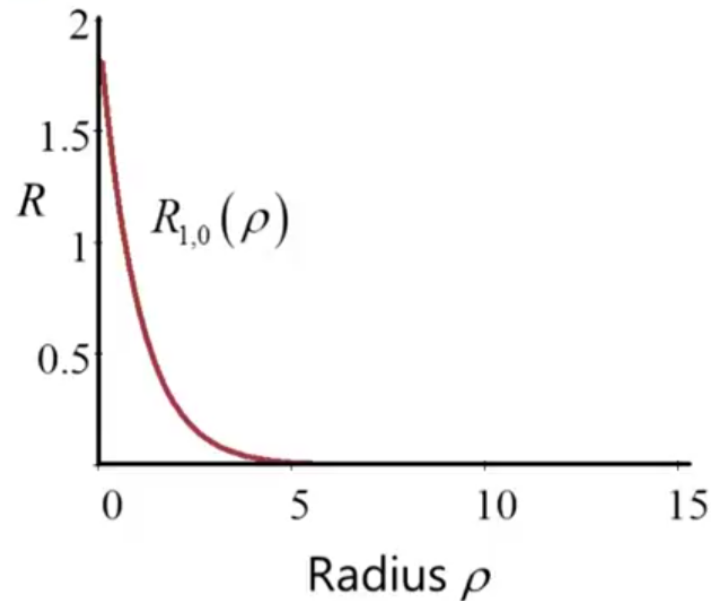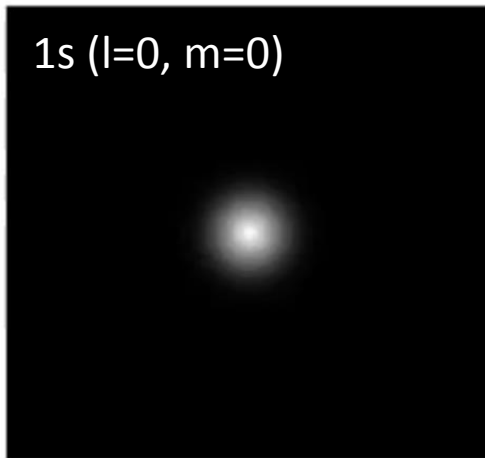# Lesson 21: The hydrogen atom solutions

Quantum Mechanics for Electronical And Electronics Engineerings

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1s (l=0, m=0)

$R_{1,0}(\rho)$

Radius ρ

Internal states of the hydrogen atom

- We start with the equation for the relative motion of electron and proton

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] U(\mathbf{r}) = E_H U(\mathbf{r})$$

- We use the spherical symmetry of this equation and change to spherical polar coordinates

- From now on, we drop the subscript r in the operator ∇^2

- In spherical polar coordinates, we have

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right]$$

- Where the term in square brackets is the operator $\nabla^2_{\theta,\phi} \equiv -\hat{L}^2/\hbar^2$ we introduced in discussing angular momentum

- Knowing the solutions to the angular momentum problem, we propose the separation

$$U(\mathbf{r}) = R(r)Y(\theta,\phi)$$

Internal states of the hydrogen atom

- The mathematics is simpler using the form $\boxed{U(\mathbf{r}) = \dfrac{1}{r}\chi(r)Y(\theta,\phi)}$

where, obviously $\chi(r) = rR(r)$

- This choice gives a convenient simplification of the radial derivatives

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\frac{\chi(r)}{r} = \frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2}$$

- Hence the Schrodinger equation becomes

$$-\frac{\hbar^2}{2\mu}Y(\theta,\phi)\frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2} + \frac{\chi(r)}{r^3}\frac{1}{2\mu}\hat{L}^2Y(\theta,\phi) + Y(\theta,\phi)V(r)\frac{\chi(r)}{r} = E_H\frac{1}{r}\chi(r)Y(\theta,\phi)$$

Dividing by $-\hbar^2\chi(r)Y(\theta,\phi)/2\mu r^3$

- And rearranging, we have

$$\boxed{\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2} + r^2\frac{2\mu}{\hbar^2}\big(E_H - V(r)\big) = \frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)}$$

