

Series expansion method
Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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Using the series expansion method, we solve the differential equation for the radial wave function for the hydrogen system. We start with

$$u''(r) - \left[\frac{l(l+1)}{r^2} + \frac{2\mu(\varepsilon_1 - Ze^2/r)}{\hbar^2} \right] u(r) = 0,$$

with

$$r = \frac{\hbar}{\sqrt{8\mu\varepsilon_1}} \rho = \frac{\rho}{2\kappa},$$

with

$$\varepsilon_1 = \frac{\hbar^2 \kappa^2}{2\mu}, \quad \kappa = \frac{\sqrt{2\mu\varepsilon_1}}{\hbar}.$$

Solution of radial part of the hydrogen atom

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4} \right] u(\rho) = 0, \quad (1)$$

with

$$\lambda = \frac{Ze^2}{\hbar} \sqrt{\frac{\mu}{2\varepsilon_1}},$$

which corresponds to the eigenvalue. Note that according to the Bohr model, $\lambda = n =$ integer since

$$\varepsilon_1 = \frac{\mu Z^2 e^4}{2n^2 \hbar^2}.$$

We solve the differential equation to determine the eigenvalue and eigenfunction.

(a) In the limit of $\rho \rightarrow 0$.

We assume that it behaves at the origin like

$$u \approx \rho^s,$$

or

$$[s(s-1) - l(l+1)]\rho^{s-2} + \lambda\rho^{s-1} - \frac{1}{4}\rho^s = 0.$$

Note that the ρ^{s-2} term dominates for small ρ .

$$s(s-1) - l(l+1) = 0,$$

or

$$(s - l - 1)(s + l) = 0,$$

or

$$s = l + 1 \text{ or } s = -l.$$

We must discard those solutions that behave as ρ^{-l} . So we get the form around $\rho = 0$:

$$u[\rho] \approx \rho^{l+1}.$$

(b) In the limit of $\rho \rightarrow \infty$,

$$\left(\frac{d^2}{d\rho^2} - \frac{1}{4}\right)u(\rho) = 0.$$

The solution for this equation is

$$u(\rho) \approx Ae^{-\rho/2} + Be^{\rho/2}.$$

The constant B should be equal to zero ($\rho \rightarrow \infty$):

$$u(\rho) \approx e^{-\rho/2}.$$

Thus we can attempt to find a solution of the form

$$u(\rho) = \rho^{l+1} e^{-\rho/2} F(\rho).$$

With this substitution, the differential equation (1) becomes

$$\frac{d^2 F(\rho)}{d\rho^2} + \left(\frac{2l+2}{\rho} - 1\right) \frac{dF(\rho)}{d\rho} + \left(\frac{\lambda}{\rho} - \frac{l+1}{\rho}\right) F(\rho) = 0.$$

We assume that

$$F(\rho) = \sum_{k=0}^{\infty} C_k \rho^k,$$

with $C_0 \neq 0$.

$$\begin{aligned} & \sum_{k=2}^{\infty} k(k-1)C_k \rho^{k-2} + \sum_{k=1}^{\infty} (2l+2)kC_k \rho^{k-2} - \sum_{k=1}^{\infty} kC_k \rho^{k-1} \\ & + \sum_{k=0}^{\infty} [\lambda - (l+1)]C_k \rho^{k-1} = 0 \end{aligned},$$

