THE OLD QUANTUM THEORY (OF RADIATION)

(1) Thomson's and Rutherford's experiments and their thoughts about pudding, potatoes, planets - and atoms

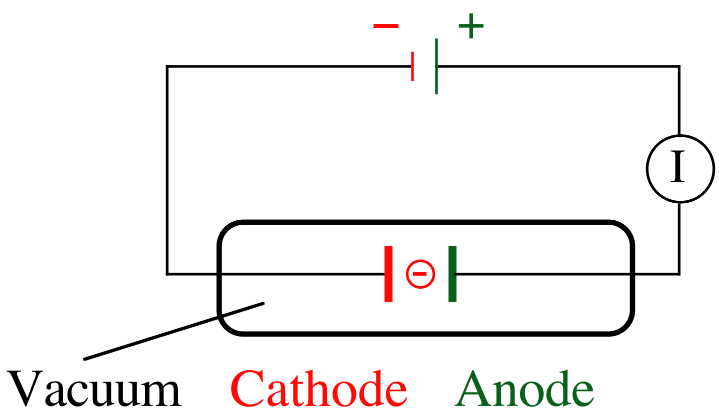
(2) Enter Einstein, cautiously, to explain the photoelectric effect, and to assists at the birth of the photon

(3) Enter Bohr, discretely, to propose a quantum model of the atom

(4) Exit Classical Physics (not quite yet ...)

1. Thomson's and Rutherford's experiments and their thoughts about pudding, potatoes, planets and atoms

- J.J. Thomson (1856-1940), successor to Maxwell and Rayleigh at the Cavendish Laboratory in Cambridge, discovered the electron in "cathode rays" in 1897



- in his setup, Thomson subjected the "rays" to combined electric and magnetic fields - a mass spectrometer (not shown) which allowed him to make guesses about their mass and charge: "... the assumption of a state of matter more finely subdivided than the atom is a somewhat startling one. ... [ionization] essentially involves the splitting up of the atom, a part of the mass of the atom [i.e., the electron(s)] getting free and becoming detached from the original atom ..."
- some of his colleagues at the Royal Society thought that he was "pulling their leg"

- the pudding model of the atom: J.J. proposed that the atom has the newly discovered electrons embedded somehow in a sphere of uniform positive charge, this sphere being the full size of the atom; concluded that the number of electrons in an atom was approximately equal to the atomic number; proposed that by analyzing possible modes of vibration of electrons in these configurations, the color of atoms could be determined

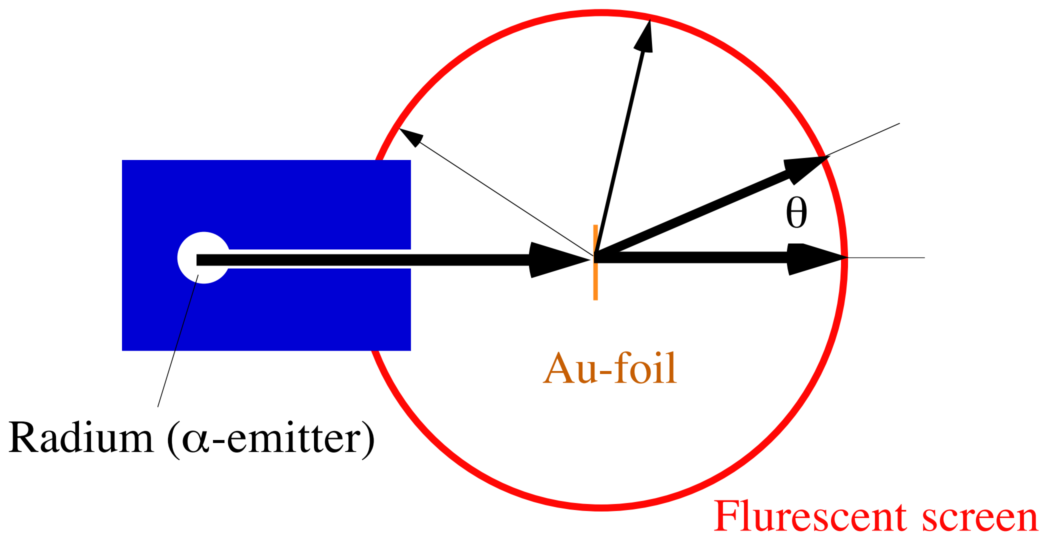
- in a stable state of the atom, electrons assumed to be stationary (or somehow nonaccelerating) - or otherwise they would radiate and so the atom would lose energy and collapse!

