

Quantum Mechanics . Module - 2

The Emergence of quantum Mechanics

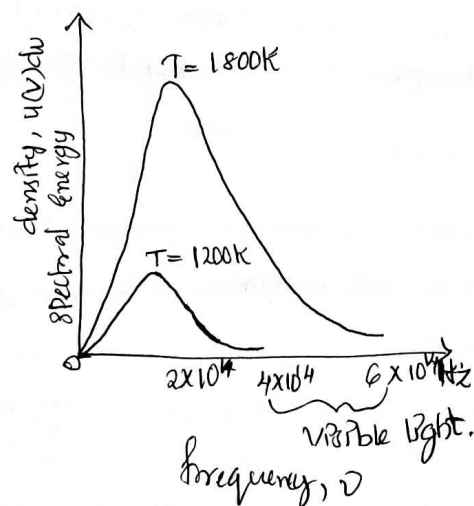
Black body radiation, - photoelectric effect - The Compton effect
- wave properties of matter and electron diffraction - The Bohr atom - The Rutherford Planetary model - The Bohr Postulates - The correspondence principle.

✓ Black body radiation

An ideal body one that absorbs all radiations incident upon it, regardless of frequency. Such a body is called a blackbody. A black body can be approximated by a hollow object with a very small hole leading to its interior. Any radiation striking the hole enters the cavity, where it is trapped by reflection back and forth until it is absorbed. The cavity walls are constantly emitting and absorbing radiation. A blackbody radiates more when it is hot than when it is cold, and the spectrum of a hot blackbody has its peak at a higher frequency than the peak in the spectrum of a cooler one.

The Ultraviolet Catastrophe

Lord Rayleigh and James Jeans started by considering the radiation inside a cavity of absolute temp. T whose walls are perfect reflectors to be a series of standing em waves. This is 3D generalization of standing waves in a stretched string.



The condition for standing waves in such a cavity is that the path length from wall to wall, whatever the direction, must be a whole number of half-wavelengths, so that a node occurs at ~~the~~ each reflecting surface. The no. of independent standing waves $G(\nu) d\nu$ in the frequency interval ν and $d\nu$ per unit volume in the cavity turned out to be,

$$G(\nu) d\nu = \frac{8\pi^2 \nu^2 d\nu}{c^3}$$

According to the theorem of equipartition of energy, a mainstay of classical physics, the average energy per degree of freedom of an entity that is a member of a system of such entities in thermal equilibrium at the temp. T is $\frac{1}{2}kT$, where k is Boltzmann's constant, $k = 1.381 \times 10^{-23} \text{ J/K}$.

A 1D harmonic oscillator has two degree of freedom, one that corresponds to its kinetic energy & one that corresponds to its potential energy. Because each standing wave in a cavity originates in an oscillating electric charge in the cavity wall, two degrees of freedom are associated with the wave and it should have an avg energy of $2(\frac{1}{2})kT$.

$$\bar{\epsilon} = kT$$

Rayleigh-Jeans formula,

$$u(\nu) d\nu = \bar{\epsilon} G(\nu) d\nu = \frac{8\pi kT}{c^3} \nu^2 d\nu$$

As the frequency ν increases towards the ultraviolet end of the spectrum, this formula predicts that the energy should increase as ν^2 . In the limit of infinitely high frequencies, $u(\nu) d\nu$ therefore should also go to infinity. In reality, of course, the energy density falls to 0 as $\nu \rightarrow \infty$. This discrepancy became known as the ultraviolet catastrophe of classical physics.