We note that

$$\sum_{k=2}^{\infty} k(k-1)C_k \rho^{k-2} = \sum_{k=1}^{\infty} k(k+1)C_{k+1} \rho^{k-1} = \sum_{k=0}^{\infty} k(k+1)C_{k+1} \rho^{k-1},$$

$$\sum_{k=1}^{\infty} (2l+2)kC_k \rho^{k-2} = \sum_{k=0}^{\infty} (2l+2)(k+1)C_{k+1} \rho^{k-1},$$

$$\sum_{k=1}^{\infty} kC_k \rho^{k-1} = \sum_{k=0}^{\infty} kC_k \rho^{k-1}.$$

Then we get

$$\sum_{k=0}^{\infty} k(k+1)C_{k+1} \rho^{k-1} + \sum_{k=0}^{\infty} (2l+2)(k+1)C_{k+1} \rho^{k-1} + \sum_{k=0}^{\infty} [-k + \lambda - (l+1)]C_k \rho^{k-1} = 0$$

or

$$\sum_{k=0}^{\infty} \{(k+1)(k+2l+2)C_{k+1} - (k+l+1-\lambda)C_k\} \rho^{k-1} = 0,$$

Since the coefficient of ρ^{k-1} should be zero, we get the recursion relation as

$$\frac{C_{k+1}}{C_k} = \frac{k+l+1-\lambda}{(k+1)(k+2l+2)}.$$

Note that

$$\frac{C_{k+1}}{C_k} \rightarrow \frac{1}{k},$$

which is the same asymptotic behavior as e^ρ . Thus, unless the series terminate, $u(\rho)$ will grow exponentially like $e^{\rho/2}$.

To avoid this, we must have

$$n_r + l + 1 - \lambda = 0,$$

or

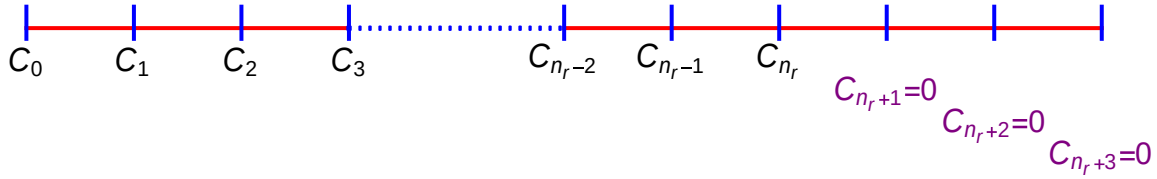
$$\lambda = n_r + l + 1,$$

for $k_{\max} = n_r$. Then we have

$$C_0, C_1, C_2, C_3, \dots, C_{n_r-1}, C_{n_r}, \quad (\text{finite terms})$$

and

$$C_{n_r+1} = C_{n_r+2} = \dots = C_\infty = 0.$$



The function F will thus be a polynomial of degree of n_r , known as an associated Laguerre polynomial.

$$\lambda = \frac{Ze^2}{\hbar} \sqrt{\frac{\mu}{2\varepsilon_1}} = l + 1 + n_r,$$

or

$$E = -\varepsilon_1 = -\frac{\mu Z^2 e^4}{2\hbar^2 (l + 1 + n_r)^2}.$$

Since $l = 0, 1, 2, 3, \dots$, $n_r = 0, 1, 2, \dots$, we introduced a principal quantum number n ,

$$n = l + 1 + n_r,$$

with $n = 1, 2, 3, \dots$

Thus, in terms of n , the energy eigenvalue can be rewritten as

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}.$$

When $n_r = 0$, $l = l_{\max}$. Thus we have

$$l_{\max} = n - 1.$$

((Note))

n : principal quantum number
 l : azimuthal quantum number
 m : Magnetic quantum number

((Note))

Coefficient of ρ^0 :

$$C_1 = \frac{(l+1-\lambda)}{1(2l+2)} C_0.$$

Coefficient of ρ^1 :

$$C_2 = \frac{(l+2-\lambda)}{2(2l+3)} C_1.$$

Coefficient of ρ^2 :

$$C_3 = \frac{(l+3-\lambda)}{3(2l+4)} C_2.$$

Coefficient of ρ^3 :

$$C_4 = \frac{(l+4-\lambda)}{4(2l+5)} C_3.$$

Coefficient of ρ^4 :

$$C_5 = \frac{(l+5-\lambda)}{5(2l+6)} C_4.$$

Coefficient of ρ^5 :

