Early Quantum Theory and The Models of the Atom

Planck's Quantum Hypothesis; Blackbody Radiation

Blackbody: An idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence. Also emits blackbody radiation

Blackbody radiation: Thermal electromagnetic radiation within or surrounding a body in thermodynamic equilibrium with its environment, emitted by a blackbody.

Blackbody radiation has a characteristic, temperature dependent curve. It is found experimentally that the wavelength at the peak of the spectrum λ_p is related to Kelvin temperature by

$$\lambda_p T = 2.90 \times 10^{-3}\ mK \qquad \text{(Wien's Law)}$$

According to classical electromagnetism, the number of electromagnetic modes in a 3-D cavity per unit frequency is proportional to the square of velocity. Thus, both the power at a given frequency and the total radiated power is unlimited as higher and higher frequencies are considered, this is unphysical as the total radiated power of a cavity is not infinite. This is called the UV catastrophe

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In 1900 Max Planck proposed an empirical formula that nicely fit the data!

$$I(\lambda, T) = \frac{2\pi h c^2 \lambda^{-5}}{e^{hc/\lambda k T} - 1}$$ (Planck's radiation formula)

Rad. Intensity at λ, and T

Boltzmann constant

Planck's constant

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

Planck explained the form of this formula by a new and radical assumption: The energy of the oscillations of atoms within molecules cannot have just any value instead each has energy which is a multiple of a minimum value related to the frequency of oscillation by

$$E = hf$$

and any vibration must have

Planck's Quantum Hypothesis

$$E = n\,h\,f \qquad n = 1, 2, 3, \ldots$$

Planck's constant

frequency

Quantum number

This formula implies energy is quantized - it only exists in discrete amounts. The smallest amount is (hf) quantum of energy

Planck was strongly against this, and tried very hard to find a classical interpretation

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Photon Theory of Light and the Photoelectric Effect

In 1905, along with the special theory of relativity Einstein made a bold move and proposed a new theory of light: Since all light comes ultimately from a radiating source, perhaps light is transmitted as tiny particles (photons) as well as waves predicted by Maxwell's EMT. Einstein proposed an experiment using photoelectric effect to test the validity of this theory.

Photoelectric effect: The emission of electrons when EM radiation such as light hits a material.

That electrons should be emitted when light shines on is consistent with classical electrodynamics however quantum and classical theory have different predictions

Classical EMT	Quantum
1) The number of $\bar{e}$ increases with increasing light intensity	1) The number of $\bar{e}$ increase with intensity
2) The maximum kinetic energy of $\bar{e}$ increases with increasing light intensity	2) K.E. of $\bar{e}$ is not affected by intensity
3) Frequency of light should not affect KE of $\bar{e}$	3) frequency of the light determines the kinetic energy
	4) If frequency is less than a threshold, no $\bar{e}$ is emitted

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As you can see, there is a stark difference between the predictions, and the experiments align with the quantum theory.

Now let's see how Quantum theory has arrived at these predictions

- In a monochromatic beam, all photons have the same energy hf
- Increasing the intensity, increases the number of photons, but does not change the energy of each photon
- According to Einstein, electron ejection is due to collision of a single electron with a single photon where photon energy is transferred to the electron and photon ceases to exist
- A minimum energy needs to be supplied to the $\bar{e}$ for it to break free from the attractive potential of the metal. This is called the Work Function W_0 of the material

$$\underbrace{hf}_{\text{photon energy}} = \underbrace{K}_{\text{KE of } \bar{e}} + \underbrace{W}_{\text{Binding energy}}$$

for the least bound $\bar{e}$

$$hf = \underbrace{K_{max}}_{\text{max KE possible for } hf} + \underbrace{W_0}_{\text{work function}}$$

