Consider the Rydberg formula:

$$\nu = K\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where ν is the frequency of emitted radiation, $K = cR$, where R is the Rydberg constant and c is the speed of light, and $n_1 < n_2$ are quantum numbers corresponding to transitions for the emitted (or absorbed) radiation.

Show that in the limit of large quantum numbers, the frequency ν corresponds to classical theory.

Answer:

To show this, we must use the Principle of Correspondence.

Assume for simplicity the mass of the nucleus to be infinite in comparison to that of the electron.

As a classical central-force problem (due to the Coulomb attraction), the electron revolves classically with angular frequency ω around the nucleus:

$$\omega = \sqrt{\frac{2W^3}{\pi^2 e^4 m}}$$

where e is the charge of the electron, m is its mass, and W is the work required to remove the electron to infinity.

Multiplying both sides of the Rydberg formula by h yields an instance of the Bohr frequency condition:

$$\begin{aligned} h\nu &= hK\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \\ &= E_1 - E_2 \end{aligned}$$

This suggests that the energy of the n^{th} stationary state is:

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

Substituting E_n for W in the equation for the classical frequency gives:

$$\omega_n = \frac{1}{n^3}\sqrt{\frac{2h^3K^3}{\pi^2 e^4 m}}$$

where ω_n is the angular frequency of the n^{th} stationary state.

Note that this equation can be solved for K (sort of):

$$K = \omega_n n^3 \sqrt{\frac{\pi^2 e^4 m}{2h^3 K}}$$

The Rydberg formula can be rewritten:

$$\begin{aligned}\nu &= K\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\\ &= K\left(\frac{n_2^2 - n_1^2}{n_1^2 n_2^2}\right)\\ &= \tau K\left(\frac{n_2 + n_1}{n_1^2 n_2^2}\right)\end{aligned}$$

where $\tau = n_2 - n_1$.

If $n_1, n_2 \gg \tau$, then n_1 and n_2 can be equated to yield:

$$\begin{aligned}\left(\frac{n_2 + n_1}{n_1^2 n_2^2}\right) &= \frac{n + n}{n^4}\\ &= \frac{2}{n^3}\end{aligned}$$

And the equation for ν can be written:

$$\nu = \tau K \frac{2}{n^3}$$

Inserting the expression for K above:

$$\nu = \tau\omega 2\sqrt{\frac{\pi^2 e^4 m}{2h^3 K}}$$

where ω is now the orbital frequency of one or the other of the two states.
e, m, h, and K are all independently measurable physical constants. Denote a constant C that describes the corresponding term:

$$C = 2\sqrt{\frac{\pi^2 e^4 m}{2h^3 K}}$$

Note that it turns out that C is 1 within experimental error (though this does not affect the results below).

Considering the above, ν can be written:

$$\nu = \tau\omega$$

The last result shows that in the limit of large quantum numbers, where the difference $n_2 - n_1$ is small in comparison to n_1 and n_2, the frequency from the Rydberg formula can be written as a term corresponding to a classical Fourier series.