PS 3

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3.1 (a) 4f state : $n=4$, $l=3$

$l=3 \Rightarrow$ There are $2l+1=7$ choices for m_l.

$s=\frac{1}{2} \Rightarrow$ There are $2s+1=2$ choices for m_s.

So that in total there are $7\times 2=14$ states in the notation of $|4,3,m_l;s=\frac{1}{2},m_s\rangle$.

We have 7 spin-down states:

$|4,3,-3;\frac{1}{2},-\frac{1}{2}\rangle$, $|4,3,-2;\frac{1}{2},-\frac{1}{2}\rangle$, $|4,3,-1;\frac{1}{2},-\frac{1}{2}\rangle$,

$|4,3,0;\frac{1}{2},-\frac{1}{2}\rangle$, $|4,3,1;\frac{1}{2},-\frac{1}{2}\rangle$, $|4,3,2;\frac{1}{2},-\frac{1}{2}\rangle$, $|4,3,3;\frac{1}{2},-\frac{1}{2}\rangle$.

and 7 spin-up states:

$|4,3,-3;\frac{1}{2},\frac{1}{2}\rangle$, $|4,3,-2;\frac{1}{2},\frac{1}{2}\rangle$, $|4,3,-1;\frac{1}{2},\frac{1}{2}\rangle$

$|4,3,0;\frac{1}{2},\frac{1}{2}\rangle$, $|4,3,1;\frac{1}{2},\frac{1}{2}\rangle$, $|4,3,2;\frac{1}{2},\frac{1}{2}\rangle$, $|4,3,3;\frac{1}{2},\frac{1}{2}\rangle$.

The 14 states all have the same energy (as the energy of H-atom only depends on n): $E_4=\frac{1}{4^2}E_1=-\frac{13.6\,\text{eV}}{16}$.

(b) For $l=3$ and $s=\frac{1}{2}$, the total angular momentum j can be $j=3-\frac{1}{2}=\frac{5}{2}$ or $j=3+\frac{1}{2}=\frac{7}{2}$.

① For $j=\frac{5}{2}$, there are $2j+1=6$ values for m_j. These states are values of m_j

$$|4,3,\tfrac{1}{2};\tfrac{5}{2},\boxed{-\tfrac{5}{2}}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{5}{2},\boxed{-\tfrac{3}{2}}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{5}{2},-\tfrac{1}{2}\rangle$$

$$|4,3,\tfrac{1}{2};\tfrac{5}{2},\tfrac{1}{2}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{5}{2},\tfrac{3}{2}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{5}{2},\tfrac{5}{2}\rangle$$

② For $j=\frac{7}{2}$, there are $2j+1=8$ values for m_j. These states are

values of m_j

$$|4,3,\tfrac{1}{2};\tfrac{7}{2},\boxed{-\tfrac{7}{2}}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{7}{2},\boxed{-\tfrac{5}{2}}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{7}{2},-\tfrac{3}{2}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{7}{2},-\tfrac{1}{2}\rangle,$$

$$|4,3,\tfrac{1}{2};\tfrac{7}{2},\tfrac{1}{2}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{7}{2},\tfrac{3}{2}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{7}{2},\tfrac{5}{2}\rangle,\quad |4,3,\tfrac{1}{2};\tfrac{7}{2},\tfrac{7}{2}\rangle.$$

We see that there are in total $6+8=14$ states, which is the same as we do in part (a).

Consider one of the 14 states $|4,3,\frac{1}{2};j,m_j\rangle$. We write it as a superposition of states in notation $|4,3,m_l;\frac{1}{2},m_s\rangle$:

$$|4,3,\tfrac{1}{2};j,m_j\rangle=\sum_{m_l,m_s}\underbrace{C(j,m_j;m_l,m_s)}_{}|4,3,m_l;\tfrac{1}{2},m_s\rangle$$

a complex number depends on j,m_j,m_l,m_s.

