

EARLY QUANTUM IDEAS AND THE BOHR MODEL

Bohr's postulates were based on the observation of discrete spectra and the results of the α -scattering experiment of Rutherford.

The postulates were

- Electrons move around the nucleus in discrete orbits. These orbits correspond to fixed energies and are stable (i.e. no radiation is emitted by such electrons)
- Radiation is emitted only when the electron jumps from one discrete orbit to another orbit of a lower energy. When electrons absorb radiation, the reverse transition occurs.
- A dynamic equilibrium exists between the centrifugal force and the coulomb force between the electron and the nucleus:

$$(z=1!) \quad \frac{(Ze)^2}{4\pi\epsilon_0 r^2} = m\omega^2 r \quad \Rightarrow \quad \omega = \frac{e^2}{4\pi\epsilon_0 m r^3}$$

The electron revolves at this frequency in the orbit. Classical electrodynamics predicts that the charge will radiate at this very frequency and lose energy. Bohr's postulates override this.

The total energy of the electron is

$$\begin{aligned} E &= E_{\text{kin}} + E_{\text{pot}} \\ &= \frac{1}{2} m\omega^2 r^2 - \frac{e^2}{4\pi\epsilon_0 r} \end{aligned}$$

Using the above obtained value of ω , we get

$$E = \frac{-e^2}{8\pi\epsilon_0 r} = -\frac{1}{2} \frac{\omega^{2/3}}{(4\pi\epsilon_0)^{2/3}} (me^4)^{1/3}$$

Bohr's important insight was to recognise that the frequency of radiation (according to the postulates) should be given by

$$h\nu = E_n - E_{n'}$$

where $h\nu$ is the radiation quantum as proposed earlier by Planck, and that this radiation must be the same as that

OPTICAL STUDIES LEADING TO THE STRUCTURE OF THE ATOM

1. Kirchoff & Bunsen 1870s observed
 - thin (sparse) gases emit discrete spectra when heated
 - on the other hand solids emit a continuous spectrum or a continuous spectrum with some discrete features
 - thin gases absorb at discrete wavelengths when they are exposed to a source emitting a continuous spectrum.

2. Balmer observed discrete lines in the visible spectrum of Hydrogen. Atomic Hydrogen is very difficult to study since it readily converts to H_2 . By 1885 he could show that the wavelengths could be very well fit by the formula
$$\lambda = B \frac{n^2}{n^2 - 4}$$
where n is an integer ≥ 3 .

B , the Balmer's constant is a special case of the Rydberg constant found later. $R_H = 4/B$ in wavenumbers.

3. In 1881 several discrete lines were observed in astrophysical spectra by Huggins, among them the so-called H_{α} line in the solar spectrum, corresponding to $n=3$ in Balmer's formula
$$\lambda_{H_{\alpha}} = 656.3 \text{ nm} = 15233 \text{ cm}^{-1}$$

4. Rydberg put together all Hydrogen line spectra (observed and analysed by Lyman, Balmer, Brackett, Paschen, Pfund) and showed that their wavelengths could be given by a single formula
$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad n_1 > n_2; \text{ both integers}$$

R_H was found to have the value 109677 cm^{-1}

5. A similar series (Fowler series) was observed in the spectrum of He^+ called the Fowler series

$$\frac{1}{\lambda} = R_{He} \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \text{ in the visible range.}$$

In particular, if two neighbouring levels are E_n & E_{n-1} for large n then

$$\begin{aligned}\frac{\omega}{2\pi} &= (E_n - E_{n-1}) \frac{1}{h} \\ &= R_H c \left[-\frac{1}{n^2} + \frac{1}{(n-1)^2} \right] \\ &= \frac{2R_H c}{n^3}\end{aligned}$$

$$\omega = \frac{4\pi R_H c}{n^3} \rightarrow \text{discrete values of } \omega$$

Using this value of ω and the previous expressions for E in terms of ω and in terms of R_H we get

$$R_H = \frac{me^4}{8\epsilon_0 h^3 c}$$

Thus, Bohr's theory could predict the Rydberg constant by invoking a correspondence between classical and quantum predictions.

There is a small difference between the predicted and observed Rydberg constants

$$R_H^{\text{theory}} = 109737 \text{ cm}^{-1} \quad \text{while} \quad R_H^{\text{exp}} = 109677 \text{ cm}^{-1}$$

This difference is readily accounted for by replacing m in the formula by the reduced mass $m_e m_p / (m_e + m_p)$ in the formulae

The quantisation of the radii immediately follows from the formula for the energy in terms of the radius:

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2}$$

As a consequence the angular momentum $L = m r^2 \omega$ should also be quantised:

$$|L| = m r^2 \omega = n \frac{h}{2\pi}$$

described by Rydberg's formula. That is

$$h\nu = E_n - E_{n'} \quad \text{and} \quad \frac{1}{\lambda} = \frac{h\nu}{c} = \frac{1}{n_1^2} - \frac{1}{n_2^2}$$

must represent the same things.

