

# Quantum Mechanics 2

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Hydrogen Atom  
The Radial Function



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# The Radial Equation

In [hydrogen 1], we have shown that the radial equation

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m}{\hbar^2} \left[ E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] R = 0$$

can be recast by defining

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}} r$$

$$\alpha = \sqrt{\frac{m}{2\hbar^2|E|} \frac{e^2}{4\pi\epsilon_0}}$$

$$R(\rho) = G(\rho)e^{-\rho/2}$$

to yield

$$\frac{d^2 G}{d\rho^2} + \left[ \frac{2}{\rho} - 1 \right] \frac{dG}{d\rho} + \left[ \frac{\alpha - 1}{\rho} - \frac{l(l+1)}{\rho^2} \right] G = 0$$



# The Radial Equation

With  $l(l + 1)$  in the last term, it is reasonable to expect that  $G(\rho)$  is of the form\*

$$G(\rho) = \rho^l L(\rho)$$

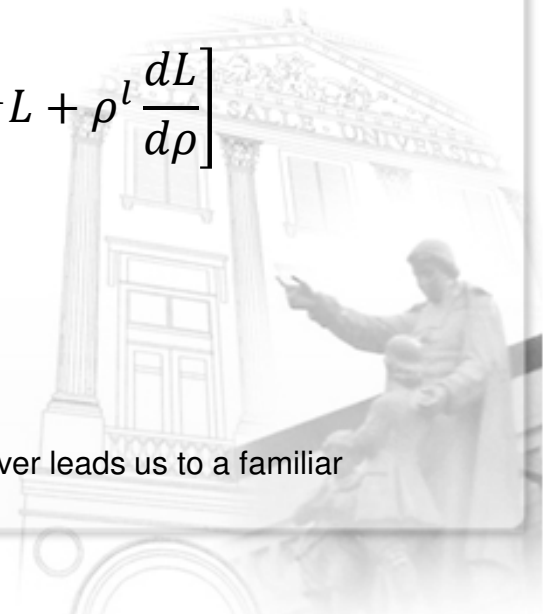
With

$$\begin{aligned}\frac{dG}{d\rho} &= l\rho^{l-1}L + \rho^l \frac{dL}{d\rho} \\ \frac{d^2G}{d\rho^2} &= l(l-1)\rho^{l-2}L + 2l\rho^{l-1} \frac{dL}{d\rho} + \rho^l \frac{d^2L}{d\rho^2}\end{aligned}$$

we have

$$\begin{aligned}l(l-1)\rho^{l-2}L + 2l\rho^{l-1} \frac{dL}{d\rho} + \rho^l \frac{d^2L}{d\rho^2} + \left[\frac{2}{\rho} - 1\right] \left[l\rho^{l-1}L + \rho^l \frac{dL}{d\rho}\right] \\ + \left[\frac{\alpha-1}{\rho} - \frac{l(l+1)}{\rho^2}\right] \rho^l L = 0\end{aligned}$$

\* We could actually skip this step and go straight to a Fröbenius solution. Doing this however leads us to a familiar differential equation.



# Associated Laguerre Equation

Rearranging according to order, we have

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

which simplifies to

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

Factoring out  $\rho^{l-1}$ , we arrive at the Associated Laguerre Equation

$$\rho \frac{d^2 L}{d\rho^2} + (k + 1 - \rho) \frac{dL}{d\rho} + sL = 0$$

where

$$k = 2l + 1$$

$$s = \alpha - l - 1$$



# Fröbenius Solution

The Associated Laguerre Equation may be solved using the Fröbenius method. Assuming a power series solution,

