Laguerre polynomials and the hydrogen wave function

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1 The radial equation: aymptotic limits

We begin by writing the radial wave equation,

$$\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}+\left(\frac{2me^2}{\hbar^2 r}+\frac{2mE}{\hbar^2}-\frac{1}{r^2}l\,(l+1)\right)\psi \quad = \quad 0$$

and finding the limiting forms as $r\to\infty$and at the origin. For large r, since $\frac{\partial\psi}{\partial r}$ is bounded,

$$\frac{\partial^2\psi}{\partial r^2}+\frac{2mE}{\hbar^2}\psi \quad = \quad 0$$

Since $E<0$, the limit has exponential solutions which we write in the form

$$\psi \quad = \quad Ae^{-\frac{1}{2}\kappa r}+Be^{+\frac{1}{2}\kappa r}$$

where

$$\kappa=\sqrt{-\frac{8mE}{\hbar^2}}$$

For the wave function to vanish at infinity, we require $B=0$.

As $r\to 0$, the equation reduces to

$$\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}-\frac{1}{r^2}l\,(l+1)\,\psi \quad = \quad 0$$

and we set $\psi=r^\alpha$. Then

$$\begin{aligned}
0 &= \frac{\partial^2 r^\alpha}{\partial r^2}+\frac{2}{r}\frac{\partial r^\alpha}{\partial r}-\frac{1}{r^2}l\,(l+1)\,r^\alpha \\
&= \alpha\,(\alpha-1)\,r^{\alpha-2}u+\frac{2}{r}\left(\alpha r^{\alpha-1}\right)-\frac{1}{r^2}l\,(l+1)\,r^\alpha u \\
&= (\alpha\,(\alpha+1)-l\,(l+1))\,r^{\alpha-2}u
\end{aligned}$$

so we have solutions

$$\alpha=l,-(l+1)$$

We require the positive powers, $\alpha=l$.

2 Transformation

First, simplify the variables. Starting with

$$\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}+\left(\frac{2me^2}{\hbar^2 r}+\frac{2mE}{\hbar^2}-\frac{1}{r^2}l\,(l+1)\right)\psi=0$$

the first two terms may be written as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\left(\frac{2me^2}{\hbar^2 r}+\frac{2mE}{\hbar^2}-\frac{1}{r^2}l\left(l+1\right)\right)\psi=0$$

Let

$$\begin{aligned}\kappa^2 &= -\frac{8mE}{\hbar^2}\\ \kappa r &= x\\ \lambda &= \frac{2me^2}{\kappa\hbar^2}\end{aligned}$$

Then multiplying by $\frac{1}{\kappa^2}$, the radial equation becomes

$$\begin{aligned}0 &= \frac{1}{\kappa^2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\left(\frac{1}{\kappa^2}\frac{2me^2}{\hbar^2 r}+\frac{1}{\kappa^2}\frac{2mE}{\hbar^2}-\frac{1}{\kappa^2}\frac{1}{r^2}l\left(l+1\right)\right)\psi\\ &= \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial\psi}{\partial x}\right)+\left(\frac{\lambda}{x}-\frac{1}{4}-\frac{l\left(l+1\right)}{x^2}\right)\psi\end{aligned}$$

