

Reminder: The Hamiltonian Eigenstate Equation in spherical coordinates for an electron in the Coulomb electric field of a proton is given by

$$H\psi_E = -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi_E}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi_E}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi_E}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi_E = E \psi_E$$

where $\psi_E(r, \theta, \phi)$ is the wave function in spherical coordinates that describes the eigenstate of the Hamiltonian with the eigenvalue E (=total energy).

We are looking for wave function that can be written as product of separate functions of the three coordinates ("separation of variables"):

$$\psi_E(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

Last time we learned that the last function, $\Phi_m(\phi)$, can be chosen as an eigenstate to the operator L_z representing the z-component of the angular momentum:

$$\frac{e^{im\phi}}{\sqrt{2\pi}} = \Phi_m(\phi) \quad m=0, \pm 1, \pm 2, \dots \quad \rightarrow \quad L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad L_z \Phi_m = m\hbar \Phi_m$$

Furthermore, the second and third term in the Hamiltonian together represent the total angular momentum squared, $L^2/2mr^2$. So the product of the 2nd and 3rd term in $\psi_E(r, \theta, \phi)$ should combine to form eigenstates of that operator, with eigenvalues $\ell(\ell+1)\hbar^2$:

$$Y_{\ell, m}(\theta, \phi) = \Theta_{\ell, m}(\theta) \cdot \Phi_m(\phi) \quad L_z Y_{\ell, m} = m\hbar Y_{\ell, m} \\ \ell = 0, 1, 2, 3, \dots; \quad m = -\ell, -\ell+1, \dots, \ell-1, \ell \quad L^2 Y_{\ell, m} = \ell(\ell+1)\hbar^2 Y_{\ell, m}$$

Here is a short table of some of these eigenstates; more information can be found on our website:

ℓ	m	$Y_{\ell m}$ (values)	$\ell(\ell+1)$
0	0	$1/\sqrt{4\pi}$	0
1	-1	$\sqrt{3/8\pi} \sin\theta \cdot e^{-i\varphi}$	2
1	0	$\sqrt{3/4\pi} \cos\theta \cdot e^{i0}$	
1	+1	$\sqrt{3/8\pi} \sin\theta \cdot e^{+i\varphi}$	
2	0		6
	± 1		
	± 2		

[**Important Aside:** In the lecture, I forgot to mention the “spectroscopic notation” for ℓ . Here it is:

$\ell = 0 \Rightarrow$ “s-state” or “S”

$\ell = 1 \Rightarrow$ “p-state” or “P”

$\ell = 2 \Rightarrow$ “d-state” or “D”

$\ell = 3 \Rightarrow$ “f-state” or “F” and so on

These make NO sense but were introduced by atomic physicists looking at spectra before they even knew about quantized angular momenta.

Plugging everything in gives the new version of the eigenstate equation for the Hamiltonian:

$$\rightarrow \underbrace{-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)}_{\text{K.E.}} \psi_E + \frac{\vec{L}^2}{2mr^2} \psi_E - \frac{e^2}{4\pi\epsilon_0 r} \psi_E = E \psi_E$$

Plugging in our Ansatz

$$\psi_E(r, \theta, \varphi) = R(r) \cdot Y_{\ell, m}(\theta, \varphi)$$

and dividing both sides by $Y_{\ell, m}$ yields

$$\psi_E(r, \theta, \varphi) = R(r) \cdot Y_{\ell, m}(\theta, \varphi) \quad \text{Ansatz, divided by } Y_{\ell, m}$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} R(r) - \frac{e^2}{4\pi\epsilon_0 r} R(r) = E R(r)$$

$$E_{n, \ell} = -\frac{1}{n^2} R_y \quad R_y = 13.6 \text{ eV} \quad \text{Rydberg}$$

$$n = 1, 2, 3, \dots \quad n \geq \ell + 1$$

The solutions for $R_{n, \ell}(r)$ exist only for certain values of E , given (for each positive integer) by $E_{n, \ell}$ (see above). They are called “Laguerre Polynomials” and “Associated Laguerre Polynomials” -> see Wikipedia for more on those; the lowest order one is

$$R_{1,0}(r) \sim e^{-r/a_0}$$

Note that E is actually independent of ℓ , while the wave function itself definitely is very different for different ℓ . So the full solution can be written by specifying three quantum numbers:

