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POLSKIE TOWARZYSTWO FIZYCZNE
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JAN BLATON

1907—1948

Obituary notice by A. RUBINOWICZ, Warsaw.

The tragic death of Professor Jan Blaton on 17th May 1948 as the result of an accident in the Tatra Mountains was a severe blow to all of us. We have lost in him, a physicist, devoted heart and soul to scientific research, a teacher who carried away his students and who kindled in them the flame of desire for independent scientific thought, a man with a character like rock crystal. The knowledge that this cruel blow need never have fallen and that a little more presence of mind might have sufficed to prevent the terrible catastrophe has alarmed us and has, if possible, plunged us all into even greater sorrow.

Jan Blaton was born on 17th May 1907 in Sporysz in the beautiful hills near the locality of Żywiec. He was the fifth and youngest child of a worker's family. Presumably it never entered his head that the mountains in which he had spent his childhood, those mountains which he loved so dearly and which in his young days he so passionately explored, were plotting his untimely death.

After his having graduated, with honours, at the gymnasium at Bielsko, we find Blaton enrolled in 1925 at the Faculty of Civil Engineering at the Lwów Institute of Technology. He was, however, more interested in theoretical problems than in technical questions and therefore he passed to the General Faculty of this Institute in order to study physics. It was here, in 1928, that I made his acquaintance. He was an uncommonly capable student, and his progress in the study of theoretical physics was astonishing. Even so, I was quite taken aback when this young enthusiast for theoretical physics came before the summer holidays after barely one year of studies to ask me for a subject for this magister examination thesis. I was, however, more astounded still when, after the holidays, he showed me the thesis almost completed. This work, on the intensities of the quadrupole lines in the Balmer series, was the first of a series of his publications concerning multipole radiation, among which we find his most valuable scientific achievements.

In 1929 he became my assistant. He held this position only for a few weeks, however, since he was at that time under court sentence for two weeks detention — the sentence remaining suspended — for the distribution of communist leaflets. Devoted, to the point of self-sacrifice, to the cause of the progress of humanity, Blaton had entered directly after he had passed his matriculation into contact with a group of students belonging to the students' union „Życie" (Life) and in spite of intense scientific work he continued to be politically active. Considerable efforts were needed to make it possible for him to remain at the Institute, if only in the character of a student.

In March 1931 Blaton took his magister degree and less than two months later he submitted a second paper for publication. Its purpose was to investigate the problem of whether, in the scattering of light quanta by atoms, two photons can be turned into one photon.

Blaton's third paper was presented to the Polish Academy of Sciences and Letters in July of the same year. In it the author endeavoured to prove that the electric field of a wave of light, despite its periodicity, causes a Stark effect.

In 1932, Blaton was awarded a National Culture Fund Scholarship and, on the basis of his thesis on the dispersion of light in the vinicity of quadrupole lines, he took his doctor's degree at the Lwów Institute of Technology. Together, in this same year, he and I wrote a report on quadrupole radiation for the „Ergebnisse der exakten Naturwissenschaften".

Continuing to benefit from the National Culture Fund Scholarship, Blaton proceeded to Munich where, under the direction of Professor Sommerfeld, he continued his studies until the advent of Hitlerism forced him to leave Germany. He then went to Zurich.

From 1933 to 1935, after his return to his native land, Blaton occupied the post of an assistant in the Department of Theoretical Physics at the University of Wilno. One of his best scientific achievements, that is his participation in the discovery of magnetic dipole lines, dates from this period. In 1933 H. Niewodniczański discovered that in mixtures of lead vapour with helium and argon there appear in the spectrum of high frequency electric discharges forbidden lines of non-ionized lead. In a letter dated November 1933, addressed to the Editors of the *Physical Review*, Blaton together with Niewodniczański came to the conclusion that one of these lines must be a magnetic dipole line not containing any admixture of electric quadrupole radiation. Niewodniczański, by investigating its Zeeman effect, confirmed this result later and thus finally discovered the magnetic dipole radiation.

The year 1934 saw Blaton submitting his thesis for admission as lecturer of Theoretical Physics at the Wilno University. In it the author shows how to calculate the intensities of magnetic dipole lines in case of any coupling.

In 1935 Blaton published a paper on quaternions, semivectors and spinors, investigating the relations between these quantities.

Blaton was appointed, in 1936, Head of the National Meteorological Institute. He occupied this post until the outbreak of the war A proof to the versatility of his intellect is the rapidity with which he mastered meteorology, a sphere of science at that time quite unknown to him. Two papers of his, quoted in meteorological textbooks, provide evidence of this. In one, the author investigates the dependence of the wave lengths of the gravitational waves on depth, employing methods used in wave mechanics. In the other, he gives for any plane fluid motion a simple kinematic relation between the rate of change of the velocity direction of the fluid motion and the radii of curvatures of the path of the fluid particles and of the stream line. Applying this formula to the dynamics of the atmosphere, he demonstrates how it is possible to calculate changes in the direction of winds with a horizontal movement in the atmosphere with a knowledge only of the coefficient of friction and the data derived from synoptic maps.

Since the post he then held involved a considerable degree of responsibility, it was necessary for Blaton to concentrate his whole mind and attention on meteorology; yet he found the time, in 1937, to write the last of his multipole papers. In it he explains how to split the radiation created by any periodic electric currents into electric and magnetic multipole radiations. Unfortunately, this paper appeared only in the *Acta Physica Polonica* and was overlooked by certain foreign authors.

During the German occupation of Poland, Blaton lived at the Jegiel District Forestry House and, in order to lecture on Theoretical Mechanics and Physics at the clandestine University, journeyed to Warsaw at regular intervals until July 1944. His enthusiasm in overcoming difficulties and the spontaneous admiration he aroused in his students are proved by the fact that amidst the difficult war conditions he managed to educate several pupils who have have already become independent scientific workers.

During the war years Blaton was also occupied with writing a textbook of mechanics. Judging from what he told me about it, it is perfectly up to date and answers all our present-day needs. So far, it has been impossible, unfortunately, to find a publisher willing to bring it out.

October 1944 found Blaton helping to organize the Marie Curie Skłodowska University in Lublin. At the outset he accepted the chair of General Physics there and in 1945 that of Theoretical Physics. From the Autumn of 1946 he was professor of Theoretical Mechanics at the Jagellonian University in Cracow.

In May 1947, at the first post-war symposium on physics in Warsaw, Blaton spoke on the collision of elementary particles in relativistic mechanics. He further developed this work during his visit to Copenhagen in the Autumn of the same year and the first few months of the next. It appeared posthumously in the publications of the Danish Academy.

In Copenhagen, Blaton also devoted much time and thought to the problem of the forces causing μ-mesons to enter into the composition of π-mesons. He surmised that these forces are caused by the electron-neutrino field. One week before his death he lectured on these deliberations at the second Warsaw symposium in May 1948, emphasizing, however, that his idea was open to criticism. Despite the fact that he did not publish his considerations we find a mention of them in a note of Professor O. Klein.

Thus it was that Jan Blaton met his death at the very moment when, following the forced inactivity of the war years, he was entering a period of increased scientific activity. He recommenced his scientific work with wonderful energy. Pitiless fate, however, plucked him from our midst at the very moment when he was entering upon the path which would possibly have led him to his life's greatest scientific achievement. Among Polish physicists his memory will remain alive for ever, just as I shall keep for ever in my soul the memory of one who was my good friend as well as a pupil dear to my heart.

In 1949 Jan Blaton was posthumously awarded a National Scientific Prize. He was being the first Polish physicist to receive it.

Papers published by the late Jan Blaton

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(1a) O natężeniu linij multipolowych w serii Balmera, Spraw. i Prace Polsk. Tow. Fiz., **5**, 17 (1930).

(2) Gibt es eine Doppelstreung von Lichtquanten? Z. Phys., **69**, 835 (1931).

(3) Über die Richtungsquantelung der Atome durch eine Lichtwelle, Bull. Int. Acad. Polonaise Sci. Lett., Série A, 599 (1931).

(4) Über die Dispersion des Lichtes in der Umgebung von Quadrupollinien, Z. Phys., **74**, 418 (1932); **82**, 684 (1935).

(5) Die Quadrupolstrahlung (with A. Rubinowicz), Erg. exakt. Naturwiss., **11**, 176 (1932).

(6) The Nature of the Forbidden Lines in the Pb I Spectrum (with H. Niewodniczański), Phys. Rev., **45**, 64 (1934).

(7) O natężeniach linij dipolowych magnetycznych. Wilno 1934.

(7a) Über die Intensitäten magnetischer Dipollinien, Z. Phys., **89**, 155 (1934).

(8) Quaternionen, Semivektoren und Spinoren, Z. Phys., **95**, 337 (1935).

(9) Versuch einer Anwendung des Fermat'schen Prinzips auf geophysikalische Wellenprobleme, Biul. Tow. Geofiz. w Warszawie, nr 14 (1937).

(10) Zur Theorie der Multipolstrahlung, Acta Phys., Polonica, **6**, 256 (1937).

(11) Zur Kinematik und Dynamik nichtstationärer Luftströmungen, Biul. Tow. Geofiz. w Warszawie, nr 15 (1938).

(12) On a Geometrical Interpretation of Energy and Momentum Conservation in Atomic Collisions and Disintegration Processes, K. Danske Vidensk. Selsk. Mat.-fys. Medd., **24**, No 20 (1950).

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ON THE THEORY OF SPONTANEOUS AND „FORCED“ *K*-CAPTURE

By Marian GÜNTHER, Institute of Theoretical Mechanics, University of Warsaw, Warsaw

(received November 27, 1948)

The main purpose of this paper is to calculate the probability of electron *K*-capture on the basis of the theory of interaction of nucleons with electron-neutrino fields *(1)*, in such a way as to avoid as far as possible all special assumptions regarding the magnitude of the nucleon radius and the behaviour of the electron wave-function inside it. Our final formulas contain only the range of the nuclear forces, i. e. the meson mass.

We shall establish also the dependence of the probability of a *K*-capture process on the atomic number Z of the element which is thus transformed into another one with the atomic number $Z—1$. Finally, we shall be led to draw some consequences regarding the hypothetical „forced“ *K*-capture probability when irradiating a suitable material by antineutrinos — this being a consequence of the neutrino-hole theory.

Hamiltonian of the problem

In order to introduce consistent notations for all the five fields (electron, neutrino, meson, proton, and neutron fields) it is necessary to give first a short survey of their basic equations.