- Ernest Rutherford (1871-1937) obtained a fellowship at age 24 to study under J.J. Thomson "That's the last potato I'll dig! [at his parents' farm in New Zealand]"

- at the Cavendish "I ... proceeded to make a systematic examination of [radioactive decay], and I found that it was of two types - one which produced intense ionization, and which was absorbed by a few centimeters of air, and the other, which produced less intense ionization, but was more penetrating. I called these alpha rays [He++] and beta rays [electrons], respectively; and when, in 1898, Villard discovered a still more penetrating type of radiation, he called it gamma-radiation [electromagnetic radiation]."

- got the 1908 Chemistry Nobel Prize for his work on radioactivity; also worked out a theory, largely wrong, of the transmutation of elements due to radioactive decay

- the best was yet to come: at the University of Manchester, he continued studying alpha rays and came up with a project for a new student, E. Marsden: "Why not let him see of any alpha particles can be scattered [off a metal foil, such as gold] through a large angle ? I may tell you in confidence that I did not believe that they would be, since we knew that the alpha-particle was a very fast, massive particle ..."



- a few days later Rutherford was told that some of the alpha-particles were coming backward: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you ... On consideration I realized that ... it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus."

- Rutherford devised a model of the atom (Rutherford's planetary model) where light electrons orbit an oppositely charged small heavy nucleus; for a hydrogen atom (consisting of just one electron orbiting a single proton), the magnitudes involved are:

$m_p = 1.6726 \times 10^{-24}$ g	$m_e = 9.1095 \times 10^{-28}$ g
$m_p / m_e = 1836.151$	
$a_0 = 5.292 \times 10^{-9}$ cm	mean separation between e and p
$R \approx 1.5 \times 10^{-13} A^{1/3}$ cm	diameter of a nucleus with a mass number A (i.e. a total number of nucleons)
$R_p \approx 1.5 \times 10^{-13}$ cm	diameter of the proton

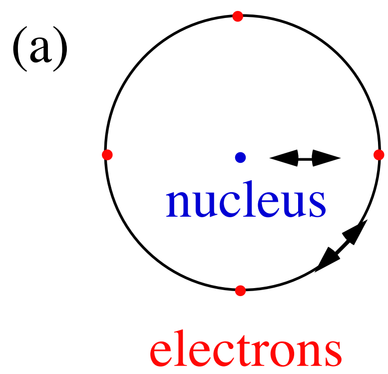
- hence,

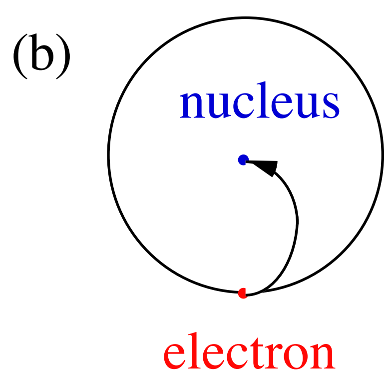
$$a_0 / R_p \approx 3.5 \times 10^4$$

which is about the ratio of a golf ball diameter to the width of a football stadium

$(a_0 / R_p)^3 \approx 4 \times 10^{13}$ atoms (and matter) are mostly empty!

- problems of Rutherford’s planetary model: (a) a ring of equidistant electrons orbiting the nucleus is mechanically unstable; (b) a system of orbiting electrons is radiatively unstable, since any orbiting motion is an accelerated one (an accelerated charge produces electromagnetic radiation; therefore, a planetary electron would quickly lose its energy and collapse onto the nucleus); (c) there’s no characteristic size of the planetary atom





