

THE OLD QUANTUM THEORY

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3 On a Heuristic Point of View about the Creation⁴³ and Conversion of Light[†]

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An essential formal difference:

- theoretical pictures of ponderable bodies

State: determined by the positions and velocities of a large, finite number of atoms and electrons

Energy: can be written as a sum over the atoms and electrons

- Maxwell's theory of electromagnetic processes in empty space

State: continuous spatial functions, finite number not sufficient

Energy: a continuous function in space for all purely electromagnetic phenomena, thus also for light

For the case of light:

Optical observations: refer to time averages, not instantaneous values

continuous functions →

lead to contradictions, if applied to the **creation and conversion of light**.

Assumption: energy of light is distributed **discontinuously** in space.

“when a light ray starting from a point is propagated, the energy is not continuously distributed over an ever increasing volume, but it consists of a finite number of energy quanta, localised in space, which move without being divided and can be absorbed or emitted only as a whole.”

1. On a Difficulty in the Theory of “Black-body Radiation”

- Definition of “resonators”

Gas molecules and electrons: moving freely and exerting upon one another conservative forces when they approach each other.

Resonator electrons: bound to points in space, by forces proportional to the distance from those points and in the direction towards those points. Far from one another. Interacting conservatively with the free molecules and electrons when close.

↑

“resonators”: they emit and absorb electromagnetic waves with definite periods.

1. On a Difficulty in the Theory of “Black-body Radiation”

- Relationship between E of **electron resonator** and of **gas molecule**

Dynamic equilibrium:

average kinetic energy of a resonator electron equals average kinetic energy of the translational motion of a gas molecule.

$$\bar{E} = \frac{R}{N} T,$$

R: gas constant

N: the number of “real molecules”

Time averages of the kinetic and potential energy of a resonator are equal to one another.

→ \bar{E} is equal to 2/3 of the kinetic energy of a free molecules of a monatomic gas

1. On a Difficulty in the Theory of “Black-body Radiation”

- Our case: take into considerations of **radiation effects**

If, because of radiation effects the time average of a resonator be larger or smaller than \bar{E} , collisions with the free electrons and molecules will lead to an energy transfer to or from the gas which has a non-vanishing average.

In **our case**, dynamic equilibrium will be possible **only, if each resonator has the average energy \bar{E} .**

1. On **a Difficulty** in the Theory of “Black-body Radiation”

- dynamic equilibrium condition considering interaction between resonator and radiation

Mr. Planck's derivation:

$$\bar{E}_\nu = \frac{L^3}{8\pi\nu^2} \rho_\nu,$$

L : speed of light

\bar{E}_ν : average energy of a resonator with eigenfrequency ν

$\rho_\nu d\nu$: energy per unit volume of that part of the radiation which has frequencies between ν and $\nu + d\nu$.

Because of conservation of radiation energy of frequency ν

$$\frac{R}{N} T = \bar{E} = \bar{E}_\nu = \frac{L^3}{8\pi\nu^2} \rho_\nu \quad \rho_\nu = \frac{R}{N} \frac{8\pi\nu^2}{L^3} T.$$

The greater we choose the range of frequencies of the resonators, the greater becomes the radiation energy in space!

2. On Planck's Determination of Elementary Quanta

- determination of elementary quanta given by Mr. Planck

$$\rho_v = \frac{\alpha}{\beta} v^2 T. \quad \rho_v = \frac{R}{N} \frac{8\pi v^2}{L^3} T.$$

↑ Planck's formula for long wavelengths and high radiation densities

By equating the Coefficients in the two formulae, we get

$$\frac{R}{N} \frac{8\pi}{L^3} = \frac{\alpha}{\beta}$$

$$N = \frac{\beta}{\alpha} \frac{8\pi R}{L^3} = 6.17 \times 10^{23},$$

Our theory work at **higher energy density and longer wavelengths**

Does not work for **short wavelengths and low radiation densities**

3. On the Entropy of the Radiation

- consider “black-body radiation” basing upon experience

In the case of “black-body radiation”, ρ is such a function of ν or that the entropy is a maximum for a given energy,

$$\delta \int_0^{\infty} \phi(\rho, \nu) d\nu = 0, \quad \text{if} \quad \delta \int_0^{\infty} \rho d\nu = 0.$$

If the temperature of a black-body radiation in a volume $\nu = 1$ increases by dT , we have

$$dS = \int_{\nu=0}^{\nu=\infty} \frac{\partial \phi}{\partial \rho} d\rho d\nu = \frac{1}{T} dE.$$



$$\frac{\partial \phi}{\partial \rho} = \frac{1}{T} *$$

black-body radiation law

4. Limiting Law for the Entropy of Monochromatic Radiation for Low Radiation Density

- Entropy of Radiation

Radiation of energy E with a frequency between ν and $\nu+d\nu$.
The entropy of this radiation is

$$S = \nu \phi(\rho, \nu) d\nu = -\frac{E}{\beta \nu} \left[\ln \frac{E}{\nu \alpha \nu^3 d\nu} - 1 \right].$$

$$\frac{\partial \phi}{\partial \rho} = \frac{1}{T^*}$$
$$\rho = \alpha \nu^3 e^{-\beta \nu / T}$$

denote the entropy of the radiation by S_0 if it occupies a volume ν_0 , we get

$$S - S_0 = \frac{E}{\beta \nu} \ln \frac{\nu}{\nu_0}.$$

Entropy of a monochromatic radiation of sufficiently small density varies with volume has the same rules as the entropy of a perfect gas or of a dilute solution

