Exercise 1

PHYS4000 Advanced Computational Quantum Mechanics

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1 Question 1

Equation 2.17 is written as:

$$\frac{d^2u_l(r)}{dr^2} + 2(E + \frac{Z}{r})u_l(r) = l(l+1)\frac{u_l(r)}{r^2} \tag{1}$$

First we need to make ρ the subject of the function which is done through the substitution of $\rho = kr$.

$$k^2\frac{d^2u_l(\rho)}{d\rho^2} + 2(-\frac{k^2}{8} + \frac{Zk}{\rho})u_l(\rho) = l(l+1)\frac{u_l(\rho)k^2}{\rho^2} \tag{2}$$

Where we have substituted for E by rearranging the definition of $k = 2\sqrt{-2E}$. We further simplify the differential Equation to the following by cancelling k^2 and multiplying the bracket:

$$\frac{d^2u_l(\rho)}{d\rho^2} - (\frac{1}{4} - \frac{2Z}{\rho k})u_l(\rho) = l(l+1)\frac{u_l(\rho)}{\rho^2} \tag{3}$$

In finding the solutions to the differential equation we rearrange it into the form...

$$\frac{d^2u_l(\rho)}{d\rho^2} - (\frac{1}{4} - \frac{2Z}{\rho k})u_l(\rho) - l(l+1)\frac{u_l(\rho)}{\rho^2} = 0 \tag{4}$$

The question presents the substitution $u_l(\rho) = \rho^{l+1}\exp\{-\rho/2\}\omega(\rho)$, which forms...

$$\frac{d^2}{d\rho^2}[\rho^{l+1}\exp\{-\rho/2\}\omega(\rho)] - (\frac{1}{4} - \frac{2Z}{\rho k})(\rho^{l+1}\exp\{-\rho/2\}\omega(\rho)) - l(l+1)\rho^{l-1}\exp\{-\rho/2\}\omega(\rho) = 0 \tag{5}$$

$$(l+1)[(l\rho^{l-1}\exp\{-\rho/2\} - \frac{1}{2}\rho^{l+1}\exp\{-\rho/2\})\omega(\rho) + \rho^l\exp\{-\rho/2\}\frac{d\omega(\rho)}{d\rho}]$$

$$-\frac{1}{2}\{[(l+1)\rho^l\exp\{-\rho/2\} - \frac{1}{2}\rho^{l+1}\exp\{-\rho/2\}]\omega(\rho) + \frac{d\omega(\rho)}{d\rho^2}\rho^{l+1}\exp\{-\rho/2\}\}$$

$$+[(l+1)\rho^l\exp\{-\rho/2\} - \frac{1}{2}\rho^{l+1}\exp\{-\rho/2\}]\frac{d\omega(\rho)}{d\rho} + \frac{d^2\omega(\rho)}{d\rho^2}\rho^{l+1}\exp\{-\rho/2\}$$

$$-(\frac{1}{4} - \frac{2Z}{k\rho})\rho^{l+1}\exp\{-\rho/2\}\omega(\rho) - l(l+1)\rho^{l-1}\exp\{-\rho/2\}\omega(\rho) = 0$$

and simplifies to

$$\frac{d^2\omega(\rho)}{d\rho^2}\rho^{l+1} + \frac{d\omega(\rho)}{d\rho}[2(l+1)\rho^l - \rho^{l+1}] - \omega(\rho)[(l+1)\rho^l - \frac{2Z}{k}\rho^l] = 0 \tag{6}$$

We now eliminate ρ^l on all terms to get:

$$\frac{d^2\omega(\rho)}{d\rho^2}\rho + [2(l+1) - \rho]\frac{d\omega(\rho)}{d\rho} - [(l+1) - \frac{2Z}{k}]\omega(\rho) = 0 \tag{7}$$

This differential equation has the form:

$$z\frac{d^2w}{dz^2} + (b - z)\frac{dw}{dz} - aw = 0 \tag{8}$$

Which has solutions in the confluent hypergeometric function;

$$F(a, b; \rho) = 1 + \frac{a}{b}\frac{\rho}{1!} + \frac{a}{b}\frac{(a+1)}{(b+1)}\frac{\rho^2}{2!} + \dots \tag{9}$$

In this case, the function will truncate so long as $a = 1 - n$ for $n = 1, 2, 3$, in this way, after the $n + 1$ term of the series and all subsequent terms must simplify to zero.

By comparing the equation we have with the general form, we can see that

$$a = l + 1 - \frac{2Z}{k} \tag{10}$$

$$b = 2(l + 1) \tag{11}$$

And knowing that the differential equation has a general solution in the form of the hypergeometric functions and that the series truncates to be a finite sum, we know that this set of equations satisfies the conditions for a solution of $\omega(\rho)$ for bound states of the hydrogen atom.

2 Question 2

The equation:

$$F(a, b; \rho) = 1 + \frac{a}{b}\frac{\rho}{1!} + \frac{a}{b}\frac{(a+1)}{(b+1)}\frac{\rho^2}{2!} + \ldots \tag{12}$$

Terminates for $a = 1 - n$, for $n \in \{1, 2, 3, \ldots\}$. This prevents the series from growing exponentially in ρ.