(a) Electron field

The differential Hamiltonian of the electron field is

$$H_{el} = \overline{\psi}\{e\varphi + \vec{\alpha}(c\vec{p} - e\vec{A}) + \beta mc^2\}\psi, \tag{1}$$

where e is the (negative) electron charge. The spinor components of ψ obey the following anticommutation relations[1]

$$[\overline{\psi}_\sigma(x), \psi_\varrho(x)]_+ = \delta_{\sigma\varrho}\delta(x-x'). \tag{2}$$

Introducing the orthonormal set of functions (c-numbers) u_n describing the different states of the electrons and being the eigenfunctions of

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[1] As argument of a function x stands for x_1, x_2, x_3.

the time-free wave equation, according to the formulas

$$E^{(e)}_u u^{(n)} = \{e\varphi + \vec{\alpha}(c\vec{p} - e\vec{A}) + \beta mc^2\} u^{(n)}, \tag{3}$$

$$\int \bar{u}^{(n)} u^{(m)} d\tau = \delta_{nm}, \tag{4}$$

we can expand the ψ function (q-number) in the series

$$\psi = \sum_n a_n u_\varrho^{(n)} \tag{5}$$

with the a's obeying the commutation relations (2)

$$[\bar{a}_n a_m]_+ = \delta_{nm}. \tag{6}$$

The total integral Hamiltonian of the electron field becomes thus

$$H_{el} = \int H_{el} d\tau = \sum_n \bar{a}_n a_n E^{(e)}_n = \sum_n N^{(e)}_n E^{(e)}_n, \quad N^{(e)}_n = \bar{a}_n a_n. \tag{7}$$

We must further remember that the application of the a_n or ψ operations to the state function means annihilation and the application of $\bar{a}_n$ or $\bar{\psi}$ — creation of electrons.

The operators $N^{(e)}_n$ describe the number of electrons occupying the n-th state with the eigenvalues 0 and 1.

When dealing with hole-theory it is also convenient to introduce the operators

$$a_n \bar{a}_n = N^{(p)}_n = 1 - N^{(e)}_n \quad \text{for} \quad E^{(e)}_n < 0, \tag{9}$$

i. e. for the states of negative energy accounting for the number of positrons, the energy of these positrons being

$$E^{(p)}_n = -E^{(e)}_n. \tag{10}$$

(b) Neutrino field

All the neutrino field quantities obey the same equations as the quantities of the electron field, the only difference being that we must put $m=0$ and $e=0$.

We shall use the following notations for the neutrino field quantities

φ	for the neutrino field, instead of	ψ	for the electron field,
b_ν	” ” ” ” ” ”	a_n	” ” ” ”
v_ν	” ” ” ” ” ”	u_n	” ” ” ”
$E^{(n)}_\nu$	” ” ” ” ” ”	$E^{(e)}_n$	” ” ” ”
$E^{(a)}_\nu$	” ” ” ” ” ”	$E^{(p)}_n$	” ” ” ”
$N^{(n)}_\nu$	” ” ” ” ” ”	$N^{(e)}_n$	” ” ” ”
$N^{(a)}_\nu$	” ” ” ” ” ”	$N^{(p)}_n$	” ” ” ”

Thus, instead of (7) we get

$$H_{\text{ntno}} = \int \mathcal{H}_{\text{ntno}} d\tau = \sum_\nu \bar{b}_\nu b_\nu E_\nu^{(n)} = \sum_\nu N_\nu^{(n)} E_\nu^{(n)} . \tag{11}$$

We shall deal here consistently with the convention that in processes like the K-capture electron and antineutrino or positron and neutrino are always created and annihilated together. Therefore, only $\bar{\varphi}\psi$- or $\bar{\psi}\varphi$-like products will appear in the interaction term.

(c) Proton and neutron fields

All that has been said about the electron field is also valid, in principle at least, for the proton and neutron fields, only the wave equations (analogous to (3)) can be more complicated owing to the forces of non electromagnetic origin.

We introduce the following notations

Ψ for proton field, Φ for neutron field, instead of ψ for electron field,
B_μ " " " A_m " " " " " a_n " " "
V_μ " " " U_m " " " " " u_n " " "
$N_\mu^{(P)}$ " " " $N_m^{(N)}$ " " " " " $N_n^{(e)}$ " " "
$E_\mu^{(P)}$ " " " $E_m^{(N)}$ " " " " " $E_n^{(e)}$ " " "

Then we have, instead of (3),

for protons $$H_{\text{pr}} = \int \mathcal{H}_{\text{pr}} d\tau = \sum_\mu \bar{B}_\mu B_\mu E_\mu^{(P)} = \sum_\mu N_\mu^{(P)} E_\mu^{(P)} \tag{12}$$

and for neutrons $$H_{\text{neutr}} = \int \mathcal{H}_{\text{neutr}} d\tau = \sum_m \bar{A}_m A_m E_m^{(N)} = \sum_m N_m^{(N)} E_m^{(N)} . \tag{13}$$

(d) Meson field

The meson field we shall deal with here is a certain combination of the charged vector and pseudosclalar fields. We shall start first with the Møller-Rosenfeld combination, enabling us to perform the calculations for the vector and the pseudoscalar parts of the field until a certain point in a uniform way, owing to the formal invariance of the equations against five dimensional rotations. To get the other combinations after the vector pseudoscalar parts have been separated means simply to ascribe different coupling constants to their interaction terms with the other fields. The equations of the Møller-Rosenfeld field are *(4)*

$$G_{\mu\nu}=\frac{\partial\chi_\nu}{\partial x_\mu}-\frac{\partial\chi_\mu}{\partial x_\nu}+S_{\mu\nu};\quad S_{\mu\nu}=-S_{\nu\mu}, \tag{14}$$

$$\sum_{\nu=0}^{4}\frac{\partial G_{\mu\nu}}{\partial x_\nu}+\mu^2\chi_\mu=M_\mu,\ (\mu,\nu=0,1,2,3,4) \tag{15}$$

$$\sum_{\nu=0}^{4}\frac{\partial\chi_\nu}{\partial x_\nu}=0. \tag{16}$$

We can get the equations (14) and (15) together with their conjugates from the following differential Lagrangian

$$L=-\tfrac{1}{2}\sum_{\mu=0}^{4}\sum_{\nu=0}^{4}G^\dagger_{\mu\nu}G_{\mu\nu}-\mu^2\sum_{\mu=0}^{4}\sum_{\mu=0}^{4}\chi^\dagger_\mu\chi_\mu+\sum_{\mu=0}^{4}\chi^\dagger_\mu M_\mu+\sum_{\mu=0}^{4}\chi_\mu M^\dagger_\mu. \tag{17}$$

To have the terms needed in our problem we must put *(5)*

$$\begin{gathered}M_\mu=g_1\psi^\dagger\gamma^{(\mu)}\varphi+g_1'\Phi^\dagger\gamma^{(\mu)}\Psi,\\ S_{\mu\nu}=\frac{g_2}{2\mu}\psi^\dagger[\gamma^{(\mu)}\gamma^{(\nu)}]_-\varphi+\frac{g_2'}{2\mu}\Phi^\dagger[\gamma^{(\mu)}\gamma^{(\nu)}]_-\Psi.\quad(\mu,\nu=0,1,2,3,4)\end{gathered} \tag{18}$$

the g's being the coupling constants. Quantities with the „†"-sign are defined as follows:

$$\psi^\dagger=i\overline{\varphi}\gamma^{(4)}=i\overline{\alpha}\beta\quad\text{(the same for }\varphi,\Phi,\Psi),$$

$$G^\dagger_{\mu\nu}=\overline{G}_{\mu\nu},\quad S^\dagger_{\mu\nu}=\overline{S}_{\mu\nu},\quad M^\dagger_\mu=M_\mu,\quad \chi^\dagger_\mu=\chi_\mu\quad(\mu,\nu=0,1,2,3), \tag{19}$$

$$G^\dagger_{\mu4}=-G_{\mu4},\quad S^\dagger_{\mu\nu}=-\overline{S}_{\mu4},\quad M^\dagger_4=-\overline{M}_4,\quad \chi^\dagger_4=-\chi_4. \tag{20}$$

The well-known relations between the γ's and the Dirac α and β operators are

$$\gamma^{(\nu)}=-i\beta\alpha_\nu\ (\nu=1,2,3);\quad \gamma^{(4)}=\beta,\quad \gamma^{(0)}=\gamma^{(1)}\gamma^{(2)}\gamma^{(3)}\gamma^{(4)}=i\alpha_1\alpha_2\alpha_3. \tag{21}$$

In order to split the field into its vector and pseudoscalar parts it is sufficient to observe that the fifth coordinate x_0 was introduced from a purely formal point of view, i. e. all field quantities are independent of it. In this way we get instead of (14), (15) and (16) two independent systems of equations:

$$\begin{gathered}\sum_{\nu=1}^{4}\frac{\partial G_{\mu\nu}}{\partial x_\nu}+\mu^2\chi^\dagger_\mu=M^\dagger_\mu,\quad \sum_{\nu=1}^{4}\frac{\partial\chi_\nu}{\partial x_\nu}=0,\\ G_{\mu\nu}=\frac{\partial\chi_\nu}{\partial x_\mu}-\frac{\partial\chi_\mu}{\partial x_\nu}+S_{\mu\nu}\quad(\mu,\nu=1,2,3,4)\end{gathered} \tag{22}$$

and
$$\sum_{\nu=1}^{4}\frac{\partial G_{0\nu}}{\partial x_\nu}+\mu^2\chi_0=M_0,\quad G_{0\nu}=-\frac{\partial\chi_0}{\partial x_\nu}+S_{0\nu}\quad(\nu=1,2,3,4), \tag{23}$$

the eqs. (22) describing the vector *(3)*, and (23) the pseudoscalar part of the field. According to the remark made before it is sufficient to change the g's in (18) into $S_{0\nu}$ and M_0 to get other combinations of these field than the Møller-Rosenfeld mixture.