5. Molecular-Theoretical Investigation of the Volume-dependence of the Entropy of Gases and Dilute Solutions

- Concerning Boltzmann's principle

If any increase of entropy can be considered as a transition to a more probable state, the entropy S_1 of a system will be a function of the probability W_1 of its instantaneous state.

If S_0 is the entropy of a certain initial state of the system considered and W the relative probability of a state with entropy S , we have in general

$$S - S_0 = \frac{R}{N} \ln W.$$

5. Molecular-Theoretical Investigation of the **Volume-dependence of the Entropy** of Gases and Dilute Solutions

- Consider a special case
 - n moving points in a volume v_0 , no direction preferred above others, number of points be so small that we neglect mutual interaction
 - a part v of the volume v_0 contains all n moving points while otherwise nothing is changed in the system

We ask: how large is the probability of this state relative to the original state?

$$W = \left(\frac{v}{v_0}\right)^n; \quad \longrightarrow \quad S - S_0 = R \frac{n}{N} \ln \frac{v}{v_0}.$$

noted that it is unnecessary to make any assumptions about the laws for this conclusion

6. Interpretation of the Expression for the Volume-dependence of the Entropy of Monochromatic Radiation according to Boltzmann's Principle

Compare two equations

$$S - S_0 = \frac{E}{\beta v} \ln \frac{v}{v_0} = \frac{R}{N} \ln \left[\left(\frac{v}{v_0} \right)^{NE/R\beta v} \right],$$

Entropy of a monochromatic radiation of sufficiently small density

$$S - S_0 = \frac{R}{N} \ln W,$$

Boltzmann's principle

If monochromatic radiation of frequency ν and energy E is enclosed (by reflecting walls) in a volume v_0 , the probability that at an arbitrary time the total radiation energy is in a part Y of the volume v_0 will be

$$W = \left(\frac{v}{v_0} \right)^{NE/R\beta v}.$$

6. Interpretation of the Expression for the Volume-dependence of the Entropy of Monochromatic Radiation according to Boltzmann's Principle

From this we then conclude :

Monochromatic radiation of low density behaves as if it consisted of **mutually independent energy quanta** of magnitude $R\beta\nu/N$.

Then it is plausible to investigate whether the laws on **creation and transformation of light** are also such as if light consisted of such energy quanta.

7. On Stokes' Rule

Consider monochromatic light which is changed by photoluminescence to light of a different frequency, assume that both the original and the changed light consist of energy quanta of magnitude $(R/N)\beta\nu$

The energy of a final light quantum can not be larger than that of an initial light quantum:

$$\frac{R}{N}\beta\nu_2 \leq \frac{R}{N}\beta\nu_1, \quad \text{or} \quad \nu_2 \leq \nu_1 \quad \text{Stokes' Rule}$$

Intensity of light produced proportional to the incident light intensity for weak illumination.

No lower limit for intensity of the incident light to produce photoluminescence.

7. On Stokes' Rule

Deviations from Stokes' rule

1. When the **number of the energy quanta** per unit volume involved in transformations is so **large**, an energy quantum of the light produced may obtain its energy from several initial energy quanta.

2. When the initial (or final) light energetically does **not** have the properties characteristic for “**black-body radiation**” according to Wien's law;

e.g. initial light produced by a body of high temperature that Wien's law no longer holds for wavelengths considered

8. On the Production of Cathode Rays by Illumination of Solids

If every energy quantum of the incident light transfers its energy to electrons independently of all other quanta, the velocity distribution of the electrons (the quality of the resulting cathode radiation) will be independent of the intensity of the incident light;

The number of electrons leaving the body should be proportional to the intensity of the incident light

$$\Pi\varepsilon = \frac{R}{N}\beta v - P,$$

ε : electrical mass of the electron

E : charge of a gram equivalent of a single-valued ion

P' : potential of that amount of negative electricity with respect to the body

9. On the Ionisation of Gases by Ultraviolet Light

- two predictions

Assume that when a gas is ionised by ultraviolet light, always one absorbed light energy quantum is used to ionise **just one** gas molecule.

the ionization energy of a molecule cannot be larger than the energy of an effective, absorbed light energy quantum.

$$R\beta\nu \geq J.$$

J: ionisation energy per
gram equivalent

Relation between the absorbed light intensity L and the number j of moles ionised by this light:

$$j = \frac{L}{R\beta\nu}.$$