Internal states of the hydrogen atom

$$\boxed{\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2} + r^2\frac{2\mu}{\hbar^2}\left(E_H - V(r)\right) = \frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2 Y(\theta,\phi)} = l(l+1)$$

- In the usual manner for a separation argument, the left hand side depends only on *r*

- And the right hand side depends only on θ and ϕ

- So both sides must be equal to a constant

- We already know what the constant is explicitly

i.e., we already know that $\hat{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1)Y_{lm}(\theta,\phi)$

- So that the constant is $l(l+1)$

Internal states of the hydrogen atom

- Hence, in addition to the $\hat{L}^2$ Eigenequation which we had already solved from our separation above, we also have

$$\frac{r^2}{\chi(r)}\frac{\partial^2 \chi(r)}{\partial r^2} + r^2 \frac{2\mu}{\hbar^2}\left(E_H - V(r)\right) = l(l+1)$$

Or, rearranging

$$-\frac{\hbar^2}{2\mu}\frac{d^2 \chi(r)}{dr^2} + \left(V(r) + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H(r)$$

which we can write as an ordinary differential equation

- All the functions and derivatives are in one variable r

- For this radial part of the wavefunction which looks like a Schrodinger wave equation with an additional effective potential energy term of the form

$$\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}$$

Central potentials

- Note incidentally that though here we have a specific form for $V(r)$

- In our assumed Coulomb potential $$V(|\mathbf{r}_e - \mathbf{r}_p|) = -\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_e - \mathbf{r}_p|}$$

- The above separation works for any potential that is only a function of *r*

- The precise form of the equation will be different for different central potentials

- We can still separate out the $\hat{L}^2$ angular momentum eigenequation with the spherical harmonic solutions

- Since a reasonable first approximation for more complicated atoms is to say that the potential is still approximately "central", approximately independent of angle

- We can continue to use the spherical harmonics as the first approximation to the angular form of the orbitals and use the "hydrogen atom" labels for them e.g, s, p, d, f, etc.

Radial equation solutions

- Using a separation of the hydrogen atom wavefunction solutions into radial and angular parts

$$U(\mathbf{r}) = R(r)Y(\theta,\phi)$$

- And rewriting the radial part using $\chi(r) = rR(r)$

We obtained the radial equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} - \left(\frac{e^2}{4\pi\varepsilon_0 r} - \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H(r)$$

- Where we know l is 0 or any positive integer

- We now choose to write our energies in the form $E_H = -\dfrac{Ry}{n^2}$

Where n for now is just an arbitrary real number

- We define a new distance unit $s = \alpha r$ where the parameter α is

$$\alpha = \frac{2}{na_0} = 2\sqrt{-\frac{2\mu}{\hbar^2}E_H}$$

Radial equation solutions

- We therefore obtain an equation

$$\frac{d^2\chi}{ds^2} - \left(\frac{l(l+1)}{s^2} - \frac{n}{s} + \frac{1}{4}\right)\chi = 0$$

- Then we write $\chi(s) = s^{l+1}L(s)\exp(-s/2)$

- So we get

$$s\frac{d^2L}{ds^2} - [s - 2(l+1)]\frac{dL}{ds} + [n - (l+1)]L = 0$$

- The technique to solve the equation is to propose a power series in s

- The power series will go on forever and hence the function will grow arbitrarily unless it "terminates" at some finite power which requires that n is an integer, and $n \geq l+1$

- The normalizable solution then becomes the finite power series know an the associated Laguerre polynomials

$$L_{n-l-1}^{2l+1}(s) = \sum_{q=0}^{n-l-1} (-1)^q \frac{(n+1)!}{(n-l-q-1)!(q+2l+1)!} s^q$$

Or equivalently

$$L_p^j(s) = \sum_{q=0}^{p} (-1)^q \frac{(P+j)!}{(p-q)!(j+q)!} s^q$$

Radial equation solutions

- Now we can work back to construct the whole solution

- In our definition $\chi(s) = s^{l+1} L(s) \exp(-s/2)$

- We now insert the associated Laguerre polynomials $\chi(s) = s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2)$