In our case, we have $a = 1 + l - \frac{2Z}{k}$, which can be rewritten as $a = 1 - (\frac{2Z}{k} - l)$.
This makes our $n = \frac{2Z}{k} - l$ and subsequently $n + l = \frac{2Z}{k}$.
We then write $n = \frac{2Z}{k}$, $\forall\, n \in \{1 + l, 2 + l, 3 + l, \ldots\}$.

3 Question 3

2.28 states:

$$\int_0^\infty dr u_{n'l}(r) u_{nl}(r) = \delta_{n'n} \tag{13}$$

Which tell us that the eigenstates are orthogonal and normalised for $n = n'$, where the kronecker delta equals unity. This will allow us to calculate the normalisation coefficients for our wave-functions, $u_{21}(r)$ and $u_{31}(r)$.

For $\mathbf{u_{21}(r)}$;

First we establish what we are substituting for ρ, with $Z = 1,\ n = 2,\ l = 1$:

$$\rho = kr = \frac{2Zr}{n}$$

$$\rho = kr = \frac{2(1)r}{2} = r$$

$$\therefore k = 1 \tag{14}$$

With $l = 1 = Z = k = 1$ we have:

$$a = l + 1 - \frac{2Z}{k}$$

$$a = 1 + 1 - 2 = 0$$

$$b = 2(l + 1)$$

$$b = 2(2) = 4$$

$$a = 0,\ b = 4 \tag{15}$$

Calculating the $\omega(kr)$

$$F(a,b;r) = 1 + \frac{a}{b}\frac{r}{1!} + \frac{a}{b}\frac{(a+1)}{(b+1)}\frac{r^2}{2!} + \dots$$

$$F(0,4;r) = 1 + \frac{0}{4}\frac{r}{1!} + \frac{0}{4}\frac{(0+1)}{(4+1)}\frac{r^2}{2!} + \dots$$

$$F(0,4;r) = \omega(r) = 1 \tag{16}$$

Substituting r for ρ to get back $u_{nl}(r)$ from $u_{nl}(\rho)$:

$$u_{nl}(r) = (kr)^{l+1}\exp\{-kr/2\}\omega(kr)$$

$$u_{21}(r) = r^{1+1}\exp\{-r/2\}(1)$$

$$u_{21}(r) = r^2\exp\{-r/2\} \tag{17}$$

We need to add a constant of normalisation to this function in order for it to belong to the Hilbert space, and we will use (13) in order to normalise.

$$\int_0^\infty (Ar^2\exp\{-r/2\})^2 dr = \delta_{n'n}$$

$$\int_0^\infty A^2 r^4\exp\{-r\}dr = \delta_{2,2} = 1$$

Tabular integration will solve the integral

F(x)	G(x)
r^4	e^{-r}
$-4r^3$	$-e^{-r}$
$12r^2$	e^{-r}
$-24r$	$-e^{-r}$
24	e^{-r}
0	$-e^{-r}$
	e^{-r}

$$\int_0^\infty A^2 r^4\exp\{-r\}dr$$

$$= A^2[-r^4\exp\{-r\} - 4r^3\exp\{-r\} - 12r^2\exp\{-r\} - 24r\exp\{-r\} - 24\exp\{-r\}]_0^\infty$$

$$= A^2[0 - (-24)]$$

$$= 24A^2 = 1$$

$$A = \frac{1}{2\sqrt{6}} \tag{18}$$

Which normalises the function to

$$u_{21}(r) = \frac{r^2}{2\sqrt{6}} \exp\{-r/2\} \tag{19}$$

as given in the problem statement.

For $\mathbf{u_{31}(r)}$:

We start in the same way, by defining the appropriate quantities starting with $Z = 1,\ n = 3,\ l = 1$. Subsequently computing parameters like k:

$$\rho = kr = \frac{2Zr}{n}$$

$$\rho = kr = \frac{2(1)r}{3} = r$$

$$\therefore k = \frac{2}{3} \tag{20}$$

a and b...

$$a = l + 1 - \frac{2Z}{k}$$

$$a = 1 + 1 - \frac{2(1)}{\frac{2}{3}}$$

$$a = 1 + 1 - 3 = -1$$

$$b = 2(l + 1)$$

$$b = 2(2) = 4$$

$$a = -1,\ b = 4 \tag{21}$$

Taking these values we compute the $\omega(\rho)$ value needed for the function.

