Appendix (Optional)[+]

- Students are encouraged to read through this appendix
- Then you will see why in Hydrogen atom
  - $\underbrace{3d,\ 3p,\ 3s}$ all correspond to $E_3 = \frac{-13.6}{3^2}$ eV
  - Given energy E_3

    only have 3s, 3p, 3d (not 3f, 3g, ...)

    OR $l = 0, 1, 2, \ldots, n-1$ (given $\underbrace{n}_{E_n}$)

[+] "Optional": Mathematical details for solving $R_{nl}(r)$ are excluded from exams.

Appendix: Solving the radial equation for H-atom

Goal: See how B.C.'s (well-behaved ψ) give

- E_n (not $E_{n\ell}$ in H-atom)
- ℓ (for given n) goes from $0, 1, \cdots, n-1$

[but short of getting all $R_{n\ell}(r)$]

Radial Eq. for given ℓ: (General)

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left[E - U(r) - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right] R = 0$$

$$U(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \text{ (H-atom) or } -\frac{Ze^2}{4\pi\varepsilon_0 r} \text{ (H-like ions)}$$

$$\boxed{\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right] R = 0} \quad (A1)$$

- To solve for $R(r)$ and E (for given ℓ)

- Focus on Bound states $\underbrace{\text{with } E<0}$

$\therefore U(r)<0$ and $U \to 0$ as $r \to \infty$

Step 1: Convenient to define

$$\boxed{\chi(r) = r \cdot R(r)} \qquad (A2)$$

- $[\chi(r)]^2 = r^2 [R(r)]^2$ is radial prob. distribution fn (See Ch. IX)
- $\underbrace{\chi(0) = 0}_{\text{[Good B.C. to handle]}}$ otherwise $R(r) = \frac{\chi(r)}{r}$ diverges at $r=0$

Note: $R(0)$ can still be finite (see "1s")

Eq. for $\chi(r)$?

$$\frac{d\chi}{dr} = R + r\frac{dR}{dr}; \quad \frac{d^2\chi}{dr^2} = \frac{dR}{dr} + \frac{dR}{dr} + r\frac{d^2R}{dr}$$

$$= \frac{1}{r}\frac{d}{dr}\left(r\frac{dR}{dr}\right)$$

Eq. (A1) becomes:

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

$$\boxed{\frac{d^2\chi}{dr^2} + \frac{2m}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right]\chi = 0} \qquad (A3)$$

Eq. (A3) : looks like a 1D problem (r)
but r ranges from 0 to ∞
$\chi(0)=0 \Rightarrow$ as if a hard wall at $r=0$

Step 2: Turn quantities into dimensionless quantities

Define: $$\rho \equiv \sqrt{-\frac{8mE}{\hbar^2}}\, r \qquad \text{(recall: } E<0\text{)}$$

$$\beta \equiv \frac{e^2}{4\pi\varepsilon_0\hbar}\sqrt{-\frac{m}{2E}}$$

[Note: More complicated than oscillator. E enters ρ and β]

$$\frac{d^2\chi}{dr^2} = -\frac{8mE}{\hbar^2}\frac{d^2\chi}{d\rho^2} \qquad [\chi \text{ becomes } \chi(\rho)]$$

Eq. (A3) becomes

$$\boxed{\frac{d^2\chi}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}\chi + \left(\frac{\beta}{\rho} - \frac{1}{4}\right)\chi = 0} \qquad (A4)$$

- To solve for $\chi(\rho)$ and β
- $\frac{\ell(\ell+1)}{\rho^2}$ term from $\sim\frac{\ell(\ell+1)}{r^2}$; $\frac{1}{\rho}$ term from $\frac{1}{r}$ in (A3)

<u>Step 3</u>: Examine (A4) behavior for large ρ (large r)

Eq. (A4) becomes $\frac{d^2\chi}{d\rho^2} - \frac{1}{4}\chi = 0$ (large ρ)

$\Rightarrow \chi \sim e^{-\frac{\rho}{2}}$ [foul out $e^{+\frac{\rho}{2}}$ by physics]

Write solutions to Eq. (A4) as:

$$\boxed{\begin{array}{l} \chi(\rho) = F(\rho)\, e^{-\rho/2} \\ \text{with } F(\rho) \text{ to be determined} \end{array}} \quad (A5)$$

<u>Step 4</u>: Eq. for $F(\rho)$?

