Bohr’s atomic model

Another interesting success of the so-called *old quantum theory* is explaining atomic spectra of hydrogen and hydrogen-like atoms. The electromagnetic radiation emitted by free atoms is concentrated at a number of discrete wavelengths. Each kind of atom has its own characteristic spectrum *i.e.* a different set of wavelengths at which the lines of the spectrum are found. To explain the discrete nature of the spectral lines, Bohr postulated (1913)

1. Electron in an atom moves in circular orbits, obeying classical mechanics, about the nucleus under Coulomb interaction thus obeying classical electromagnetic theory.

2. Of all the infinite set of orbits possible in classical mechanics, electron moves only in those for which its orbital angular momentum is an integral multiple of $\hbar/2\pi$, *i.e.* $L = n\hbar$, which is a departure from classical mechanics. Further, electron moving in such an orbit does not loose energy by electromagnetic radiation, though it is in accelerated motion, thereby defying classical electromagnetic theory on the way.

3. Electromagnetic radiation is emitted if electron, initially moving in an orbit with energy $E_i$, jumps discontinuously to another orbit of energy $E_f$ and the frequency of the emitted radiation is $\nu = (E_i - E_f)/\hbar$.

Based on these postulates of Bohr, calculation of the energy of an atomic electron moving in one of the allowed orbits is straightforward. From postulate 1, an electron of charge $-e$ and mass $m$ moving round a nucleus of charge $Ze$ and mass $M$ in an orbit of radius $r$ with velocity $v$, we get

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = \frac{mv^2}{r}. \quad (33)$$

From postulate 2, we get

$$L = mvr = n\hbar, \quad n = 1, 2, 3, \ldots \quad (34)$$

These two together give us

$$r = \frac{4\pi\epsilon_0 \hbar^2 n^2}{mc^2 Z} = a_0 \frac{n^2}{Z} \quad (35)$$

$$v = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{n\hbar} \quad (36)$$

where, $a_0 \approx 5.3\text{nm}$ is known as *Bohr radius*. The ratio between the speed of electron in the first Bohr orbit ($n = 1$) and the speed of light is equal to a dimensionless constant $\alpha$, known as *fine structure constant*:

$$\alpha = \frac{v_1}{c} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{hc} = \frac{1}{137}. \quad (37)$$
which actually gives the strength of electromagnetic coupling. Now the kinetic and
potential energy of this electron, using (33), are,

\[ K = \frac{mv^2}{2} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{2r} \]

\[ V = -\int_r^\infty \frac{Ze^2}{4\pi\epsilon_0 r^2} dr = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}. \]

Therefore, the total energy of the electron, \( E = K + V \), moving in an orbit specified
by \( n \) of equation (34) is,

\[ E = -\frac{mZ^2e^4}{(4\pi\epsilon_0)^22\hbar^2} \frac{1}{n^2} = -\frac{R Z}{n^2}, \quad n = 1, 2, 3, \ldots \] (38)

\textit{i.e.} the quantization of orbital angular momentum leads to quantization of orbital
energy. \( R = 13.6\text{eV} \) is called Rydberg constant. From postulate 3, the frequency of
electromagnetic radiation emitted when the electron makes transition from quantum
state \( (E_i, n_i) \) to the quantum state \( (E_f, n_f) \) is given by,

\[ \nu = \frac{E_i - E_f}{\hbar} = \left( \frac{1}{4\pi\epsilon_0} \right)^2 \frac{mZ^2e^4}{4\pi\hbar^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \] (39)

The above expression (39) explains the discrete atomic spectral lines \textit{i.e.} discrete fre-
quency of electromagnetic radiation when electron jumps around among the discrete
energy levels of the atom.

Direct confirmation that the energy states of an atom are quantized came from
the \textbf{experiment of Frank and Hertz} (1914). The experiment provided not only
the evidence of discrete energy states of Hg atom but actually measured the energy
differences between its quantum states.