$$F(a, b; \rho) = 1 + \frac{a}{b}\frac{\rho}{1!} + \frac{a}{b}\frac{(a+1)}{(b+1)}\frac{\rho^2}{2!} + \ldots$$

$$F(-1, 4; \rho) = 1 + \frac{-1}{4}\frac{\rho}{1!} + \frac{-1}{4}\frac{(-1+1)}{(4+1)}\frac{\rho^2}{2!} + \ldots$$

$$F(-1, 4; \rho) = 1 - \frac{\rho}{4} \tag{22}$$

Replacing ρ with $\frac{2}{3}r$

$$\omega(\frac{2}{3}r) = F(-1, 4; \frac{2}{3}r) = 1 - \frac{1}{4}\frac{2}{3}r \tag{23}$$

$$\omega(\frac{2}{3}r) = 1 - \frac{r}{6} \tag{24}$$

We now make the appropriate substitutions as follows:

$$u_{nl}(r) = (kr)^{l+1} \exp\{-kr/2\}\omega(kr)$$

$$u_{31}(r) = (\frac{2}{3}r)^{1+1} \exp\left\{-\frac{r}{2}\frac{2}{3}\right\}(1 - \frac{r}{6})$$

$$u_{31}(r) = (\frac{4}{9})r^2 \exp\left\{-\frac{r}{3}\right\}(1 - \frac{r}{6})$$

And add the necessary normalisation coefficient A:

$$u_{31}(r) = A(\frac{4}{9})r^2 \exp\left\{-\frac{r}{3}\right\}(1-\frac{r}{6}) \tag{25}$$

As last time we now use the normalisation condition of Equation 13 to determine the normalisation coefficient

$$\int_0^\infty dr u_{n'l}(r) u_{nl}(r) = \delta_{n'n}$$

$$\int_0^\infty (A(\frac{4}{9})r^2 \exp\left\{-\frac{r}{3}\right\}(1-\frac{r}{6}))^2 dr = \delta_{3'3}$$

$$\int_0^\infty A^2(\frac{16}{81}) \exp\left\{-\frac{2r}{3}\right\}(r^4 - \frac{r^5}{3} + \frac{r^6}{36})dr = \delta_{3,3} = 1$$

$$A^2(\frac{16}{81}) \int_0^\infty \exp\left\{-\frac{2r}{3}\right\}(r^4 - \frac{r^5}{3} + \frac{r^6}{36})dr = 1 \tag{26}$$

As before, the form of integral we have is an exponent multiplied by a polynomial, so we know that tabular integration will solve the integral:

F(x)	G(x)
$r^4 - \frac{r^5}{3} + \frac{r^6}{36}$	$\exp\{-\frac{2r}{3}\}$
$-(4r^3 - \frac{5}{3}r^4 + \frac{6}{36}r^5)$	$-\frac{3}{2}\exp\{-\frac{2r}{3}\}$
$12r^2 - \frac{20}{3}r^3 + \frac{5}{6}r^4$	$\frac{9}{4}\exp\{-\frac{2r}{3}\}$
$-(24r - 20r^2 + \frac{20}{6}r^3)$	$-\frac{27}{8}\exp\{-\frac{2r}{3}\}$
$24 - 40r + 10r^2$	$\frac{81}{16}\exp\{-\frac{2r}{3}\}$
$-(-40 + 20r)$	$-\frac{243}{32}\exp\{-\frac{2r}{3}\}$
20	$\frac{729}{64}\exp\{-\frac{2r}{3}\}$
0	$-\frac{2187}{128}\exp\{-\frac{2r}{3}\}$

Resulting in the final integral

$$A^2(\frac{16}{81}) \int_0^\infty \exp\left\{-\frac{2r}{3}\right\}(r^4 - \frac{r^5}{3} + \frac{r^6}{36})dr$$

$$= A^2(\frac{16}{81})[-\frac{3}{2}\exp\left\{-\frac{2r}{3}\right\}(r^4 - \frac{r^5}{3} + \frac{r^6}{36}) - \frac{9}{4}\exp\left\{-\frac{2r}{3}\right\}(4r^3 - \frac{5}{3}r^4 + \frac{6}{36}r^5)$$

$$-\frac{27}{8}\exp\left\{-\frac{2r}{3}\right\}(12r^2 - \frac{20}{3}r^3 + \frac{5}{6}r^4) - \frac{81}{16}\exp\left\{-\frac{2r}{3}\right\}(24r - 20r^2 + \frac{20}{6}r^3)$$

$$-\frac{243}{32}\exp\left\{-\frac{2r}{3}\right\}(24 - 40r + 10r^2) - \frac{729}{64}\exp\left\{-\frac{2r}{3}\right\}(-40 + 20r) - 20\frac{2187}{128}\exp\left\{-\frac{2r}{3}\right\}]_0^\infty = 1$$

Which in the limits of the integration will evaluate to:

$$= A^2(\frac{16}{81})(\frac{2187}{32}) = 1$$

$$= \frac{27}{2}A^2 = 1$$

$$A = \frac{2}{3\sqrt{6}} \tag{27}$$

When finally substituted into the function for u:

$$u_{31}(r) = \frac{2}{3\sqrt{6}}(\frac{4}{9})r^2 \exp\left\{-\frac{r}{3}\right\}(1 - \frac{r}{6}) \tag{28}$$

$$u_{31}(r) = \frac{8r^2}{27\sqrt{6}} \exp\left\{-\frac{r}{3}\right\}(1 - \frac{r}{6}) \tag{29}$$