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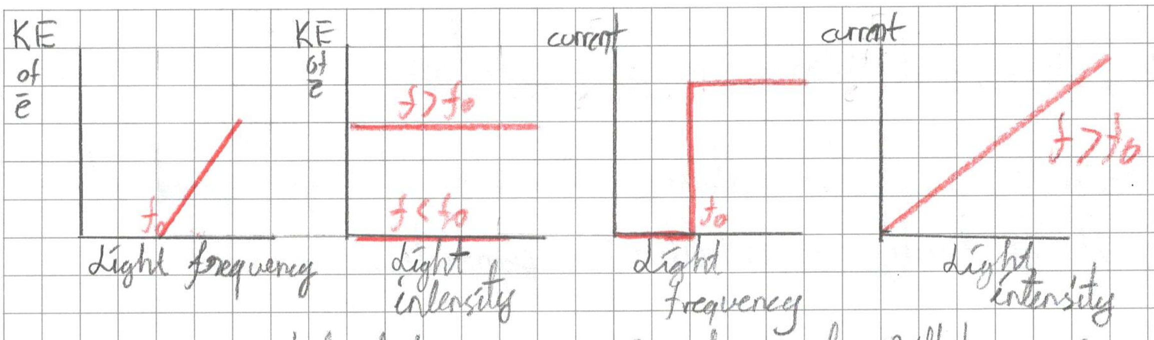

The photoelectric experiments of Millikan in 1913-1914 confirmed the photon theory

Example: Photon energy

Calculate the energy of a photon of blue light $\lambda = 450nm$ in air (or vacuum)

$$E = hf = \frac{hc}{\lambda} = \frac{(6.63\times10^{-34}\,J.s)(3.0\times10^{8}\,m/s)}{(4.5\times10^{-7}\,m)} = 4.4\times10^{-19}\,J$$

or

$$\frac{4.4\times10^{-19}\,J}{1.60\times10^{-19}\,J/eV} = 2.8eV$$

Example: Photoelectron speed and energy

What is the kinetic energy and the speed of an electron ejected from a sodium surface whose work function is $W_0 = 2.28eV$ when illuminated by a light of wavelength (a) 410nm (b) 550nm

a) $hf = \frac{hc}{\lambda} = 4.85\times10^{-19}\,J = 3.03eV$

$$K_{max} = 3.03eV - 2.28eV = 0.75eV$$

$$K = \frac{1}{2}mv^2 = \frac{1}{2}\,9.11\times10^{-31}\,kg\ v^2$$

$$V_{max} = \sqrt{\frac{2K}{m}} = 5.1\times10^{5}\,m/s$$

b) $hf = hc/\lambda = 2.26eV$. $\bar{e}$ does not eject

Energy, Mass, and Momentum of a photon

Because a photon always travels at the speed of light, it is truly a relativistic particle.

$$K = E = hf$$

The momentum of a photon can be obtained from the relativistic formula $E^2 = p^2c^2 + m^2c^4$ where $m=0$

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda}$$

Wave-Particle Duality, the principle of Complementarity

Compton effect, photoelectric effect and etc

light is a particle!

Young's experiment, other classic experiments:

light is a wave!

Niels Bohr:

Both are correct! (wave-particle duality)

Principle of complementarity: Wave and particle aspects of light complement each other

This is a fundamental fact of nature

Although the use of wave-particle duality has worked well in physics, the meaning or interpretation has not been satisfactorily resolved.

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Wave Nature of Matter

De Broglie proposed that particles also have a wave dual just like EM waves have a particle dual. For a particle having a linear momentum $p = mv$ the wave dual has λ

$$\boxed{\lambda = h/p}$$ de Broglie wavelength

notice that p can be classic or relativistic

example: Wavelength of a ball:

Calculate the de Broglie wavelength of a 0,20 kg ball moving with a speed of 15 m/s

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.6 \times 10^{-34}\ J.s}{(0,20\ kg)(15\ m/s)} = 2,2 \times 10^{-34}\ m$$

As you can see, ordinary objects have too small wavelength to be observed. However elementary particles, such as electrons have a clearly observable wave dual.