$$[n, \ell, m \rightarrow \text{"orbital"}]$$

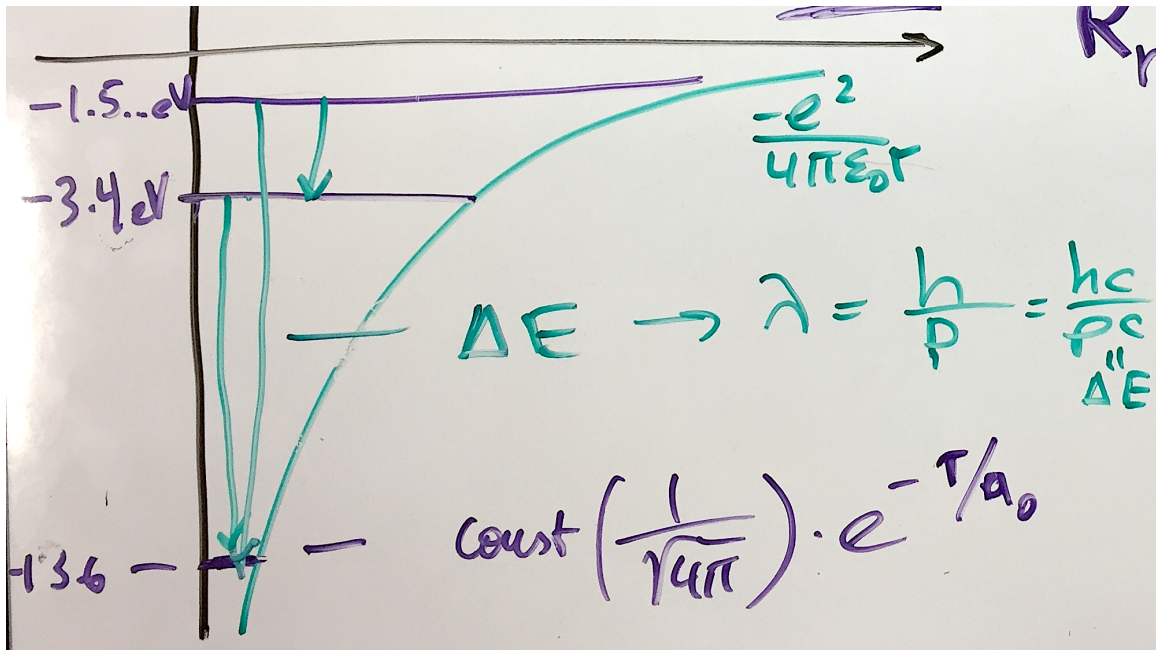
With the requirement that

$n = 1, 2, 3, \dots$ (main quantum number),

$\ell = 0, 1, \dots, n-1$ (total angular momentum quantum number = s, p, d, f, ...)

$m = 0, \pm 1, \dots, \pm \ell$

Here is a pictorial representation of the possible energy levels and the transitions that produce the distinctive wave lengths (spectral lines) in hydrogen:



Here is a summary on how to calculate the Rydberg constant and the Bohr radius:

$$\alpha_{em} = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.036}$$

Fine Structure constant

$$R_H = \alpha^2 \cdot \frac{mc^2}{2}$$

electron: $mc^2 = 511 \text{ keV}$

$$E_n = -\frac{1}{h^2} \alpha^2 Z^2 \cdot \frac{mc^2}{2}$$

$$\psi_E(R, \theta, \varphi) = R(r) \cdot \underbrace{\Theta_{e,m}(\theta)}_{\text{Legendre polynomial}} \cdot \underbrace{\Phi_m(\varphi)}_{\text{Eigenstate to } \vec{L}^2}$$

Spherical Harmonics

$$a_0 = \frac{\hbar}{\alpha mc}$$

$\approx 0.05 \text{ nm}$
 $0.5 \text{ \AA}$

Bohr radius

Note that the equation at the bottom left describes the energy levels not only for a Hydrogen atom, but really for ANY system of a bound positive nucleus and a negatively charged particle (like electron, muon, antiproton,...). Here Z is the total charge of the positively charged nucleus in units of $+e$ (= total number of protons in the nucleus) and m is the mass of the negatively charged object (with an assumed charge of $-e$).

Strictly speaking this assumes that the negatively charged object has MUCH less mass than the positively charged nucleus, which is a good assumption for electrons but not so good for muons and clearly bad for antiprotons. For better precision, you must replace the mass m with the REDUCED MASS $\mu = m*M/(m + M)$, where m is the mass of the negative particle and M is the mass of the nucleus.

Correspondingly, the Bohr radius also depends on the (reduced) mass, and it should have a $1/Z$ in front (i.e. it scales with the inverse of the positive charge).