Where $s = (2/na_0)r$

- Since our radial solution was $\chi(r) = rR(r)$

We now have $R(r = na_0 s/2) \propto \dfrac{1}{r} s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2)$

$$\propto s^l L_{n-l-1}^{2l+1}(s) \exp(-s/2)$$

Radial equation solutions – normalization

- We formally introduce a normalization coefficient *A* so

$$R(r = na_0 s/2) \propto \frac{1}{A} s^l L_{n-l-1}^{2l+1}(s) \exp(-s/2)$$

- The full normalization integral of the wavefunction $U(\mathbf{r}) = R(r)Y(\theta, \phi)$

Would be $1 = \int\limits_{r=0}^{\infty} \int\limits_{\theta=0}^{\pi} \int\limits_{\phi=0}^{2\pi} |R(r)Y(\theta, \phi)|^2 r^2 \sin\theta \, d\theta \, d\phi \, dr$

- But we have already normalized the spherical harmonics, so we are left with the radial normalization

- Radial normalization would be $1 = \int\limits_0^{\infty} R(r) r^2 dr$

- We could show $\int\limits_0^{\infty} s^{2l} \left[L_{n-l-1}^{2l+1}(s) \right]^2 \exp(-s) s^2 ds = \frac{2n(n+l)!}{(n-l-1)!}$

- So the normalized radial wavefunction becomes

$$R(r) = \left[\frac{(n-l-1)!}{2n(n+l)!} \left(\frac{2}{na_0} \right)^3 \right]^{1/2} \left(\frac{2r}{na_0} \right)^l L_{n-l-1}^{2l+1}(\frac{2r}{na_0}) \exp(-\frac{r}{na_0})$$

Hydrogen atom radial wavefunctions

- We write the wavefunctions using the Bohr radius a_0 as the unit of radial distance, so we have a dimensionless radial distance $\rho = r / a_0$
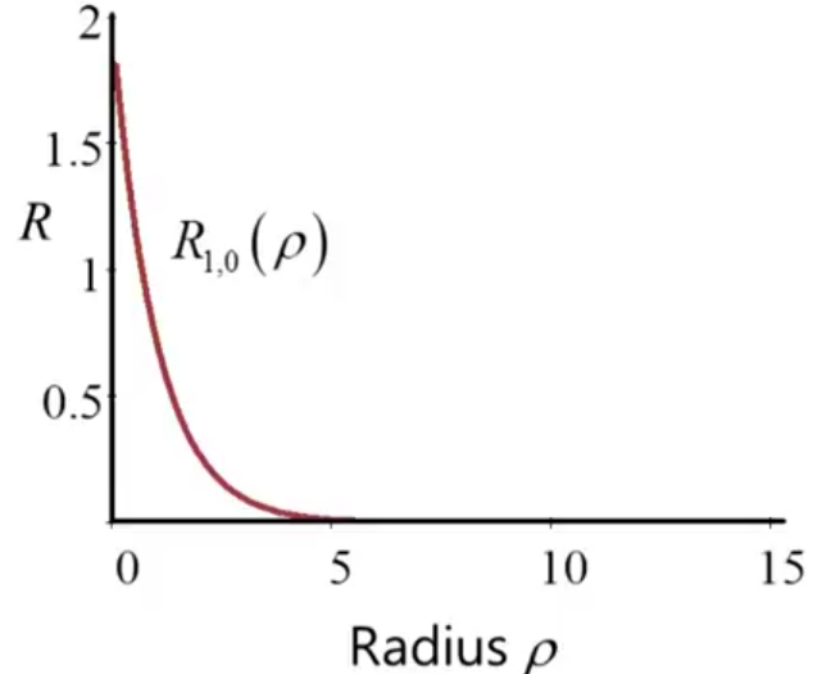
- And we introduce the subscripts