$$L(\rho) = \sum_{m=0}^{\infty} a_m \rho^{m+b}$$

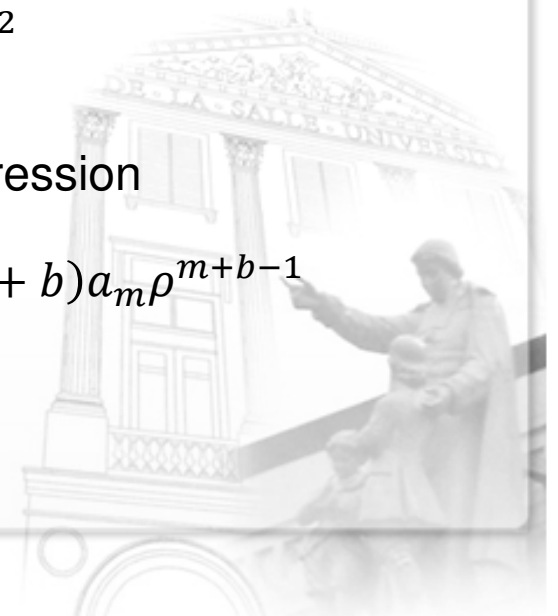
we have

$$\frac{dL}{d\rho} = \sum_{m=0}^{\infty} (m+b) a_m \rho^{m+b-1}$$

$$\frac{d^2L}{d\rho^2} = \sum_{m=0}^{\infty} (m+b)(m+b-1) a_m \rho^{m+b-2}$$

The differential equation then reduces to a power series expression

$$\begin{aligned} & \rho \sum_{m=0}^{\infty} (m+b)(m+b-1) a_m \rho^{m+b-2} + (k+1) \sum_{m=0}^{\infty} (m+b) a_m \rho^{m+b-1} \\ & - \rho \sum_{m=0}^{\infty} (m+n) a_m \rho^{m+b-1} + s \sum_{m=0}^{\infty} a_m \rho^{m+b} = 0 \end{aligned}$$



# Fröbenius Solution

The expression can be rearranged in terms of powers of  $\rho$

$$\sum_{m=0} (m+b)[(m+b-1)+(k+1)]a_m\rho^{m+b-1} + \sum_{m=0} (s-m-b)a_m\rho^{m+b} = 0$$

The first term can be split as

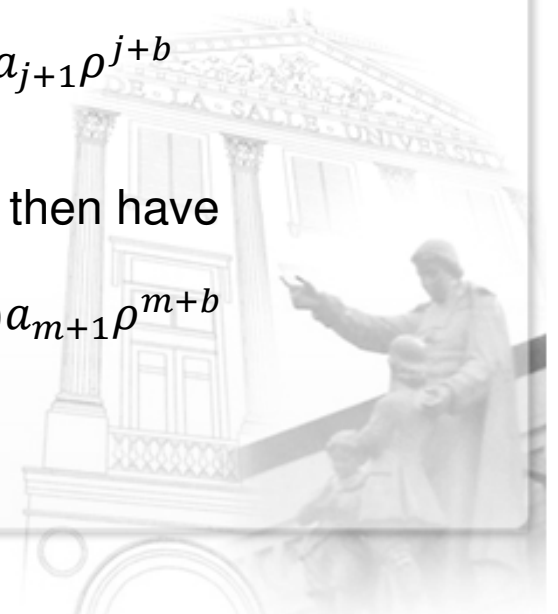
$$b(b+k)a_0\rho^{b-1} + \sum_{m=1} (m+b)(m+b+k)a_m\rho^{m+b-1}$$

and by replacing  $m \rightarrow j = m - 1$  rewritten as

$$b(b+k)a_0\rho^{b-1} + \sum_{j=0} (j+b+1)(j+b+k+1)a_{j+1}\rho^{j+b}$$

Since  $j$  is a dummy index, we can replace it back with  $m$ . We then have

$$b(b+k)a_0\rho^{b-1} + \sum_{m=0} (m+b+1)(m+b+k+1)a_{m+1}\rho^{m+b} \\ + \sum_{m=0} (s-m-b)a_m\rho^{m+b} = 0$$



# Indicial and Recurrence Relations

Invoking linear independence, the coefficients of each power vanish separately. Thus,

$$b(b + k)a_0 = 0$$

$$(m + b + 1)(m + b + k + 1)a_{m+1} + (s - m - b)a_m = 0$$

The first expression yields the **indicial equation**

$$b(b + k) = 0$$

suggesting that  $b = 0, -k$ . Taking  $b = 0$  so that we have a series of positive powers, the second equation becomes

$$(m + 1)(m + k + 1)a_{m+1} + (s - m)a_m = 0$$

This yields the **recursion relation**

$$a_{m+1} = \frac{(m - s)}{(m + 1)(m + k + 1)} a_m$$



# Termination of the Series

At large  $m$ ,

$$a_{m+1} \approx \frac{a_m}{m}$$

Just like in [\[harmonic oscillator 4\]](#), this indicates that the power series diverges as  $\rho \rightarrow \infty$  unless the series terminates. This implies that there must exist a positive integer  $m = N$  such that

$$a_{N+1} = \frac{(N - s)}{(N + 1)(N + k + 1)} a_N = 0$$

Thus,  $s = N$  and

$$s = \alpha - l - 1 \geq 0$$

As the angular momentum quantum number  $l$  is a positive definite integer [\[spherical harmonics 1\]](#), then  $\alpha$  must be an integer  $n$  such that

$$n \geq l + 1$$





# The Principal Quantum Number

The expression

$$n \geq l + 1$$

not only restricts the possible values of the angular momentum quantum number  $l$ , it also provides a condition on the eigenenergies of the atom

