

ATOMIC STRUCTURE

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ENERGY LEVELS AND SPECTRA

The various permitted orbits involve different electron energies.

$$E = -\frac{e^2}{8\pi\epsilon_0 r}$$

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n}$$

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

$$E_n = -\frac{m e^4}{8 \epsilon_0^2 h^2} \left(\frac{1}{n^2} \right) = \frac{E_1}{n^2}, n = 1, 2, 3, \dots$$

$$E_1 = -2.18 \times 10^{-18} \text{ J} = -13.6 \text{ eV}$$

This equation specifies the energy levels of the H atom.

→ They are negative.

→ They are discrete.

→ Other energies are not allowed.

E_1 is called the **ground state**.

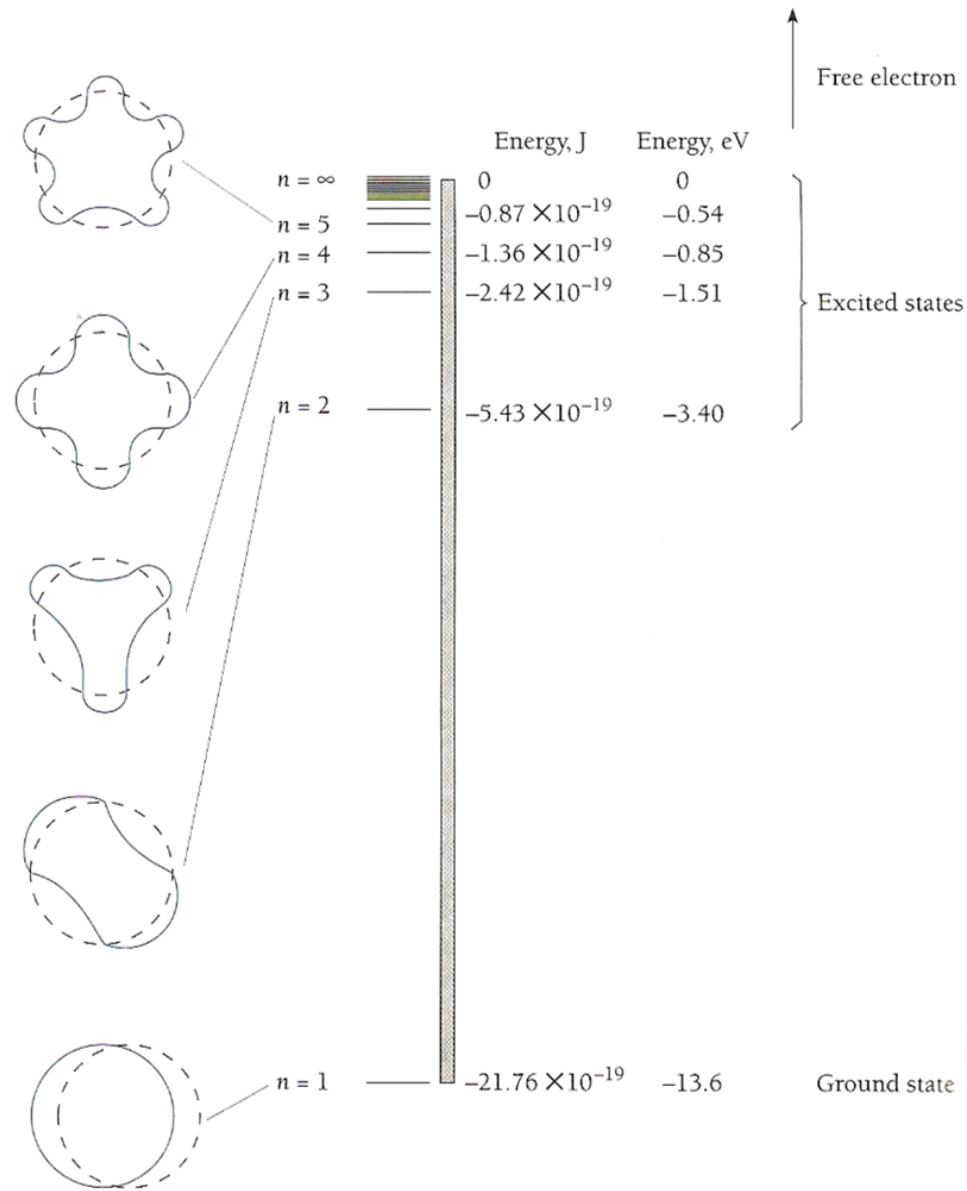
E_2 , E_3 , E_4 , ... are called **excited states**.