Now let

$$\psi=e^{-x/2}x^l Z\left(x\right)$$

Then

$$\begin{aligned}\frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial\left(e^{-x/2}x^l Z\psi\right)}{\partial x}\right) &= \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\left(-\frac{1}{2}e^{-x/2}x^l Z+le^{-x/2}x^{l-1}Z+e^{-x/2}x^l Z'\right)\right)\\ &= \frac{1}{x^2}\frac{\partial}{\partial x}\left(-\frac{1}{2}e^{-x/2}x^{l+2}Z+le^{-x/2}x^{l+1}Z+e^{-x/2}x^{l+2}Z'\right)\\ &= \frac{1}{x^2}\left(\frac{1}{4}e^{-x/2}x^{l+2}Z-\frac{1}{2}le^{-x/2}x^{l+1}Z-\frac{1}{2}e^{-x/2}x^{l+2}Z'\right)\\ &\quad+\frac{1}{x^2}\left(-\frac{1}{2}\left(l+2\right)e^{-x/2}x^{l+1}Z+l\left(l+1\right)e^{-x/2}x^l Z+\left(l+2\right)e^{-x/2}x^{l+1}Z'\right)\\ &\quad+\frac{1}{x^2}\left(-\frac{1}{2}e^{-x/2}x^{l+2}Z'+le^{-x/2}x^{l+1}Z'+e^{-x/2}x^{l+2}Z''\right)\\ &= \frac{1}{4}e^{-x/2}x^l Z-\frac{1}{2}le^{-x/2}x^{l-1}Z-\frac{1}{2}e^{-x/2}x^l Z'\\ &\quad-\frac{1}{2}\left(l+2\right)e^{-x/2}x^{l-1}Z+l\left(l+1\right)e^{-x/2}x^{l-2}Z+\left(l+2\right)e^{-x/2}x^{l-1}Z'\\ &\quad-\frac{1}{2}e^{-x/2}x^l Z'+le^{-x/2}x^{l-1}Z'+e^{-x/2}x^l Z''\end{aligned}$$

so, cancelling the common exponential, the radial equation is transformed to

$$\begin{aligned}0 &= \frac{1}{4}x^l Z-\frac{1}{2}lx^{l-1}Z-\frac{1}{2}x^l Z'\\ &\quad-\frac{1}{2}\left(l+2\right)x^{l-1}Z+l\left(l+1\right)x^{l-2}Z+\left(l+2\right)x^{l-1}Z'\\ &\quad-\frac{1}{2}x^l Z'+lx^{l-1}Z'+x^l Z''\\ &\quad+\lambda x^{l-1}Z-\frac{1}{4}x^l Z-l\left(l+1\right)x^{l-2}Z\end{aligned}$$

Collecting terms,

$$\begin{aligned} 0 &= x^l Z'' + (2l+2-x)\, x^{l-1} Z' \\ &\quad + \left(-\frac{1}{2} l x^{l-1} - \frac{1}{2}(l+2)\, x^{l-1} + \lambda x^{l-1} + l\,(l+1)\, x^{l-2} - l\,(l+1)\, x^{l-2} \right) Z \\ &= x^l Z'' + (2\,(l+1) - x)\, x^{l-1} Z' \\ &\quad + (-\,(l+1) + \lambda)\, x^{l-1} Z \end{aligned}$$

Dividing by x^{l-1}, Z must satisfy

$$xZ'' + (2\,(l+1) - x)\, Z' + (\lambda - (l+1))\, Z = 0$$

Let

$$\begin{aligned} k &= 2l+1 \\ \alpha &= \lambda - (l+1) \end{aligned}$$

Then

$$xZ'' + (k+1-x)\, Z' + \alpha Z = 0$$

This is the associated Laguerre equation.

3 The Laguerre equation

A useful set of polynomials, the Laguerre functions, is given by the solutions to the Laguerre equation,

$$x\frac{d^2 L_\alpha}{dx^2} + (1-x)\frac{dL_\alpha}{dx} + \alpha L_\alpha = 0$$

and for $\alpha = n$, the associated Laguerre polynimials,

$$L_n^k(x) = (-1)^k \frac{d^k}{dx^k} L_{n+k}(x)$$

which satisfy

$$x\frac{d^2 L_n^k}{dx^2} + (k+1-x)\frac{dL_n^k}{dx} + \alpha L_n^k = 0$$

Exercise: Derive the associated Laguerre equation by differentiating the Laguerre equation k times. For the Laguerre equation, we assume a solution of the form