Introducing the canonical variables π_μ by means of the Lagrangian (17)

$$\pi_\mu = \frac{\partial L}{\partial \dot{\chi}_\mu} = -\frac{1}{ic} G^\dagger_{4\mu}, \quad \pi^\dagger_\mu = \frac{\partial L}{\partial \dot{\chi}^\dagger_\mu} = -\frac{1}{ic} G_{4\mu}, \quad (\mu = 0,1,2,3,4) \tag{24}$$

from which it follows that

$$\pi_4 = \pi^\dagger_4 = 0, \quad \pi^\dagger_\nu = \bar{\pi}_\nu, \ (\nu = 0,1,2,3) \tag{25}$$

and eliminating χ_4 and $\chi^\dagger_4$ as having vanishing dynamical conjugates with the help of the equations (15) and (24), as follows:

$$\chi_4 = \frac{1}{\mu^2} M_4 + \frac{ic}{\mu^2} \sum_{\nu=1}^{3} \frac{\partial \pi^\dagger_\nu}{\partial x_\nu}, \quad \chi^\dagger_4 = \frac{1}{\mu^2} M^\dagger_4 + \frac{ic}{\mu^2} \sum_{\nu=1}^{3} \frac{\partial \pi_\nu}{\partial x_\nu} \tag{26}$$

we get the differential Hamiltonian of the meson field and the interaction in the form

$$\boldsymbol{H}_{\text{mez}} = \boldsymbol{H}^{(0)}_{\text{vect}} + \boldsymbol{H}^{(0)}_{\text{ps}} + \boldsymbol{H}'_{\text{vect}} + \boldsymbol{H}'_{\text{ps}}. \tag{27}$$

These four terms correspond to the vector and pseudoscalar parts of the field and to the interaction of the vector and pseudoscalar parts with other fields respectively, and are

$$\boldsymbol{H}^{(0)}_{\text{vect}} = \text{rot}\ \vec{\bar{\chi}} \cdot \text{rot}\ \vec{\bar{\chi}} + c^2(\vec{\bar{\pi}}, \vec{\pi}) + \frac{c^2}{\mu^2} \text{div}\ \vec{\bar{\pi}} \cdot \text{div}\ \vec{\pi} + \mu^2 \vec{\bar{\chi}}, \vec{\chi}, \tag{28}$$

$$\boldsymbol{H}^{(0)}_{\text{ps}} = \text{grad}\ \bar{\chi}_0 \cdot \text{grad}\ \chi_0 + c^2 \pi_0 + \mu^3 \bar{\chi}_0 \chi_0, \tag{29}$$

$$\begin{aligned} \boldsymbol{H}_{\text{vect}} = \vec{\bar{S}}_1\, \text{rot}\ \vec{\chi} + \vec{S}_1\, \text{rot}\ \vec{\bar{\chi}} + \vec{\bar{S}}_1 \vec{S} - \frac{ic}{\mu^2} M_4\, \text{div}\ \vec{\pi} + \frac{ic}{\mu^2} \bar{M}_4\, \text{div}\ \vec{\bar{\pi}} + \frac{1}{\mu^2} \bar{M}_4 M_4 \\ - \vec{\bar{\chi}}, \vec{M} - \vec{\chi} \vec{\bar{M}} - ic \vec{\pi}, \vec{S}_{4\cdot} + ic \vec{\pi} \vec{S}_{\cdot 0}, \end{aligned} \tag{30}$$

$$\begin{aligned} \boldsymbol{H}'_{\text{ps}} = \vec{\bar{S}}_{\cdot 0}, \text{grad}\ \chi_0 + \vec{S}_{\cdot 0}, \text{grad}\ \bar{\chi}_0 + \vec{\bar{S}}_{\cdot 0} \vec{S}_{\cdot 0} \\ - \bar{\chi}_0 M_0 - \chi_0 \bar{M}_0 - ic \bar{\pi}_0 \bar{S}_{40} + ic \pi_0 S_{40}. \end{aligned} \tag{31}$$

Ordinary threedimensional notations have been used in these formulas, the threedimensional vectors occuring there, having the components:

$$\begin{gathered} \vec{\chi} = (\chi_1, \chi_2, \chi_3), \quad \vec{\pi} = (\pi_1, \pi_2, \pi_3), \quad \vec{M} = (M_1, M_2, M_3) \\ \vec{S} = (S_{23}, S_{31}, S_{12}), \quad \vec{S}_{4\cdot} = (S_{41}, S_{42}, S_{43}), \quad \vec{S}_{\cdot 0} = (S_{10}, S_{20}, S_{30}). \end{gathered} \tag{32}$$

Finally, to quantize the Hamiltonian according to Bose statistics, we postulate the usual commutation relations:

$$[\pi(x), \chi_\mu(x')]_- = [\bar{\pi}(x), \bar{\chi}_\mu(x')]_- = -it_1\,\delta_{\mu\nu}\,\delta(x-x') \qquad (33)$$

all other pairs of meson field quantities commuting.

(d) Total Hamiltonian

In order to get the total Hamiltonian of all the fields, we must add the integral hamiltonians of these fields and those of the interaction terms (space integrals of eqs. (30) and (31)) and — strictly speaking — the terms due to electromagnetic interactions also (the one, at least, which corresponds to the interaction between protons and electrons). But, as we shall see later, we need only know the form of the zero Hamiltonian for the meson field and the „meson" interaction terms given by the equations (28), (29), (30) and (31).

Canonical transformation of the Hamiltonian

The „source" quantities in the interaction terms (30) and (31) of the meson field Hamiltonian can be divided into two groups with respect to their magnitude in the case of slow „source" particles (electrons, protons, etc.). Namely, there are quantities as $\vec{M}$, M_0, $\vec{S}_{4\cdot}$, S_{40} the expectation values of which vanish for slow particles with vanishing velocity, and others as M_4, $\vec{S}$, $\vec{S}_{\cdot 0}$ with non-vanishing expectation values.

As we shall limit ourselves to nonrelativistic velocities for protons and neutrons contained in the nucleus (and even for the electrons in the K-shell), we can eliminate, in this approximation, the meson quantities $\vec{\chi}$, χ_0, $\vec{\pi}$, π_0 from the interaction terms by a procedure equivalent to the introduction of the static Yukawa potential instead of them. We can do this by means of a suitable canonical transformation of the Hamiltonian. We proceed as follows: first of all, we divide the sum of $\boldsymbol{H}'_{\text{vect}}$ and $\boldsymbol{H}'_{\text{ps}}$ into three parts:

the „big" one

$$\begin{aligned} \boldsymbol{H}^{(1)} = \bar{\vec{S}} \operatorname{rot} \vec{\chi} + \vec{S} \operatorname{rot} \bar{\vec{\chi}} - \frac{ic}{\mu^2} M_4 \operatorname{div} \vec{\pi} + \frac{ic}{\mu^2} \bar{M}_4 \operatorname{div} \bar{\vec{\pi}} \\ + \bar{\vec{S}}_{\cdot 0}, \operatorname{grad} \chi_0 + \vec{S}_{\cdot 0}, \operatorname{grad} \bar{\chi}_0, \end{aligned} \qquad (34)$$

the „small“ one

$$H^{(2)}=-\overline{\vec{\chi}}\vec{M}-\vec{\chi}\overline{\vec{M}}-ic\overline{\vec{\pi}}\overline{\vec{S}}_{4\cdot}+ic\vec{\pi}\vec{S}_{4\cdot}-\overline{\chi}_0M_0-\chi_0\overline{M}_0-ic\overline{\pi}_0\overline{S}_{40}+ic\pi_0S_{40} \tag{35}$$

and finally

$$H'=\overline{\vec{S}}\vec{S}+\frac{1}{\mu^2}\overline{M}_4M_4+\overline{\vec{S}}_{\cdot 0}\vec{S}_{\cdot 0}, \tag{36}$$

the last one not containing meson field quantities at all. We write down the transformation matrix in the form e^{iK} and have for every operator Q

$$\widetilde{Q}=e^{iK}Qe^{-iK}, \tag{37}$$

where $\widetilde{Q}$ means the operator in the „new“ coordinates. We have thus

$$\begin{aligned}\widetilde{H}_{\text{mez}}&=e^{iK}(H^{(0)}_{\text{vect}}+H^{(0)}_{\text{ps}}+H'_{\text{vect}}+H'_{\text{ps}})e^{-iK}=\\&=(1+iK-\tfrac{1}{2}K^2+\dots)(H^{(0)}_{\text{vect}}+H^{(0)}_{\text{ps}}+H^{(1)}+H^{(2)}+H'')\\&\qquad\qquad\times(1-iK-\tfrac{1}{2}K^2+\dots)=\\&=H^{(0)}_{\text{vect}}+H^{(0)}_{\text{ps}}+i[K,H^{(0)}_{\text{vect}}+H^{(0)}_{\text{ps}}]_-+H^{(1)}+i[K,H^{(1)}]_-\\&\qquad\qquad-\tfrac{1}{2}[K,[K,H^{(0)}_{\text{vect}}+H^{(0)}_{\text{ps}}]_-]_-+H''+\dots\end{aligned} \tag{38}$$

If we choose now K to satisfy

$$[K,H^{(0)}_{\text{vect}}+H^{(0)}_{\text{ps}}]_-=iH^{(1)}, \tag{39}$$

we get

$$\widetilde{H}_{\text{mez}}=H^{(0)}_{\text{vect}}+H^{(0)}_{\text{ps}}+\frac{i}{2}[K,H^{(1)}]_-+H''. \tag{40}$$

Now, introducing the Yukawa potential function *(7)*

$$V(r)=\frac{1}{4\pi}\,\frac{e^{-\mu r}}{r} \tag{41}$$

which satisfies the „static“ meson field equation

$$\{\Delta-\mu^2\}V(r)=0 \quad \text{for} \quad r\neq 0 \tag{42}$$

and remembering the formula

$$\int V(r)\,\{\Delta-\mu^2\}\varphi(r)\,d\tau=\int V(r)\{\Delta-\mu^2\}\varphi-\varphi\{\Delta-\mu^2\}V(r)]\,d\tau=-\varphi(0) \tag{43}$$

valid for arbitrary functions φ, we get for K satisfying (39) the expression

$$\begin{aligned}K=\frac{1}{\hbar}\int\!\!\int V(x-x')\Big\{&\frac{i}{c}\,\overline{M}_4(x)\,\text{div}'\,\vec{\chi}(x)-\frac{i}{c}\,M_4(x)\,\text{div}'\,\overline{\vec{\chi}}(x')\\&-\vec{S}(x)\,\text{rot}'\,\vec{\pi}(x)-\overline{\vec{S}}(x)\,\text{rot}\,\overline{\vec{\pi}}(x)\\&-\overline{\vec{S}}_{\cdot 0}(x)\,\text{grad}'\,\overline{\pi}_0(x)-\vec{S}_{\cdot 0}(x)\,\text{grad}'\,\overline{\pi}_0(x)\Big\}\,d\tau\,d\tau'.\end{aligned} \tag{44}$$