n – the principal quantum number, and
l – the angular momentum quantum number

to index the various functions $R_{n,l}$

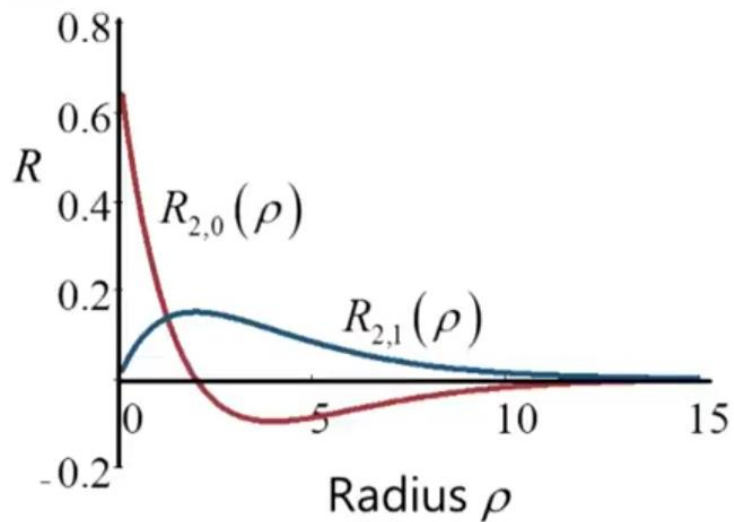**Principal quantum number n=1**
Angular momentum quantum number l=0

$$R_{1,0}(\rho) = 2\exp(-\rho)$$

Radial wavefunctions – n=2

$l=0$ $\qquad R_{2,0}(\rho) = \dfrac{\sqrt{2}}{4}(2-\rho)\exp(-\rho/2)$

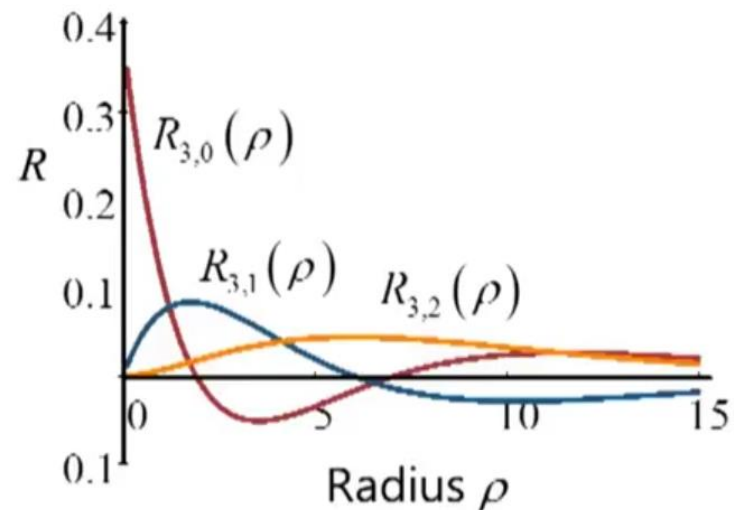$l=1$ $\qquad R_{2,1}(\rho) = \dfrac{\sqrt{6}}{12}\rho\exp(-\rho/2)$
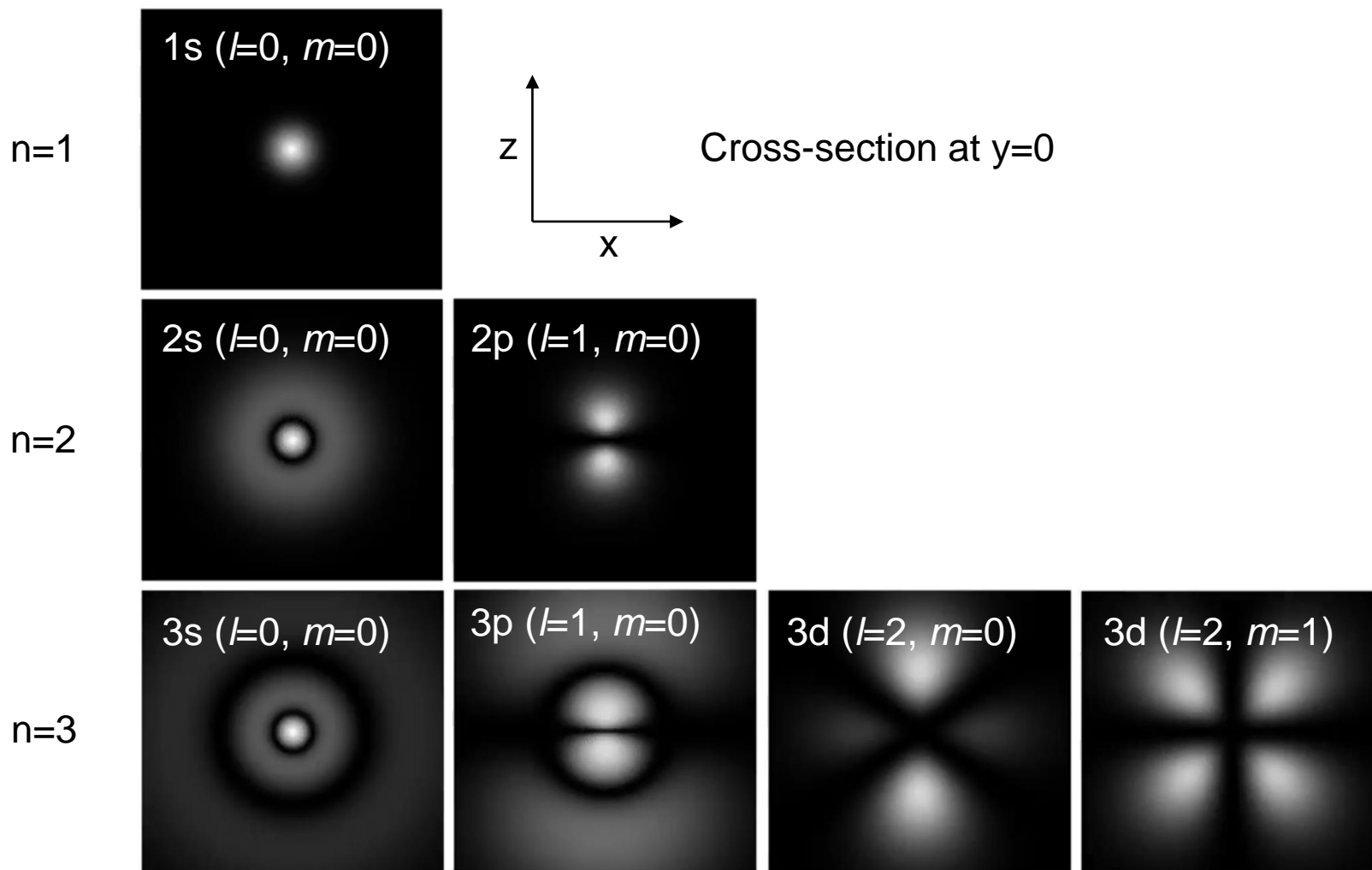
Radial wavefunction – n=3