$$L_\alpha = \sum_{s=0}^{\infty} a_s x^s$$

Then

$$\begin{aligned} \frac{dL_\alpha}{dx} &= \sum_{s=1}^{\infty} s a_s x^{s-1} \\ \frac{d^2 L_\alpha}{dx^2} &= \sum_{s=2}^{\infty} s\,(s-1)\, a_s x^{s-2} \end{aligned}$$

so that

$$
\begin{aligned}
x\sum_{s=2}^{\infty}s\left(s-1\right)a_{s}x^{s-2}+\left(1-x\right)\sum_{s=1}^{\infty}sa_{s}x^{s-1}+\alpha\sum_{s=0}^{\infty}a_{s}x^{s} &= 0 \\
\sum_{s=2}^{\infty}s\left(s-1\right)a_{s}x^{s-1}+\sum_{s=1}^{\infty}sa_{s}x^{s-1}-\sum_{s=1}^{\infty}sa_{s}x^{s}+\alpha\sum_{s=0}^{\infty}a_{s}x^{s} &= 0 \\
\sum_{m=1}^{\infty}m\left(m+1\right)a_{m+1}x^{m}+\sum_{m=0}^{\infty}\left(m+1\right)a_{m+1}x^{m}-\sum_{m=1}^{\infty}ma_{m}x^{m}+\alpha\sum_{m=0}^{\infty}a_{m}x^{m} &= 0
\end{aligned}
$$

The $m=0$ term is

$$a_1+\alpha a_0=0$$

For all $m>0$,

$$
\begin{aligned}
\left(m\left(m+1\right)a_{m+1}+\left(m+1\right)a_{m+1}-ma_{m}+\alpha a_{m}\right)x^{m} &= 0 \\
\left(m+1\right)^{2}a_{m+1}+\left(\alpha-m\right)a_{m} &= 0
\end{aligned}
$$

and therefore

$$a_{m+1} = -\frac{\alpha-m}{\left(m+1\right)^{2}}a_{m}$$

For $m=0$ this formula also gives $a_1=-\alpha a_0$ so we may extend this formula to all m. Iterate this series:

$$
\begin{aligned}
a_m &= -\frac{\alpha-m+1}{m^2}a_{m-1} \\
&= \left(-1\right)^{2}\frac{\left(\alpha-m+1\right)\left(\alpha-m+2\right)}{m^{2}\left(m-1\right)^{2}}a_{m-2} \\
&= \left(-1\right)^{k}\frac{\left(\alpha-m+1\right)\left(\alpha-m+2\right)\cdots\left(\alpha-m+k\right)}{m^{2}\cdots\left(m-k+1\right)^{2}}a_{m-k}
\end{aligned}
$$

so that for $k=m$,

$$
\begin{aligned}
a_m &= \left(-1\right)^{m}\frac{\left(\alpha-m+1\right)\left(\alpha-m+2\right)\cdots\alpha}{m^{2}\cdots 1^{2}}a_{0} \\
&= \left(-1\right)^{m}\frac{\Gamma\left(\alpha+1\right)}{m!m!\Gamma\left(\alpha-m+1\right)}a_{0}
\end{aligned}
$$

where the Γ function satisfies

$$
\begin{aligned}
\Gamma\left(m\right) &= \left(m-1\right)! \\
\Gamma\left(\alpha+1\right) &= \alpha\Gamma\left(\alpha\right)
\end{aligned}
$$

The solution is

$$L_{\alpha}\left(x\right)=a_{0}\sum_{m=0}^{\infty}\frac{\Gamma\left(\alpha+1\right)}{m!m!\Gamma\left(\alpha-m+1\right)}\left(-1\right)^{m}x^{m}$$