To verify it, we must use the commutation relations (33) and the formula (43). In order to show how the calculation runs, we shall calculate for instance the following commutator

$$\begin{aligned}&\left[\int\!\!\int \overline{M}_4(x)V(x-x')\,\mathrm{div}'\,\vec{\chi}(x')\,d\tau d\tau', H^{(0)}_{\mathrm{vect}}\right]_-\\ &=c^2\left[\int\!\!\int \overline{M}_4(x)V(x-x')\,\mathrm{div}'\,\vec{\chi}(x')\,d\tau d\tau', \int \overline{\vec{\pi}}(x''),\vec{\pi}(x'')\,d\tau''\right]_-\\ &+\frac{c^2}{\mu^2}\left[\int\!\!\int \overline{M}_4(x)V(x-x')\,\mathrm{div}'\,\vec{\chi}(x')\,d\tau d\tau', \int \mathrm{div}''\,\overline{\vec{\pi}}(x'')\,\mathrm{div}''\,\vec{\pi}(x'')\,d\tau''\right]_-.\end{aligned} \tag{45}$$

Taking into account the commutation relations (33) and performing some partial integrations, we have

$$\begin{aligned}&\left[\int\!\!\int \overline{M}_4(x)V(x-x')\,\mathrm{div}'\,\vec{\chi}(x')\,d\tau\,d\tau', \int \overline{\vec{\pi}}(x'')\vec{\pi}(x'')\,d\tau''\right]_- =\\ &=i\hbar\int\!\!\int\!\!\int \overline{M}(x)V(x-x')\overline{\vec{\pi}}(x'')\,\nabla'\delta(x-x'')\,d\tau\,d\tau' d\tau'' =\\ &=i\hbar\int\!\!\int \overline{M}_4(x)V(x-x')\,\mathrm{div}'\,\overline{\vec{\pi}}(x')\,d\tau\,d\tau',\end{aligned} \tag{46}$$

similarly

$$\begin{aligned}&\left[\int\!\!\int \overline{M}_4(x)V(x-x')\,\mathrm{div}'\,\vec{\chi}(x')\,d\tau\,d\tau', \int \mathrm{div}''\,\overline{\vec{\pi}}(x'')\,\mathrm{div}''\,\vec{\pi}(x'')\,d\tau''\right]_- =\\ &=-i\hbar\int\!\!\int V(x-x')\,\Delta'\{\overline{M}_4(x)\,\mathrm{div}'\,\overline{\vec{\pi}}(x')\}\,d\tau d\tau',\end{aligned} \tag{47}$$

and finally, with the help of (43),

$$\begin{aligned}&\left[\int\!\!\int \overline{M}_4(x)V(x-x')\,\mathrm{div}'\,\vec{\chi}(x')\,d\tau\,d\tau', H^{(0)}_{\mathrm{vect}}\right]_-\\ &=-\frac{i\hbar c^2}{\mu^2}\int\!\!\int V(x-x')\,\{\Delta'-\mu^2\}\,\{\overline{M}(x)\,\mathrm{div}'\,\overline{\vec{\pi}}(x'')\}\,d\tau d\tau'\\ &=\frac{i\hbar c^2}{\mu^2}\int \overline{M}(x)\,\mathrm{div}\,\overline{\vec{\pi}}(x')\,d\tau,\end{aligned} \tag{48}$$

where the Yukawa potential has disappeared. Calculations with other commutators are similar. While performing the partial integrations mentioned above, we must pay special attention never to introduce second derivatives of V into volume integrals or first derivatives into surface integrals.

The only term we have to calculate in our problem is now

$$H=\frac{i}{2}[K,H^{(1)}]_- + H'', \tag{49}$$

this being valid also if we perform the transformation taking into account other parts of the total Hamiltonian corresponding to other fields. Indeed, we can easily verify that the commutators of K with the zero Hamiltonians of those fields (electron, neutrino, proton and neutron fields) and the electrostatical interaction terms between them, have their zero matrix element corresponding to the K-capture process. The other terms, for which this element does not vanish, are either small for non-relativistic velocities of the particles, or can be neglected because of their being proportional to higher powers of the coupling constants.

After somewhat lengthy calculations, but proceeding along the same lines as in the example given above, we get

$$\begin{aligned}[K,H^{(1)}] = \int\!\!\int V(x-x')\Delta'\Big\{ & -\frac{i}{\mu^2}\overline{M}_4(x)\,M_4(x') - \frac{i}{\mu^2}M_4(x)\overline{M}_4(x') \\ & - i\overline{\vec{S}}_{\cdot 0}(x)\vec{S}_{\cdot 0}(x') - i\vec{S}_{\cdot 0}(x)\overline{\vec{S}}_{\cdot 0}(x') - i\vec{S}(x)\overline{\vec{S}}(x') - i\overline{\vec{S}}(x)\vec{S}(x')\Big\}d\tau d\tau' \\ & -2i\int\!\!\int \vec{S}(x)\ \mathrm{div}'\ \overline{\vec{S}}(x')\,\nabla' V(x-x')\,d\tau d\tau' \\ & +2i\int\!\!\int \vec{S}_{\cdot 0}(x)\{\nabla' V(x-x')\times \mathrm{rot}'\ \overline{\vec{S}}_{\cdot 0}(x')\}\,d\tau d\tau' + (\ldots).\end{aligned} \tag{50}$$

Finally, owing to the eqs. (36), (43) and (49), we get

$$\begin{aligned}H = \int\!\!\int V(x-x')\{\overline{M}_4(x)M_4(x') + \mu^2\overline{\vec{S}}_{\cdot 0}(x)\vec{S}_{\cdot 0}(x') + \mu^2\overline{\vec{S}}(x)\vec{S}(x')\}\,d\tau d\tau' \\ + \int\!\!\int \vec{S}(x)\ \mathrm{div}'\ \overline{\vec{S}}(x')\,\nabla' V(x-x')\,d\tau d\tau' \\ - \int\!\!\int \vec{S}_{\cdot 0}(x),\{\nabla\ V(x-x')\times \mathrm{rot}'\ \overline{\vec{S}}_{\cdot 0}(x')\}\,d\tau d\tau' + (\ldots),\end{aligned} \tag{51}$$

where the terms marked (...) appear due to non-commutativity of the „source" quantities (as a consequence of the anticommutation rules of the form (2)), but have no matrix elements corresponding to our problem. It is convenient to express the quantities M_4, S, $S_{\cdot 0}$ with the help of Dirac's ϱ and σ matrices, getting thus

$$\begin{aligned}M_4 = g_1 i\overline{\psi}\varphi + g_1' i\overline{\Phi}\Psi, \quad \vec{S} = -\frac{g_2}{\mu}\overline{\psi}\varrho_3\vec{\sigma}\varphi - \frac{g_2'}{\mu}\overline{\Phi}\varrho_3\vec{\sigma}\Psi \\ \vec{S}_{\cdot 0} = -\frac{g_2}{\mu}\overline{\psi}\vec{\sigma}\varphi - \frac{g_2'}{\mu}\overline{\Phi}\vec{\sigma}\Psi\end{aligned} \tag{52}$$

where

$$\vec{\sigma} = -i\alpha_1\alpha_2\alpha_3\vec{\alpha}; \quad \varrho_3 = \beta. \tag{53}$$

We must bear in mind that we may also change the coupling constants g_2, g_2' for $S_{\cdot 0}$ in order to get a more general field than the Møller-Rosenfeld mixture.

The transition matrix element

The matrix element H corresponding to the K-capture process is easily seen to be

$$
\begin{aligned}
H_K = & \iint V(x-x')\,\{g_1 g_1' \overline{U}(x) V(x)\, \overline{v}(x') u(x') \\
& + g_2 g_2' (\overline{U}(x) \vec{\sigma} V(x), \overline{v}(x') \vec{\sigma} u(x') + \overline{U}(x)\, \varrho_3 \vec{\sigma} V(x), \overline{v}(x') \varrho_3 \vec{\sigma} u(x'))\} d\tau d\tau' \\
& + \frac{1}{\mu^2} \iint g_2 g_2' \overline{U}(x)\, \varrho_3 \vec{\sigma} V(x) \operatorname{div}' \{\overline{v}(x')\, \varrho_3 \vec{\sigma} u(x')\}\, \nabla' V(x-x')\, d\tau d\tau' \\
& - \frac{1}{\mu^2} \iint g_2 g_2' \overline{U}(x) \vec{\sigma} V(x), (\nabla' V(x-x') \times \operatorname{rot}' \{\overline{v}(x') \vec{\sigma} u(x')\})\, d\tau d\tau'.
\end{aligned}
\tag{54}
$$

The functions u and v describe the neutron and proton states, respectively, the latter superseding the former in our process, u is the electron function in the K-shell, v that of the neutrino plane wave. In our further calculations we shall neglect the last two terms in (54). We can do this — as shown in the appendix — by assuming the ratio of the nuclear radius a (being defined, e. g., as the mean extension of the u and v functions) and the range of nuclear forces $1/\mu$ to be great in comparison with the fine structure constant multiplied by the atomic number:

$$Z\alpha \ll a\mu. \tag{55}$$

It might also be shown that when dealing with these terms one would be forced to make special assumptions about the behaviour of the electron function inside of the nucleus which we shall avoid.

On the other hand, in order to be able to perform the further calculation without special knowledge about the behaviour of the u and v functions, we must assume the range of the meson forces $1/\mu$ to be great in comparison to the nuclear radius a, so that we must complete the inequality (55) to

$$Z\alpha \ll a\mu \ll 1. \tag{56}$$

If the last condition can be fulfilled we may write

$$H_K = \int V(r)\{g_1 g_1' (\widetilde{1})\, \overline{v}(x) u(x) + g_2 g_2' ((\widetilde{\varrho_3 \vec{\sigma}}), \overline{v}(x) \varrho_3 \sigma u(x) + (\widetilde{\vec{\sigma}}), \overline{v}(x) \sigma u(x))\} d\tau, \tag{57}$$

where the radius vector $\vec{r}$ is to be taken from the electric centre of the nucleus, and

$$(\widetilde{1}) = \int \overline{U}(x) V(x)\, d\tau, \quad (\widetilde{\vec{\sigma}}) = \int \overline{U}(x) \vec{\sigma} V(x)\, d\tau, \quad (\widetilde{\varrho_3 \vec{\sigma}}) = \int \overline{U}(x) \varrho_3 \vec{\sigma} V(x)\, d\tau. \tag{58}$$

For the more general meson field than the Møller-Rosenfeld field we should have

$$H_K=\int V(\vec{r})\{g_1g_1'(\widetilde{1})\bar{v}(x)u(x)+g_2g_2'(\widetilde{\vec{\varrho_3\sigma}}),\bar{v}(x)\varrho_3\vec{\sigma}u(x)+g_3g_3'(\widetilde{\vec{\sigma}}),\bar{v}(x)\vec{\sigma}u(x)\}d\tau. \tag{57'}$$

It is understood also that the approximation (57) or (57′) is valid if the neutrino wave length is great in comparison with the range of the meson forces $1/\mu$, i. e. if the neutrino energy is small in comparison with the meson rest energy.