Example: Wavelength of an electron

Determine the wavelength of an electron accelerated through 100 V

$$\frac{1}{2}mv^2 = eV \qquad v = \sqrt{\frac{2eV}{m}} = \sqrt{\frac{2(1,6 \times 10^{-19} c)(100 V)}{(9.1 \times 10^{-31} kg)}} =$$

$$= 5.9 \times 10^6\ m/s$$

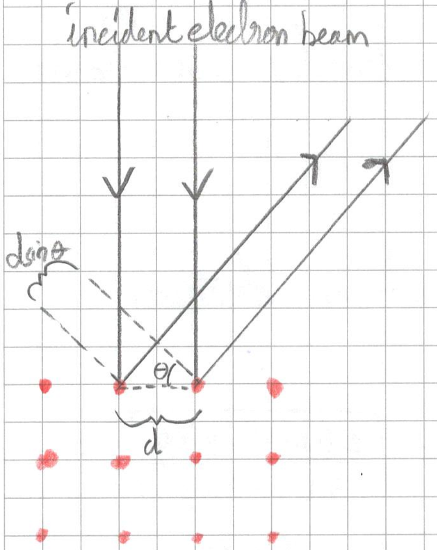
then

$$\lambda = \frac{h}{mv} = \frac{(6.63\times10^{-34}\,J.s)}{(9.1\times10^{-31}kg)(5.9\times10^{6}m/s)} = 1.2\times10^{-10}\,m$$

$$= 0.12\,nm$$

Ex: Electron diffraction.

The wave nature of electrons is manifested in experiments where an electron beam interacts with the atoms on the surface of a solid. By studying the angular distribution of the diffracted electrons, one can indirectly measure the geometrical arrangement of atoms. Assume that the electrons strike perpendicular to the surface of a solid, and their energy is low, $K = 100\,eV$, so that they interact only with the surface layer of atoms. If the smallest angle which a diffraction angle occurs is at 24°, what is the separation d between the atoms on the surface?



Treating the electrons as waves

$$d\sin\theta = \lambda$$

λ is related to the (non-relativistic) KE

$$K = \frac{p^2}{2m_e} = \frac{h^2}{2m_e\lambda^2}$$

Thus

$$\lambda = \frac{h}{\sqrt{2m_e K}} = \frac{(6.63\times10^{-34}J.s)}{\sqrt{2(9.11\times10^{-31}kg)(100eV)(1.6\times10^{-19}J/eV)}}$$

$$= 0.123\,nm$$

Surface interatomic spacing: $d = \frac{\lambda}{\sin\theta} = \frac{0.123\,nm}{\sin 24°} = 0.30\,nm$

Atomic Spectra: Key to the structure of Atom

In low density gasses, the atoms are sufficiently far from each other, so that we can assume the line spectrum (absorbtion or emission) is dominated by individual atoms

Hydrogen is the simplest atom. The spacing between lines decreases in a regular way. In 1885 J. J. Balmer (1825–1898) showed that the four lines in the visible portion of the hydrogen spectrum obey

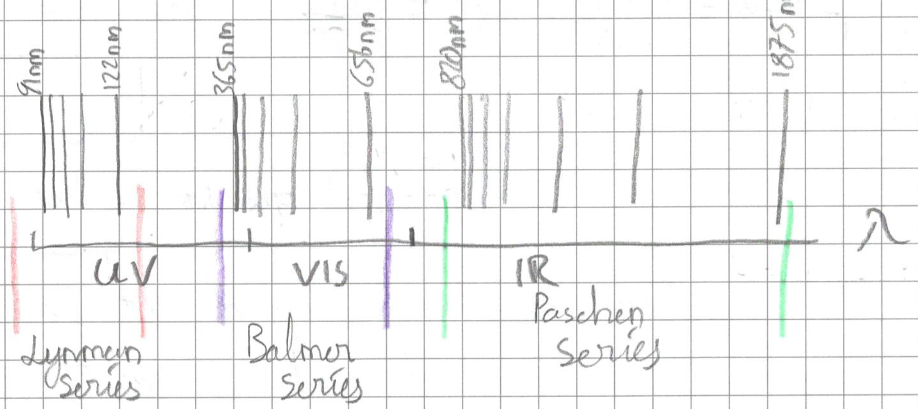
Balmer series $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ $n=3,4,\dots$