4 Quantization

Consider the large m limit of our solution for $L_{\alpha}\left(x\right)$. As $\alpha-1$ becomes negligible in the numerator, the coefficients become

$$a_m = \frac{\left(m-\alpha-1\right)\left(m-\alpha-2\right)\cdots\left(m-\left(\alpha-1\right)+1-m\right)}{m!m!}a_{0}$$

$$
\begin{aligned}
&\approx \frac{m(m-1)(m-2)\cdots 1}{m!m!}(\alpha-1)a_0 \\
&= (\alpha-1)a_0\frac{1}{m!}
\end{aligned}
$$

so asymptotically the series approaches

$$L_\alpha(x) \sim (\alpha-1)a_0\sum_{m=0}^{\infty}\frac{1}{m!}x^m \sim e^x$$

This means that if the series extends to large m, the radial wave function becomes

$$\psi = e^{-x/2}x^l Z(x) \sim e^{+x/2}x^l$$

and diverges. The only way to avoid this is by taking $\alpha \equiv i$ to be a non-negative integer so that the series terminates

$$
\begin{aligned}
a_m &= (-1)^m\frac{(i-m+1)(i-m+2)\cdots\alpha}{m^2\cdots 1^2}a_0 \\
a_i &= (-1)^i\frac{1}{i!}a_0 \\
a_{i+1} &= 0
\end{aligned}
$$

and $L_n(x)$ is a polynomial.

Returning to our definitions for the radial wave function

$$
\begin{aligned}
\kappa^2 &= -\frac{8mE}{\hbar^2} \\
\kappa r &= x \\
\lambda &= \frac{2me^2}{\kappa\hbar^2}
\end{aligned}
$$

and

$$i = \lambda-(l+1)$$

We therefore get a quantization condition,

$$\lambda = i+l+1 \equiv n$$

where

$$
\begin{aligned}
n &= \frac{2me^2}{\kappa\hbar^2} \\
&= \frac{2me^2}{\hbar^2\sqrt{-\frac{8mE}{\hbar^2}}} \\
&= \frac{2me^2}{\hbar\sqrt{-8mE}}
\end{aligned}
$$

Solving for the energy

$$
\begin{aligned}
-8mE_n &= \frac{4m^2e^4}{n^2\hbar^2} \\
E_n &= -\frac{me^4}{2n^2\hbar^2}
\end{aligned}
$$

Neglecting fine structure, these are the energy levels of hydrogen. Notice that in order for i to be a positive integer, we must have

$$n \geq l+1$$

The final polynomials are:

$$L_{\alpha}^{k}(x) = L_{n-l-1}^{2l+1}(\kappa r)$$

so that the complete wave function is

$$\Psi(r,\theta,\varphi,l,m_l,m_s) = Ae^{-\kappa r/2}(\kappa r)^l L_{n-l-1}^{2l+1}(\kappa r) Y_{lm}(\theta,\varphi)\chi(\alpha,\beta)$$

where A gives the normalization.

5 Appendix: The associated Laguerre equation

The associated polynomials solve a related set of equations given by differentiating the Laguerre equation for L_{n+k}, k times:

$$\begin{aligned} 0 &= \frac{d^k}{dx^k}\left(x\frac{d^2L_{n+k}}{dx^2} + (1-x)\frac{dL_{n+k}}{dx} + (n+k)L_{n+k}\right) \\ &= \frac{d^k}{dx^k}\left(x\frac{d^2L_{n+k}}{dx^2}\right) + \frac{d^k}{dx^k}\left((1-x)\frac{dL_{n+k}}{dx}\right) + (n+k)\frac{d^kL_{n+k}}{dx^k} \end{aligned}$$

For the first term,

$$\begin{aligned} \frac{d}{dx}\left(x\frac{d^2L_{n+k}}{dx^2}\right) &= x\frac{d^3L_{n+k}}{dx^3} + \frac{d^2L_{n+k}}{dx^2} \\ \frac{d^2}{dx^2}\left(x\frac{d^2L_{n+k}}{dx^2}\right) &= x\frac{d^4L_{n+k}}{dx^4} + 2\frac{d^3L_{n+k}}{dx^3} \\ \frac{d^3}{dx^3}\left(x\frac{d^2L_{n+k}}{dx^2}\right) &= x\frac{d^5L_{n+k}}{dx^5} + 3\frac{d^4L_{n+k}}{dx^4} \end{aligned}$$