We must insert now for u the solutions of the Dirac equations for the K-shell, for v the neutrino plane wave, and then average the square of the absolute value of H with respect to:

1) two different orientations of the spins of the electrons in the K-shell,

2) two different orientations of the neutrino spin with respect to its motion,

3) all possible directions of the rejected neutrino,

as the transition probability depends only on this mean value.

The Dirac equation of an electron in the central electrostatic field of the nucleus of charge $-Ze$ is

$$\left\{\left(\frac{E}{c}+\frac{Ze^2}{cr}\right)+i\hbar\vec{\alpha}\nabla-\beta mc\right\}u=0. \tag{59}$$

If we use the customary representation for the α_i and β matrices:

$$\alpha_1=\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix},\quad \alpha_2=\begin{pmatrix}0&0&0&-i\\0&0&i&0\\0&-i&0&0\\i&0&0&0\end{pmatrix},$$
$$\alpha_3=\begin{pmatrix}0&0&1&0\\0&0&0&-1\\1&0&0&0\\0&-1&0&0\end{pmatrix},\quad \beta=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}, \tag{60}$$

we get the following form of the two solutions for the K-electrons

$$\begin{aligned}
u^{(1)}_{1/2}&=f'(r)\frac{1}{\sqrt{4\pi}}, & u^{(1)}_{-1/2}&=0,\\
u^{(2)}_{1/2}&=0, & u^{(2)}_{-1/2}&=f'(r)\frac{1}{\sqrt{4\pi}},\\
u^{(3)}_{1/2}&=f(r)\frac{1}{\sqrt{4\pi}}\cos\vartheta, \qquad \text{or} & u^{(3)}_{-1/2}&=f(r)\frac{1}{\sqrt{4\pi}}\sin\vartheta e^{-i\varphi},\\
u^{(4)}_{1/2}&=f(r)\frac{1}{\sqrt{4\pi}}\sin\vartheta e^{i\varphi}, & u^{(4)}_{-1/2}&=-f(r)\frac{1}{\sqrt{4\pi}}\cos\vartheta.
\end{aligned} \tag{61}$$

These solutions belong to the common lowest energy value

$$E_K = mc^2\sqrt{1-Z^2\alpha^2}, \quad \alpha = e^2/\hbar c \tag{62}$$

and correspond to the two possible orientations of the spin of the electron, so that if we introduce the angular momentum operator

$$\vec{m} = -i\hbar(\vec{r}\times\vec{\nabla}) + \tfrac{1}{2}\hbar\vec{\sigma}, \tag{63}$$

we will have for its z-component:

$$m_z u_{1/2} = \tfrac{1}{2}u_{1/2}, \quad m_z u_{-1/2} = -\tfrac{1}{2}u_{-1/2}. \tag{64}$$

The functions $f(r)$ and $f'(r)$ satisfy the equations

$$\begin{gathered} \left(\frac{E_K}{c} + \hbar\frac{Z\alpha}{r} + mc\right)f + i\hbar\frac{df'}{dr} = 0, \\ \left(\frac{E_K}{c} + \hbar\frac{Z\alpha}{r} - mc\right)f' + i\hbar\left(\frac{df}{dr} + \frac{2}{r}f\right) = 0 \end{gathered} \tag{65}$$

and are

$$\begin{gathered} f = ic\sqrt{1-\sqrt{1-Z^2\alpha^2}}\, r^{\sqrt{1-Z^2\alpha^2}}\, e^{-\frac{mc}{\hbar}Z\alpha r} \\ f' = C\sqrt{1+\sqrt{1-Z^2\alpha^2}}\, r^{\sqrt{1-Z^2\alpha^2}}\, e^{-\frac{mc}{\hbar}Z\alpha r} \end{gathered} \tag{66}$$

with the normalization factor

$$C = \left(2\frac{Z\alpha mc}{\hbar}\right)^{\sqrt{1-Z^2\alpha^2}+1/2} \frac{1}{\sqrt{2\Gamma(2\sqrt{1-Z^2\alpha^2}+1}}. \tag{67}$$

The neutrino function v satisfies the equation

$$\left\{\frac{E^{(n)}}{c} - \vec{\alpha}\vec{p}\right\}v = 0, \quad (\vec{p} = -i\hbar\nabla) \tag{68}$$

the plane wave solution of which is given by

$$v = \frac{\varepsilon}{\sqrt{\Omega}}e^{i\vec{k}\vec{x}}, \tag{69}$$

where Ω is the periodicity volume in which we normalize it, $\vec{k}$ the wave vector, ε the unit spinor satisfying the equations

$$E^{(n)}\varepsilon = \hbar c\vec{\alpha}\vec{k}\varepsilon \quad (70) \qquad \text{or} \qquad E^{(n)}\varepsilon = \hbar c|\vec{k}|(\vec{\alpha},\vec{k}_0)\varepsilon \quad (\bar{\varepsilon}\varepsilon = 1) \quad (70')$$

where $\vec{k}_0$ is the unit vector in the direction of wave propagation. The operator $(\vec{\alpha},\vec{k}_0)$ has two eigenvalues equal to 1, belonging to positive neutrino energy, and two eigenvalues equal to —1, belonging to negative energy. We have thus

$$E^{(n)}_{(+)} = -E^{(a)}_{(-)} = \hbar c|\vec{k}|, \quad E^{(a)}_{(+)} = -E^{(n)}_{(-)} = \hbar c|\vec{k}|, \tag{71}$$

and

$$\varepsilon^{(+)} = (\vec{a}, \vec{k}_0)\,\varepsilon^{(+)}, \quad -\varepsilon^{(-)} = (\vec{a}, \vec{k}_0)\,\varepsilon^{(-)}, \tag{72}$$

where $E^{(n)}$ and $E^{(a)}$ mean the neutrino and antineutrino energies respectively, the subscripts „+“ and „—“ being easily understood to refer to positive and negative energies. It is useful for the sequel to write the eqs. (71) in the form

$$\tfrac{1}{2}\{1 \mp (\vec{a}, \vec{k}_0)\}\,\varepsilon^{(\pm)} = 0, \quad \tfrac{1}{2}\{1 \pm (\vec{a}, \vec{k}_0)\}\varepsilon^{(\pm)} = \varepsilon^{(\pm)}. \tag{72'}$$

Inserting (61) and (69) into (54), we get

$$H_K = \frac{\bar{\varepsilon}}{\sqrt{\Omega}} \}g_1 g_1'(\tilde{1}) + g_2 g_2'(\widetilde{(\varrho_3 \vec{\sigma})}, \varrho_3 \vec{\sigma} + (\tilde{\vec{\sigma}}), \vec{\sigma})\} \int V(r)\, e^{-i \vec{k}\vec{x}}\, u\, d\tau. \tag{73}$$

If, as mentioned above,

$$\mu \gg |\vec{k}|, \quad \text{i. e.} \quad \hbar \mu c \gg E^{(n)}, \tag{74}$$

we can write

$$\int V(r)\, e^{-i \vec{k}\vec{x}}\, u\, d\tau = \frac{1}{4\pi} \int \frac{e^{-\mu r - i \vec{k}\vec{x}}}{r}\, u\, d\tau \simeq \frac{1}{4\pi} \int \frac{e^{-\mu r}}{r}\, u\, d\tau. \tag{75}$$

If we further assume, as may safely be done, that the meson mass is great in comparison with the mass of the electron

$$\hbar \mu c \gg mc^2, \tag{76}$$

we get finally after elementary calculations with the help of eqs. (61), (66), (67)

$$\frac{1}{4\pi} \int \frac{e^{-\mu r}}{r}\, u\, d\tau = N \chi^{(+)} \quad \text{where}$$
$$N = \frac{1}{\sqrt{4\pi\mu}} \sqrt{1 + \sqrt{1 - Z^2\alpha^2}} \left(2 Z \alpha \frac{mc}{\hbar \mu}\right)^{\sqrt{1 - Z^2\alpha^2} + 1/2} \frac{\Gamma(\sqrt{1 - Z^2\alpha^2} + 1)}{\sqrt{2\Gamma(2\sqrt{1 - Z^2\alpha^2} + 1)}} \tag{77}$$

and where (cf. (60))

$$\chi^{(\pm)}_{+1/2} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}; \quad \chi^{(+)}_{-1/2} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{78}$$

are the unit „eigenspinors“ of the β-operator, belonging to the eigen value 1. If we introduce formally the two other „eigenspinors“ of this operator, namely

$$\chi^{(-)}_{+1/2}=\begin{pmatrix}0\\0\\0\\1\end{pmatrix},\quad \chi^{(-)}_{-1/2}=\begin{pmatrix}0\\0\\1\\0\end{pmatrix} \tag{78}$$

we shall have

$$\tfrac{1}{2}(1\mp\varrho_3)\chi^{(\pm)}=0,\quad \tfrac{1}{2}(1\pm\varrho_3)\chi^{(\pm)}=\chi^{(\pm)}, \tag{79}$$

two equations which are similar to (72′).

Instead of (73), we get

$$H_K=\frac{N}{\sqrt{\Omega}}\,\bar{\varepsilon}\{g_1g_1'(\widetilde{1})+g_2g_2'(\widetilde{(\varrho_3\vec{\sigma})},\varrho_3\vec{\sigma}+\widetilde{(\vec{\sigma})},\vec{\sigma}\}\chi^{(+)}. \tag{80}$$

Now, we are able to perform the above mentioned averaging of the square of the absolute value of the expression (80). We denote by

$$Q=\frac{N}{\sqrt{\Omega}}\{g_1g_1'(\widetilde{1})+g_2g_2'(\widetilde{(\varrho_3\vec{\sigma})},\varrho_3\bar{\vec{\sigma}}+\widetilde{(\vec{\sigma})},\vec{\sigma})\} \tag{81}$$

the most important operator in (80), which is of the type of Dirac's α and β operators, and average with respect to the neutrino spin orientations first. This average value is (owing to (72′))

$$\begin{aligned}\tfrac{1}{2}S_{\varepsilon^{(\pm)}}|H_K|^2&=\tfrac{1}{2}S_{\varepsilon^{(\pm)}}(\bar{\chi}^{(+)}Q\varepsilon\cdot\bar{\varepsilon}Q\chi^{(+)})\\&=\tfrac{1}{2}S_{\varepsilon}(\bar{\chi}^{(+)}\bar{Q}\tfrac{1}{2}\{1\pm(\vec{\alpha}\vec{k}_0)\}\varepsilon\cdot\bar{\varepsilon}Q\chi^{(+)})=\tfrac{1}{2}\bar{\chi}^{(+)}Q\tfrac{1}{2}\{1\pm(\vec{\alpha}\vec{k}_0)\}Q\chi^{(+)}\end{aligned} \tag{82}$$

$S_{\varepsilon^{(\pm)}}$ denoting the summation over positive *or* negative energies only, while S_ε over *both* of them (we reserve the summation over $\varepsilon^{(-)}$ for the case of „forced“ K-capture). Now we can easily average over all possible k-directions, by simply dropping out $(\vec{\alpha},\vec{k}_0)$.