\textbf{Wilson-Sommerfeld quantization rules}

To interpret two rather successful quantization rules – Planck’s quantization of en-
ergy (10), \( \epsilon = nh\nu \) and Bohr’s quantization of angular momentum (34), \( L = nh \)
of an electron moving in a circular orbit – in a consistent way, Wilson and Sommer-
feld (1916) offered a scheme that included both Planck and Bohr quantization rules
as special cases. Wilson-Sommerfeld quantization rule states that – \textit{for any physical
system in which the coordinates are periodic functions of time, the quantum condition for each coordinate is}

\[ \oint p_q dq = n_q\hbar \] (40)

where \( q \) is one of the coordinates, \( p_q \) is the momentum associated with that coordinate,
\( n_q \) is a quantum number which takes on integral values and integration is taken over
one period of the coordinate \( q \). For instance, \( (q, p_q) \) for one dimensional simple
harmonic oscillator is \( (x, p_x) \), displacement from center and linear momentum, for
electron moving in an orbit it is angle and orbital angular momentum \( (\theta, L_\theta) \). Most
of the time, equation (40) is referred as quantization of action variable, \( J = \oint p_x dq = n_x \hbar \), where \( J \) is the action.

The rule for quantization of cavity radiation by Planck (10) can be derived from action quantization (40). Considering an one-dimensional simple harmonic oscillator (a whole lot of which made up the cavity radiation), the task is to calculate the quantization integral \( \oint p_x dx \), where the instantaneous position \( x \) and momentum \( p_x \) are related by the total energy \( E \),

\[
E = \frac{p_x^2}{2m} + \frac{kx^2}{2} \Rightarrow \frac{p_x^2}{2mE} + \frac{x^2}{2E/k} = 1. \tag{41}
\]

A plot in two-dimensional space having having coordinates \( x \) and \( p_x \), called phase space, the motion of simple harmonic oscillator traces out an ellipse, \( x^2/a^2 + p_x^2/b^2 = 1 \), semi-axes being

\[
a = \sqrt{\frac{2E}{k}} \quad \text{and} \quad b = \sqrt{2mE}. \tag{42}
\]

The value of \( \oint p_x dx \) is just equal to the area enclosed by the above ellipse, thus

\[
\oint p_x dx = \pi ab = \pi \sqrt{\frac{2E}{k}} \frac{2mEi}{\sqrt{k/m}} = \frac{2\pi E}{\sqrt{k/m}}. \tag{43}
\]

Since, for an linear oscillator, the frequency of oscillation is related to \( k \) and \( m \) as \( \sqrt{k/m} = 2\pi \nu \), Wilson - Sommerfeld quantization rule (40) leads to Planck’s quantization (10),

\[
\oint p_x dx = \frac{E}{\nu} = n_x \hbar \Rightarrow E = n_x \hbar \nu. \tag{44}
\]

That is, the only allowed states of oscillation are those represented in the phase space by a series of ellipse with quantized area \( \oint p_x dx = \hbar \). The area between two successive ellipses, \( i.e. \) states of oscillation, is equal to \( \hbar \). Hence, Planck’s energy quantization is equivalent to the quantization of action.

Similarly, Bohr’s quantization of orbital angular momentum follows from action quantization. For an electron moving in a circular orbit, the appropriate coordinate is the angle \( \theta \), which is a periodic function of time, and corresponding momentum is orbital angular momentum \( L \), which is a constant (angular momentum is conserved for inverse-square laws). From (40) it follows that,

\[
\oint p_\theta d\theta = n_\theta \hbar \Rightarrow \oint L d\theta = \hbar. \tag{45}
\]

Since \( L \) is constant, we have \( \oint L d\theta = L \int_0^{2\pi} d\theta = 2\pi L \) and thus

\[
2\pi L = n\hbar \Rightarrow L = n\hbar \tag{46}
\]

which is Bohr’s quantization condition. A more physical interpretation of the Bohr’s orbital angular momentum quantization comes from de Broglie’s hypothesis of wave-particle duality.
**Motivation for action discretization – classical adiabatic invariants**

*Pendulum with variable string length*: Consider an ideal pendulum consisting of a massless string of length $l$ with a mass $m$ attached and undergoing simple harmonic motion of small amplitude $A$ i.e. small angle $\theta$. The equation of motion of the pendulum, for small $\theta$, is

$$mg\sin \theta = -F = -m\frac{d^2x}{dt^2} \Rightarrow \frac{d^2\theta}{dt^2} = -\frac{g}{l} \theta. \quad (47)$$