Planck radiation formula

In 1900 the German physicist Max ~~Planck~~ Planck used "lucky guesswork" to come up with a formula for the spectral energy density of blackbody radiation:

$$\text{Planck's radiation formula, } u(\nu) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/kT}}$$

Here h is a const. whose value is Planck's const.

$$h = 6.626 \times 10^{-34} \text{ J.s}$$

At high frequencies, $h\nu \gg kT$ and $e^{h\nu/kT} \rightarrow \infty$, which means that $u(\nu) d\nu \rightarrow 0$ as observed. No more ultraviolet catastrophe. At low frequencies, where the Rayleigh-Jeans formula is a good approximation to the data, $h\nu \ll kT$ and $h\nu/kT \ll 1$. In general,

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

If x is small, $e^x \approx 1 + x$, and so for $h\nu/kT \ll 1$ we have

$$\frac{1}{e^{h\nu/kT} - 1} \approx \frac{1}{1 + \frac{h\nu}{kT} - 1} \approx \frac{kT}{h\nu} \quad h\nu \ll kT$$

Thus at low frequencies Planck's formula becomes

$$u(\nu) d\nu \approx \frac{8\pi h}{c^3} \nu^3 \left(\frac{kT}{h\nu} \right) d\nu \approx \frac{8\pi kT}{c^3} \nu^2 d\nu$$

which is the Rayleigh-Jeans formula.

Photoelectric effect

The energy of e^- liberated by light depend on the frequency of the light.

During his exp. on em waves, Hertz noticed that sparks occurred more readily in the air gap of his transmitter when ultraviolet light was directed at one of the metal balls. He did not follow up this observations, but others did. They soon discovered that the cause was electrons emitted when the frequency of the light was sufficiently high. This phenomenon is known as photoelectric effect. And the emitted e^- are called photoelectrons.

- (1) within the limits of experimental accuracy (about 10^{-9} s), there is no time interval b/w the arrival of light at a metal surface and the emission of photoelectrons. However, because the energy in an em wave is supposed to be spread across the wave fronts, a period of time should elapse before an individual electron accumulates enough energy to leave the metal. A detectable photoelectron current results ~~on~~ when 10^{-6} W/m² of em energy is absorbed by a sodium surface. A layer of sodium 1 atom thick and 1 m² in area contains about 10^{19} atoms, so if the incident light is absorbed in the uppermost atomic layer, each atom receives energy at an avg rate of 10^{-25} W.

At this rate over a month would be needed for an atom to accumulate energy of the magnitude that photoelectrons from a sodium surface are observed to have.

(2) A bright light yields more photoelectrons than a dim one of the same frequency, but the e^- energies remain the same. The em theory of light, on the contrary, predicts that the more intense the light, the greater the energies of the e^- .

(3) The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light. At frequencies below a certain critical frequency ν_0 , which is characteristic of each particular metal, no electrons are ~~not~~ emitted. Above ν_0 the photoelectrons range in energy from 0 to a max. value that increases linearly with increasing frequency. This observation also, cannot be explained by the em theory of light.

Quantum theory of light

There must be a minimum energy ϕ for an e^- to escape from a particular metal surface or else electrons would pour out all the time. This energy is called the work function of the metal, & is related to ν_0 by the formula,

$$\phi = h\nu_0$$

The greater the work fn of the metal, the more energy is needed for an e^- to leave its surface & the higher the critical frequency for photoelectric emission to ~~occur~~ occur.

According to Einstein, the photoelectric effect in a given metal should obey the equation,

$$\text{photoelectric effect, } h\nu = KE_{\max} + \phi$$

where $h\nu \rightarrow$ ~~photoelectric~~ photon energy.

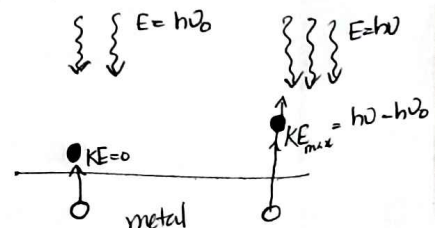
$KE_{\max} \rightarrow$ photoelectron energy proportional to the stopping potential.

$\phi \rightarrow$ min. energy needed for an e^- to leave the metal.