Denoting the angular mean value by $\langle\ldots\ldots\rangle$, we get thus

$$\langle\tfrac{1}{2}S_{\varepsilon^{(\pm)}}|H_K|^2\rangle=\tfrac{1}{4}\bar{\chi}^{(+)}\bar{Q}Q\chi^{(+)}. \tag{83}$$

Finally, we perform the summation over both possible orientations of the electron spin in the K-orbit, and get in a similar way as before thanks to (79)

$$|H_K|^2=S_{\chi^{(+)}}\langle\tfrac{1}{2}S_{\varepsilon^{(\pm)}}|H_K|^2\rangle=Tr\{\bar{Q}Q(1+\varrho_3)\} \tag{84}$$

but without the factor $\frac{1}{2}$ before $S_{\chi^{(+)}}$, owing to the fact that there are two electrons on the K-orbit. Inserting the expression (81) and calculating according to well-known rules the „trace“ of the expression $\{\bar{Q}Q(1+\varrho_3)\}$, we get

$$|H_K|^2 = \frac{1}{8\pi\mu\Omega}\{(g_1g_1')^2(\tilde{1})^2 + (g_2g_2')^2|\widetilde{\overrightarrow{(\varrho_3\sigma)}} + \widetilde{\overrightarrow{(\sigma)}}|^2\}\left(2Z\alpha\frac{mc}{\hbar\mu}\right)^{2\sqrt{1-Z^2\alpha^2}+1} \times \frac{\Gamma(\sqrt{1-Z^2\alpha^2}+1)\,\Gamma(\sqrt{1-Z^2\alpha^2}+2)}{2\Gamma(2\sqrt{1-Z^2\alpha^2}+1)}. \tag{85}$$

To deal with more general combinations of the vector and pseudoscalar meson fields we must replace the bracket expression by

$$\{(g_1g_1')^2|(\tilde{1})|^2 + |g_2g_2'\widetilde{\overrightarrow{(\varrho_3\sigma)}} + g_3g_3'\widetilde{\overrightarrow{(\sigma)}}|^2\}. \tag{85'}$$

Transition probabilities

In order to get a suitable survey of the possible phenomena it is convenient to deal shortly with the perturbation method for the case of resonance absorption. The basic equations in our case are *(8)*

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|P\rangle^* &= \sum_I |I\rangle^*\langle I|H|P\rangle \exp\left\{\frac{it}{\hbar}(H_P-H_I)\right\},\\ i\hbar\frac{\partial}{\partial t}|I\rangle^* &= |P\rangle^*\langle P|H|I\rangle \exp\left\{\frac{it}{\hbar}(H_I-H_P)\right\} +\\ &\quad + \sum_{F_I}|F_I\rangle^*\langle F_I|H|I\rangle \exp\left\{\frac{it}{\hbar}(H_I-H_{F_I})\right\},\\ i\hbar\frac{\partial}{\partial t}|F_I\rangle^* &= |I\rangle^*\langle I|H|F_I\rangle \exp\left\{\frac{it}{\hbar}(H_{F_I}-H_I)\right\}, \end{aligned} \tag{86}$$

where we have used Dirac's bracket notation (thus, $\langle\ldots\rangle$ does not mean angular average, as in the preceding section), the suffixes P, I, F_I refer to primary, intermediate, and final states respectively, the sum $\sum_{F_I}$ means summation over all F_I with fixed I.

The $|P\rangle^*$ state corresponds in our case to an atom of atomic number Z with 2 electrons in the K-shell, and to no neutrino in the positive energy range. We may postulate further in this $|P\rangle^*$ state the existence of antineutrino radiation in space, corresponding in the neutrino-hole formalism to some unoccupied states of the neutrino negative energy range. In this way we shall be led to the aforesaid „forced“ K-capture in case of a suitable (negative) energy difference between the initial and the final energy of the atomic system.

The $|I\rangle^*$ states correspond to the atomic system after the K-capture process and one additional neutrino more than in the $|P\rangle^*$ state. We call this state „intermediate" only from a somewhat formal point of view, owing to a possible „reabsorption" of the neutrino („re-emission" of an antineutrino).

The $|F_I\rangle^*$ states correspond to this „reabsorption", with the atomic system back again in the primary configuration. It is necessary to ascribe to these states two indices, F and I, the first indicating the neutrino which has been absorbed, the second the emitted one.

The approximate solutions of the equations (86) for $|P\rangle^*$ and $|I\rangle^*$ are

$$|P\rangle^* = e^{-\frac{\Gamma}{2}t}$$

$$|I\rangle^* = \langle P|H|I\rangle \frac{e^{-\frac{\Gamma}{2}t}\, e^{\frac{it}{\hbar}(H_I - H_P)} - e^{-\frac{r}{2}t}}{H_P - H_I + i\hbar\frac{\gamma - \Gamma}{2}}, \tag{87}$$

where

$$\gamma = \frac{2\pi}{\hbar}\{|\langle I|H|F_I\rangle|^2 \varrho(H_{F_I})\}_{H_{F_I}=H_P}, \tag{88}$$

and where $\varrho(H_{F_I})$ is the final state density per energy interval, while

$$\Gamma = \frac{i}{\hbar}\sum|\langle P|H|I\rangle|^2 \frac{1 - \exp\frac{it}{\hbar}(H_P - H_I + i\hbar\,\tfrac{1}{2}(\gamma - \Gamma))}{H_P - H_I + i\hbar\,\tfrac{1}{2}(\gamma - \Gamma)}, \tag{89}$$

which gives:

(a)
$$\Gamma = \frac{2\pi}{\hbar}\{|\langle P|H|I\rangle|^2 \varrho(H_I)\}_{H_I=H_P}, \tag{89'}$$

where $\varrho(H_I)$ is the density of intermediate states, if the energy conservation condition $H_I = H_P$ demands the emission of a neutrino of positive energy, or if the „width" of the antineutrino line is great in comparison to that given by γ when dealing with negative neutrino energy; or by

(b)
$$R(\Gamma) = \Theta\Gamma_P \frac{|\langle P|H|I\rangle|^2}{(H_P - H_I)^2 + \left(\frac{\hbar\gamma}{2}\right)^2} \tag{89''}$$

if we deal with a very „narrow" antineutrino line,

$$\Theta = \int \varrho(H_I)\,dH_I \tag{90}$$

being the total number of antineutrinos contained in it.

We can now see that:

(1) In the positive energy range of the neutrinos the density of the intermediate $|I\rangle^*$ states is the maximum possible one, owing to Pauli's exclusion principle:

$$\varrho(H_I) = \varrho_P = \frac{\Omega (E^{(n)})^2}{\pi^2 \hbar^3 c^3} = \frac{\Omega k^2}{\pi \hbar c} = \frac{4\Omega}{\hbar c \lambda}, \tag{91'}$$

where Ω is the periodicity volume, whereas the final-state density $\varrho(H_{F_I})$ vanishes:

$$\varrho(H_{F_I}) = 0, \tag{91}$$

corresponding to the fact that only one neutrino can be reabsorbed, namely this one which has been emitted first, and this leads exactly to the restitution of the primary state $|P\rangle^*$ only.

(2) In the negative energy range of the neutrinos the intermediatestate density $\varrho(H_I)$ is determined by the intensity of the assumed antineutrino radiation, so that if we designate by $I(E^{(a)})$ the number of the antineutrinos of energy between $E^{(a)}$ and $E^{(a)} + dE^{(a)}$ passing in unit time perpendicularly through unit area, we will have

$$\varrho(H_I) = \frac{1}{c} \Omega I(H_I). \tag{92}$$

The final state density $\varrho(H_{F_I})$ is now at its maximum, because of the presence of neutrinos occupying the negative states of energy. Thus

$$\varrho(H_{F_I}) = \varrho_P. \tag{92'}$$

In order to know with which of these two cases we have to do, we must realize that

$$H_P - H_I = (E^{(P)} + E_K^{(e)}) - (E^{(N)} + E^{(n)}) \quad \text{or} \quad = (E^{(P)} + E_K^{(e)} + E^{(a)}) - E^{(N)}, \tag{93}$$

where $E_K^{(e)}$ is given by (62). The condition $H_P - H_I = 0$ leads thus to

$$E^{(n)} = -E^{(a)} = (E^{(P)} - E^{(N)}) + E_K^{(e)} = \Delta Q \tag{94}$$

ΔQ meaning the mass difference measured in energy units between the atomic weights of the Z and the $Z-1$ isobars (nucleus + electron shell).