Rydberg constant

Later experiments showed quantized behaviour also in IR (Paschen series) and UV (Lyman series)

Lyman series $\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$, $n=2,3,\dots$ 91–122 nm

$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$ $n=4,5,\dots$ 820–1875 nm



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The Bohr Model

The quantum theory of light laid by Einstein and Planck motivated Bohr to incorporate this idea to the atomic model. Rutherford's model had a lot of issues, including its failure to explain atomic spectra. Bohr postulated that, there exists quantized orbits around the nucleus that an $\bar{e}$ can exist without radiating energy (not possible classically). He called these orbits stationary states. Light is emitted only when the electron jumps from one stationary state to another

$$\underbrace{hf}_{\text{emitted photon}} = \underbrace{E_U}_{\text{upper stationary state}} - \underbrace{E_L}_{\text{lower stationary state}}$$

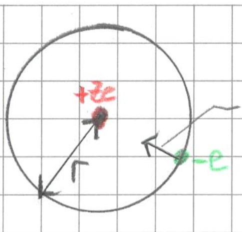
Bohr went for the simplest atom, Hydrogen, to convince the scientific community. He assumed the angular momentum of the electron is quantized

$$L = I\omega = mr^2 \, v/r = mvr = n \frac{h}{2\pi}$$

$\boxed{\text{Bohr's quantum condition}}$

$\boxed{n = 1, 2, 3, \ldots \text{ principal quantum number}}$

Notice that this equation is phenomenological, it does not have a theoretical background. Let us see it in action, by predicting the wavelengths of emitted light



$$F = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(e)}{r^2}$$

An electron on a classical circular orbit around nuclei would have an acceleration v^2/r_n. The force is due to Coulomb's law

$$F = \frac{1}{4\pi\epsilon_0} \frac{\overbrace{(Ze)}^{\text{charge of nucleus}}\overbrace{(e)}^{\text{charge of electron}}}{\underbrace{r_n^2}_{\text{radius of the orbital}}}$$

for hydrogen atom, $Z = +1$

$$F = ma$$

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n^2} = \frac{mv^2}{r_n}$$

$$V = nh/2\pi m r_n$$ (from Bohr's quantization criteria)

$$r_n = \frac{Ze^2}{4\pi\epsilon_0 mv^2} = \frac{Ze^2 4\pi^2 m r_n^2}{4\pi\epsilon_0 n^2 h^2}$$

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2} = \frac{n^2}{Z} r_1$$

$$r_1 = \frac{h^2 \epsilon_0}{\pi m e^2} = \frac{(1)^2 (6.626 \times 10^{-34}\ J.s)^2 (8.85 \times 10^{-12}\ C^2/N.m^2)}{\pi\ (9.11 \times 10^{-34}\ kg)(1.602 \times 10^{-19}\ C)^2}$$

$$\boxed{r_1 = 0.529 \times 10^{-10}\ m}$$ Bohr radius

$$r_n = \frac{n^2}{Z} (0.529 \times 10^{-10}\ m) \qquad n = 1, 2, 3, \ldots$$

The total energy E_n for an electron in the n^{th} orbit is the sum of kinetic plus the potential energy