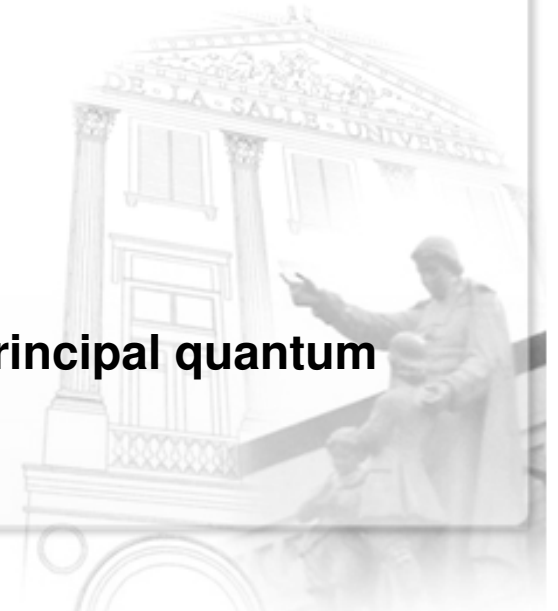
$$\alpha = \sqrt{\frac{m}{2\hbar^2|E|} \frac{e^2}{4\pi\epsilon_0}} = n$$

Thus, as to be expected for bound systems, the energy eigenvalues of the Hydrogen atom are quantized

$$E_n = -\frac{me^4}{(4\pi\epsilon_0)^2 2n^2\hbar^2} = \frac{E_1}{n^2} = -\frac{13.6eV}{n^2}$$

This is the same expression obtained by [\[Bohr\]](#).

Since eigenenergy is specified by  $n$ , the latter is called the **principal quantum number**.



# Recursion

The power series expression of the Radial function  $L(\rho)$  may be evaluated using the recursion relation

$$a_{m+1} = \frac{-(s - m)}{(m + 1)(m + k + 1)} a_m$$

For  $m = 0$ ,

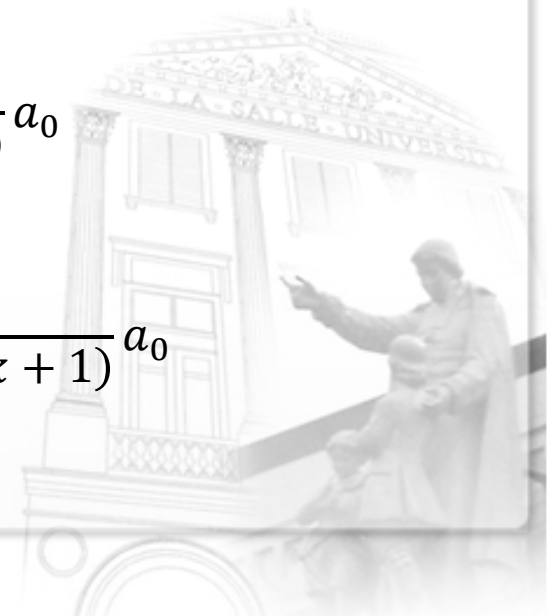
$$a_1 = \frac{-s}{(1)(k + 1)} a_0$$

For  $m = 1$ ,

$$a_2 = \frac{-(s - 1)}{(2)(k + 2)} a_1 = \frac{s(s - 1)}{(2)(1)(k + 2)(k + 1)} a_0$$

For  $m = 2$ .

$$a_3 = \frac{-(s - 2)}{(3)(k + 3)} a_2 = \frac{-s(s - 1)(s - 2)}{(3)(2)(1)(k + 3)(k + 2)(k + 1)} a_0$$



# Associated Laguerre Polynomials

By induction,

$$a_m = (-1)^m \frac{s(s-1)(s-2)\cdots(s-m+1)}{m!(k+m)(k+m-1)\cdots(k+1)} a_0 = (-1)^m \frac{s!k!}{(s-m)!m!(k+m)!} a_0$$

If we take\*

$$a_0 = \frac{(s+k)!}{s!k!}$$

then

$$a_m = (-1)^m \frac{(s+k)!}{(s-m)!m!(k+m)!}$$

and we have the associated Laguerre polynomials

$$L_s^k(\rho) = \sum_{m=0}^s (-1)^m \frac{(s+k)!}{(s-m)!m!(k+m)!} \rho^m$$

\* Taken from the normalization of the [\[Associated Laguerre\]](#) Polynomials