Subst. (A5) into (A4) gives eq. for $F(\rho)$ as:

$$\boxed{\frac{d^2F}{d\rho^2} - \frac{dF}{d\rho} - \frac{\ell(\ell+1)}{\rho^2}F + \frac{\beta}{\rho}F = 0} \quad (A6)$$

- Recall: $\chi(0) = 0 \Rightarrow F(0) = 0$
- (A6) to solve for $F(\rho)$ and β

Step 5: Series solution to Eq. (A6)

Write $\boxed{F(\rho) = \sum_{p=1}^{\infty} a_p \rho^p}$ (A7)

- Series starts from "$p=1$ term"
  ["$p=0$" term? $a_0 = 0$ because $F(0)=0$]
- Need to determine a_p
- The point "p starts counting from 1" is important. If another number is going to hit p, the smallest one is $p=1$.

Comes from physics ($\chi(0) = 0$ for well-behaved $R(r)$)

Find recursive relation: Plug (A7) into (A6)

$$\frac{dF}{d\rho} = \sum_{p=1}^{\infty} p\, a_p \rho^{p-1}$$

$$\frac{d^2F}{d\rho^2} = \sum_{p=1}^{\infty} p(p-1) a_p \rho^{p-2} = \sum_{p=2}^{\infty} p(p-1) a_p \rho^{p-2}$$

$$= \sum_{p=1}^{\infty} (p+1)p\, a_{p+1} \rho^{p-1}$$

$$\frac{F}{\rho^2} = \sum_{p=1}^{\infty} a_p \rho^{p-2} = a_1 \rho^{-1} + \sum_{p=2}^{\infty} a_p \rho^{p-2}$$

$$= a_1 \rho^{-1} + \sum_{p=1}^{\infty} a_{p+1} \rho^{p-1}$$

$$\frac{F}{\rho} = \sum_{p=1}^{\infty} a_p \rho^{p-1}$$

Eq. (A6) reads:

$$-\ell(\ell+1) a_1 \underbrace{\rho^{-1}} + \sum_{p=1}^{\infty} \left[(p+1) p a_{p+1} - p a_p - \ell(\ell+1) a_{p+1} + \beta a_p \right] \underbrace{\rho^{p-1}} = 0$$

- The coefficient of each power of ρ must vanish

So, $a_1 = 0$ unless $\ell = 0$

AND $$\frac{a_{p+1}}{a_p} = \frac{p - \beta}{p(p+1) - \ell(\ell+1)} \qquad (A8)$$

- All the results for H-atom follow from Eq. (A8)
- Note special form: Both numerator and denominator will be important (when we impose the well-behaving $F(\rho)$ requirement).

<u>Step 6:</u> Check if behavior implied by (A8) is OK or not

Inspect Eq. (A8) for $p \to \infty$ terms

$$\frac{a_{p+1}}{a_p} \to \frac{1}{p}$$ Is this OK?

No! It is bad!

Consider $\underbrace{e^{+\rho} = \sum_{p=0}^{\infty} \frac{\rho^p}{p!}}$

Take two consecutive terms: $\frac{a_{p+1}}{a_p} = \frac{\frac{1}{(p+1)!}}{\frac{1}{p!}} = \frac{1}{p+1} \to \frac{1}{p}$

$\therefore$ If Eq. (A7) remains a series, its asymptotic behavior is $e^{+\rho}$

Back to Eq. (A5), $\chi(\rho) = F(\rho)\, e^{-\rho/2} \sim \underbrace{e^{+\rho/2}}$

blows up as $\rho \to \infty$ ($r \to \infty$)

not the physical (acceptable) behavior for QM wavefunction

∴ $\boxed{\text{Need to truncate series into polynomial.}}$

Step 7: Extract Results

Key Result #1

$$\frac{a_{p+1}}{a_p} = \frac{p-\beta}{p(p+1)-l(l+1)} \qquad (A8)$$

- looks like denomintor will diverge when p hits l (that's bad)
- $\boxed{\text{Avoided by requiring } a_p = 0 \text{ for values of } p \text{ with } p \le l}$ (A9)

Why? If not, some $a_p \neq 0$ for $p<l$, then (A8) will take us to a_{p+1}, a_{p+2} and so on. Sooner or later, we get to a_p with $p=l$. Then $a_{p+1} = \infty \cdot a_{(p=l)} = \infty$, $a_{p+2} = \infty$, ..., so $F(\rho) \to \infty$!

∴ Given l, the first non-zero coefficient should be a_p $(p>l)$.

