The Correspondence Principle

a) The correspondence principle states that in situations where the quantum-mechanical effects have little effect, classical and quantum calculations should yield the same results. Such an example is for large quantum numbers, \( n \), where the energy levels approach becoming continuous (not discrete), so \( E_n = E_0/n^2 \).

b) Consider the case of large \( n \) and look at the frequency of the photon emitted when an electron makes a transition from the state \( n \rightarrow n-1 \).

From Bohr's theory, \( E_n = -\frac{Z^2E_0}{n^2} \) where \( E_0 = \frac{mk^2e^4}{2\hbar^2} \)

where \( n = 1, 2, 3, \ldots \)

\[
E_{ph} = |E_{n+1} - E_n| = Z^2E_0 \left[ \frac{1}{(n-1)^2} - \frac{1}{n^2} \right]
\]

\[
= Z^2E_0 \left[ \frac{n^2 - (n-1)^2}{n^2(n-1)^2} \right] = Z^2E_0 \left[ \frac{n^2 - (n^2 - 2n + 1)}{n^2(n-1)^2} \right]
\]

\[
= Z^2E_0 \left( \frac{2n-1}{n^2(n-1)^2} \right)
\]

and \( E_{ph} = \hbar f_{ph} \)

\[
f_{ph} = \frac{Z^2E_0(2n-1)}{n^2(n-1)^2\hbar} = \frac{Z^2(2n-1)mk^2e^4}{n^2(n-1)^2\hbar^2} = \frac{Z^2mk^2e^4(2n-1)}{4\pi\hbar^3 n^2(n-1)^2}
\]

c) In the case of large \( n \), \( (n-1) \approx n \), \( (2n-1) \approx 2n \)

\[
f_{ph} \approx \frac{Z^2mk^2e^42n}{4\pi\hbar^3 n^4} = \frac{Z^2mk^2e^4}{2\pi\hbar^3 n^3}, \text{ as required}
\]
Consider an electron orbiting the nucleus according to Bohr’s theory:

For the \( n^{th} \) energy level,

\[
L = n\hbar = r_n m v_n \quad \text{(ang. m\text{v}m)}
\]

also \( r_n = n^2 a_0 \) where \( a_0 = \frac{\hbar^2}{2mke^2} \)

now to determine the frequency of oscillation of the electron
(also predicted to be the frequency of the radiated photon)
- classically

\[
f_c = \frac{1}{T} \quad \text{and we know classically,}
\]

\[
\omega = \frac{\text{distance}}{\text{time}} = \frac{2\pi r_n}{T}
\]

\[
\therefore f_c = \frac{1}{T} = \left( \frac{2\pi r_n}{\omega} \right)^{-1} = \left( \frac{2\pi r_n}{n\hbar/\lambda} \right)^{-1} = \left( \frac{2\pi \hbar}{n\hbar} \right)^{-1}
\]

\[
= \left[ \frac{2\pi m (n^2 \hbar^2 \left( \frac{Zmke^2}{n^4\hbar^4} \right)^2 \cdot \frac{1}{n^4\hbar^4}} {2\pi \hbar} \right]^{-1}
\]

\[
= \frac{n\hbar \cdot Z^2 m^2 k e^4}{n^4 \hbar^4} \cdot \frac{1}{2\pi \hbar}
\]

\[
= \frac{Z^2 m^2 k e^4}{2\pi \hbar^3 n^3} \quad \text{≈ } f_{qu} \text{ in the case of large quantum number, } n.
\]

Thus, both the classical & quantum approach to deriving
the frequency of the emitted photon agrees in the
large \( n \) limit — as required by the correspondence principle.
\[ \frac{\Delta \lambda}{\lambda} = -\frac{\Delta \mu}{\mu} \]

Now, the wavelength of the spectral lines is given by
\[ \frac{1}{\lambda_{mn}} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \] - the Rydberg-Ritz formula.

Bohr's theory predicts that
\[ R = \frac{m_e^2 e^4}{4\pi \hbar^2 c^3} \rightarrow \frac{\mu^2 e^4}{4\pi \hbar^2 c^3} \]

where \( \mu = \text{reduced mass} \).

\[ \frac{1}{\lambda} = \mu C \]

where \( C = \frac{k^2 e^4}{4\pi \hbar^2 c^3} \cdot \left( \frac{1}{m^2} - \frac{1}{n^2} \right) = \text{constant for a given } m \& n. \]

\[ \lambda = C \mu \text{ or } \lambda = C' \mu^{-1} \]

where \( C' \) is a constant.

