

Chemistry I - CY1001
Introductory Quantum Mechanics and Spectroscopy
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Lecture – 08

Lecture 5: Part I - The quantum mechanics of Hydrogen atom

Welcome back to the lectures on CY1001 or introductory chemistry. In this group of lectures consisting of several thoughts, I shall describe the quantum mechanics associated with the hydrogen atom, the solution of the Schrodinger equation I will give you the results. The solution of the Schrodinger equation has its first major achievement in arriving at the spectra of the hydrogen atom which were known for many decades before that and it is the spectra of the hydrogen atom which prompted Niels Bohr who came up with his first model of quantizing the energy and quantizing the angular momentum of an atom.

Schrodinger equation of course does this using his prescription and to the wave function and we shall see some of the details in the calculation of the energies and in the calculation of probabilities of the electrons and so on.

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The image shows a digital whiteboard with handwritten notes. At the top, the Schrodinger equation is written as $\hat{H}\psi = E\psi$ with $\psi(x, y, z)$ below it. To the left, a diagram shows a nucleus labeled $+Ze$ and an electron labeled e^- at a distance r . To the right, the reduced mass μ is defined as $\mu = \frac{m_e m_p}{m_e + m_p}$. Below this, it is noted that $\mu \approx \frac{m_e m_p}{m_p}$ and $m_p \gg m_e$. At the bottom, the approximation $\mu \approx m_e$ is written. The NPTEL logo is visible in the bottom left corner of the whiteboard.

So, this is part I of the quantum mechanics of hydrogen atom and in the solution of this equation $\hat{H}\psi$ is equal to $E\psi$, where now ψ is three dimensional Cartesian co-

ordinate. We do use a classical starting point of the nucleus with an electron somewhere and the nucleus having a positive charge plus $z e$; z is 1 and the electron with a minus charge and the distance of r .

I shall not describe this as a 2 body problem even though that is the right way of doing it. The 2 body problem and then remove the centre mass from the 2 body problem and study only the relevant motion of the 2 particle system, which in this case the relative mass or the reduced mass for the 2 particle system is the mass of the electron, times the mass of the proton divided by the mass of the electron plus that of the proton which is approximately the mass of the electron divided by the times mass of the proton divided by the mass of the proton; since m_p is much much greater than m_e and therefore, μ turns out to be approximately m_e ; when you cancel the m_p .

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$\mu \approx m_e$

$m_e.$

Hamiltonian for electron.

$$\hat{H} = \frac{1}{2m_e} \hat{p}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$p_x^2 + p_y^2 + p_z^2$

We shall worry about making the approximation and write the mass as nothing but the mass of the electron therefore, we needed the Hamiltonian for the electron. So, let us assume that the nucleus is stationary; does not contribute to the overall kinetic energy of the atom and that is already there in the centre of mass which is not considered here. Therefore, if you write the kinetic energy and the potential energy operator for the hydrogen atom, it will be in terms of the operators it will be p square; 1 by $2 m_e$ minus $z e$ square by $4 \pi \epsilon_0 r$, which is the classical columbic energy of interaction between the positive and the negative charge.

And this p square which is an operators is given by p_x square plus p_y square plus p_z square the three components of the momentum, in a co-ordinate system which is probably fixed in the nucleus itself for arguments