$$C_6 = \frac{(l+6-\lambda)}{6(2l+7)} C_5$$

Radial wave function

(i) For $n_r = 0$, $\lambda = n = l + 1 + n_r = l + 1$

$$F(\rho) = C_0.$$

(ii) For $n_r = 1$, $\lambda = n = l + 1 + n_r = l + 2$

$$F(\rho) = C_0 + C_1 \rho = C_0 \left(1 - \frac{1}{2l+2} \rho\right).$$

with

$$C_1 = \frac{l+1-\lambda}{2(1+l)} C_0 = -\frac{1}{2l+2} C_0.$$

(iii) For $n_r = 2$, $\lambda = n = l + 1 + n_r = l + 3$

$$F(\rho) = C_0 + C_1 \rho + C_2 \rho^2 = C_0 \left[1 - \frac{1}{l+1} \rho + \frac{1}{(2l+2)(2l+3)} \rho^2\right] C_0,$$

with

$$C_1 = \frac{l+1-\lambda}{2(1+l)} C_0 = -\frac{1}{(l+1)} C_0.$$

$$C_2 = \frac{l+2-\lambda}{2(2l+3)} C_1 = -\frac{1}{2(2l+3)} C_1 = \frac{1}{(2l+2)(2l+3)} C_0.$$

(iv) For $n_r = 3$, $\lambda = l + 1 + n_r = l + 4$

$$\begin{aligned} F(\rho) &= C_0 + C_1 \rho + C_2 \rho^2 + C_3 \rho^3 \\ &= \left[1 - \frac{3}{2l+2} \rho + \frac{3}{(2l+2)(2l+3)} \rho^2 - \frac{1}{(2l+2)(2l+3)(2l+4)} \rho^3\right] C_0 \end{aligned}$$

with

$$C_1 = \frac{l+1-\lambda}{2(1+l)} C_0 = -\frac{3}{2l+2} C_0,$$

$$C_2 = \frac{l+2-\lambda}{2(2l+3)} C_1 = \frac{3}{(2l+2)(2l+3)} C_0,$$

$$C_3 = \frac{l+3-\lambda}{3(2l+4)} C_2 = -\frac{1}{(2l+2)(2l+3)(2l+4)} C_0 \dots$$

((Physics))

We discuss the radial wave function for a given n ($=1, 2, 3, 4, \dots$). Since

$$n = l + 1 + n_r,$$

When n is given, l should be equal to

$$l = n - 1, \quad \text{for } n_r = 0, \quad (C_0)$$

$$l = n - 2, \quad \text{for } n_r = 1, \quad (C_0 + C_1 \rho)$$

$$l = n - 3, \quad \text{for } n_r = 2, \quad (C_0 + C_1 \rho + C_2 \rho^2)$$

.....

$$l = 1, \quad \text{for } n_r = n - 2, \quad (C_0 + C_1 \rho + C_2 \rho^2 + \dots + C_{n-2} \rho^{n-2})$$

$$l = 0, \quad \text{for } n_r = n - 1. \quad (C_0 + C_1 \rho + C_2 \rho^2 + \dots + C_{n-1} \rho^{n-1})$$

(i) $n = 1$

$$l = 0 \quad n_r = 0 \quad \text{(1s)}$$

$$F(\rho) = C_0.$$

(i) $n = 2$

$$l = 1 \quad n_r = 0 \quad \text{(2p)}$$

$$F(\rho) = C_0.$$

$$l = 0 \quad n_r = 1 \quad \text{(2s)}$$

$$F(\rho) = C_0(1 - \frac{1}{2l+2}\rho) = C_0(1 - \frac{1}{2}\rho) = \frac{C_0}{2}(2 - \rho).$$