2. Enter Einstein, cautiously, to explain the photoeffect, and assists at the birth of the photon

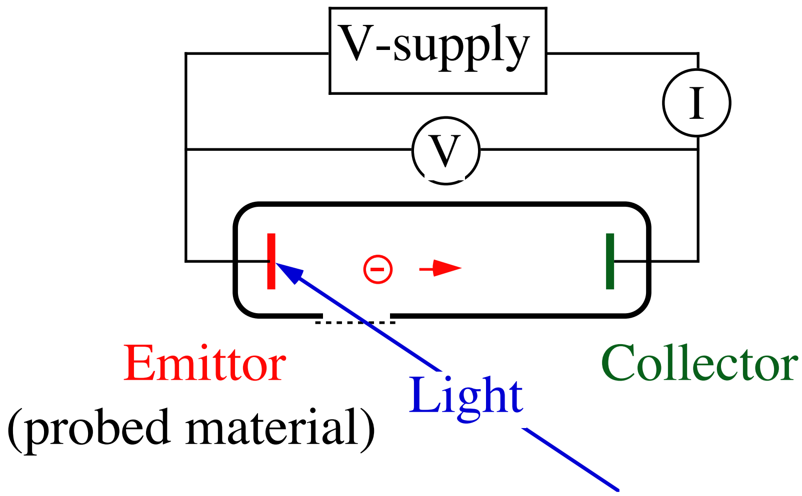
- Albert Einstein (1879-1955)

  "Subtle is the Lord, but malicious He is not."

- one of Einstein's 1905 papers accounts for the Brownian motion (i.e., motion of microscopically visible particles suspended in liquids) as due to collisions between those particles and the molecules of the liquid: "The atomic theory has triumphed. ... its adversaries, at last overcome, now renounce one after the other their misgivings which were for so long both legitimate and useful." (J. Perrin)

- in March 1905, thinking about the black-body radiation law, came up with the light-quantum hypothesis: monochromatic black-body radiation behaves as if it consisted of mutually independent energy quanta of magnitude $h\nu$ (hypothesis justified by a similarity between the thermodynamic behavior of light and that of an ideal gas) and a heuristic principle: light itself (i.e., electromagnetic radiation in vacuum) consists of particle-like energy quanta, dubbed (in 1926) photons
- this was quite an audacious thing to say – since the properties of light in vacuum were described by the mathematically unassailable and experimentally demonstrated Maxwell equations! Hmmm ...
- proposed an explanation of the photoelectric effect
- the photoelectric effect, discovered by Hertz in 1887 and studied mainly by J.J. Thomson and P. Lenard, was still a frontier subject in 1905

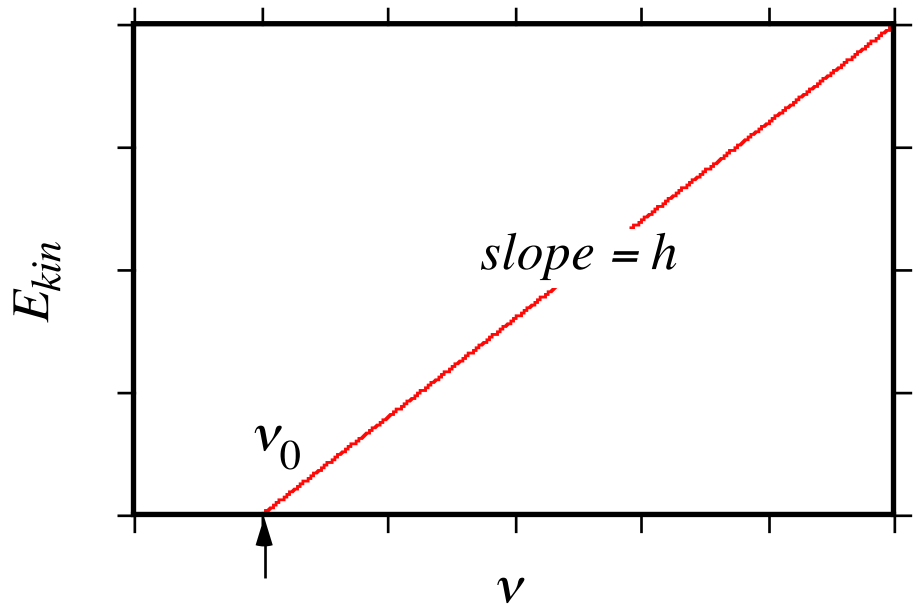
- Thomson was the first to state that the photoelectric current consists of electrons; Lenard measured the kinetic energy of the photoelectrons and found that this is independent of the light's intensity, unlike the photocurrent which is; however, whether there's a photocurrent or not depends on the light's color (i.e., frequency)