Because, $\phi = h\nu_0$

$$\text{then, } h\nu = KE_{\max} + h\nu_0$$

$$KE_{\max} = h\nu - h\nu_0 = h(\nu - \nu_0)$$



Imp 4 marks / 15/2

COMPTON EFFECT

Such a collision: an x-ray photon strikes an e^- and is scattered away from its original direction of motion while the electron receives an impulse and begins to move. We can think of the photon as losing an amount of energy in the collision that is the same as the KE gained by the e^- , although actually separate photons are involved. If the initial photon has the frequency ν associated with it, the scattered photon has the lower frequency ν' , where

loss in photon energy = gain in e^- energy.

$$h\nu - h\nu' = KE$$

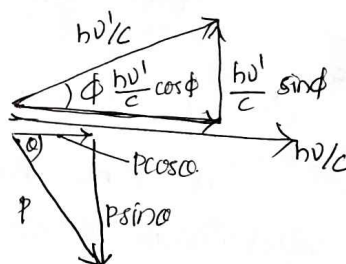
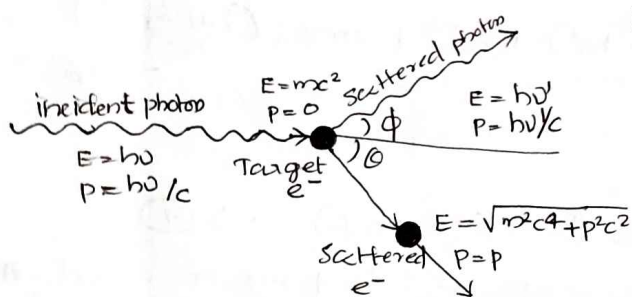
Momentum of a massless particle is related to its energy by the formula,

$$E = pc$$

Since the energy of a photon is $h\nu$, its momentum is,

photon momentum,

$$p = \frac{E}{c} = \frac{h\nu}{c}$$



The initial photon momentum is $h\nu/c$, the scattered photon momentum is $h\nu'/c$, and the initial & final e^- momenta are respectively 0 and p . In the original photon direction,

Initial momentum = final momentum

$$\frac{h\nu}{c} + 0 = \frac{h\nu'}{c} \cos \phi + p \cos \theta \quad \text{--- (1)}$$

are \perp to this direction,

Initial momentum = final momentum

$$0 = \frac{h\nu'}{c} \sin \phi - p \sin \theta \quad \text{--- (2)}$$

The angle ϕ is that b/w the directions of the initial and scattered photons, and θ is that b/w the directions of the initial photon and the recoil e^- . (1) & (2) are related the wavelength

difference b/w initial and scattered photons with the angle ϕ between their directions, both of which are readily measurable quantities.

Using (1) & (2) by C,

$$pc \cos \phi = h\nu - h\nu' \cos \phi$$

$$pc \sin \phi = h\nu' \sin \phi$$

By squaring each of these eqns & adding the new ones together, the angle ϕ is eliminated leaving,

$$p^2 c^2 = (h\nu)^2 - 2(h\nu)(h\nu') \cos \phi + (h\nu')^2 \rightarrow (3)$$

equating the 2 expressions for the total energy of the particle,

$$E = KE + mc^2 \rightarrow (4)$$

$$E = \sqrt{m^2 c^4 + p^2 c^2} \rightarrow (5)$$

we have,

$$(KE + mc^2)^2 = m^2 c^4 + p^2 c^2$$

$$p^2 c^2 = KE^2 + 2mc^2 KE$$

since,

$$KE = h\nu - h\nu'$$

we have,

$$p^2 c^2 = (h\nu)^2 - 2(h\nu)(h\nu') + (h\nu')^2 + 2mc^2 (h\nu - h\nu') \rightarrow (6)$$

Sub. \downarrow $p^2 c^2$
value of

$$2mc^2 (h\nu - h\nu') = 2(h\nu)(h\nu') (1 - \cos \phi) \rightarrow (7)$$

The relationship is simpler when expressed in terms of wavelength λ , dividing by $2h^2 c^2$,

$$\frac{mc}{h} \left(\frac{\nu}{c} - \frac{\nu'}{c} \right) = \frac{\nu}{c} \frac{\nu'}{c} (1 - \cos \phi)$$

and so, since $\nu/c = 1/\lambda$ & $\nu'/c = 1/\lambda'$

$$\frac{mc}{h} \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right) = \frac{1 - \cos \phi}{\lambda \lambda'}$$