Then we act the Hamiltonian on this state:

$$\hat{H_0}|4,3,\tfrac{1}{2};j,m_j\rangle=\sum_{m_l,m_s}C(j,m_j;m_l,m_s)\,\hat{H_0}|4,3,m_l;\tfrac{1}{2},m_s\rangle$$

$$=\sum_{m_l,m_s}C(j,m_j;m_l,m_s)\,E_4|4,3,m_l;\tfrac{1}{2},m_s\rangle$$

$$=E_4|4,3,\tfrac{1}{2};j,m_j\rangle,$$

Hence $|4,3,\frac{1}{2};j,m_j\rangle$ is an eigenstate of $\hat{H_0}$, with corresponding energy $E_4=-\frac{13.6\,eV}{16}$.

(c) The spin-orbit interaction term

$$\hat{H}_{so} = f(r)\, \vec{S} \cdot \vec{L} = \frac{1}{2} f(r) \left(J^2 - L^2 - S^2 \right),$$

where $\vec{J} = \vec{L} + \vec{S}$ is the total angular momentum,

For a given angular state $|j, m_j\rangle$, we have:

$$J^2 |j, m_j\rangle = j(j+1)\hbar^2 |j, m_j\rangle ,$$

which similarly holds for l and s.

Hence $$\hat{H}'_{so} | 4, 3, \tfrac{1}{2} ; j, m_j\rangle = \frac{1}{2} f(r)\, \hbar^2 \left[j(j+1) - l(l+1) - s(s+1) \right] | 4, 3, \tfrac{1}{2} ; j, m_j\rangle ,$$

and the expectation value is

$$\langle \hat{H}'_{so} \rangle = \frac{1}{2} \langle f(r) \rangle \left[j(j+1) - 12 - \frac{3}{4} \right] \hbar^2 \quad \text{for } l = 3 \text{ and } s = \frac{1}{2} ,$$

① For $j = l - s = \frac{5}{2}$, $\langle \hat{H}'_{so} \rangle = -2 \langle f(r) \rangle \hbar^2$.

② For $j = l + s = \frac{7}{2}$, $\langle \hat{H}'_{so} \rangle = \frac{3}{2} \langle f(r) \rangle \hbar^2$.

Since $\hat{H}'_{so}$ only depends on J^2, L^2, S^2 but not on m_j, we can treat the states with the same j as degenerate states and simplify the problem into a 2-state problem,

We define $|j = \frac{5}{2}, m_j\rangle$ as $|1\rangle$ (6 states) $\rightarrow$ $\underline{{}^2f_{5/2}}$

define $|j = \frac{7}{2}, m_j\rangle$ as $|2\rangle$ (8 states) $\rightarrow$ $\underline{{}^2f_{7/2}}$

term symbol

Then we set up the 2x2 matrix as:

$$H_{mn} = \begin{bmatrix} E_4 - 2\langle f(r) \rangle \hbar^2 & 0 \\ 0 & E_4 + \frac{3}{2} \langle f(r) \rangle \hbar^2 \end{bmatrix}$$

(This is actually a 14x14 matrix reduced to a 2x2 matrix)

where $\langle \hat{H}_0 + \hat{H}'_{so} \rangle_{11} = E_4 - 2\langle f(r) \rangle \hbar^2$,

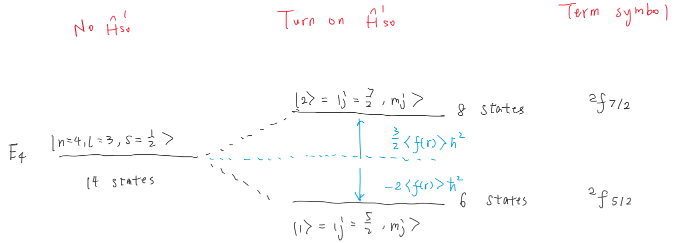
$\langle \hat{H}_0 + \hat{H}'_{so} \rangle_{22} = E_4 + \frac{3}{2}\langle f(r) \rangle \hbar^2$, (we denote $\langle \hat{H} \rangle_{ij} = \langle i | \hat{H} | j \rangle$)

$$\langle \hat{H}_0 + \hat{H}'_{so} \rangle_{12} = \underbrace{\langle \hat{H}_0 \rangle_{12}}_{\downarrow} + \underbrace{\langle \hat{H}'_{so} \rangle_{12}}_{\downarrow} = 0,$$

$\langle \hat{H}_0 \rangle_{12} = 0$ by orthogonality. $\langle \hat{H}'_{so} \rangle \propto \langle f(r) \rangle_{12} \langle j = \frac{5}{2}, m_j | j = \frac{7}{2}, m_j \rangle = 0$

similarly $\langle \hat{H}_0 + \hat{H}'_{so} \rangle_{21} = 0$,

The 2x2 matrix has 2 eigenstates $|1\rangle$ and $|2\rangle$ with eigenenergies $E_4 - 2\langle f(r) \rangle \hbar^2$ and $E_4 + \frac{3}{2}\langle f(r) \rangle \hbar^2$ respectively.