In the following formulas we may insert $|H_K|^2$ from the preceding section instead of $|\langle I|H|F_I\rangle|^2$ and $|\langle P|H|I\rangle|^2$ and introduce an important new quantity, namely the transition probability corresponding to maximum density of states:

$$\Gamma_P = \frac{2\pi}{\hbar} |H_K|^2 \varrho_P = \frac{(E^{(n)})^2}{4\pi^2 \hbar^4 c^3 \mu} \{(g_1 g_1')^2 |(\widetilde{1})|^2 + |g_2 g_2' (\widetilde{\varrho_3 \vec{\sigma}})|^2 + g_3 g_3' (\breve{\vec{\sigma}})|^2\}$$
$$\times \left(2Za \frac{mc}{\hbar \mu}\right)^{2\sqrt{1-Z^2a^2}+1} \frac{\Gamma(\sqrt{1-Z^2a^2}+1)\,\Gamma(\sqrt{1-Z^2a^2}+2)}{2\Gamma(2\sqrt{1-Z^2a^2}+1)}. \tag{95}$$

Thus, we are led to the following conclusions:

(1) „*Spontaneous*“ *K-capture.* In this case we have $\Delta Q > 0$, i. e. the energy of the atom with atomic number Z is greater than that of its isobar of atomic number $Z-1$ in which it is transmuted. It is quite obvious that it is only this that we observe in all the natural K-emitters. As $\Delta Q = E^{(n)}$, we have to do with real emission of the (positive energy) neutrino and may write

$$\gamma = 0, \quad \Gamma = \Gamma_P. \tag{96}$$

The mean lifetime of such a K-emitter is given by

$$t_0 = 1/\Gamma_P. \qquad (97$$

(2) „*Forced*“ *K-capture.* The energy condition would now demand $\Delta Q < 0$, i. e. the isobar $Z-1$ to possess greater energy than that of atomic number Z, and the gap to be filled up by the absorbed antineutrino. We have now

$$\gamma = \Gamma_P, \tag{98}$$

but for Γ we must still distinguish between the two cases of „wide“ and „narrow“ antineutrino lines: (a) „*wide*“ *line*

$$\begin{aligned}\Gamma = \frac{2\pi}{\hbar}|H_K|^2\frac{I(E)\Omega}{c} = \frac{I(E)}{4\hbar\mu c}\{g_1 g_1')^2|(\widetilde{1})|^2 + |g_2 g_2'\widetilde{(\varrho_3\vec{\sigma})} + g_3 g_3'\widetilde{(\vec{\sigma})}|^2\} \\ \times\left(2Z\alpha\frac{mc}{\hbar\mu}\right)^{2\sqrt{1-Z^2\alpha^2}+1}\frac{\Gamma(\sqrt{1-Z^2\alpha^2}+1)\,\Gamma(\sqrt{1-Z^2\alpha^2}+2)}{2\Gamma(2\sqrt{1-Z^2\alpha^2}+1)},\end{aligned} \tag{99}$$

where $I(E)$ is the number of antineutrinos of energy in the interval $(E_1, E+dE)$ passing in unit of time unit of area perpendicular to the direction of their motion. We get as before for the mean lifetime

$$t_0 = 1/\Gamma. \tag{97'}$$

(b) „*narrow*“ *line.* According to (89″), (95) and (98) the transition probability per unit time is

$$R(\Gamma) = \frac{2\Theta}{\pi\hbar\varrho_P}\,\frac{\left(\frac{\hbar\Gamma_P}{2}\right)^2}{(H_P - H_I)^2 + \left(\frac{\hbar\Gamma_P}{2}\right)^2}. \tag{100}$$

Taking into account that the total number of antineutrinos passing in unit time unit perpendicular area is $\Theta c/\Omega$, we get thanks to (91) and (93) the following expression for the total cross-section for a single antineutrino

$$\sigma_K = \frac{\lambda^2}{2\pi} \frac{\left(\frac{\hbar \Gamma_P}{2}\right)^2}{(E^{(a)}+\Delta Q)^2+\left(\frac{\hbar \Gamma_P}{2}\right)^2}, \tag{101}$$

where λ is the wave-length of the antineutrino, and Γ_P is still given by (95).

Discussion of the orders of magnitude *(9)*.

We shall compare first the order of magnitude of the gg'-coefficients, which we get by inserting the known experimental data for several K-emitters into the eqs. (95) and (97), with those given by Yukawa. We assume $(\widetilde{1})$, $\widetilde{(\varrho_3\vec{\sigma})}$, $\widetilde{(\vec{\sigma})}$ to be of order one, but this order can be smaller when the transition is forbidden by nuclear selection rules, so that we may compare the short life K-emitters only and establish the upper limit for the gg'-estimations, as they will be underestimated in general. We must further pay special attention to those short life K-emitters which possess small A's, because, owing to (95) and (97), the mean lifetime should then have the tendency to decrease with increasing Z. While performing these estimations, we assume that the meson mass is 200 times that of the electron.

As a first example we choose the K-reaction

$${}^{7}_{4}Be \xrightarrow[K]{} {}^{7}_{3}Li\,.$$

The half lifetime τ is in this case 53 days, so that the energy difference ΔQ between ${}^{7}_{4}Be$ and ${}^{7}_{3}Li$, as calculated from their mass defects, is

$$t_0 = \tau \ln 2 = 6{,}61 \times 10^6 \text{ s.}$$

and we have for the bracket expression in (95), with sufficient approximation,

$$\{(g_1 g_1')^2|(\widetilde{1})|^2 + |g_2 g_2' \widetilde{(\varrho_3\vec{\sigma})} + g_3 g_3' \widetilde{(\vec{\sigma})}|^2\} \approx \frac{8\pi^2\mu\hbar^4 c^3}{(\Delta\Omega)^2}\,\frac{1}{t_0}\,2\left\{\frac{200}{2\times 4}\times 137\right\}^3$$
$$= (2\pi)^4 \times 8 \times 10^{-51}.$$

The g and g' coefficients estimated by Yukawa are given approximately by

$$\frac{(g/2\pi)^2}{\hbar c} \simeq \frac{1}{10}, \quad g'/2\pi \simeq 4 \times 10^{-17},$$

so that

$$(gg')^2 \simeq (2\pi)^4 \times 5 \times 10^{-51},$$

which gives the same order of magnitude as our estimation. Because ΔQ has not been measured for other K-emitters, we will only give one more example, namely that of the reaction

$${}^{65}_{31}Ga \xrightarrow[K]{} {}^{65}_{30}Zn.$$

In this case we can be sure that $\Delta \leqslant 2mc^2$ as there is no $\overset{+}{\beta}$ radioactivity accompanying the K-capture. The half lifetime τ of ${}^{65}_{31}Ga$ is the shortest one among all „pure“ K-emitters and equals 15 min. Thus

$$t_0 = \tau / ln 2 = 1{,}29 \times 10^3 \text{ s}.$$

If we carry out the estimation in the same way as before, putting simply $\Delta Q = 2mc^2$, we get

$$\{g_1 g_1')^2 |\widetilde{(1)}|^2 + |(g_2 g_2')(\widetilde{\varrho_3 \vec{\sigma}}) + (g_3 g_3')\,(\tilde{\vec{\sigma}})|^2\} \approx (2\pi)^4 \times 27 \times 10^{-51},$$

which gives the same order of magnitude as for ${}^{7}_{4}Be$.

The probability of „forced“ K-capture — if such a K-capture exists — would be in general many orders of magnitude smaller than the probability of „spontaneous“ K-capture.

If the formula (99) applies — this would be the case, e. g., when irradiating a suitable element by the broad spectral line of antineutrinos produced together whith electrons by a $\bar{\beta}$ emitter — the ratio of probabilities of „forced“ and „spontaneous“ K-captures will be of the order of magnitude of the ratio between the radiation density owing to the presence of these emitters to the maximum state density provided by Pauli's principle. We shall estimate the order of magnitude of this ratio in the centre of a sphere of radius R containing the uniformly distributed emitter, which we can choose to be radium C possessing the half lifetime

$$\tau_R = 19{,}5 \text{ min.}, \quad t_R = \tau_R / ln\, 2$$

and the maximum β-ray energy

$$E_{\max} = -3{,}15 \text{ MeV}.$$

After elementary calculations we get for the intensity in the sphere

$$I = \frac{3L}{16\pi^2 t_R E_{\max}} \frac{\nu}{R^2} = 13 \times 10^{21} \frac{\nu}{R} \qquad (R \text{ in cm}),$$

where L is the Loschmidt number and ν the number of gram molecules of *Ra* contained in the sphere. If we calculate now the maximum energy density (91), assuming for instance $E=2mc^2$, we get

$$I_R/I_{\max}=6\times 10^{-23}\,\nu/R^2,$$

where $I_{\max}$ is the radiation density corresponding to the states density ϱ_P.

If we assume two elements — one of which is a natural K-emitter and the other the hypothetical „forced" K-emitter — to have equal $|H_K|^2$ and equal absolute values $|\Delta Q|=2mc^2$ and place ν' moles of the latter in the centre of our sphere, we get for the number of these „forced" K-processes in unit time

$$\frac{1}{t'}L\nu'\frac{I_R}{I_{\max}}=40\times\frac{\nu'\nu}{t'R^2},$$

t' being the mean lifetime of the natural K-emitter.

I wish to express my deepest thanks to Prof. A. Rubinowicz, to whom I owe the idea of this paper, for his suggestions and constant interest during the work.

Appendix.

We have still to discuss the order of magnitude of the last two terms in (54) which we have neglected.

Using the same approximation as in (54) (based on the assumption (55)), we get for these two terms

$$\frac{1}{\mu^2}g_2g_2'\widetilde{(\varrho_3\vec{\sigma})},\int\frac{V_r(r)}{r}\vec{r}\,\mathrm{div}\,\{\bar{v}(r)\varrho_3\vec{\sigma}u(r)\}d\tau$$

and (a)

$$-\frac{1}{\mu^2}g_2g_2'(\widetilde{\vec{\sigma}}),\int\frac{V_r(r)}{r}(\vec{r}\times\mathrm{rot}\,\{\bar{v}(r)\vec{\sigma}u(r)\}d\tau$$

respectively, where $V_r(r)=dV(r)/dr$.

We can easily see that

$$\begin{aligned}\mathrm{div}\,\{\bar{v}(r)\varrho_3\vec{\sigma}u(r)\}&=\bar{v}(r)\varrho_3(\vec{\sigma})\nabla u(r)+\overline{\bar{u}(r)\varrho_3(\vec{\sigma}\nabla)v(r)}=\\&=i\bar{v}(r)\varrho_2\vec{\alpha}\nabla u(r)-i\overline{\bar{u}(r)\varrho_2\vec{\alpha}\nabla v(r)}.\end{aligned}\qquad\text{(b)}$$

Thanks to (56) and (69), this is equal to

$$\bar{v}(r)\varrho_2\left\{\varrho_3\frac{mc}{\hbar}-\frac{E}{\hbar c}-\frac{Z\alpha}{r}\right\}u(r)-\bar{v}(r)\varrho_2(\vec{\alpha}\vec{k})u(r)$$

which, strictly speaking, would even lead to divergent integrals, owing to the term Za/r, if we assumed a too small nuclear radius. In order that the last expression be small, for every r, in comparison with

$$\mu\,\bar{v}(r)u(r) \quad \text{and like terms} \qquad (c)$$

we must put $Za/a \ll \mu$, thus giving us the condition (55).

Performing the integration in (a) shows that when div $\{\bar{v}(r)\varrho_3\sigma u(r)\}$ is small in comparison with the (c) — terms the first term in (a) is small in comparison with the other terms in (54) and can thus be neglected.