- Einstein proposed a "simple explanation:" a photon impinging on a substance gives all its energy, $h\nu$, to a single electron (independently of other photons and electrons); the electron escapes from the substance with a kinetic energy, E_{kin}, diminished by its binding energy, W_0, in the substance (W_0 is called the work function):

$$E_{kin} = h\nu - W_0$$

- Einstein's formula represents the second coming of h, independent of the black-body radiation law; it's equal to the slope of the E_{kin} versus ν dependence, which can be determined experimentally and should be the same for all materials



- the work function

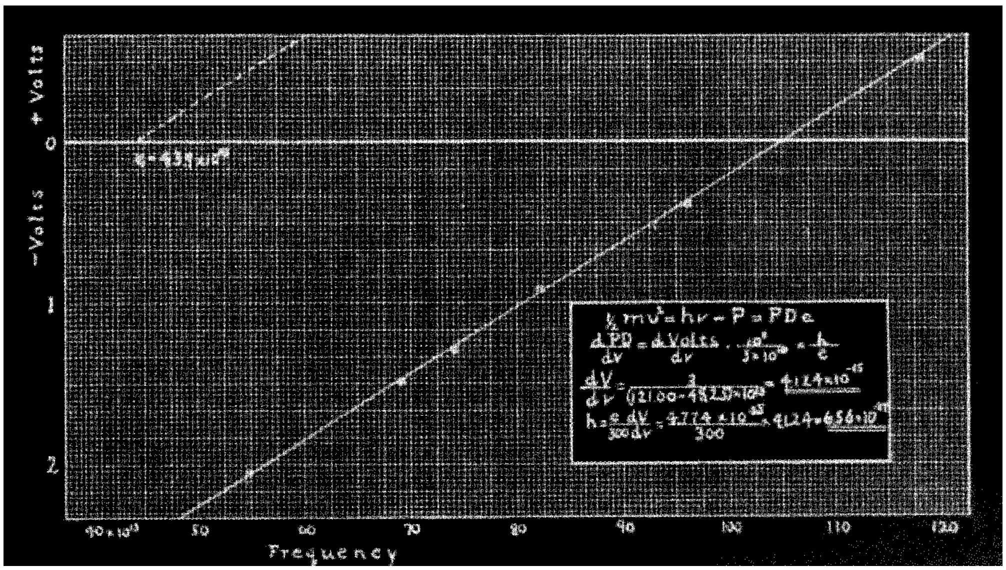
  $W_0 = h\nu_0$

  is material-dependent

- Einstein's explanation of the photoeffect met with much incredulity; the problem was a lack of reliable data to test the theory against; Einstein himself was extremely cautious ...

- only in 1915, R.A. Millikan (University of Chicago) was able to carry out measurements accurate enough to prove Einstein right; the value of Planck's constant that Millikan obtained was within 0.5% of today's value
- note that the kinetic energy of an electron, E_{kin}, is defined by the potential V the electron is subjected to and by the electron's charge

$$E_{kin} = eV$$



- in 1916-17, Einstein produced three more papers on radiation; in one of them, he derives the black-body distribution law in the way presented in the previous seminar; in the others, he completes the particle picture of the photon: a photon is a state of the electromagnetic field with a definite frequency and wavevector

- photon's energy, E, and momentum, p, are

$$E = h\nu \qquad\qquad p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} = \frac{hk}{2\pi} \equiv \hbar k$$

  (it took Einstein 12 years to write these side by side)

- in 1924 (two years after receiving the Physics Nobel Prize for the photoeffect), Einstein writes a popular article for *Berliner Tageblatt* about light: "... radiation behaves as if it consisted of discrete energy projectiles, not only in regard to energy transfer, but also in regard to momentum transfer ..."

- BUT: What about electromagnetic waves? What are they really and where do they come from?

3. Enter Bohr, discretely, to propose a quantum model of the atom

- Niels Bohr (1885-1962)

  "The opposite of a right statement is a wrong statement. The opposite of a deep truth can also be a deep truth."