This gives the energy levels in terms of the Rydberg constant

$$E_n = - R_H \frac{hc}{n^2} \quad \text{Energy is (discretised or quantised)}$$

This energy must be the same as that given by the classical laws (which are used in the postulates)

$$-\frac{e^2}{8\pi\epsilon_0 r_n} = -R_H \frac{hc}{n^2} \quad \text{(radii are also quantised)}$$

$$r_n = \frac{e^2 n^2}{R_H \cdot 8\pi\epsilon_0 hc}$$

At this point discrete energy levels and discrete radii are explained, but the Rydberg constant is not yet predicted or determined based on the postulates alone. Further, the emission frequency ν in the above expression does not match $\omega/2\pi$ that would be classically expected.

Bohr's model is an ad-hoc mix of classical and new (quantum or "discrete") ideas, in particular it uses classical force laws that allow arbitrary radii, but imposes only certain "allowed" orbits and energies.

To make sense of this Bohr put forth the correspondence principle. This principle states that in the limit of large size (scale) the new ideas must merge with or correspond to the classical ones.

Specifically, for the frequency of the emitted radiation he proposed that the frequency of radiation predicted by the new formula for large n should match the classical frequency.

Thus angular momentum quantisation is a result of the Bohr's postulates and the correspondence principle. It is sometimes stated as one of the postulates, but this does not seem right.

Quantisation of the radius also gives a size of the atom.

$$r_1 = \frac{h^2 \epsilon_0}{\pi m e^2} = 0.529 \text{ \AA}$$

which is given the special symbol a_0 and is treated a fundamental unit of length in the context of atoms and molecules, along with the electron charge e and Planck's constant. That is, we have a system of atomic units in which

$$m_e = 1, \quad e = 1, \quad \hbar = 1, \quad a_0 = 1 \quad (e \text{ in CGS units})$$

The discrete energy levels are

$$E_n = - \frac{e^4 m_e}{32 \pi^2 \hbar^2 \epsilon_0^2} \frac{1}{n^2} \quad \left(\frac{e^2}{4 \pi \epsilon_0} = 1 \text{ in MKS} \right)$$

which in "atomic units" becomes

$$E_n = - \frac{1}{2} \frac{1}{n^2}$$

Schrodinger Eqn for the Hydrogen Atom

$$\left[\frac{-\hbar^2}{2m_e} \nabla^2 + V(\vec{r}) \right] \Psi = -i\hbar \frac{\partial \Psi}{\partial t} \quad \text{where } \Psi(\vec{r}, t) \equiv \Psi(\vec{r}, t)$$

$$V(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Due to the time and angle independent nature of V the equation get simplified in two ways. First the time dependence on the RHS of the equation gets replaced by the energy eigenvalue. Second the Hamiltonian when written in spherical coordinates, allows the separation of $\Psi(\vec{r})$ into a product of radial-only and angular-only parts. Thus we get the form

$$\left[-\nabla^2 + \frac{2m_e}{\hbar^2} \cdot \frac{Ze^2}{4\pi\epsilon_0 r} \right] \Psi(r) = \frac{2m_e E}{\hbar^2} \Psi \quad \text{where } \Psi(\vec{r}, t) = e^{-iEt/\hbar} \Psi(\vec{r})$$

Written in spherical coordinates and with the substitution

$$k = \frac{m_e Z e^2}{4\pi\epsilon_0 \hbar^2}$$

$$K = \sqrt{2m|E|} / \hbar$$

and using

$$\nabla_{\text{sph}}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \hat{L}^2 \quad \hat{L}^2 \text{ is the angular momentum operator}$$

and $\Psi(\vec{r}) = R(r) Y(\theta, \phi)$, we get

$$\nabla^2 \Psi(\vec{r}) = \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \hat{L}^2 \right] R(r) Y(\theta, \phi)$$

$$= \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) R Y + \frac{1}{r^2} L^2 R Y \quad Y: \text{ spherical harmonics.}$$

$$= \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) R Y + \frac{l(l+1)}{r^2} R Y \quad \text{since } \hat{L}^2 Y = l(l+1) \hbar^2 Y$$

Thus, the Schrödinger eqn becomes

$$-\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right] R(r) Y(\theta, \phi) + \frac{2a}{r} R(r) Y(\theta, \phi) = k^2 R(r) Y(\theta, \phi)$$

which simplifies to

$$-\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] R(r) + \frac{2a}{r} R(r) = k^2 R(r)$$