The pattern is emerging:

$$\frac{d^k}{dx^k}\left(x\frac{d^2L_{n+k}}{dx^2}\right) = x\frac{d^{k+2}L_{n+k}}{dx^{k+2}} + k\frac{d^{k+1}L_{n+k}}{dx^{k+1}}$$

Check one more derivative to complete the induction:

$$\frac{d^{k+1}}{dx^{k+1}}\left(x\frac{d^2L_{n+k}}{dx^2}\right) = \frac{d}{dx}\left(x\frac{d^{(k+1)+2}L_{n+k}}{dx^{(k+1)+2}} + (k+1)\frac{d^{(k+1)+1}L_{n+k}}{dx^{(k+1)+1}}\right)$$

so the form is correct.

For the second term, we need

$$\begin{aligned} \frac{d^k}{dx^k}\left((1-x)\frac{dL_{n+k}}{dx}\right) &= \frac{d^k}{dx^k}\left(\frac{dL_{n+k}}{dx} - x\frac{dL_{n+k}}{dx}\right) \\ &= \frac{d^{k+1}L_{n+k}}{dx^{k+1}} - \frac{d^k}{dx^k}\left(x\frac{dL_{n+k}}{dx}\right) \end{aligned}$$

Look at the last part,

$$\begin{aligned} \frac{d}{dx}\left(x\frac{dL_{n+k}}{dx}\right) &= x\frac{d^2L_{n+k}}{dx^2} + \frac{dL_{n+k}}{dx} \\ \frac{d^2}{dx^2}\left(x\frac{dL_{n+k}}{dx}\right) &= x\frac{d^3L_{n+k}}{dx^3} + 2\frac{d^2L_{n+k}}{dx^2} \end{aligned}$$

so we guess that the generic term is

$$\frac{d^k}{dx^k}\left(x\frac{dL_{n+k}}{dx}\right) = x\frac{d^{k+1}L_{n+k}}{dx^{k+1}} + k\frac{d^kL_{n+k}}{dx^k}$$

and check one more:

$$\begin{aligned}\frac{d^{k+1}}{dx^{k+1}}\left(x\frac{dL_{n+k}}{dx}\right) &= \frac{d^{k+1}L_{n+k}}{dx^{k+1}} + x\frac{d^{k+2}L_{n+k}}{dx^{k+2}} + k\frac{d^{k+1}L_{n+k}}{dx^{k+1}} \\ &= x\frac{d^{(k+1)+1}L_{n+k}}{dx^{(k+1)+1}} + (k+1)\frac{d^{k+1}L_{n+k}}{dx^{k+1}}\end{aligned}$$

Therefore, returning to the equation,

$$\begin{aligned}0 &= \frac{d^k}{dx^k}\left(x\frac{d^2L_{n+k}}{dx^2}\right) + \frac{d^k}{dx^k}\left((1-x)\frac{dL_{n+k}}{dx}\right) + (n+k)\frac{d^kL_{n+k}}{dx^k} \\ &= x\frac{d^{k+2}L_{n+k}}{dx^{k+2}} + k\frac{d^{k+1}L_{n+k}}{dx^{k+1}} + \frac{d^{k+1}L_{n+k}}{dx^{k+1}} - x\frac{d^{k+1}L_{n+k}}{dx^{k+1}} - k\frac{d^kL_{n+k}}{dx^k} + (n+k)\frac{d^kL_{n+k}}{dx^k} \\ &= x\frac{d^2}{dx^2}\left(\frac{d^kL_{n+k}}{dx^k}\right) + (k+1-x)\frac{d}{dx}\left(\frac{d^kL_{n+k}}{dx^k}\right) + n\left(\frac{d^kL_{n+k}}{dx^k}\right)\end{aligned}$$

and, inserting a minus sign, the associated Laguerre equation is

$$x\frac{d^2L_n^k}{dx^2} + (k+1-x)\frac{dL_n^k}{dx} + nL_n^k = 0$$