ar - \alpha br^2 e^{-\alpha r}$, and $u''(r)$ is equal to $2b e^{-\alpha r} - 2\alpha(a + 2br) e^{-\alpha r} + \alpha^2(ar + br^2) e^{-\alpha r}$; this is $e^{-\alpha r}$ times $2b - 2\alpha(a + 2br) + \alpha^2(ar + br^2)$ here. We substitute this n . So, next step is going to be.

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• Substitute this in the equation for u

• Equate coefficients for the

$$E = -\frac{1}{2^2} \cdot \left(\frac{Z^2 e^4 m}{32 \pi^2 \epsilon_0^2 \hbar^2} \right)$$
$$u(r) = (ar + br^2 + cr^3)$$
$$E = -\frac{1}{3^2} \left(\frac{Z^2 e^4 m}{32 \pi^2 \epsilon_0^2 \hbar^2} \right)$$

The energy for a state with $l=0$ is $-\frac{13.6 Z^2}{n^2}$
where n is the degree of polynomial for $u(r)$

Substitute this in the equation for u , then equate coefficients for the equal powers of r . To do that and you are going to find that E comes out to be in this case as 1 over 2 square Z square e raise to 4 m over 32 π square ϵ_0 square \hbar cross square. You go further if I take $u r$ to be as ar plus br square plus cr cubed and substitute in the equation you would find that E comes out to be minus 1 over 3 square Z square e raise to 4 n over 32 π square ϵ_0 square \hbar cross square.

So, if you do this exercise what you will conclude is that the energy for a state with l equal to 0 is minus $13.6 Z$ square over n square where, n is the degree of polynomial for $u r$.

So, I will leave that for you. You can go to higher and higher powers. As an illustration let us also take a case of l equals 1 .

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$l=1: u(r) \text{ as } r \rightarrow 0 \sim r^{l+1} = r^2$
 $u(r) = r^2 e^{-\alpha r}$
 $u'(r) = 2r e^{-\alpha r} - \alpha r^2 e^{-\alpha r}$
 $u''(r) = 2e^{-\alpha r} - (2\alpha r e^{-\alpha r}) \times 2 + \alpha^2 r^2 e^{-\alpha r}$
 $= 2e^{-\alpha r} + 4\alpha r e^{-\alpha r} + \alpha^2 r^2 e^{-\alpha r}$
 $-\frac{\hbar^2}{2m} [2 + 4\alpha r + \alpha^2 r^2] e^{-\alpha r} + \frac{2\hbar^2}{2m r^2} \cdot r^2 e^{-\alpha r} - \frac{Ze^2}{4\pi\epsilon_0} \cdot r e^{-\alpha r} = E r^2 e^{-\alpha r}$
 $-\frac{\hbar^2}{2m} + \frac{2\hbar^2}{2m} = 0$
 $-\frac{\hbar^2}{2m} + \frac{2\hbar^2}{2m} = 0$

Now, remember for l equals 1 u as r tends to 0 goes as r raised to 1 plus 1 which is r squared. So, the minimum power of r that you take is r squared. In this case I am going to take u as r squared e raised to minus αr . Therefore, u' is going to be $2r e$ raised to minus αr minus $\alpha r^2 e$ raised to minus αr and u'' is going to be equal to $2 e$ raised to minus αr minus $2\alpha r e$ raised to minus αr times 2 plus $\alpha^2 r^2 e$ raised to minus αr . So, this comes out to be $2 e$ raised to minus αr plus $4\alpha r e$ raised to minus αr plus $\alpha^2 r^2 e$ raised to minus αr .

Let us substitute this in the equation. So, I get minus \hbar^2 over $2m$ plus $4\alpha r$ plus $\alpha^2 r^2$ e raised to minus αr plus now 1 is not 0 so I am going to get $2\hbar^2$ over $2m r^2$ and I have $r^2 e$ raised to minus αr minus $\frac{Ze^2}{4\pi\epsilon_0} \cdot r e$ raised to minus αr is equal to $E r^2 e$ raised to minus αr . $E e$ raised to minus αr cancels throughout. And when I equate the terms of equal powers of r I get minus \hbar^2 over m plus $2\hbar^2$ over $2m$ and this term actually cancels to 0 which is cancelling. So, let us do that, this term cancels with the first term this is 0.

Equate the terms with power r and I get minus \hbar^2 times 4α over $2m$ minus $\frac{Ze^2}{4\pi\epsilon_0}$ equals 0 and this gives me the energy. And the last

term $E r^2$ term would actually cancel with this α^2 term that basically it give me E equals minus mod E which we already know.

So, the energy is determined by this term in green, so this cancels again this gives me 2.

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The image shows a whiteboard with the following handwritten equations and text:

$$-\frac{2\hbar^2}{m}\alpha = \left(\frac{Ze^2}{4\pi\epsilon_0}\right)$$

$$\alpha^2 = \frac{1}{4} \left[\frac{m^2}{\hbar^4} \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \right]$$

$$\frac{2m|E|}{\hbar^2} = \frac{1}{4} \left[\frac{m^2}{\hbar^4} \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \right]$$

$$|E| = \frac{1}{4} \left[\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \right]$$

$$E = -\frac{1}{4} 13.6 Z^2$$

$r^2 \rightarrow \frac{1}{2^2} (\quad)$ The degree of polynomial for $u(r)$ determines the energy.