Compton effect, $\boxed{\lambda' - \lambda = \frac{h}{mc} (1 - \cos \phi)} \rightarrow (8)$

eqn (8) gives the change in wavelength expected for a photon that is scattered through the angle ϕ by a particle of rest mass m . This change is independent of the wavelength λ of the incident photon. The quantity, Compton wavelength, $\lambda_c = h/mc \rightarrow (9)$

is called the Compton wavelength of the scattering particle. For an e^-
 $\lambda_c = 2.426 \times 10^{-12} \text{ m}$, which is 2.426 pm ($1 \text{ pm} = 10^{-12} \text{ m}$). In terms
of λ_c ; eqn (8) becomes,

$$\lambda' - \lambda = \lambda_c (1 - \cos \phi)$$

The Compton effect is the chief means by which x-rays lose energy when they pass through matter.

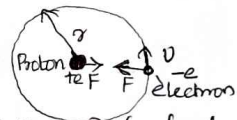
Electron orbits

The planetary models of the atom and why it fails

The Rutherford model of the atom, so convincingly confirmed by experiment, pictures a tiny, massive, +vely charged nucleus surrounded at a relatively great distance by enough electrons to render the atom electrically neutral as a whole. The e^- s cannot be stationary in this model, because there is nothing that can keep them in place against the electric force pulling them to the nucleus. If the e^- s are in motion, however, dynamically stable orbits like those of the planets around the sun are possible.

Let us look at the classical dynamics of the hydrogen atom, whose single electron makes it the simplest of all atoms. We assume a circular e^- orbit for convenience, though it might as reasonably be assumed to be elliptical in shape. The centripetal force,

$$F_c = \frac{mv^2}{r}$$



holding the e^- in an orbit 'r' from the nucleus is provided by the electric force,

$$F_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$$

between them. The condition for a dynamically stable orbit is

$$F_c = F_e$$

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$$

the e^- velocity v is therefore related to its orbit's radius r by the formula,

$$\text{Electron velocity, } v = \frac{e}{\sqrt{4\pi\epsilon_0 m r}}$$

The total energy E of the e^- in a hydrogen atom is the sum of its kinetic and PEs, which are,

$$KE = \frac{1}{2}mv^2, \quad PE = \frac{-e^2}{4\pi\epsilon_0 r}$$

Hence,

$$E = KE + PE = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0 r}$$

Sub. for v from eqn. (V)

$$E = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r}$$

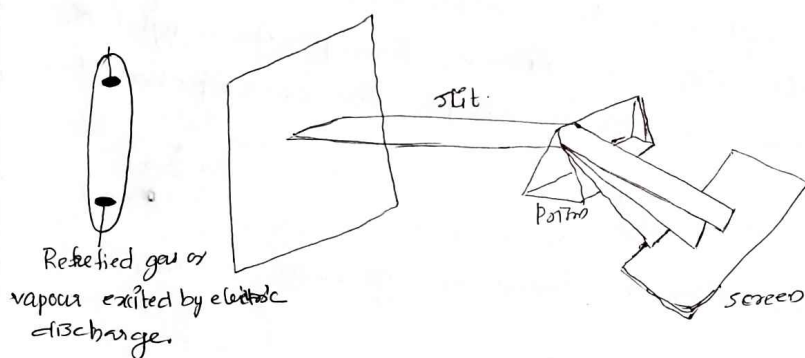
total energy of hydrogen atom,

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

The total energy of the e^- is negative. This holds for every atomic e^- and reflects the fact that it is bound to the nucleus. If E were greater than zero, an e^- would not follow a closed orbit around the nucleus.

Atomic Spectra.

When an atomic gas or vapour at somewhat less than atm pressure is suitably 'excited', usually by passing an electric current through it, the emitted radiation has a spectrum which contains certain specific wavelengths only. An idealized arrangement for observing such atomic spectra.