- a theorist familiar with the work of Planck and Einstein, joined Rutherford at Manchester in 1912 - to study radioactivity (not Rutherford's model of the atom, which was largely ignored; in fact even Rutherford was quite reticent about it, in his book and at conferences)

- Bohr came up with the idea that radioactive displacement implied that both the α- and β-particles originate in the nucleus - but Rutherford dissuaded him from publishing it

- in 1913, back in Copenhagen, Bohr proposed a model of the atom; Bohr's model represents the third coming of h; Bohr set out to resolve the difficulties of the planetary model by introducing a new "hypothesis for which there will be given no attempt at a mechanical foundation (as it seems hopeless) ... The assumption of mechanical forces is not a priori self-evident, for one must assume that there are forces in nature of a kind completely different from the usual mechanical [and electromagnetic] sort ... [An example of this is] the radiation law for high frequencies ...“

- apart from the precedent of the black-body distribution law, Bohr could lean on massive experimental evidence about spectroscopic behavior of atoms, dating back to the alkali spectra discovered by Kirchhoff and Bunsen; in 1860, A. Ångström measured the emission spectra of atomic hydrogen in the VIS range whereupon J. Balmer found, in 1885, that the hydrogen lines occur at frequencies given by

$$\nu_{mn} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

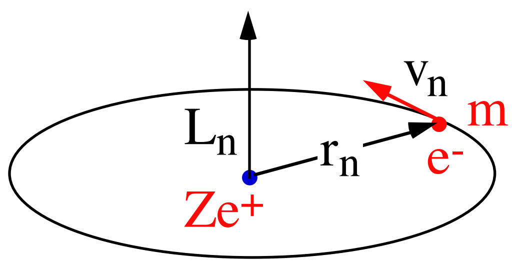
where $m = 2,3,4,5$, $n = 3,4,5,6$, and $R \approx 3 \times 10^{15}$ Hz is now called the Rydberg constant; Balmer's formula remained a curiosity until Bohr put his hands on it

- Bohr's atomic hypothesis (formulated for the H-atom):

(a) an atom possesses discrete stationary states $|1\rangle, |2\rangle, |3\rangle, |4\rangle$ ... with angular momenta $L_1, L_2, L_3, L_4, \ldots$; the state, $|1\rangle$, with the lowest angular momentum, L_1, is stable (the ground state); other states are unstable

(b) the angular momentum, L_n, of a stationary state is given by

$$L_n = m\mathrm{v}_n r_n = n\hbar \qquad \text{with} \qquad n = 1, 2, 3, \ldots$$



- from the balance between the Coulomb and centrifugal forces

$$\frac{Ze^2}{r_n^2} = \frac{m\mathrm{v}_n^2}{r_n}$$

the radius of the electron's orbit can be obtained

$$r_n = \frac{n^2\hbar^2}{Ze^2 m}$$

- since, classically, the energy of a bound state is

$$E_n = -\frac{L_n^2}{2mr_n}$$

we have for the energy of a stationary state

$$E_n = -\frac{Z^2 e^4 m}{2\hbar^2}\frac{1}{n^2}$$

(c) when an atom changes its state (undergoes a transition), the energy difference, $|E_n - E_m|$, of any two states $|m\rangle, |n\rangle$ is equal to a single light quantum of energy

$$|E_n - E_m| = h\nu_{nm} = \frac{Z^2 e^4 m}{2\hbar^2}\left|\frac{1}{n^2} - \frac{1}{m^2}\right|$$