$E_\infty = 0$ ← electron is not bound to the nucleus.

E_1 is the **ionization energy**.

$E = +ve$ ← free electron & has no quantum condition to fulfill.

ENERGY LEVELS AND SPECTRA



ENERGY LEVELS AND SPECTRA

What is the origin of line spectra and do they follow from Bohr's model?

If the quantum number of the initial (higher-energy) state is n_i and the quantum number of the final (lower-energy) state is n_f , then:

initial energy - final energy = emitted photon energy

$$E_i - E_f = h\nu$$

$$E_i - E_f = E_I \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = -E_I \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\nu = \frac{E_i - E_f}{h} = -\frac{E_I}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The
Hydrogen
spectrum

ENERGY LEVELS AND SPECTRA

$$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Series		wavelength	
Lyman	$n_f = 1$	$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{1^2} - \frac{1}{n_i^2} \right)$	$n = 2, 3, 4, \dots$
Balmer	$n_f = 2$	$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right)$	$n = 3, 4, 5, \dots$
Paschen	$n_f = 3$	$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{3^2} - \frac{1}{n_i^2} \right)$	$n = 4, 5, 6, \dots$
Brackett	$n_f = 4$	$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{4^2} - \frac{1}{n_i^2} \right)$	$n = 5, 6, 7, \dots$
Pfund	$n_f = 5$	$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{5^2} - \frac{1}{n_i^2} \right)$	$n = 6, 7, 8, \dots$

ENERGY LEVELS AND SPECTRA

Can Bohr's model predict the Rydberg constant?

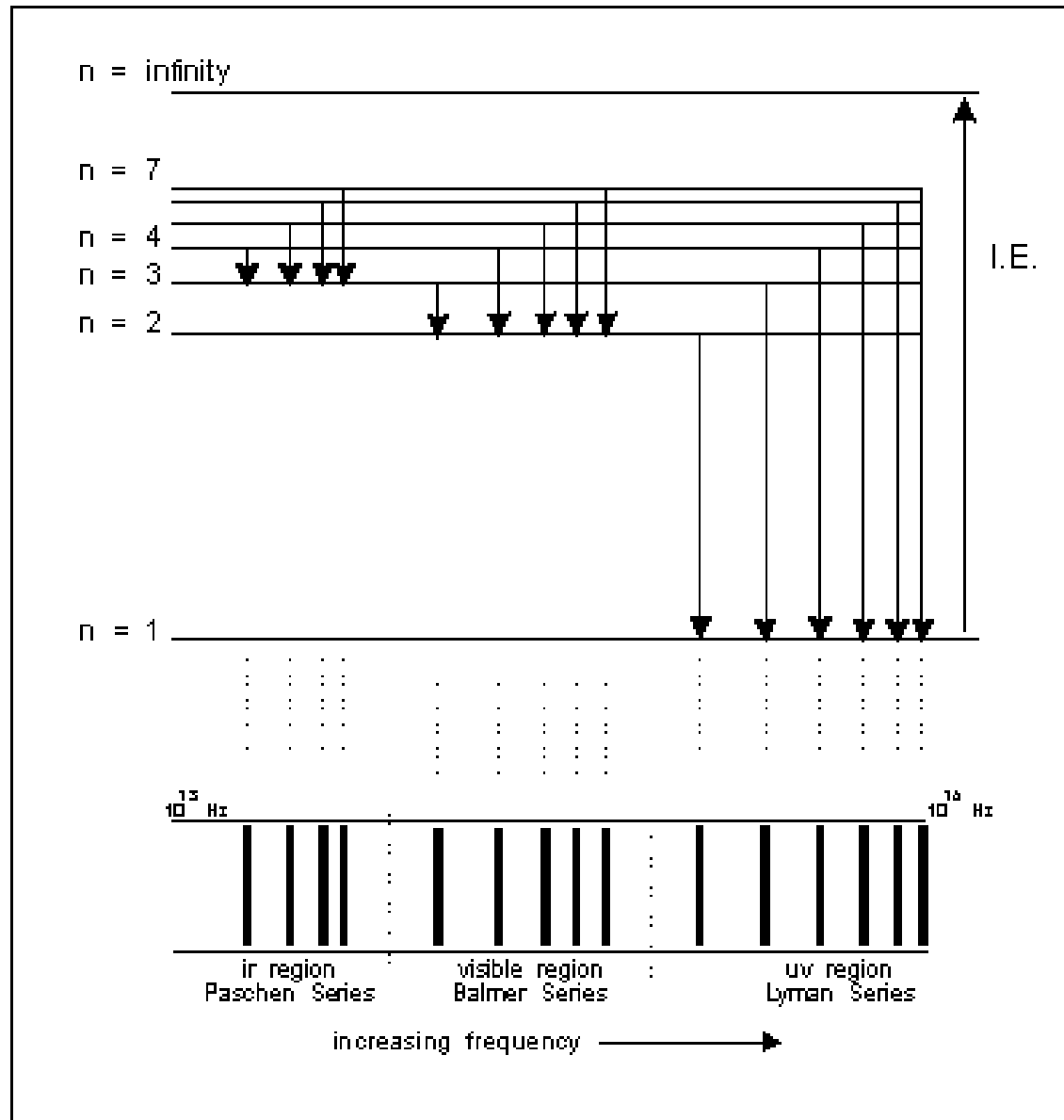
$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \dots$$

