Quantum Physics PY1T20/PYU11P20

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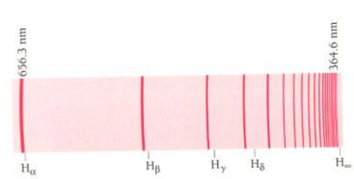
Lecture 7: The hydrogen atom

Structure of the (hydrogen) atom:

- planetary model
- energy and orbit radius
- "Bohr" model
- allowed energy levels
- line spectra formula
- correspondence principle



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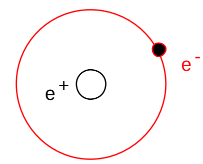
Structure of the (hydrogen) atom

Rutherford: small, massive +ve nucleus, surrounded by -ve electrons at (relatively) large distance….

Planetary model of hydrogen:
electron (e^-) orbiting proton (e^+)
with speed v, at radius r



Electrical force: $$F_e = \frac{e^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$$ *(mass × centr. accel)*

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

As r decreases, v increases

The hydrogen atom (continued)

Electron energy $E = KE + PE$

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

KE (non-relativistic) = $m\mathrm{v}^2/2$

$$KE = \frac{m}{2}\left(\frac{e}{\sqrt{4\pi\varepsilon_o m r}}\right)^2 = \frac{e^2}{8\pi\varepsilon_o r}$$

PE (electric) = qV *(V: potential due to proton)*

$$PE = (-e)\left(\frac{e}{4\pi\varepsilon_o r}\right) = -\frac{e^2}{4\pi\varepsilon_o r}$$

$$E = KE + PE = \frac{e^2}{8\pi\varepsilon_o r} - \frac{e^2}{4\pi\varepsilon_o r} = -\frac{e^2}{8\pi\varepsilon_o r}$$

The Bohr (deBroglie) hydrogen atom

Classically, any radius possible, therefore any energy possible!

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

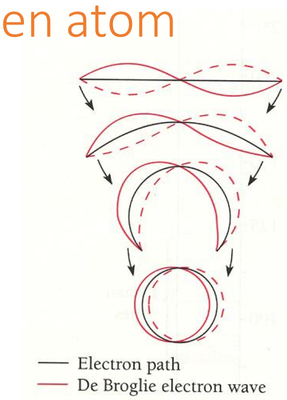
Fact 1: energy required to remove electron from hydrogen (eg. by photoelectric effect) is always the same E = 13.6 eV (corresponds to special radius = 5.3×10^{-11} m)

Fact 2: EM Theory requires an *accelerating* charge to radiate (emit EM waves, lose energy, causing orbit to collapse!)

...should be looking for special orbits which do not radiate?
(radiation to be associated with "transitions" between orbits)

The Bohr (deBroglie) hydrogen atom

Suggestion: "An electron can circle a nucleus without losing energy if its orbit contains an integral number of de Broglie wavelengths"



Test?

$$\mathrm{v} = \frac{e}{\sqrt{4\pi\varepsilon_o m r}} \quad \textit{and} \quad \lambda = h/m\mathrm{v}$$

$$\lambda = h/e\sqrt{\frac{4\pi\varepsilon_o r}{m}} \quad \textit{substitute} \quad r = 5.3\times 10^{-11}\ \mathrm{m}$$

$$\lambda = 33\ x10^{-11}\ \mathrm{m} \quad = 2\pi(5.3\times 10^{-11}\ \mathrm{m}) = 2\pi r$$

In general, $\boxed{n\lambda = 2\pi r_n}$ n=1,2,3….. *See patterns in text*

Allowed Values of Radius

$$n\lambda = n\,{}^{h}\!/_{e}\sqrt{\frac{4\pi\varepsilon_o r_n}{m}} = 2\pi r_n$$

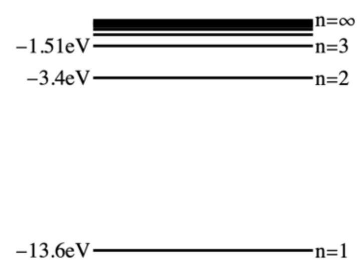
$$r_n = \frac{n^2 h^2 \varepsilon_o}{\pi m e^2} = n^2 a_o$$

Allowed <u>radii</u> proportional to n^2

Bohr radius (a_o) - *unfortunate label?* Corresponds to n=1

Exercise: insert values of constants, show $a_o = 5.292 \times 10^{-11}$ m

Allowed Values of Energy



Allowed <u>radii</u> implies allowed <u>energies</u>

$$E_n = -\frac{e^2}{8\pi\varepsilon_o r_n} = -\frac{e^2}{8\pi\varepsilon_o\left(\dfrac{n^2 h^2 \varepsilon_o}{\pi m e^2}\right)}$$

$$E_n = -\frac{me^4}{8\varepsilon_o^2 h^2}\left({}^{1}\!/_{n^2}\right) = -2.18\,x10^{-18}\left({}^{1}\!/_{n^2}\right)J = -13.6\left({}^{1}\!/_{n^2}\right)eV$$

$$E_n = E_1\left({}^{1}\!/_{n^2}\right) \quad where \quad E_1 = -13.6\ eV$$

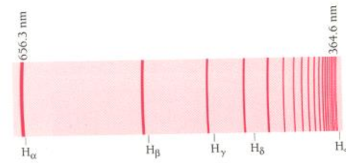
Energy is proportional to $1/n^2$ - *compare particle in box?*