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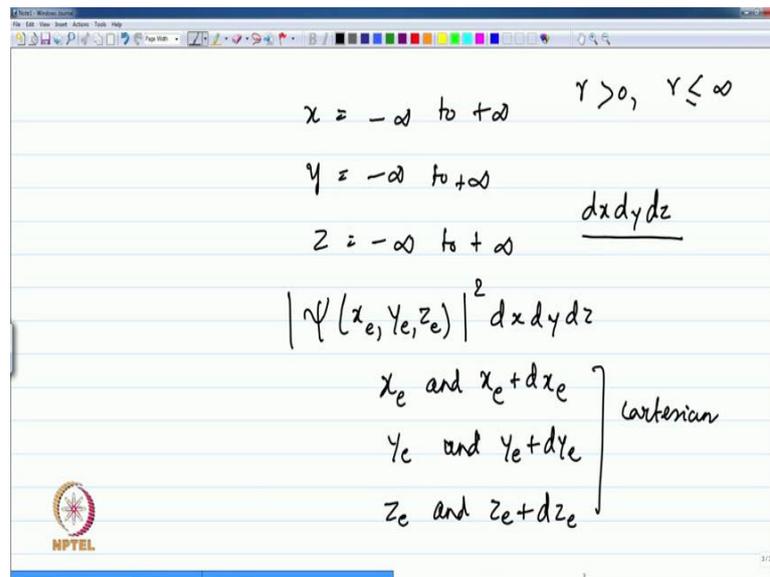
$$\hat{H} = -\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{ze^2}{4\pi\epsilon_0 r}$$

$x = -\infty$ to $+\infty$ $r > 0, r \leq \infty$
 $y = -\infty$ to $+\infty$
 $z = -\infty$ to $+\infty$

And then of course, p_x is replaced by the derivative operators so that the Hamiltonian becomes minus \hbar square by $2m_e$; $\text{d}ou$ square by $\text{d}ou x_e$ square plus $\text{d}ou$ square by $\text{d}ou y_e$ square plus $\text{d}ou$ square by $\text{d}ou z_e$ square, where these are the coordinates of the electron with respect to that origin. And then you have the potential energy minus $z e$ square by $4\pi\epsilon_0 r$ and r is in principle greater than 0 and less than or equal to infinity; at infinity of course, the coulombic interaction is 0.

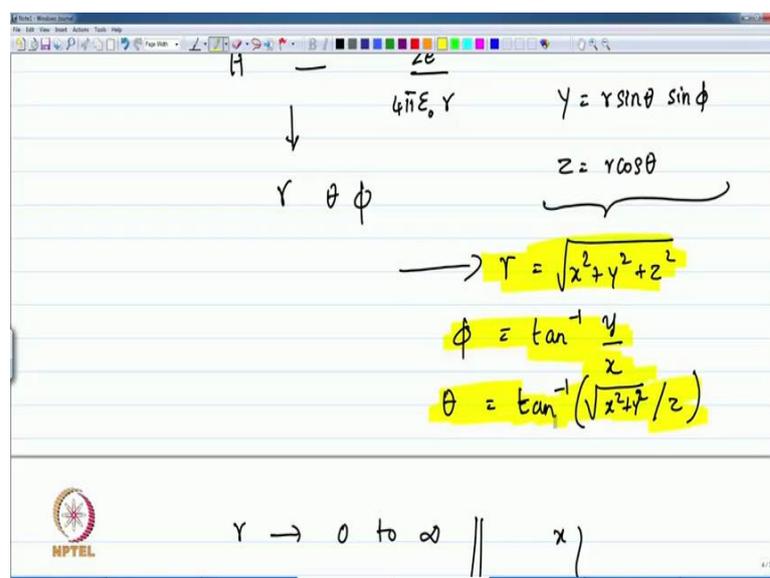
Therefore here the boundary includes the entire three dimensional world, the whole universe. So, the boundaries are explicitly x is from minus infinity to plus infinity, y is from minus infinity to plus infinity and also z is from minus infinity to plus infinity, so this is the three dimensional region and the volume element that we talk about for the particle.

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For the electron probability is the psi is the volume element is d x, d y, d z and then the probability is psi x e, y e, z e absolute square; d x, d y, d z. As the probability of finding the electron in the region or in the cube between x e and x e plus d x e; y e and y e plus d y e and z e than z e plus d z e. This is the three dimensional Cartesian coordinate representation for the hydrogen electron problem; the nucleus electron problem.