- this we recognize as the Balmer formula if

$$R = \frac{Z^2 e^4 m}{4\pi\hbar^3}$$

which simplifies for the hydrogen atom to

$$R = \frac{e^4 m}{4\pi\hbar^3} = 3.28 \times 10^{15}\ \text{Hz}$$

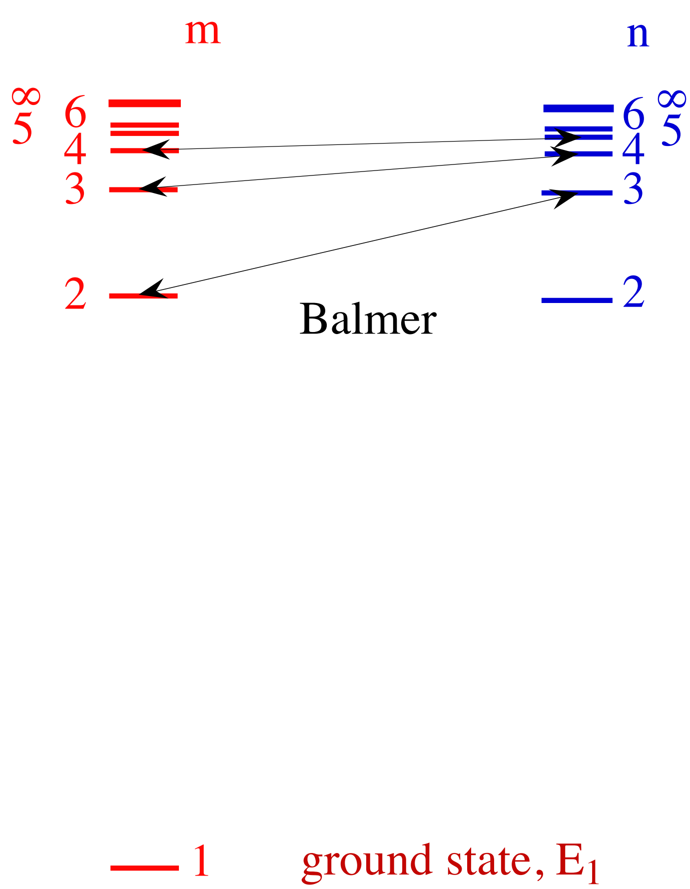
- thus Bohr's model renders the value of the Rydberg constant; this was a great triumph of the model

- the ground-state energy and the ground-state orbit radius (Bohr radius) are

$$E_1 = -\frac{e^4 m}{2\hbar^2} = 13.6057\ \text{eV} \qquad \& \qquad r_1 = \frac{\hbar^2}{e^2 m} = 0.529\ \text{Å}$$

where 1 eV = 1.6022×10^{-19} J and 1 Å = 10^{-8} cm

- for $n > m$, the transition $|n\rangle \rightarrow |m\rangle$ corresponds to emission and the $|m\rangle \rightarrow |n\rangle$ transition corresponds to absorption of the light quantum (photon) $h\nu_{nm}$



- there are infinitely many bound states and infinitely many transitions; all hydrogen spectra thereby interpreted
- in each stationary state, the atom has a size

$$r_n = \frac{n^2}{Z} r_1$$

- Bohr's model of the atom is also a model of where light comes from

- a twist: what about the emission spectrum of He^+ where $Z = 2$?

$$\Delta E \equiv E_n - E_m = \frac{Z^2 e^4 m}{2\hbar^2}\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \text{for } n > m$$

and hence

$$\frac{\Delta E(He^+)}{\Delta E(H)} = \frac{Z^2(He^+)}{Z^2(H)} = 4$$

- Experiment:

$$\frac{\Delta E(He^+)}{\Delta E(H)} = 4.0016 \qquad \text{(Pickering, in 1896, at Harvard)}$$

- Bohr's correction:

$$m \to \mu \equiv \frac{mM}{m + M}$$

and hence

$$\frac{\Delta E(He^+)}{\Delta E(H)} = \frac{Z^2(He^+)\mu(He^+)}{Z^2(H)\mu(H)} = 4.00163$$

which is an agreement within an accuracy that was unprecedented in spectroscopy

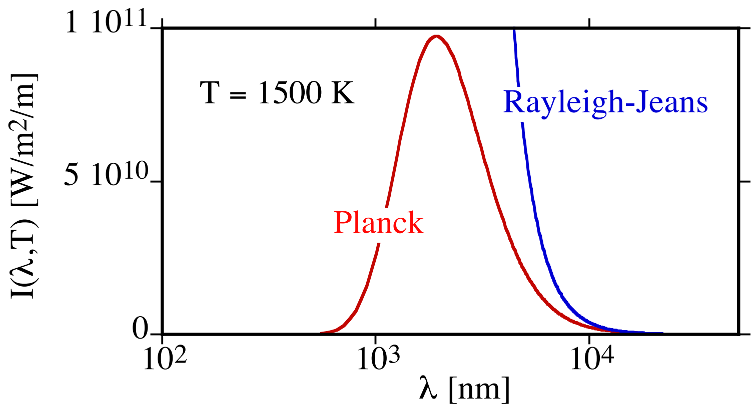
- Einstein's reaction: "This is an enormous achievement. The theory of Bohr must then be right."