So, I get minus $2\hbar^2$ over m α equals $Z e^2$ over $4\pi\epsilon_0$. So, α^2 is equal to m^2 over \hbar^4 $Z^2 e^4$ over $4\pi\epsilon_0^2$ and $1/4$ here. So, α^2 is $1/4 m^2$ over \hbar^4 $Z^2 e^4$ over $4\pi\epsilon_0^2$. And α^2 is nothing but $2m|E|$ over \hbar^2 which is equal to one-fourth m^2 over \hbar^4 $Z^2 e^4$ over $4\pi\epsilon_0^2$.

And you see this again gives me after simplifying modulus of E equals one-fourth of m over $2\hbar^2$ $Z^2 e^4$ over $4\pi\epsilon_0^2$, which is nothing but E equals minus one-fourth $13.6 Z^2$. So, again we see that the power r^2 leaves to energy $1/2^2$ times at minus $13.6 Z^2$.

So, what we conclude in this through this and you can keep trying it for other else that the degree of polynomial for $u(r)$ determines the energy.

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$$U(r) = \sum_{l=1}^n a_l r^l$$

$$E_n = -\frac{13.6 Z^2}{n^2} \quad (E_n \text{ does not depend on } l)$$

$$\psi_{n,l,m} = R_{nl}(r) Y_{lm}(\theta, \phi)$$

$$l \leq (n-1) \Rightarrow l = 0, 1, 2, \dots, (n-1)$$

$$-l \leq m_l \leq l \Rightarrow m_l = -l, -(l-1), \dots, 0, 1, 2, \dots, l-1$$

Number of electrons in the n^{th} level

$n \rightarrow (0, 1, \dots, l-1)$ l levels
 \downarrow
 $(2l+1)$ states m_l \rightarrow 2 electrons due to Pauli exclusion principle

Then what does it give me? That if $U(r)$ is summation i equals 1 through n $a_i r^i$ then the energy comes out to be it depends on n minus $13.6 Z^2$ over n^2 . Keep in mind that E does not depend on l . So, this is quite a coincidence for hydrogen atom E_n does not depend on l . But r does, so the wave function is written as n, l and m and this is $R_{nl}(r) Y_{lm}(\theta, \phi)$. So, r depends on l , but the energy does not. And what is also found in this solution when you do it that l is restricted to below n minus 1. So, this means l can be 0, 1, 2, and so on up to n minus 1.

Other thing is that m_l ; let me write it m_l is restricted to be below between minus l plus l implies m_l as from minus l minus l plus 1 so on 0 1 2 up to l plus 1. So, the number of electrons in the n th level will be. So, for each n I have energy levels with the same energy because it depends only on n 0 1 up to l minus 1; l levels. And for each l I have $2l + 1$ states with m_l , and for each there can be two electrons due to Pauli exclusion principle.

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Handwritten mathematical derivation on a whiteboard showing the calculation of the maximum number of electrons in the n^{th} level. The text is written in black ink, with some steps in red and the final result in green.

$$\begin{aligned} & \text{Number of electrons in the } n^{\text{th}} \text{ level} \\ & \sum_{l=0}^{n-1} (2l+1) \cdot 2 \\ & = 4 \cdot \sum_{l=0}^{n-1} l + 2 \sum_{l=0}^{n-1} 1 \\ & = 4 \frac{n(n-1)}{2} + 2 \times n \\ & = 2n^2 - 2n + 2n \\ & = 2n^2 \end{aligned}$$

Number of electrons (maximum) in the n^{th} level = $2n^2$

So, what we get is number of electrons in the n^{th} level is going to be summation $2l + 1$ times 2 l equal to 0 to n minus 1 . So, this gives me 4 summation l equals 0 to n minus 1 plus 2 summation l equals 0 to n minus 1 minus 1 . So, this comes out to be $4 \frac{n(n-1)}{2} + 2 \times n$. So, this is going to be $2n^2 - 2n + 2n$. So, this comes out to be $2n^2$. So, number of electrons maximum in the n^{th} level is equal to $2n^2$.

So, what I have done in this lecture is given to you an indication has to how hydrogen atom problem is solved.

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CONCLUDE

- Set up the Schrödinger equation for Hydrogen-like systems
- Take $u(r) = \sum_{i=1}^n (a_i r^i) e^{-\alpha r}$ $\alpha = \sqrt{\frac{2m|E|}{\hbar^2}}$
- Found $E_n = -\frac{13.6 Z^2}{n^2}$
- E depends only on n
 $R_{nl} Y_{ln} = \psi_{nlm}$
- n^{th} level can accommodate $2n^2$ electrons

So, to conclude this lecture what we have done is: one, set up the Schrodinger equation for hydrogen like systems. Two, taken $u(r)$ to be equal to summation i equals 1 through n $a_i r^i e^{-\alpha r}$ where α is square root of $2m|E|$ over \hbar cross square. Then found E_n to be equal to minus $13.6 Z^2$ over n^2 where n reverse to this power. And finally, E depends only on n $R_{nl} Y_{ln}$ is the wave function ψ_{nlm} . And n -th level can accommodate $2n^2$ electrons.

With this we stop the discussion on hydrogen atom, and next week we will begin with numerical solution of this radial equation.