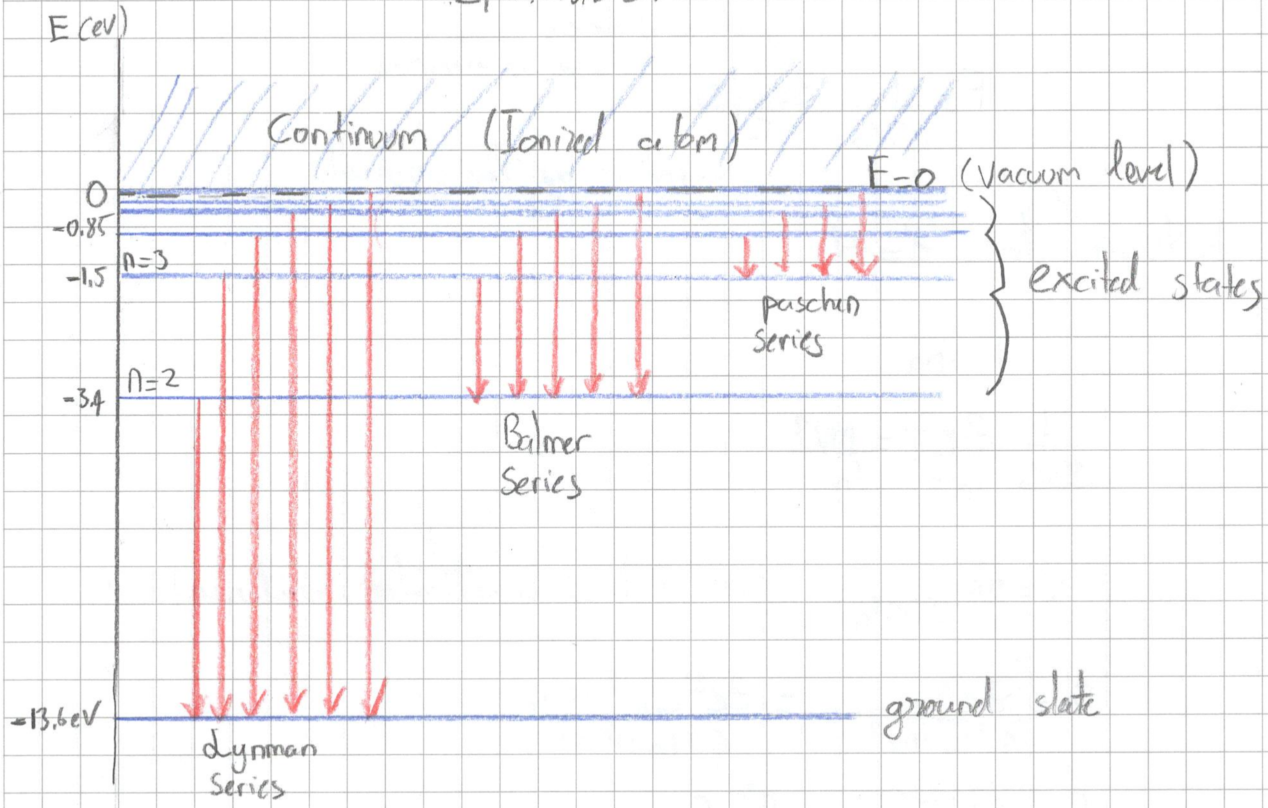
$$E_n = \frac{1}{2} mv^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n} = -\left(\frac{Z^2 e^4 m}{8\epsilon_0^2 h^2}\right)\left(\frac{1}{n^2}\right)$$

$$n = 1, 2, 3, \ldots$$

$$E_n = -(13.6\ eV)\frac{Z^2}{n^2}$$

The lowest energy for Hydrogen like atom is

$$E_1 = -13.6\ eV$$



$$\frac{1}{\lambda} = \frac{hf}{hc} = \frac{1}{hc}(E_n - E_{n'}) = \frac{Z^2 e^4 m}{8\epsilon_0^2 h^3 c}\left(\frac{1}{(n')^2} - \frac{1}{(n)^2}\right)$$

Where n is the upper state, and n' is the lower state

Although the concepts introduced by Bohr's theory is still widely used in Si electronics and spectroscopy, the theory is not valid. The electrons do not orbit around the nucleus in a definitive fashion. This contradicts with other experiments.

Bohr's theory breaks down for the next simplest atom He. It can not predict why some lines are brighter, nor the closely spaced lines (called fine structure)