No $\hat{H}'_{so}$
Turn on $\hat{H}'_{so}$
Term symbol
$|2\rangle = |j = \frac{7}{2}, m_j\rangle$
8 states
$^2f_{7/2}$
E_4
$|n=4, l=3, s=\frac{1}{2}\rangle$
14 states
$\frac{3}{2}\langle f(r) \rangle \hbar^2$
$-2\langle f(r) \rangle \hbar^2$
6 states
$^2f_{5/2}$
$|1\rangle = |j = \frac{5}{2}, m_j\rangle$

3.2. (a) $[H'_{so}, L_z] = [f(r)\vec{S}\cdot\vec{L}, L_z]$

$= f(r)[S_xL_x + S_yL_y + S_zL_z, L_z]$

$= f(r)\left(S_x[L_x, L_z] + S_y[L_y, L_z] + S_z[L_z, L_z]\right)$

$= f(r)\, i\hbar\left(-S_xL_y + S_yL_x\right)$

$\neq 0$

$$\left(\begin{array}{l} [L_i, L_j] = i\hbar\,\epsilon_{ijk}L_k, \\ \epsilon_{ijk} = \begin{cases} 1, & \text{even permutation of } i,j,k \\ -1, & \text{odd permutation of } i,j,k \end{cases} \end{array} \right)$$

Hence H'_{so} does not commute with L_z.

Similarly $[H'_{so}, S_z] = f(r)\, i\hbar\left(-S_yL_x + S_xL_y\right) \neq 0$.

Hence $\hat{H}_{so}$ also does not commute with S_z.

(b) $[H'_{so}, L^2] = f(r)\,[S_xL_x + S_yL_y + S_zL_z, L^2]$

$$= f(r)\left(S_x[L_x, L^2] + S_y[L_y, L^2] + S_z[L_z, L^2] \right)$$

$$= 0 \qquad ([L_i, L^2] = 0)$$

Similarly $[H'_{so}, S^2] = 0$ as $[S_i, L^2] = 0$.

Hence $\hat{H}_{so}$ commutes with L^2 and S^2.

3.3.

As discussed in 3.1, for $l = 3$ and $s = \frac{1}{2}$, the total angular momentum j can be $\frac{5}{2}$ or $\frac{7}{2}$.

The energy shift due to spin-orbit coupling is:

$$E_{so} = \langle \hat{H}'_{so} \rangle = \frac{1}{2}\langle f(r)\rangle [j(j+1) - l(l+1) - s(s+1)]\,\hbar^2$$

For $j = \frac{5}{2}$, $E_{so} = -2\hbar^2 \langle f(r) \rangle$.

For $j = \frac{7}{2}$, $E_{so} = \frac{3}{2}\hbar^2 \langle f(r) \rangle$.

The Landé g-factor $g_{Landé} = 1 + \frac{j(j+1) - l(l+1) - s(s+1)}{2j(j+1)}$.

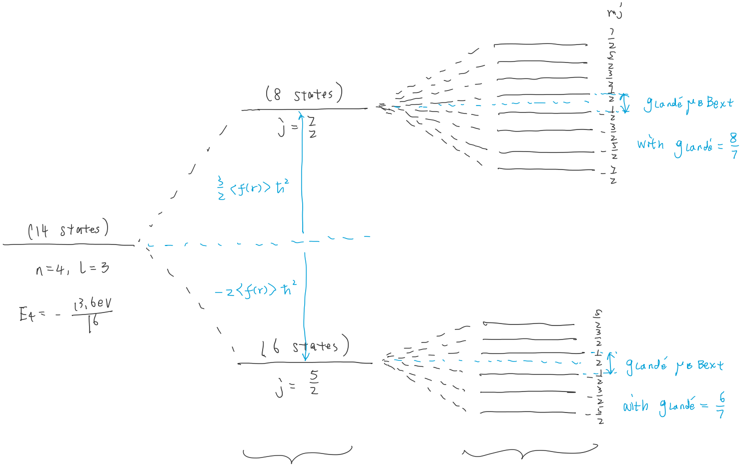
For $j = \frac{5}{2}$, $g_{Landé} = \frac{6}{7}$

For $j = \frac{7}{2}$, $g_{Landé} = \frac{8}{7}$

And $E_{Zeeman} = g_{Landé}\,\mu_B B_{ext}\, m_j$, which depends on m_j.