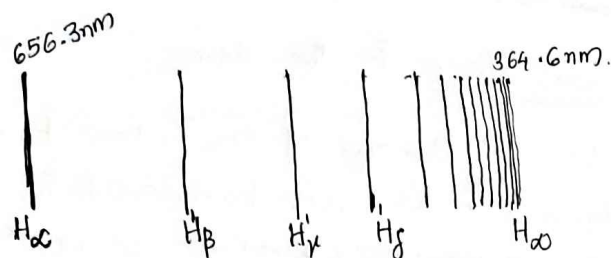


Actual spectrometers use diffraction grating. Every element displays a unique line spectrum when a sample of it in the vapor phase is excited. Spectroscopy is therefore a useful tool for analysing the composition of an unknown substance.

When white light is passed through a gas, the gas is found to absorb light of certain of the wavelengths present in its emission spectrum. The resulting absorption line spectrum consists of a bright background crossed by dark lines that correspond to the missing wavelengths; emission spectra consists of bright lines on a dark background. The spectrum of sunlight has dark lines in it because the luminous part of the sun, which radiates very nearly like a blackbody heated to 5500K, is surrounded by an envelop of cooler gas that absorb certain wavelengths only. Most other stars have spectra of this kind.

Spectral series

A century ago the wavelengths in the spectrum of an element were found to fall into sets called spectral series. The 1st such series was discovered by J.J. Balmer in 1885 in the course of a study of the visible part of the hydrogen spectrum.



The line with the longest wavelength, 656.3 nm, is designated H_α , the next, whose wavelength is 486.3 nm, is designated H_β and so on. As the wavelength decreases, the lines are found closer together and weaker in intensity until the series limit at 364.6 nm is reached, beyond which there are no further separate lines but only a faint continuous spectrum. Balmer's formula for the wavelength of this series is,

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

The quantity R , known as the Rydberg constant, has the value

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

The H_α line corresponds to $n=3$, the H_β line to $n=4$, and so on. The series limit corresponds to $n=\infty$, so that it occurs at a wavelength of $4/R$, in agreement with experiment.

The Balmer series contains wavelengths in the visible portion of the hydrogen spectrum. The spectral lines of hydrogen in the ultraviolet and infrared regions fall into several other series. In the ultraviolet the Lyman series contains the wavelengths given by the formula.

$$\text{Lyman} \quad \frac{1}{\lambda} = R \left[\frac{1}{1^2} - \frac{1}{n^2} \right] \quad n = 2, 3, 4, \dots$$

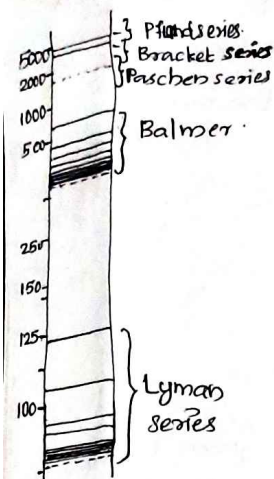
In the infrared, 3 spectral series have been found whose lines have the wavelength specified by formulas,

$$\text{Paschen} \quad \frac{1}{\lambda} = R \left[\frac{1}{3^2} - \frac{1}{n^2} \right] \quad n = 4, 5, 6, \dots$$

$$\text{Brackett} \quad \frac{1}{\lambda} = R \left[\frac{1}{4^2} - \frac{1}{n^2} \right] \quad n = 5, 6, 7, \dots$$

$$\text{Pfund } \frac{1}{\lambda} = R \left(\frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, \dots$$

These spectral series of hydrogen are plotted in terms of wavelength. Bracket series evidently overlap the Paschen & Pfund series. The value of R is the same in all eqn.



The Bohr Atom

Electron waves in the atom

The 1st theory of the atom to meet with any success was put forward in 1913 by Niels Bohr. The concept of matter waves leads in a natural way to this theory, as de Broglie found,

and this is the route that will be followed here. Bohr himself used a different approach, since de Broglie's work came a decade later, which makes his achievement all the more remarkable. The results are exactly the same, however.