4. Exit Classical Physics (not quite yet ...)

- classical mechanics (which includes Maxwell's electrodynamics) is a special case of a more general theory, quantum mechanics

- the correspondence principle (Bohr's invention) is an expression of this connection: under conditions that quantum mechanics can predict, a quantum mechanical treatment coincides with a classical one

- example: the black body radiation law



the (classical) Rayleigh-Jeans law

$$I_{R-J}(\lambda,T) = \frac{2\pi ckT}{\lambda^4}$$

becomes a special case of the (quantum) Planck law

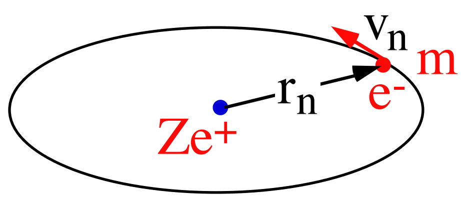
$$I(\lambda,T) = \frac{2\pi hc^2}{\lambda^5}\frac{1}{\exp\left[\frac{hc}{\lambda kT}\right]-1}$$

which happens under a condition that can be predicted from the quantum side, namely for

$$\frac{hc}{\lambda kT} = \frac{h\nu}{kT} << 1 \qquad \text{i.e., for} \quad h\nu << kT$$

when the spacing between energy levels is much smaller than kT and therefore the levels behave as if they were continuous

- what about the correspondence principle for Bohr's atom?



a classical H-atom represents an accelerated dipole expected to radiate at a frequency equal to the frequency of the electron's orbiting motion

$$f_n = \frac{v_n}{2\pi r_n}$$

with

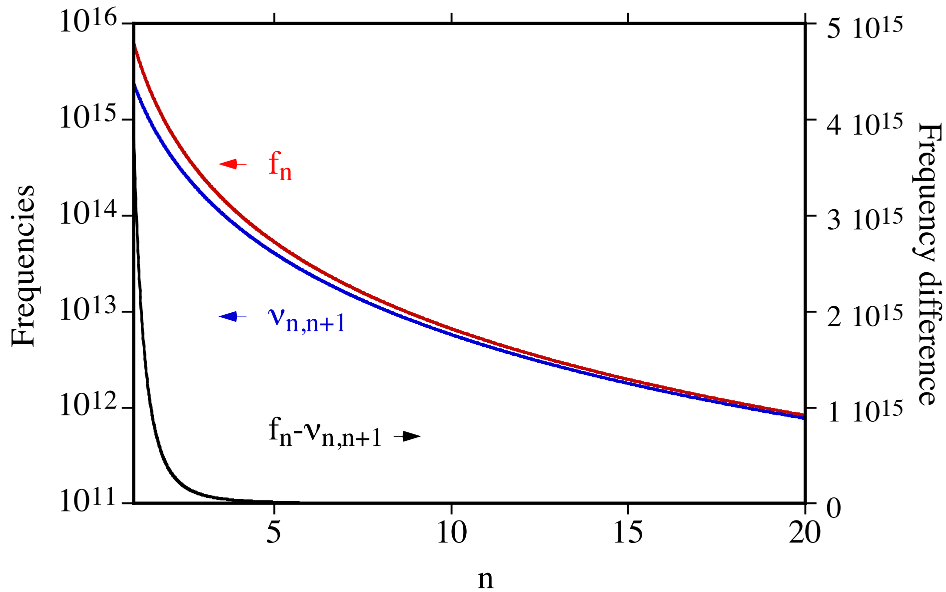
$$r_n = \frac{Ze^2}{m v_n^2} \qquad \& \qquad v_n = \left(\frac{2E_n}{m}\right)^{1/2} \qquad \& \qquad r_n = \frac{Ze^2}{2E_n}$$

hence

$$f_n = \frac{(2E_n^3 m)^{1/2}}{\pi Z e^2} = \frac{4\pi^2 m Z^2 e^4}{n^3 h^3} = \frac{2R}{n^3}$$

But: the quantum frequency of the radiation is

$$\nu_{n,n+1} = R\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) \approx \frac{2R}{n^3} \qquad \text{for } n \text{ large}$$



- hence for high *n*, when the atomic levels come so close to one another that a change from one to the next is almost continuous, the atom produces the same radiation as a corresponding classical dipole