(ii) $n = 3$

$$l = 2 \quad n_r = 0 \quad (3d)$$

$$F(\rho) = C_0,$$

$$l = 1 \quad n_r = 1 \quad (3p)$$

$$F(\rho) = C_0(1 - \frac{1}{2l+2}\rho) = \frac{C_0}{4}(4 - \rho).$$

$$l = 0 \quad n_r = 2 \quad (3s)$$

$$\begin{aligned} F(\rho) &= C_0[1 - \frac{1}{l+1}\rho + \frac{1}{(2l+2)(2l+3)}\rho^2] \\ &= \frac{C_0}{6}(6 - 6\rho + \rho^2) \end{aligned}$$

(iii) $n = 4$

$$l = 3 \quad n_r = 0 \quad (4f)$$

$$F(\rho) = C_0.$$

$$l = 2 \quad n_r = 1 \quad (4d)$$

$$F(\rho) = C_0(1 - \frac{1}{2l+2}\rho) = \frac{C_0}{6}(6 - \rho).$$

$$l = 1 \quad n_r = 2 \quad (4p)$$

$$\begin{aligned} F(\rho) &= C_0[1 - \frac{1}{l+1}\rho + \frac{1}{(2l+2)(2l+3)}\rho^2]_0 \\ &= \frac{C_0}{20}(20 - 10\rho + \rho^2) \end{aligned}$$

$$l = 0, \quad n_r = 3 \quad (4s)$$

$$\begin{aligned}
F(\rho) &= \left[1 - \frac{3}{2l+2} \rho + \frac{3}{(2l+2)(2l+3)} \rho^2 - \frac{1}{(2l+2)(2l+3)(2l+4)} \rho^3 \right] C_0 \\
&= \frac{C_0}{24} (24 - 36\rho + 12\rho^2 - \rho^3)
\end{aligned}$$

We note that $F(\rho)$ coincides with the **associated Laguerrel polynomial** $L_{n-l-1}^{2l+1}(x)$.

$n = 1$

$l = 0$	1
---------	---

$n = 2$

$l = 0$	$2 - \rho$
---------	------------

$l = 1$	1
---------	---

$n = 3$

$l = 0$	$\frac{1}{2}(6 - 6\rho + \rho^2)$
---------	-----------------------------------

$l = 1$	$4 - \rho$
---------	------------

$l = 2$	1
---------	---

$n = 4$

$l = 0$	$\frac{1}{6}(24 - 36\rho + 12\rho^2 - \rho^3)$
---------	--

$l = 1$	$\frac{1}{2}(20 - 10\rho + \rho^2)$
---------	-------------------------------------

$l = 2$	$6 - \rho$
---------	------------

$l = 3$	1
---------	---

$n = 5$

$$l = 0 \quad \frac{1}{24}(120 - 240\rho + 120\rho^2 - 20\rho^3 + \rho^4)$$

$$l = 1 \quad \frac{1}{6}(120 - 90\rho + 18\rho^2 - \rho^3)$$

$$l = 2 \quad \frac{1}{2}(42 - 14\rho + \rho^2)$$

$$l = 3 \quad 8 - \rho$$

$$l = 4 \quad 1$$

APPENDIX

Method of series expansion

((**Mathematica-1**))

Series expansion: radial part of the hydrogen atom

```
Clear["Global`*"];
```

```
vchange[Eq_, ψ_, x_, z_, f_] :=
```

```
Eq /. {D[ψ[x], {x, n_}] := Nest[ $\left(\frac{1}{D[f, z]} D[\#, z] \&\right)$ , ψ[z], n],  
ψ[x] := ψ[z], x := f}
```

$$\text{Seq1} = \frac{(2 e^2 r Z \mu - 2 r^2 \epsilon_1 \mu - \ell \hbar^2 - \ell^2 \hbar^2) u[r]}{r^2 \hbar^2} + u''[r] == 0$$

$$\frac{(2 e^2 r Z \mu - 2 r^2 \epsilon_1 \mu - \ell \hbar^2 - \ell^2 \hbar^2) u[r]}{r^2 \hbar^2} + u''[r] == 0$$

```
Seq2 = vchange[Seq1, u, r, ρ,  $\frac{\hbar \rho}{\sqrt{8 \mu \epsilon_1}}$ ] // PowerExpand
```