Let us examine the equation in the limit $r \rightarrow \infty$ and instead of $R(r)$ consider the function $R(r) = \frac{u(r)}{r}$.

$$\left[\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m}{\hbar^2} \left[E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)}{r^2} \right] R = 0 \right]$$

as $r \rightarrow \infty$ the second and third terms go to zero

and we get $\frac{d^2 u}{dr^2} + \frac{2mE}{\hbar^2} u = 0$

$$u = e^{\pm kr} ; \quad R = e^{-kr}/r \quad \text{or} \quad e^{kr}/r$$

The former solution is physically acceptable

For the general case (r finite) we seek a solution of the form

$$R(r) = u(r) e^{-kr} / r \quad \text{THIS } u \text{ is not the same as before}$$

where $u(r)$ is a polynomial.

We write instead in terms of a dimensionless variable $\rho = 2Kr$

Then

$$R(r) \rightarrow \tilde{R}(2Kr) = \tilde{R}(\rho)$$

$$\tilde{R}'' + \frac{2}{\rho} \tilde{R}' + \left[-\frac{1}{4} + \frac{B}{K\rho} - l(l+1) \right] \tilde{R} = 0$$

To match the necessary asymptotic form we do a trial soln:

$$\tilde{R} = \rho^\mu \sum a_n \rho^n e^{-\rho/2}$$

Substitute this in the radial differential equation to get equal powers of ρ together.

- This series must terminate at some value of ν .
- Since this eqn is to be valid $\forall \rho$ and RHS = 0, we can obtain a relationship (recurrence relationship) between the coeff

The smallest ^{power} non-vanishing term is that of $\rho^{\mu-2}$, and for this term we obtain

$$a_0 \mu(\mu-1) + a_0 2\mu - a_0 l(l+1) = 0$$

a_0 is the lowest power coeff, which is by definition non-zero.

$$\text{Hence } \mu(\mu+1) = l(l+1)$$

$$\Rightarrow \mu = l \quad \text{or} \quad \mu = -l-1.$$

If we choose the former we get

$$R = \rho^l \sum_{\nu} a_{\nu} \rho^{\nu} e^{-\rho/2}$$

which remains finite as $\rho \rightarrow 0$ $\mu = l$ case

but if we choose $\mu \rightarrow -l-1$ it diverges as $\rho \rightarrow 0$. $\mu = -l-1$ case

Hence the solution is $\mu = l$.

The general recurrence relation [for $\rho^{\nu+l-2}$] is

$$a_{\nu} (\nu+l)(\nu+l-1) + a_{\nu} 2(\nu+l) - a_{\nu} l(l+1) - a_{\nu-1} (\nu+l-1) + a_{\nu-1} \left(\frac{B}{K} - 1 \right) = 0$$

$$a_{\nu} = \frac{\nu+l - B/K}{\nu(\nu+2l+1)} a_{\nu-1}$$

For this series to terminate, $a_{\nu} = 0$ for some ν_{\max} .

$$\therefore \frac{\nu_{\max} + l - B/K}{\nu_{\max} (\nu_{\max} + 2l + 1)} a_{\nu_{\max}-1} = 0$$

By definition $a_{\nu_{\max}-1} \neq 0$

$$\text{Hence } \nu_{\max} + l - \frac{B}{k} = 0$$

$$\nu_{\max} = \frac{B}{k} - l \quad \left(\Rightarrow \frac{B}{k} \text{ is an integer} \right)$$

Since $\nu_{\max} > 1$, we obtain $l \leq \frac{B}{k} - 1$

B/k is an integer (n), which implies that

$$E = - \frac{m_e Z^2 e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \frac{1}{n^2}$$

which is exactly the Bohr formula. This expression for E has come about through mainly two conditions

- (1) the wavefunction should vanish at ∞ and stay finite at 0
- (2) the series solution must terminate

This forces a lowest power of ρ and a highest power of ρ and the requirement that B/k is an integer.

Going back to $\tilde{R} = e^{-\rho/2} \rho^l \sum a_\nu \rho^\nu$

$$\text{we get } R_{n,l} = N_{n,l} \exp(-k_n r) r^l \underbrace{L_{n-1}^{2l+1}(2k_n r)}_{\text{Laguerre Polynomials}}$$

$$k_n = \frac{1}{n} \frac{m_e Z e^2}{\hbar^2 4\pi\epsilon_0} \quad \text{is the scaling for the radius,}$$

$$r_n = \frac{1}{k_n}$$

$$E_n = \hbar^2 k_n^2 / 2m$$

$$\int |R_{n,l}|^2 r^2 dr = 1 \quad \text{gives } N_{n,l}$$