Key Result #2

To truncate into a polynomial

$$\frac{a_{p+1}}{a_p} = \frac{p-\beta}{p(p+1)-\ell(\ell+1)} \qquad \text{(A8)}$$

0

["p starts from 1", see (A7)]

Truncation imposes

(A10) $\boxed{\beta = n}$ (takes on an integer n that starts counting from 1, i.e. $n = 1, 2, 3, \ldots$)

Plus from (A9)

(A9) $n > \ell$ [denominator $\neq 0$]

Then, $a_p = 0$ by (A8) for $p > n$

The resulting polynomial is the associated Laguerre function

(A10) and (A9) are the familiar H-atom results you met in earlier courses

$$\underbrace{\beta = n}_{\substack{\uparrow \\ \text{acceptable} \\ \text{wavefunction}}} \Rightarrow \frac{e^2}{4\pi\varepsilon_0\hbar}\sqrt{-\frac{m}{2E}} = n \qquad n = 1, 2, 3, \ldots$$

$$\Rightarrow E = \boxed{E_n = \frac{-me^4}{2(4\pi\varepsilon_0)^2\hbar^2} \cdot \frac{1}{n^2}} \qquad \text{(A11)}$$

n = principal quantum number

- well-known H-atom energies
- E_n (instead of $E_{n\ell}$ for general $U(r)$)
- Same E_n $\underbrace{\begin{pmatrix} \text{for } \ell < n \text{ or} \\ \ell = 0, 1, \ldots, n-1 \end{pmatrix}}_{\text{this is how } \ell \text{ enters into result}}$ (A12)

$[n > \ell]$

$$\text{(A9)} \Rightarrow \underbrace{\ell < n}_{\ell = 1 \quad \text{"p states"}} \quad \begin{cases} 2p \\ 3p \\ 4p \\ \vdots \end{cases}$$

- (A11) & (A12) are the standard results

Remarks

- For those who want to see more clearly what (A8) says, take $l=2$ as an example

$$\frac{a_{p+1}}{a_p} = \frac{p-\beta}{p(p+1)-6} \qquad (A8')$$

- First of all, we better have $p>3$ (then denominator is OK)
  - If β hits 3, only $a_3 \neq 0$, $a_4 = a_5 = \cdots = 0$, $\underbrace{a_1 = a_2 = 0}_{(A9)}$

    $\left[\beta = 3 \Rightarrow E_3 = -\frac{13.6}{3^2}\,\text{eV}\right]$

    This is 3d.
  - If β hits 4, then $\underbrace{a_3 \neq 0, a_4 \neq 0}_{\text{different polynomial}}$, $a_5 = a_6 = \cdots = 0$

    Energy is $E_4 = -\frac{13.6}{4^2}\,\text{eV}$

    This is 4d.
  - 5d, 6d, $\cdots$ follow similarly

[This is using (A8) with a given l]

$$\frac{a_{p+1}}{a_p} = \frac{p-\beta}{p(p+1)-\ell(\ell+1)} \qquad \text{(A8)}$$

- Let's say β takes on 3 $\Rightarrow E_3 = \frac{-13.6}{9}$ eV
  - $\ell=2$, only $a_3 \neq 0$ "3d" Energy $= E_3$
  - $\ell=1$, $\underbrace{a_2 \neq 0,\ a_3 \neq 0}_{\text{a different polynomial}}$ "3p" Energy $= E_3$
  - $\ell=0$, $\underbrace{a_1 \neq 0,\ a_2 \neq 0,\ a_3 \neq 0}_{\text{yet another polynomial}}$ "3s" Energy $= \underbrace{E_3}_{\text{same energy } E_3 \text{ for H-atom}}$

"$n\ell$"

$R_{32} \sim \frac{\chi_{32}}{r} \sim \frac{r^3}{r} \sim r^2$ term only (3d)

$R_{31} \sim r^2, r$ terms only (3p)

$R_{30} \sim r^2, r, r^0$ terms (3s)

then $Y_{\ell m_\ell}(\theta,\phi)$

[This is using (A8) for given β.]

See table for $\psi_{3\ell m_\ell}(r,\theta,\phi)$

$$\psi_{n l m_l}(r, \theta, \phi) = R_{n l}(r)\, Y_{l m_l}(\theta, \phi)$$

Normalized Wave Functions of the Hydrogen Atom for $n = 1$, 2, and 3*

	n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$	
	1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$	ψ_{100}
	2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	ψ_{200}
	2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$	ψ_{210}
	2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$	ψ_{211} and ψ_{21-1}
3s	3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	ψ_{300}
3p	3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos\theta$	ψ_{310}
	3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin\theta\, e^{\pm i\phi}$	ψ_{311} and ψ_{31-1}
3d	3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3\cos^2\theta - 1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2\theta - 1)$	ψ_{320}
	3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin\theta\cos\theta\, e^{\pm i\phi}$	ψ_{321} and ψ_{32-1}
	3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$	ψ_{322} and ψ_{32-2}

$R_{nl}(r)$