We start by examining the wave behaviour of an electron in orbit around a hydrogen nucleus. The de Broglie wavelength of this e^- is,

$$\lambda = h/mv$$

where the e^- velocity v is that given by,

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

Hence

orbital e^-
wavelength,

$$\lambda = \frac{h}{e} \sqrt{\frac{4\pi\epsilon_0 r}{m}}$$

By substituting $5.3 \times 10^{-11} \text{ m}$ for the radius r of the e^- orbit, we find the e^- wavelength to be,

$$\lambda = \frac{6.63 \times 10^{-34} \text{ J.s}}{1.6 \times 10^{-19} \text{ C}} \times \sqrt{\frac{(4\pi)(8.85 \times 10^{-12} \text{ C}^2/\text{N.m}^2)(5.3 \times 10^{-11} \text{ m})}{9.1 \times 10^{-31} \text{ kg}}}$$

$$\lambda = 33 \times 10^{-11} \text{ m}$$

This wavelength is exactly the same as the circumference of the e^- orbit.

$$2\pi r = 33 \times 10^{-11} \text{ m}$$

The orbit of the e^- in a hydrogen atom corresponds to one complete e^- wave joined on itself.

Quantization in the atomic world.

If the quantum no. of the initial (higher energy) state is n_i and the quantum number of the final (lower-energy) state is n_f , we are asserting that,

$$\text{Initial energy} - \text{final energy} = \text{photon energy.}$$

$$E_i - E_f = h\nu$$

where ' ν ' is the frequency of the emitted photon, we have

$$E_i - E_f = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = -E_1 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

We recall that E_1 is the negative quantity (-13.6 eV , in fact), so $-E_1$ is a true quantity. The frequency of the photon released in this transition is therefore

$$\nu = \frac{E_i - E_f}{h} = -\frac{E_1}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Since $\lambda = c/\nu$, $1/\lambda = \nu/c$ and

Hydrogen spectrum,
$$1/\lambda = -\frac{E_1}{ch} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Eqn states that the radiation emitted by excited hydrogen atoms should contain certain wavelengths only. These wavelengths, furthermore, fall into definite sequences that depend upon the quantum number n_f of the final energy level of the electron. Since $n_i > n_f$ in each case, in order that there be an excess of energy to be given off as a photon, the calculated formulas for the first 5 series are,

Lyman $n_f = 1$; $1/\lambda = -\frac{E_1}{ch} \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$ $n = 2, 3, 4, \dots$

Balmer $n_f = 2$; $1/\lambda = -\frac{E_1}{ch} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$ $n = 3, 4, 5, \dots$

Paschen $n_f = 3$; $1/\lambda = -\frac{E_1}{ch} \left(\frac{1}{3^2} - \frac{1}{n^2} \right)$ $n = 4, 5, 6, \dots$

Brackett $n_f = 4$; $1/\lambda = -\frac{E_1}{ch} \left(\frac{1}{4^2} - \frac{1}{n^2} \right)$ $n = 5, 6, 7, \dots$

Pfund $n_f = 5$; $1/\lambda = -\frac{E_1}{ch} \left(\frac{1}{5^2} - \frac{1}{n^2} \right)$ $n = 6, 7, 8, \dots$

These sequences are identical in form with the empirical spectral series discussed earlier. The Lyman series corresponds to $n_f = 1$; the Balmer series corresponds to $n_f = 2$; the Paschen series corresponds to $n_f = 3$; the Brackett series corresponds to $n_f = 4$; and the Pfund series corresponds to $n_f = 5$.

Correspondence Principle

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

Quantum physics, so different from classical physics in the microworld beyond reach of our senses, must nevertheless give the same result as classical physics in the macroworld where experiments show that the latter is valid. We have already seen that this basic requirement is true for the wave theory of moving bodies. We shall now find that it is also true for Bohr's model of the hydrogen atom.

According to electromagnetic theory, an e^- moving in a circular orbit radiates em waves whose frequencies are equal to its frequency of revolution and to harmonics of the frequency. In a hydrogen atom the electron's speed is,

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 m r}} \quad r - \text{radius of the orbit.}$$

frequency of revolution f' of the e^- is,

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

The radius r_n of a stable orbit is given by in terms of its quantum number 'n' by,

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

and so the frequency of revolution is,

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