$$\frac{8 \epsilon_1 \mu \left(\frac{e^2 Z \sqrt{\mu} \rho \hbar}{\sqrt{2} \sqrt{\epsilon_1}} - \ell \hbar^2 - \ell^2 \hbar^2 - \frac{\rho^2 \hbar^2}{4} \right) u[\rho]}{\rho^2 \hbar^4} + \frac{8 \epsilon_1 \mu u''[\rho]}{\hbar^2} == 0$$

$$\lambda = \frac{Z e^2}{\hbar} \sqrt{\frac{\mu}{2 \epsilon_1}}$$

$$\text{rule1} = \left\{ \epsilon_1 \rightarrow \frac{1}{2} \left(\frac{\sqrt{\mu} Z e^2}{\hbar} \frac{1}{\lambda} \right)^2 \right\};$$

Seq3 = Seq2 /. rule1 // PowerExpand;

Seq4 = Solve[Seq3, $u''[\rho]$]

$$\left\{ \left\{ u''[\rho] \rightarrow \frac{(4\ell + 4\ell^2 - 4\lambda\rho + \rho^2) u[\rho]}{4\rho^2} \right\} \right\}$$

$$F = D[u[\rho], \{\rho, 2\}] - \frac{\ell(\ell+1)}{\rho^2} u[\rho] + \left(\frac{\lambda}{\rho} - \frac{1}{4} \right) u[\rho];$$

rule1 = { $u \rightarrow (\#^s \&)$ };

F /. rule1 // Simplify

$$-\frac{1}{4} \rho^{-2+s} (4s - 4s^2 + 4\ell + 4\ell^2 + \rho(-4\lambda + \rho))$$

rule2 = { $u \rightarrow \left(\#^{1+\ell} \text{Exp}\left[-\frac{\#}{2}\right] F1[\#] \& \right)$ };

eq1 = F /. rule2 // Simplify

$$-e^{-\rho/2} \rho^\ell ((1+\ell-\lambda) F1[\rho] + (-2-2\ell+\rho) F1'[\rho] - \rho F1''[\rho])$$

$$\text{eq2} = -((1+\ell-\lambda) F1[\rho] + (-2-2\ell+\rho) F1'[\rho] - \rho F1''[\rho])$$

$$-(1+\ell-\lambda) F1[\rho] - (-2-2\ell+\rho) F1'[\rho] + \rho F1''[\rho]$$

rule3 = { $F1 \rightarrow \left(\sum_{k=0}^{10} c[k] \#^k \& \right)$ };

eq3 = eq2 /. rule3 // Expand;

```
list1 = Table[{n, Coefficient[eq3, ρ, n]}, {n, 0, 9}] // Simplify;
list1 // TableForm
```

```
0      (-1 - ℓ + λ) C[0] + 2 (1 + ℓ) C[1]
1      (-2 - ℓ + λ) C[1] + 2 (3 + 2 ℓ) C[2]
2      (-3 - ℓ + λ) C[2] + 6 (2 + ℓ) C[3]
3      (-4 - ℓ + λ) C[3] + 4 (5 + 2 ℓ) C[4]
4      (-5 - ℓ + λ) C[4] + 10 (3 + ℓ) C[5]
5      (-6 - ℓ + λ) C[5] + 6 (7 + 2 ℓ) C[6]
6      (-7 - ℓ + λ) C[6] + 14 (4 + ℓ) C[7]
7      (-8 - ℓ + λ) C[7] + 8 (9 + 2 ℓ) C[8]
8      (-9 - ℓ + λ) C[8] + 18 (5 + ℓ) C[9]
9      (-10 - ℓ + λ) C[9] + 10 (11 + 2 ℓ) C[10]
```