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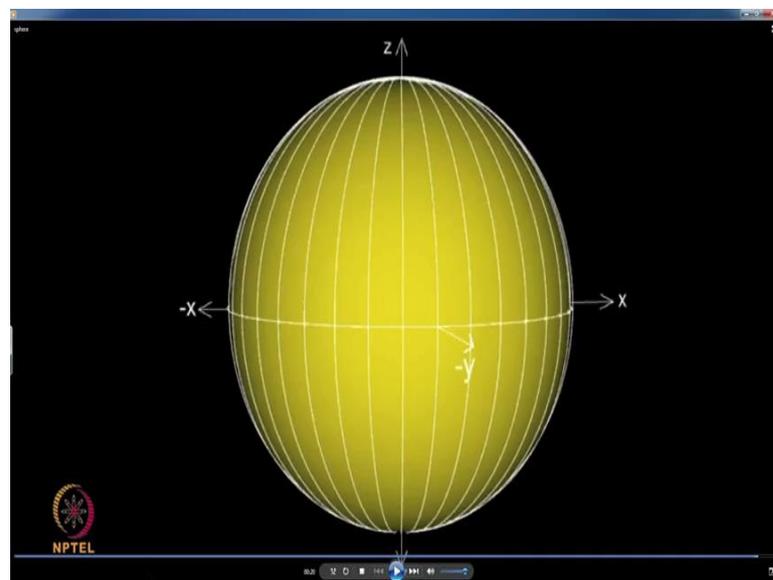
Instead of Cartesian coordinates in the case of hydrogen atom, one uses spherical polar coordinates and the reason for that is that, if you look at the hydrogen atom the potential

energy is spherically symmetric. Therefore, the important contribution to the stability of the hydrogen atom which is the binding energy between that coulombic charges being spherically symmetrical, the system is better described using the spherical polar coordinates which if you recall have three variables; the various of the sphere and then the polar angles theta and phi on the sphere.

The standard relations for these are x is equal to $r \sin \theta \cos \phi$ and y is $r \sin \theta \sin \phi$ and z is $r \cos \theta$. These are the coefficients for the transformation between polar and Cartesian coordinates and the inverse transformation is of course, r is square root of $x^2 + y^2 + z^2$ and if you take the ratio of x by y or $\sin \theta$ cancels off and you have $\cos \phi$ or ϕ is $\tan^{-1} y/x$, and the last relation is θ which is given in terms of \tan^{-1} ; square root of $x^2 + y^2$ divided by z .

So, the coordinate transformation allows you to either use the spherical or the Cartesian coordinate by using the relationship between them and this one animation gives you the relation or the visualization of the spherical polar coordinate system and the values between 3D animation.

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Here the relation between the Cartesian and the spherical system is given for a given one value of r , the radius of this sphere and you can see that if you fix a polar axis, call it as an axis then the polar angle θ is the angle θ varying from 0 to π as shown by these different radii.

So, that is the variation of theta and theta varies from 0 to pi only and the other angle is of course, the azimuthal angle phi which is perpendicular in a plane perpendicular to this and if you rotate this arc; semi arc by 2 pi you generate the surface of this sphere. So, that is it the azimuthal angle phi with respect to a chosen x axis. So that is a spherical coordinate system in which you can see the variation in theta given by these the different arcs and the value of phi corresponding to each one of these arcs, starting from the x axis here at some arbitrary point and then going around the x axis to the plus y, to the minus x to the minus y and back you have 2 pi.

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$$\begin{array}{l}
 r \rightarrow 0 \text{ to } \infty \\
 \theta \rightarrow 0 \text{ to } \pi \\
 \phi \rightarrow 0 \text{ to } 2\pi
 \end{array}
 \left\| \begin{array}{l}
 x \\
 y \\
 z
 \end{array} \right\} -\infty \text{ to } +\infty$$

$$dx dy dz \rightarrow r^2 dr \sin \theta d\theta d\phi$$

Therefore, if we recall our lecture component r varies from 0 to infinity being the radius of the sphere, the sphere is from 0 radius to all over the universe and theta varies from 0 to pi as if the polar angle varying from 0 to pi as you have seen with respect to the z axis and the phi which goes around the circle in 2 pi; phi is 0 to 2 pi. And these are relations in parallel to the x, y, z; all going from minus infinity to plus infinity in the Cartesian axis in taking care of the whole universal space. Therefore, these are the limits and dx, dy, dz which is a volume element in Cartesian coordinate space, will have to be expressed in terms of the volume elements in spherical polar coordinate system and that is given by r square, d r sin theta, d theta d phi.

