

Exercise 1

PHYS4000 Advanced Computational Quantum Mechanics

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1 Question 1

Equation 2.17 is written as:

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

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

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

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:

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

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

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

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

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

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

and simplifies to

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

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

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

This differential equation has the form:

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

Which has solutions in the confluent hypergeometric function;

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

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

$$a = l + 1 - \frac{2Z}{k} \quad (10)$$

$$b = 2(l + 1) \quad (11)$$

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:

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

Terminates for $a = 1 - n$, for $n \in \{1, 2, 3, \dots\}$. 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 $n = \frac{2Z}{k}$, $\forall n \in \{1 + l, 2 + l, 3 + l, \dots\}$.

3 Question 3

2.28 states:

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

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 $\mathbf{u}_{21}(\mathbf{r})$;

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

$$\begin{aligned} \rho = kr &= \frac{2Zr}{n} \\ \rho = kr &= \frac{2(1)r}{2} = r \\ \therefore k &= 1 \end{aligned} \quad (14)$$

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

$$\begin{aligned} a &= l + 1 - \frac{2Z}{k} \\ a &= 1 + 1 - 2 = 0 \\ b &= 2(l + 1) \\ b &= 2(2) = 4 \end{aligned}$$

$$a = 0, b = 4 \quad (15)$$

Calculating the $\omega(kr)$

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

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

$$F(0, 4; r) = \omega(r) = 1 \quad (16)$$

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

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

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

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

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}

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

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

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

$$= 24A^2 = 1$$

$$A = \frac{1}{2\sqrt{6}} \quad (18)$$

Which normalises the function to

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

as given in the problem statement.

For $\mathbf{u}_{31}(\mathbf{r})$:

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

$$\begin{aligned} \rho = kr &= \frac{2Zr}{n} \\ \rho = kr &= \frac{2(1)r}{3} = r \\ \therefore k &= \frac{2}{3} \end{aligned} \quad (20)$$

a and $b \dots$

$$\begin{aligned} a &= l + 1 - \frac{2Z}{k} \\ a &= 1 + 1 - \frac{2(1)}{\frac{2}{3}} \\ a &= 1 + 1 - 3 = -1 \\ b &= 2(l + 1) \\ b &= 2(2) = 4 \\ a &= -1, \quad b = 4 \end{aligned} \quad (21)$$

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

$$\begin{aligned} F(a, b; \rho) &= 1 + \frac{a}{b} \frac{\rho}{1!} + \frac{a(a+1)}{b(b+1)} \frac{\rho^2}{2!} + \dots \\ F(-1, 4; \rho) &= 1 + \frac{-1}{4} \frac{\rho}{1!} + \frac{-1(-1+1)}{4(4+1)} \frac{\rho^2}{2!} + \dots \\ F(-1, 4; \rho) &= 1 - \frac{\rho}{4} \end{aligned} \quad (22)$$

Replacing ρ with $\frac{2}{3}r$

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

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

We now make the appropriate substitutions as follows:

$$\begin{aligned} u_{nl}(r) &= (kr)^{l+1} \exp\{-kr/2\} \omega(kr) \\ u_{31}(r) &= \left(\frac{2}{3}r\right)^{1+1} \exp\left\{-\frac{r}{2} \frac{2}{3}\right\} \left(1 - \frac{r}{6}\right) \\ u_{31}(r) &= \left(\frac{4}{9}\right)r^2 \exp\left\{-\frac{r}{3}\right\} \left(1 - \frac{r}{6}\right) \end{aligned}$$

And add the necessary normalisation coefficient A :

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

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

$$\begin{aligned} \int_0^\infty dr u_{n'l}(r) u_{nl}(r) &= \delta_{n'n} \\ \int_0^\infty \left(A\left(\frac{4}{9}\right)r^2 \exp\left\{-\frac{r}{3}\right\}\left(1 - \frac{r}{6}\right)\right)^2 dr &= \delta_{3'3} \\ \int_0^\infty A^2\left(\frac{16}{81}\right) \exp\left\{-\frac{2r}{3}\right\} \left(r^4 - \frac{r^5}{3} + \frac{r^6}{36}\right) dr &= \delta_{3,3} = 1 \\ A^2\left(\frac{16}{81}\right) \int_0^\infty \exp\left\{-\frac{2r}{3}\right\} \left(r^4 - \frac{r^5}{3} + \frac{r^6}{36}\right) dr &= 1 \end{aligned} \quad (26)$$

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

Resulting in the final integral

$$\begin{aligned} &A^2\left(\frac{16}{81}\right) \int_0^\infty \exp\left\{-\frac{2r}{3}\right\} \left(r^4 - \frac{r^5}{3} + \frac{r^6}{36}\right) dr \\ &= A^2\left(\frac{16}{81}\right) \left[-\frac{3}{2} \exp\left\{-\frac{2r}{3}\right\} \left(r^4 - \frac{r^5}{3} + \frac{r^6}{36}\right) - \frac{9}{4} \exp\left\{-\frac{2r}{3}\right\} \left(4r^3 - \frac{5}{3}r^4 + \frac{6}{36}r^5\right) \right. \\ &\quad \left. - \frac{27}{8} \exp\left\{-\frac{2r}{3}\right\} \left(12r^2 - \frac{20}{3}r^3 + \frac{5}{6}r^4\right) - \frac{81}{16} \exp\left\{-\frac{2r}{3}\right\} \left(24r - 20r^2 + \frac{20}{6}r^3\right) \right. \\ &\quad \left. - \frac{243}{32} \exp\left\{-\frac{2r}{3}\right\} \left(24 - 40r + 10r^2\right) - \frac{729}{64} \exp\left\{-\frac{2r}{3}\right\} \left(-40 + 20r\right) - 20 \frac{2187}{128} \exp\left\{-\frac{2r}{3}\right\} \right]_0^\infty = 1 \end{aligned}$$

Which in the limits of the integration will evaluate to:

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

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

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

When finally substituted into the function for u :

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

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