We sketch the weak Zeeman splitting for $l=3$ and $\hat{H}'_{so} \gg \hat{H}'_{Zeeman}$.

$\hat{H}_0$	$\hat{H}_0 + \hat{H}'_{so}$	$\hat{H}_0 + \hat{H}'_{so} + \hat{H}'_{Zeeman}$
No spin-orbit interaction	With spin-orbit interaction	With spin-orbit interaction
$\vec{B}_{ext} = 0$	$\vec{B}_{ext} = 0$	$\vec{B}_{ext} \neq 0$

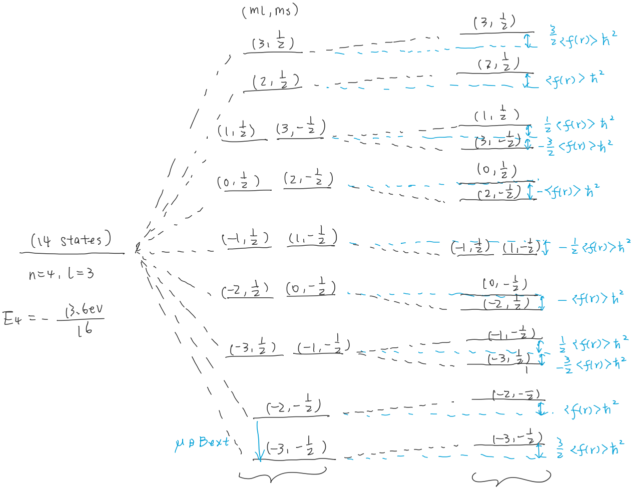

m_j
$\frac{7}{2}$ $\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$ $-\frac{1}{2}$ $-\frac{3}{2}$ $-\frac{5}{2}$ $-\frac{7}{2}$
(8 states)
$j = \frac{7}{2}$
$g_{Landé}\,\mu_B B_{ext}$
with $g_{Landé} = \frac{8}{7}$
$\frac{3}{2}\langle f(r)\rangle \hbar^2$
(14 states)
$n=4,\ l=3$
$E_4 = -\frac{13.6eV}{16}$
$-2\langle f(r)\rangle \hbar^2$
(6 states)
$j = \frac{5}{2}$
$\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$ $-\frac{1}{2}$ $-\frac{3}{2}$ $-\frac{5}{2}$
$g_{Landé}\,\mu_B B_{ext}$
with $g_{Landé} = \frac{6}{7}$

$E_{so} = \frac{1}{2}\langle f(r)\rangle [j(j+1) - l(l+1) - s(s+1)]\hbar^2$ $\quad$ $E_{Zeeman} = g_{Landé}\, \mu_B B_{ext}\, m_j$

3.4.

We consider the strong field Zeeman splitting for $l=3$ and $\hat{H}'_{so} \ll \hat{H}'_{Zeeman}$.

$\hat{H}_0$	$\hat{H}_0 + \hat{H}'_{Zeeman}$	$\hat{H}_0 + \hat{H}'_{Zeeman} + \hat{H}'_{so}$
No spin-orbit interaction	No spin-orbit interaction	With spin-orbit interaction
$\vec{B}_{ext} = 0$	$\vec{B}_{ext} \neq 0$	$\vec{B}_{ext} \neq 0$