Those of you who are not familiar with this transformation must go back and look at to the coordinate transformation and simple differentials expressed from one coordinate to the other.

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$\phi \rightarrow 0 \text{ to } 2\pi$

$dx dy dz \rightarrow r^2 dr \sin \theta d\theta d\phi$

$dx dy dz = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix} dr d\theta d\phi$

← Jacobian

And the relations are given by what is known as the Jacobian, the magnitude of the Jacobian. The Jacobian being the partial derivative of x with respect to r, x with respect to theta and x with respect to phi and the partial derivative of y with respect to r; with respect to theta and with respect to phi and likewise the partial derivative of z with respect to r and with respect to theta, with respect to phi. The determinant of this multiplied by d r d theta, d phi, this is called the Jacobian and this is in elementary transformation matrix that transforms volume elements from one coordinate system to another coordinate system and this Jacobian with the magnitude has the r square sin theta, with the d r, d theta, d phi.

Therefore, when you calculate the volume elements and when you calculate the probabilities using polar coordinate system, if you are using Cartesian coordinates transform the relation from Cartesian to the polar and these are the mathematical formulas already well known and derived from elementary differential calculus, keep the mind.

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$$\hat{H} = -\frac{\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r}$$

↓
Spherical Polar coordinates

$r \theta \phi$

$$\frac{\partial \psi(x, y, z)}{\partial x}$$

$$\psi(x, y, z) \Rightarrow \bar{\psi}(r, \theta, \phi)$$

Therefore now we have this Hamiltonian expressed in terms of minus h bar square by 2 m e; dou square by dou x e square plus dou square by dou y e square plus dou square by dou z e square minus h z e square by 4 pi epsilon naught r, this needs to be changed to spherical polar coordinates.

That is not a trivial exercise, but it is not a hard exercise. The derivates for example, dou by dou x of any function of x, y, z are expressed in another coordinate system like r theta phi, if you have to express phi in terms or r theta phi. The derivatives are expressed using the partial derivatives of the coordinates with respect to the new coordinates.

So, for example dou by dou x of psi if you wanted to write the appropriate wave function in the polar coordinate namely psi x, y, z is replaced by the corresponding substitution of the x and y and z using r theta phi using this function.

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The image shows a digital whiteboard with the following content:

At the top, the partial derivative with respect to x is written as $\frac{\partial}{\partial x}$.

Below that, the wave function is expressed in spherical coordinates: $\psi(x, y, z) \Rightarrow \bar{\Psi}(r, \theta, \phi)$.

The main derivation is the chain rule:
$$\rightarrow \frac{\partial \psi}{\partial x} = \left[\frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} \right] \bar{\Psi}(r, \theta, \phi)$$

Below this, the second-order partial derivatives are listed: $\frac{\partial^2}{\partial x^2}$, $\frac{\partial^2}{\partial y^2}$, and $\frac{\partial^2}{\partial z^2}$.

At the bottom left, there is an NPTEL logo.

Then there is a very simple partial derivative change rule, which tells you how to calculate $\frac{\partial \psi}{\partial x}$ as nothing other than $\frac{\partial \psi}{\partial r} \frac{\partial r}{\partial x}$ plus $\frac{\partial \psi}{\partial \theta} \frac{\partial \theta}{\partial x}$ plus $\frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial x}$ acting on the wave function $\psi(r, \theta, \phi)$.

So, this is the transformation of the derivative form of the Cartesian coordinate into the corresponding polar coordinates and of course, you can calculate $\frac{\partial r}{\partial x}$; $\frac{\partial \theta}{\partial x}$ and $\frac{\partial \phi}{\partial x}$ from the inverse relations that you already have; already have that.

