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

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2}\right]R = 0$$

can be recast by defining

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

$$\alpha = \sqrt{\frac{m}{2\hbar^2|E|}}\frac{e^2}{4\pi\varepsilon_0}$$

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

to yield

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

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

$$\frac{dG}{d\rho} = l\rho^{l-1}L + \rho^l \frac{dL}{d\rho}$$

$$\frac{d^2G}{d\rho^2} = l(l-1)\rho^{l-2}L + 2l\rho^{l-1}\frac{dL}{d\rho} + \rho^l \frac{d^2L}{d\rho^2}$$

we have

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

* 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

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

which simplifies to

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

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

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

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,

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

we have

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

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

The differential equation then reduces to a power series expression

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

Fröbenius Solution

The expression can be rearranged in terms of powers of ρ

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

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 $m\to j=m-1$ 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 $\rho \to \infty$ unless the series terminates. This implies that there must exist a positive integer $m = N$ such at 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 α 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

$$\alpha = \sqrt{\frac{m}{2\hbar^2|E|}}\frac{e^2}{4\pi\varepsilon_0} = n$$

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

$$E_n = -\frac{me^4}{(4\pi\varepsilon_0)^2 2n^2\hbar^2} = \frac{E_1}{n^2} = -\frac{13.6eV}{n^2}$$

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*

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

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