In this case energy is <u>negative</u>, -ve sign is included in E_1

Experimental Evidence for Bohr model

From optical emission spectrum of hydrogen:
Consists of line spectra

Balmer series; <u>fitted</u> to formula



$$1/\lambda = R\left(1/2^2 - 1/n^2\right) \quad for\ \ n = 3, 4, 5 \ldots.$$

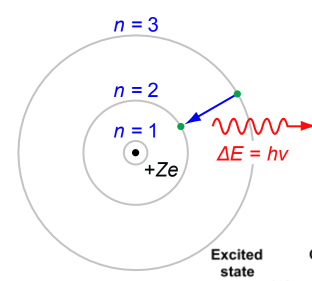
Experimental value of $R = 1.097 \times 10^7\ \mathrm{m}^{-1}$
In general, use two integers n_i (initial) and n_f (final)

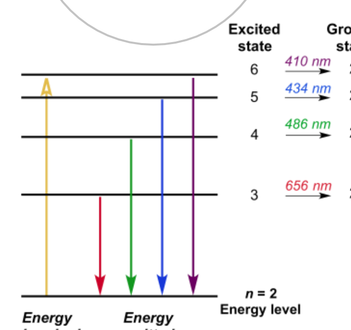
$$1/\lambda = R\left(1/n_f^2 - 1/n_i^2\right) \quad for\ \ n_i > n_f$$

Where $n_f = 1$ (Lyman), $= 2$ (Balmer), $= 3$ (Paschen) etc

Connect expt. with Bohr model

$$1/\lambda = R\left(1/n_f^2 - 1/n_i^2\right) \qquad E_n = -\frac{me^4}{8\varepsilon_o^2 h^2}\left(1/n^2\right)$$





optical emission: result of a "down transition" of electron from a higher energy orbit (n_i) to a lower energy orbit (n_f)
Energy difference is emitted as a photon:

$$\hbar\omega = E_{n_i} - E_{n_f} = -\frac{me^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \frac{me^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad \Rightarrow \quad R = \frac{me^4}{8\varepsilon_0^2 h^3 c}$$

Centre-of-mass correction

$$R = \frac{me^4}{8\varepsilon_o^2 h^3 c} = 1.097\ x10^7\ \mathrm{m}^{-1}$$

This value of R agreed with expt. of the time!
However, later (more accurate) experiments gave $R_{expt} = 1.0967785$
whereas model gave $R = 1.0973731$

Replace m with $m^* = mM/(m + M) = 0.99945(m)$
In centre-of-mass description of electron (m) and proton (M)

Correspondence Principle

"The greater the quantum number…….
the closer Quantum Physics approaches Classical Physics!"

Correspondence Principle

Compare orbit frequency (f) and emitted photon frequency ($\omega/2\pi$)

$$f = \frac{\mathrm{v}}{2\pi r} = \frac{e}{2\pi\sqrt{4\pi\varepsilon_o mr^3}} = \frac{me^4}{8\varepsilon_o^2 h^3}\left(\frac{2}{n^3}\right)$$

$$\omega/2\pi = E/h\ \frac{me^4}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Note same pre-factor! Write $n_i = n$ and $n_f = n - p$

$$\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = \left(\frac{1}{(n-p)^2} - \frac{1}{n^2}\right) = \left(\frac{2np - p^2}{n^2(n-p)^2}\right) \approx \left(\frac{2p}{n^3}\right)$$

When $n >> p$, $(2np - p^2) \sim 2np$ and $(n - p)^2 \sim n^2$
then $\omega/2\pi \sim pf$ and letting p=1, a transition: n to $(n$-1) gives $\omega/2\pi \sim f$

Bohr criterion for allowed orbits

The Bohr requirement for orbits can also be stated as:

"angular momentum is quantised in units of ħ"

$$mvr = n\left(\frac{h}{2\pi}\right) = n\hbar$$

$$\Rightarrow 2\pi r = n\left(\frac{h}{mv}\right) = n\lambda$$

i.e. this condition is equivalent to "fitting de Broglie wavelengths"

In fact, the concept of quantised angular momentum $n\hbar$ is the fuller and broader criterion, with further consequences to be seen; the other is merely illustrative, not factual.
Complete description of atom requires at least three different quantum numbers (see later lectures)

Bohr model: rights and wrongs

- The Bohr model gives the correct energy levels for the hydrogen atom, if one includes only the Coulomb potential.
- It does not correctly give the degeneracies of these levels.
- In a real atom there are corrections to the Coulomb force : 'spin-orbit coupling', 'hyperfine coupling', which slightly change the energy levels.
- The Bohr model also makes some conceptual errors:
    - It suggests the electron has a well-defined orbit in the atom. It doesn't – uncertainty principle!
    - It suggests the ground-state has angular momentum (n=1). It doesn't – the electron in the ground state is not 'orbiting' around the nucleus at all.
- Nonetheless it provides an impressively good account of the basic physics.