From this, you can calculate the derivative of r with respect to x, y and z, the derivative of phi with respect to x, y and z and the derivative of theta with respect to x, y and z. Therefore the partial derivatives that you need to calculate for expressing the kinetic energy in spherical coordinate system involves three such quantities namely $\frac{\partial^2}{\partial x^2}$ which is operating this once more, but being careful that the terms contain already r, theta and phi and therefore, the partial derivatives have to be taken carefully and you have to do the same thing for $\frac{\partial^2}{\partial y^2}$ and $\frac{\partial^2}{\partial z^2}$.

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Handwritten mathematical derivations for partial derivatives of the wave function ψ with respect to y and z in spherical coordinates. The first part shows the derivative with respect to y as a sum of three terms: $\frac{\partial x}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi}$. The second part shows the derivative with respect to z as a sum of three terms: $\frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi}$. The wave function is denoted as $\bar{\psi}(r, \theta, \phi)$.

Therefore let me summarize this particular part of the lecture with the corresponding expressions namely $\frac{\partial \psi}{\partial y}$ as $\frac{\partial x}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi}$ acting on the wave function ψ of r θ and ϕ . And similarly $\frac{\partial \psi}{\partial z}$ as $\frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi}$ acting on the corresponding wave functions ψ r θ ϕ . These are the derivative equivalence and you calculate likewise the $\frac{\partial^2}{\partial y^2}$ terms, the $\frac{\partial^2}{\partial z^2}$ terms and the $\frac{\partial^2}{\partial z^2}$ term.

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Handwritten summary of the Hamiltonian operator for a hydrogen atom in spherical coordinates. The title is "Summary Hydrogen atom - spherical polar". The Hamiltonian is given as $H = -\frac{\hbar^2}{2m_e} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin^2 \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} - \frac{Ze^2}{4\pi\epsilon_0 r}$. Below this, the Schrödinger equation is written as $\hat{H} \bar{\psi}(r, \theta, \phi) = E \bar{\psi}(r, \theta, \phi)$ and $\hat{H} \psi(x, y, z) = E \psi(x, y, z)$, with arrows indicating the correspondence between the two forms.

So, the summary of doing that calculation and if you are doing it for the first time about 2 to 3 hours is what the time that you have to give, in order to add all these terms and cancel and arrive at the final form, but I will write the final magic form that everybody uses for solving the hydrogen atom.

Hamiltonian in polar spherical coordinates: the Hamiltonian is minus \hbar^2 by $2m_e$, $\frac{1}{r^2} \frac{d}{dr} (r^2 \frac{d}{dr}) + \frac{1}{r^2 \sin^2 \theta} \frac{d}{d\theta} (\sin^2 \theta \frac{d}{d\theta}) + \frac{1}{r^2 \sin^2 \theta} \frac{d^2}{d\phi^2}$ all of which is the transformation of the derivatives to the spherical polar form. And therefore, this is nothing but the kinetic energy term in terms of the spherical polar coordinates with the potential energy minus $\frac{ze^2}{4\pi\epsilon_0 r}$ and the equation that you are looking for solving is the $H\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$ instead of the $H\psi(x, y, z) = E\psi(x, y, z)$.

The wave functions are different in the different coordinate systems, but please remember the energy which is independent on the coordinate representation will not be different between different coordinate system, how you represent your coordinates should not lead to any changes in the eigen value for the hydrogen electron and therefore, the traditional method is to use the spherical polar coordinates and that allows the wave function to be separated into an r dependent wave function only, (Refer Time: 20:21) θ dependent wave function only and the ϕ dependent wave function only. If you recall the particularly the two dimensional box where we had an x, y dependent wave function being separated into an x only wave function term and an y only wave function term and we were able to get the energies and the solutions etcetera.

Therefore, separation of variables is far more detailed here in the case of hydrogen atom and let me stop with this as the focal point for the next part of the lecture on what is called the substitution of the wave function in terms of the three radial only polar θ angle dependent only and azimuthal angle ϕ dependent only functions and how we separate these into three different equations - we will not solve them, but in the second part we will look at the solution and in the third part we will see some physical representations of the wave functions themselves; the real and the imaginary parts. So let me start with part 1, here we will continue exactly from this in the next part until then.

Thank you.