Differentiating both sides w.r.t. \( \mu \),
\[ \frac{d\lambda}{d\mu} = C' \left( -\mu^{-2} \right) = -\left( C' \mu^{-1} \right) \mu^{-1} \lambda \]

\[ \frac{d\lambda}{\lambda} = -\frac{d\mu}{\mu} \]

as required. \( \therefore \frac{\Delta \lambda}{\lambda} = -\frac{\Delta \mu}{\mu} \)

For the case of the Balmer red line, \( \lambda = 656.3 \text{ nm for hydrogen.} \)

For hydrogen, \( \mu = \frac{m_e M_H}{m_e + M_H} = \frac{m_e}{1 + \frac{m_e}{M_H}} \) now, \( m_e = 9.1094 \times 10^{-31} \text{ kg} \)
\( M_H = 1.6726 \times 10^{-27} \text{ kg} \)
\( M_D = 2M_H \)

\[ \Delta \lambda = -\frac{\Delta \mu}{\mu} \lambda \]

\[ \Delta \mu = \left( \frac{m_e M_D}{m_e + M_D} \right) - \left( \frac{m_e M_H}{m_e + M_H} \right) \]

\[ D = \text{deuterium} \]

\[ \Delta \mu = \frac{M_e}{1 + \frac{m_e}{2M_H}} - \frac{M_e}{1 + \frac{m_e}{M_H}} = (0.999728 - 0.999455) m_e \]
\[ \Delta \mu = 0.000272 \text{ me} \]

\[ \Delta \lambda = -\Delta \mu \cdot \frac{\lambda}{\mu_n} = -\frac{0.000272 \text{ me}}{0.999456 \text{ me}} \lambda = -0.000272 \lambda \]

\[ \Delta \lambda = 0.18 \text{ nm} (0.179) \]

\[ \lambda \approx 656.3 \text{ nm} \]
4.50 Singly ionised helium, $\text{He}^+$, is hydrogen-like in the sense that it is made up of a nucleus of charge $+2e$ & orbited by a single electron.

a) From the Bohr theory

$$E_n = -\frac{2^2 E_0}{n^2}$$ where $E_0 = +13.6$ eV.

To obtain the energy levels corresponding to $\text{He}^+$:

$$\begin{array}{c|c}
 n & E_n \text{ (eV)} \\
\hline
1 & -54.4 \\
2 & -13.6 \\
3 & -6.04 \\
4 & -3.40 \\
5 & -2.18 \\
\infty & 0 \quad \text{i.e. the electron is free} \Rightarrow \text{ionisation energy of } \text{He}^+ = 54.4 \text{ eV}
\end{array}$$

For the case of hydrogen, H:

$$\begin{array}{c|c}
 n & E_n \text{ (eV)} \\
\hline
1 & -13.6 \\
2 & -3.40 \\
3 & -1.51 \\
4 & -0.85 \\
5 & -0.54 \\
\infty & 0
\end{array}$$

b) $K_\alpha$ and $K_\beta$ spectral lines occur for $n=2 \rightarrow 1$ & $n=3 \rightarrow 1$ respectively.

For hydrogen: $K_\alpha$, $E_{K_\alpha} = -3.40 - (-13.6) = 10.2$ eV

$$h\nu = \frac{hc}{\lambda} \Rightarrow \lambda_{K_\alpha} = \frac{hc}{E_{K_\alpha}} = \frac{1239.8}{10.2} = 121.5 \text{ nm}$$
For hydrogen: \( K \beta \) \( E_{K\beta} = -1.51 - (-13.6) = 12.09 \text{eV} \)
\[ \Rightarrow \lambda_{K\beta} = \frac{1239.8}{12.09} = 102.5 \text{nm} \]

Now, \( E_0 = \frac{m_e^2 e^4}{2\hbar^2} = 13.6 \text{ eV} \) using reduced mass, \( E_0 = \mu \frac{e^4}{2\hbar^2} \)
\[ \mu = 0.999457 \text{ Me} \]
\[ \Rightarrow E_0 \text{ reduced} = 13.59 \text{ eV} \]
\[ \Rightarrow \text{no significant change in energy difference due to reduced mass correction.} \]

For He\(^+\): the Balmer series corresponds to electron transitions where the final level of the electron is \( n=2 \).