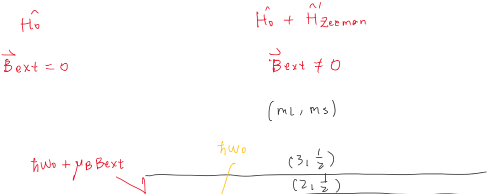

(ml, ms)
(14 states)
n=4, l=3
$E_4 = -\frac{13.6\text{eV}}{16}$
$(3,\frac{1}{2})$
$(2,\frac{1}{2})$
$(1,\frac{1}{2})$ $(3,-\frac{1}{2})$
$(0,\frac{1}{2})$ $(2,-\frac{1}{2})$
$(-1,\frac{1}{2})$ $(1,-\frac{1}{2})$
$(-2,\frac{1}{2})$ $(0,-\frac{1}{2})$
$(-3,\frac{1}{2})$ $(-1,-\frac{1}{2})$
$(-2,-\frac{1}{2})$
$(-3,-\frac{1}{2})$
$\mu_B B_{ext}$
$\frac{3}{2}\langle f(r)\rangle \hbar^2$
$\langle f(r)\rangle \hbar^2$
$\frac{1}{2}\langle f(r)\rangle \hbar^2$
$-\frac{3}{2}\langle f(r)\rangle \hbar^2$
$-\langle f(r)\rangle \hbar^2$
$-\frac{1}{2}\langle f(r)\rangle \hbar^2$
$-\langle f(r)\rangle \hbar^2$
$\frac{1}{2}\langle f(r)\rangle \hbar^2$
$-\frac{3}{2}\langle f(r)\rangle \hbar^2$
$\langle f(r)\rangle \hbar^2$
$\frac{3}{2}\langle f(r)\rangle \hbar^2$

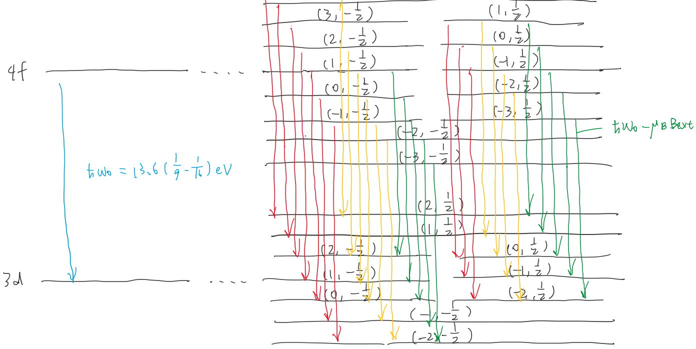
$E_{Zeeman} = \mu_B B_{ext}(m_l + 2m_s)$ $E_{so} = \langle f(r)\rangle \hbar^2 m_l m_s$.

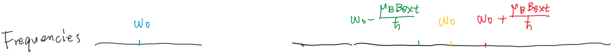
3.5.

We consider the transitions between 4f to 3d state.

And we have $E_{Zeeman} = \mu_B B_{ext}(m_l + 2m_s)$.


$\hat{H}_0$
$\vec{B}_{ext} = 0$
$\hat{H}_0 + \hat{H}'_{Zeeman}$
$\vec{B}_{ext} \neq 0$
(m_l, m_s)
$\hbar\omega_0$
$\hbar\omega_0 + \mu_B B_{ext}$
$(3,\frac{1}{2})$
$(2,\frac{1}{2})$


4f
3d
$\hbar\omega_0 = 13.6\left(\frac{1}{9}-\frac{1}{16}\right)$ eV
$\hbar\omega_0 - \mu_B B_{ext}$
(3, −1/2)
(2, −1/2)
(1, −1/2)
(0, −1/2)
(−1, −1/2)
(−2, −1/2)
(−3, −1/2)
(1, 1/2)
(0, 1/2)
(−1, 1/2)
(−2, 1/2)
(−3, 1/2)
(2, 1/2)
(1, 1/2)
(0, 1/2)
(−1, 1/2)
(−2, 1/2)
(2, −1/2)
(1, −1/2)
(0, −1/2)
(−1, −1/2)
(−2, −1/2)


Frequencies
ω_0
$\omega_0 - \frac{\mu_B B_{ext}}{\hbar}$
ω_0
$\omega_0 + \frac{\mu_B B_{ext}}{\hbar}$

By the selection rule $\Delta m_L = 0, \pm 1$ and $\Delta m_s = 0$, we find that there are three spectral lines when $\vec{B}_{ext} \neq 0$ with frequencies $\left(\omega_0 - \frac{\mu_B B_{ext}}{\hbar}, \omega_0, \omega_0 + \frac{\mu_B B_{ext}}{\hbar}\right)$, where $\omega_0 = \frac{1}{\hbar} \cdot 13.6\left(\frac{1}{9} - \frac{1}{16}\right)$ eV.