$$R = 1.097 \times 10^7 \text{ m}^{-1}$$

$$\frac{1}{\lambda} = -\frac{E_I}{ch} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$-\frac{E_I}{ch} = \frac{me^4}{8\epsilon_0^2 ch^3} = 1.097 \times 10^7 \text{ m}^{-1}$$

ENERGY LEVELS AND SPECTRA



ENERGY LEVELS AND SPECTRA

Remember...

A photon is emitted when an electron jumps from one energy level to a lower level.

CORRESPONDENCE PRINCIPLE

Quantum physics in the microworld must give the same results as classical physics in the macroworld.

How this is applied to the Bohr's model of the H model?

- According to EM theory, an electron moving in a circular orbit radiates EM waves.
- The frequencies of these radiation are equal to its frequency of revolution and to its harmonics.
- The electron speed in a H atom is:
- The frequency of revolution f of the electron:

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$$

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

$$f = \frac{\text{electron speed}}{\text{orbit circumference}} = \frac{v}{2\pi r} = \frac{e}{2\pi \sqrt{4\pi\epsilon_0 mr^3}}$$

$$f = \frac{me^4}{8\epsilon_0^2 h^3} \left(\frac{2}{n^3} \right) = -\frac{E_I}{h} \left(\frac{2}{n^3} \right)$$

CORRESPONDENCE PRINCIPLE

Under what circumstances should the Bohr atom behave classically?

• When the electron orbit is so large we might be able to measure it directly. We have:

$$\nu = -\frac{E_I}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Let $n_i \rightarrow n$ & $n_f \rightarrow n - p$ (where $p = 1, 2, 3, \dots$)

$$\nu = -\frac{E_I}{h} \left[\frac{1}{(n-p)^2} - \frac{1}{n^2} \right] = -\frac{E_I}{h} \left[\frac{2np - p^2}{n^2(n-p)^2} \right]$$

When both n_i & n_f are very large then $n \gg p$

$$\begin{aligned} 2np - p^2 &\approx 2np \\ (n-p)^2 &\approx n^2 \end{aligned}$$

$$\nu = -\frac{E_I}{h} \left(\frac{2p}{n^3} \right)$$

$$f = -\frac{E_I}{h} \left(\frac{2}{n^3} \right)$$

CORRESPONDENCE PRINCIPLE

Under what circumstances should the Bohr atom behave classically?

- The requirement that quantum physics give the same results as classical physics in the limit of large quantum number was called by Bohr the **correspondence principle**.
- Bohr used the correspondence principle in reverse to look for the condition for orbit stability.
- A stable orbit must have orbital angular momenta of:

$$mvr = \frac{nh}{2\pi}, \quad n = 1, 2, 3, \dots$$

$$n\lambda = 2\pi r$$

CORRESPONDENCE PRINCIPLE

Remember...

The greater the quantum number, the closer quantum physics approaches classical physics.