For He\(^+\) \( L_\alpha \Rightarrow n=3 \rightarrow 2 \)
\[ \Rightarrow \lambda_{L\alpha} = \frac{1239.8}{7.56} = 164.0 \text{ eV} \]

\( E_{L\beta} = -3.40 - (-13.6) = 10.20 \text{ eV} \)
\[ \Rightarrow \lambda_{L\beta} = \frac{1239.8}{10.20} = 121.5 \text{ eV} \]

\( d) \ E_n = -\frac{E_0}{n^2} \) (hydrogen) \[ \Rightarrow \text{energy levels of He}^+ \text{ match up with energy levels of (2n)} \text{ for hydrogen.} \]

\( (\text{He}^+) \)
Problem 5

Suppose Coulomb's electric force was of the form
\[ \mathbf{F} = -br^2 \hat{r} \]
\( \hat{r} \) indicates attractive force

Recalculating Bohr's theory:
\[ \sum \mathbf{F} = ma \Rightarrow br^2 = \frac{mv^2}{r} \tag{1} \]
angular momentum is quantised
\[ (L = \ell) rmv = \ell \hbar \tag{2} \]

a) To obtain an expression for the radius:
\[ r = \frac{n \hbar}{mv} \]
from (1) \[ v^2 = \frac{br^3}{m} \]
\[ \therefore v = \sqrt{\frac{br^3}{m}} \tag{3} \]
\[ \therefore r = \frac{n \hbar m^{1/2}}{m b^{1/2} r^{3/2}} \]
\[ r^{5/2} = \frac{n \hbar}{m b^{1/2} r^{3/2}} \]
squaring both sides:
\[ r^5 = \frac{n^2 \hbar^2}{m b} \]
\[ \therefore r \propto n^{2/5}, \quad as \ required \]

b) To determine the speed of the electron:
\[ v = \sqrt{\frac{br^3}{m}} \Rightarrow v^2 = \frac{b}{m} (\frac{n^2 \hbar^2}{m b})^{3/5} = \frac{(n^2 \hbar^2)^{3/5}}{m^{3/5}} b^{2/5} \]
\[ \therefore v = \left[ \frac{n^2 \hbar^2 b^{3/5}}{m^{3/5}} \right]^{1/5} \]
Problem 5 (cont’d)

e) We know \( F = -\frac{dU}{dr} \)

\[ U = -\int F \, dr \Rightarrow U = -\int -br^2 \, dr = \frac{br^3}{3} \]

and so \( U \propto r^3 \), as required.

d) \( E_{ tot} = K + U \) and \( K = \frac{1}{2}mv^2 \) : Recall \( \frac{mv^2}{r} = br^2 \)

\[ \Rightarrow E_{ tot} = \frac{1}{2}br^3 + \frac{br^3}{3} \]

\[ \Rightarrow E_{ tot} \propto r^3 \text{ and since } r \propto n^{2/5} \]

\[ \Rightarrow E_{ tot} \propto (n^{2/5})^3 \]

\[ \Rightarrow E_{ tot} \propto n^{6/5} \text{, as required.} \]

e) Now consider the case when \( \vec{F} = -\frac{b}{r} \hat{r} \)

In this case,

\[ \frac{mv^2}{r} = \frac{b}{r} \quad (1) \]

\[ \Rightarrow v^2 = \frac{b}{m} = \text{constant} \]

also, \( L = nh = rmv \)

\[ \Rightarrow r = \frac{nh}{mv} = \text{constant} \cdot n \]

\[ U = -\int F \, dr = -\int \frac{b}{r} \, dr = b \ln r \]
Problem 6

Consider the following hypothetical atom:

It has only 2 excited state (energy levels)

If a vapour of this type of atom was used in the Franck-Hertz experiment, expect inelastic collisions to occur when an excite electron from ground state to any excited state or ionisation.

\[
\begin{array}{ccccccc}
\text{current} & \text{at } & 4.0 & \text{ground level electron} & \text{excites to } 4.0 \text{eV level} \\
& & 7.0 & \text{"} & 7.0 \text{eV level} \\
& & 12.0 & \text{"} & 12.0 \text{eV level} \\
& & 14.0 & \text{"} & 14.0 \text{eV level} \\
& & 16.0 & \text{"} & 16.0 \text{eV level} \\
\end{array}
\]

At 9.0 eV atomic electron is ionised
\Rightarrow incident electron loses energy & so current drops.

- 12.0 incident electron has three collisions, each time losing 4.0 eV to atomic electron.
- 14.0 incident electron has two collisions, each time losing 7.0 eV to atomic electron.

1 collision: 4.0, 7.0
2 collisions: 8.0, 14.0, 11.0
3 collisions: 12.0, 15.0, 18.0, 20.0
4 collisions: 16.0, 19.0, ...

\[
\begin{array}{ccccccc}
4+4+4 & 4+4+7 & 4+7+7 & 7+7+7 \\
\end{array}
\]