3.6.

(a) In atomic unit, length is in unit of Bohr radius a_0, energy is in unit of Hatree energy E_h.

$$\Rightarrow \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{a_0^2}\left(\frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2}\right) = \frac{1}{a_0^2}\nabla'^2,$$

where $x' = \frac{x}{a_0}$, $y' = \frac{y}{a_0}$, $z' = \frac{z}{a_0}$ are the coordinates in atomic unit.

$$\text{Then } \hat{H}_{\text{Helium}} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$= -\frac{\hbar^2}{2ma_0^2}\nabla_1'^2 - \frac{2e^2}{4\pi\varepsilon_0 a_0}\frac{1}{\left(\frac{r_1}{a_0}\right)} - \frac{\hbar^2}{2ma_0^2}\nabla_2'^2 - \frac{2e^2}{4\pi\varepsilon_0 a_0}\frac{1}{\left(\frac{r_2}{a_0}\right)} + \frac{e^2}{4\pi\varepsilon_0 a_0}\frac{1}{\left(\frac{r_{12}}{a_0}\right)},$$

$$= E_h\left(-\frac{1}{2}\nabla_1'^2 - \frac{2}{r_1'} - \frac{1}{2}\nabla_2'^2 - \frac{2}{r_2'} + \frac{1}{r_{12}'}\right),$$

where $E_h = \frac{e^2}{4\pi\varepsilon_0 a_0}$, and $r_1' = \frac{r_1}{a_0}$, $r_2' = \frac{r_2}{a_0}$, $r_{12}' = \frac{r_{12}}{a_0}$.

Hence $\hat{H}_{\text{Helium}}$ in atomic unit is:

$$\hat{H}_{\text{Helium}} = -\frac{1}{2}\nabla_1'^2 - \frac{2}{r_1'} - \frac{1}{2}\nabla_2'^2 - \frac{2}{r_2'} + \frac{1}{r_{12}'}$$

(b) In atomic unit, we consider $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$.

We act this Hamiltonian on wavefunction $\psi(\vec{r}) = Ae^{-Zr}$:

$$\begin{aligned}
\hat{H}\psi(\vec{r}) &= \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)Ae^{-Zr} \\
&= -\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(Ar^2\frac{\partial}{\partial r}e^{-Zr}\right) - \frac{AZ}{r}e^{-Zr} \\
&= \frac{AZ}{2r^2}\left(-Zr^2e^{-Zr} + 2re^{-Zr}\right) - \frac{AZ}{r}e^{-Zr} \\
&= -\frac{Z^2}{2}Ae^{-Zr} = -\frac{Z^2}{2}\psi(\vec{r}),
\end{aligned}$$

(In spherical coordinate, if only consider r-part, $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$)

which means that $\psi(\vec{r})$ is an eigenstate of $\hat{H}$ with eigenenergy $-\frac{Z^2}{2}$.

In SI unit, the eigenenergy is $-\frac{Z^2}{2}E_h = -\frac{Z^2e^2}{8\pi\varepsilon_0 a_0}$.

Then we normalize the wavefunction $\psi(\vec{r})$ by let $\int|\psi(\vec{r})|^2 d^3r = 1$:

$$\int_0^\infty A^2 e^{-2Zr}\boxed{4\pi}\, r^2\, dr = 1$$

(θ, ϕ part $\int_0^{2\pi}\int_0^{\pi}\sin\theta\, d\theta\, d\phi = 4\pi$)

$$A^2\frac{4\pi}{(2Z)^3}\int_0^\infty e^{-2Zr}(2Zr)^2\, d(2Zr) = 1$$

($\int_0^\infty e^{-\beta x}x^n\, dx = \frac{1}{\beta^{n+1}}n!$, with $\beta = 1$, $n = 2$)

$$A^2\frac{\pi}{2Z^3}(2!) = 1$$

$$\Rightarrow A = \sqrt{\frac{Z^3}{\pi}}.$$

The prefactor is found as $A = \sqrt{\frac{Z^3}{\pi}}$ by normalization.