Determination of recursion formula

$$\text{rule4} = \left\{ \mathbf{F1} \rightarrow \left(\sum_{n=k-3}^{k+3} \mathbf{C[n]} \#^n \& \right) \right\};$$

```
eq4 = (eq2 / ρ-4+k) /. rule4 // Expand;
list2 = Table[{n, Coefficient[eq4, ρ, n]}, {n, 0, 7}] // Simplify;
list2 // TableForm
```

```
0      (-3 + k) (-2 + k + 2 ℓ) C[-3 + k]
1      - (-2 + k + ℓ - λ) C[-3 + k] + (-2 + k) (-1 + k + 2 ℓ) C[-2 + k]
2      - (-1 + k + ℓ - λ) C[-2 + k] + (-1 + k) (k + 2 ℓ) C[-1 + k]
3      - (k + ℓ - λ) C[-1 + k] + k (1 + k + 2 ℓ) C[k]
4      - (1 + k + ℓ - λ) C[k] + (1 + k) (2 + k + 2 ℓ) C[1 + k]
5      - (2 + k + ℓ - λ) C[1 + k] + (2 + k) (3 + k + 2 ℓ) C[2 + k]
6      - (3 + k + ℓ - λ) C[2 + k] + (3 + k) (4 + k + 2 ℓ) C[3 + k]
7      - (4 + k + ℓ - λ) C[3 + k]
```

```
eq5 = list2[[5, 2]] == 0
```

$$- (1 + k + \ell - \lambda) C[k] + (1 + k) (2 + k + 2 \ell) C[1 + k] == 0$$

```
Solve[eq5, C[k + 1]]
```

$$\left\{ \left\{ C[1 + k] \rightarrow \frac{(1 + k + \ell - \lambda) C[k]}{(1 + k) (2 + k + 2 \ell)} \right\} \right\}$$

((Mathematica-2))

Radial wave function

Hydrogenic atom: Radial wave function

```
Clear["Global`*"];
```

```
rwave[n_, ℓ_, r_] :=
```

$$\frac{1}{\sqrt{(n+\ell)!}} \left(2^{1+\ell} a^{-\ell-\frac{3}{2}} e^{-\frac{Zr}{a n}} n^{-\ell-2} Z^{\ell+\frac{3}{2}} r^{\ell} \sqrt{(n-\ell-1)!} \right. \\ \left. \text{LaguerreL}\left[-1+n-\ell, 1+2\ell, \frac{2Zr}{a n}\right] \right)$$

```
Table[rwave[n, ℓ, r], {n, 1, 3}, {ℓ, 0, n-1}] // TableForm[#, \\
TableHeadings -> {{\"n=1\", \"n=2\", \"n=3\"}, \\
{\"ℓ=0\", \"ℓ=1\", \"ℓ=2\"}}] &
```

	$\ell=0$	$\ell=1$	$\ell=2$
n=1	$\frac{2 e^{-\frac{r Z}{a}} Z^{3/2}}{a^{3/2}}$		
n=2	$\frac{e^{-\frac{r Z}{2 a}} Z^{3/2} \left(2-\frac{r Z}{a}\right)}{2 \sqrt{2} a^{3/2}}$	$\frac{e^{-\frac{r Z}{2 a}} r Z^{5/2}}{2 \sqrt{6} a^{5/2}}$	
n=3	$\frac{2 e^{-\frac{r Z}{3 a}} Z^{3/2} \left(27 a^2-18 a r Z+2 r^2 Z^2\right)}{81 \sqrt{3} a^{7/2}}$	$\frac{\sqrt{\frac{2}{3}} e^{-\frac{r Z}{3 a}} r Z^{5/2} \left(4-\frac{2 r Z}{3 a}\right)}{27 a^{5/2}}$	$\frac{2 \sqrt{\frac{2}{15}} e^{-\frac{r Z}{3 a}} r^2 Z^{7/2}}{81 a^{7/2}}$