The solution of the above differential equation is

$$\theta = A \cos(2\pi\nu t + \alpha), \quad \text{where} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{g}{l}}. \quad (48)$$

The force acting on the mass $m$ when the pendulum makes an instanteneous angle $\theta$ is,

$$F = mg \cos \theta + \frac{mv^2}{l} \approx mg \left(1 - \frac{\theta^2}{2}\right) + ml\ddot{\theta}^2 \quad (49)$$

$$= mg \left[1 - \frac{A^2}{2} \cos^2(2\pi\nu t + \alpha)\right] + mlA^2(2\pi\nu)^2 \sin^2(2\pi\nu t + \alpha) \quad (50)$$

Clearly, the force $F$ is time-dependent and maximum when $\theta = 0$. Let us calculate the average force $\langle F \rangle$ over one complete time period of motion,

$$\langle F \rangle = \frac{1}{T} \int_0^T F \, dt = mg \frac{1}{T} \int_0^T dt - \frac{mgA^2}{2T} \int_0^T \cos^2(2\pi\nu t + \alpha) \, dt + \frac{mlA^24\pi^2\nu^2}{T} \int_0^T \sin^2(2\pi\nu t + \alpha) \, dt$$

$$= mg + \frac{1}{4} mgA^2. \quad (51)$$

The kinetic energy of the pendulum is,

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}ml^2\ddot{\theta}^2 = \frac{1}{2}ml^2A^24\pi^2\nu^2 \sin^2(2\pi\nu t + \alpha). \quad (52)$$

Therefore the total energy of the pendulum, using (48) is,

$$E = KE_{\text{max}} = \frac{1}{2}mlA^2 \times 4\pi^2\nu^2l = \frac{1}{2}mgA^2l. \quad (53)$$

The action $J = \oint p_\theta d\theta$ being,

$$J = ml^2 \oint \dot{\theta} d\theta = ml^2A^24\pi^2\nu^2 \int_0^T \sin^2(2\pi\nu t + \alpha) \, dt = ml^2A^24\pi^2\nu^2 \frac{T}{2} = \frac{E}{\nu}, \quad (54)$$

which is a constant.

Next consider an external agency to shorten length of the string slowly by pulling it smoothly – the string is shorten by $\Delta l$ over a time spanning many periods such that change of length over one period $\delta l$ satisfies $\delta l/l \ll 1$. Such a slow change in a parameter of the system is termed as *adiabatic* while the system itself is undergoing harmonic motion throughout the time. Work done by external agency over one period is

$$\delta W = \langle F \rangle \delta l = mg \delta l + \frac{1}{4} mgA^2 \delta l \quad (55)$$
where the first term is work done against gravity and second term is the increase in kinetic energy $\delta E$ as the mass goes up. Energy of the pendulum for fixed length is $E_{\text{max}} = mg^2A^2l/2$, therefore,

$$\frac{\delta E}{E} = \frac{1}{2} \frac{\delta l}{l}. \quad (56)$$

Shortening the length $l$ by $\delta l$ results in increase of frequency $\delta \nu$,

$$\delta \nu = \delta \left( \frac{1}{2\pi} \sqrt{\frac{g}{l}} \right) = -\frac{1}{2} \frac{\delta l}{l} \nu \implies \left| \frac{\delta \nu}{\nu} \right| = \frac{1}{2} \frac{\delta l}{l} \quad (57)$$

Putting the above two equations (56, 57) together we obtain,

$$\frac{\delta E}{E} = \frac{\delta \nu}{\nu}$$

which upon integration yield adiabatic invariant (an adiabatic invariant is a property of a physical system which stays constant when changes are made slowly)

$$\frac{E}{\nu} \approx \text{constant.} \quad (58)$$

The action for the system, where the angular momentum is given by $p_{\theta} = ml^2\dot{\theta}$, is

$$\oint p_{\theta} d\theta = \frac{E}{\nu} \quad (59)$$

The motion of the pendulum when its length changes slowly over time is not quite periodic over each cycle. However, the classical action remains approximately constant as long the change is very slow $\Rightarrow$ the classical action is an adiabatic invariant. Wilson and Sommerfeld formulated action quantization by equating the quantum number of a system with its classical adiabatic invariant.