$l=0$ $\qquad R_{3,0}(\rho) = \dfrac{2\sqrt{3}}{27}\left(3-2\rho+\dfrac{2}{9}\rho^2\right)\exp(-\rho/3)$

$l=1$ $\qquad R_{3,1}(\rho) = \dfrac{\sqrt{6}}{81}\rho\left(4-\dfrac{2}{3}\rho\right)\exp(-\rho/3)$

$l=2$ $\qquad R_{3,2}(\rho) = \dfrac{2\sqrt{30}}{1215}\rho^2\exp(-\rho/3)$

Hydrogen orbital probability density

Behavior of the complete hydrogen solutions

(i)   The overall "size" of the wavefunctions becomes larger with larger n

(ii) The number of zeros in the wavefunction is n-1. The radial wavefunctions have n-l-1 zeros and the spherical harmonics have l nodal "circles"

- The radial wavefunctions appear to have an additional zero at r=0 for all $l \geq 1$, but this is already counted because the spherical harmonics have at least one nodal "circle" for all which already gives a zero as r->0 in these cases.

- In summary of the quantum numbers for the so-called principal quantum number n=1,2,3,…

And

$$l \leq n-1$$

- We already deduced that l is a positive or zero integer.

- We also now know the eigenenergies. Given the possible values for n

$$E_H = -\frac{Ry}{n^2}$$

Note the energy does not depend on l (or m)

Thank you for your attention!