In a similar way, we get the same condition (55) when the second term in (a) has to be neglected.

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(4) Møller, Det. Kgl. Dansk. Vidensk. Selsk. Math.-fysiske Medd., XVIII/6, 5 (1941).

(5) Møller, ibid., XVIII/6, 7 (1941).

(6) Wentzel, loc. cit., p. 79, eq. (12.39).

(7) Wentzel, loc. cit., pp. 43, 44.

(8) See e. g. Heitler, *The Quantum Theory of Radiation*, p. 139, eq. (13), (1944).

(9) All nuclear data from J. Mattauch, *Nuclear Physics Tables* (1946).

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A NOTE ON THE INVARIANT FORMULATION OF THE QUANTUM FIELD THEORY

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The Schrödinger equation is written in a relativistically invariant form in the general case where the interaction-energy density is not a scalar. The invariance may be exhibited without introducing a generalization called „infinitely-many-time formalism". The autonomy of the formulation of Tomonaga, i. e., its independence of the Lagrangean and Hamiltonian formalisms, is emphasized.

The famous relativistically invariant formulation of the theory of quantized fields developed by Tomonaga (1946) consists of two decisive steps: (a) The transition to the interaction representation where the field variables obey interaction-free field equations and covariant commutation relations. (b) The rewritting of the Schrödinger equation in an invariant form:

$$i\frac{\delta\Psi[S]}{\delta S_P}=H(P)\Psi[S]. \tag{1}$$

(1) is not yet sufficiently general as it applies only to the case of a scalar Hamiltonian density of interaction. In general, the operator H is not a scalar but may be represented as the four-four component of a tensor $I_{\mu\nu}$. The special case of a scalar H is contained in the more general one if $I_{\mu\nu}$ is of the form $-H\delta_{\mu\nu}$.

An interesting feature of the Tomonaga theory is that it permits to forget the Lagrangean and Hamiltonian formalisms: The field equations and the commutation relations in the interaction representation are sufficiently simple to be regarded as primary concepts. They are understandable by someone who has never heard, e. g., about the canonically conjugated momenta. The tensor $I_{\mu\nu}$ may be postulated (similarly as there was always postulated a Lagrangean) and we are not obliged to remember that its four-four component is identical with (the interaction part of) a Hamiltonian. This statement seems to the author not quite trivial since there exist possibilities of theories which are not derivable from a Hamiltonian formalism but which might be expressed in terms of the Tomonaga formulation[1].

The replacement of the planes $t=$const. by more general space-like surfaces (i. e. the so called infinitely-many-time formalism) has been introduced in order to give the Schrödinger equation an invariant form. However, it is evident that in the frame of the restricted relativity, it is not necessary to use this last generalization in order to write the Schrödinger equation in an invariant form. In the theory of special relativity a space-like plane Σ is also an invariant concept so that we do not need to introduce arbitrary surfaces.

We consider a functional $\Psi[\Sigma]$ and define a „normal derivative of $\Psi[\Sigma]$ in the plane Σ_0". We take a set of planes Σ_l parallel to Σ_0 and form the differential quotient

$$\frac{\Psi[\Sigma_l]-\Psi[\Sigma_0]}{l},$$

where l means the four-dimensional distance between the hyperplanes Σ_l and Σ_0. If the limes exists for $\Sigma_l \to \Sigma_0$ it will be denoted by

$$\frac{d\Psi[\Sigma_0]}{d\Sigma_0}$$

and called „the normal derivative in the plane Σ_0".

Given is a tensor $I_{\mu\nu}$, then we may write the equation

$$i\,\frac{d\Psi[\Sigma]}{d\Sigma}=\int\limits_{\Sigma} d\sigma_\mu I_{\mu\nu} n_\nu \cdot \Psi[\Sigma], \tag{2}$$

where $\int\limits_{\Sigma} d\sigma_\mu$ denotes the surface integral over the plane Σ and n_ν is a unit vector normal to the plane Σ ($n_\nu n_\nu=-1$). For definitness, we may also assume that n_ν points to the future, ($n_0>0$). (2) is an invariant equation since it makes use only of geometrical concepts independent of any special frame of reference.

If the system may be expressed in terms of the Hamiltonian formalism then I_{00} will be identical with the interaction part of a Hamiltonian and (2) will be equivalent to the Schrödinger equation in the interaction representation. To see this, it is sufficient to write (2) in a special Lorentz frame in which the planes $t=$const. are parallel

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[1] As examples of non-Hamiltonian systems we mention the theories where the interaction is cutt off (spread out) by means of integral (Peierls & Mc Manus) or differential operators (J. Rayski, 1947).

to the plane Σ_0. In this system of reference the functional $\Psi[\Sigma]$ may be replaced by a function of t, while the normal derivative becomes the usual derivative with respect to t. Moreover, $n_\mu I_{\mu\nu} n_\nu = I_{00} = H$ so that we get from (2) the traditional Schrödinger equation

$$i\frac{d\Psi(t)}{dt} = \int d^3x H \cdot \Psi(t). \tag{2'}$$

By comparing (2) with (2′) we recognize the double meaning of the variable t in the Schrödinger equation. In $H(xyzt)$ it appears as a space-time variable, while in $\Psi(t)$ it is only a substitute for the four-dimensional distance between two parallel space-like planes.

Of course, the restriction to planes may be as well abandoned. It is easily seen how (2) should be generalized for arbitrary space-like surfaces S:

$$i\frac{\delta\Psi[S]}{\delta S} = n_\mu(P)\, I_{\mu\nu}(P)\, n_\nu(P) \cdot \Psi[S]. \tag{3}$$

In case $I_{\mu\nu} = -H\delta_{\mu\nu}$ the equation (3) becomes the equation (1) of Tomonaga. Let us denote by C that part of $S+\delta S_{P_0}$ which does not overlap S. The points on C will be denoted by P_C. For reasons of consistency it is required that (a) C contracts to the point P_0 $(P_C^\mu - P_0^\mu \rightarrow 0)$ and (b) the angle between any normal to the surface C and the normal $n_\mu(P_0)$ tends to zero: $n_\mu(P_C) - n_\mu(P_0) \rightarrow 0$ for $\delta S \rightarrow 0$. Due to these conditions the variations are weak and the functional derivative $\delta/\delta S_{P_0}$ refers to and only to the properties of the surface S in the vicinity of the point P_0.

A formulation equivalent to our (3) has been given by Matthews (1949) by means of a generalization of the Hamiltonian: $H = n_\mu I_{\mu\nu} n_\nu$.

(2) is a special case of (3), namely, we may replace in (3) the surface S by a plane Σ and, by means of a set of successive local variations δS, we may perform a transition to another plane $\Sigma + d\Sigma$ parallel to Σ. By summing up the local variations we obtain in limes the equation (2)[2].

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[2] By taking (2) as basic equation of the theory, we are released from the condition of integrability which was necessary in case of (3). This is of importance for the formalisms with a spread out interaction — energy density.

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INFLUENCE OF TORSIONAL VIBRATIONS OF LUMINESCENT MOLECULES ON THE FUNDAMENTAL POLARIZATION OF PHOTOLUMINESCENCE OF SOLUTIONS

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The observed values of fundamental polarization are always smaller than those to be expected on the ground of theoretical considerations. This fact can be explained (at least partially) by the influence of torsional vibrations of fluorescent molecules on the rate of polarization of photoluminescence. Some conclusions can be drawn from the difference between theoretical and experimental values of the polarization. This note contains some provisional results of theoretical investigation. A fuller report is intended to be published shortly.

According to Pauling (1930) and Stern (1931) the molecules (and parts of molecules) in many crystals can rotate if the temperature of the crystal is sufficiently high. At low temperatures the molecules carry out small oscillations (torsional vibrations) about their equilibrium orientations. The energy levels and the corresponding eigenfunctions approach in the case of diatomic molecules to those of a two dimensional oscillator. The case of polyatomic molecules (three finite principal moments of inertia) was studied by Mrs W. Hanus (to be published shortly). In the last case the levels and eigenfunctions of the lowest torsional vibration states are very nearly those of a three-dimensional harmonic oscillator. Thus molecules in crystals must possess an amount of torsional vibration energy even in their lowest state („zero point energy").

There is no doubt that similar torsional vibrations are carried out by luminescent molecules in solid (vitreous) or very viscous solutions. These vibrations (and sometimes also some of the normal internal vibrations of molecules) must cause a partial depolarization of photoluminescence. Since this cause persists down to the lowest temperatures (zero point energy!) it cannot be thoroughly eliminated by choosing suitable experimental conditions[1]. Hence, the explanation of the fact

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[1] In contradistinction to the two other thus far known causes, i. e. to the Brownian rotation of luminescent molecules and the transference of the excitation energy from one molecule to another.

that the observed values of the fundamental polarization[2] are always smaller than those to be expected on the ground of theoretical considerations.

A theory of the fundamental polarization for molecules at absolute rest (not executing torsional vibrations) was given by the present writer (1935, 1936). According to it, the fundamental polarization for the case in which the same virtual electronic oscillator is responsible for the absorption as well as for the emission of light is given by[3]

$$P_0 = \frac{3\sum\limits_{i=1}^{3}\Gamma_i^2 - \Big(\sum\limits_{j=1}^{3}\Gamma_j\Big)^2}{\sum\limits_{i=1}^{3}\Gamma_i^2 + 3\Big(\sum\limits_{j=1}^{3}\Gamma_j\Big)^2}, \tag{1}$$

where Γ_j denote the relative principal transition probabilities along the three mutually perpendicular (principal) axes of the virtual electronic oscillator.

From (1) one obtains $P_0 = 1/2$ for a linear oscillator ($\Gamma_1 \neq 0$, $\Gamma_2 = \Gamma_3 = 0$), $P_0 = 1/7$ for a symmetrical flat oscillator ($\Gamma_1 = \Gamma_2 \neq 0$, $\Gamma_3 = 0$) and $P_0 = 0$ for a spherical oscillator ($\Gamma_1 = \Gamma_2 = \Gamma_3 \neq 0$).

Let us now take into consideration the influence of the torsional vibrations of luminescent molecules on the rate of polarization. In this note we restrict ourselves to two simplest cases. Let γ denote the angle of deviation of one of the principal axes from its equilibrium orientation and let the average value of $\cos^2\gamma$ be $\overline{\cos^2\gamma} = 1 - \overline{\sin^2\gamma} = 1 - \varepsilon$. Provided the distribution of γ be axially symmetrical, a linear virtual oscillator becomes (owing to the torsional vibrations) equivalent to an axially symmetrical spatial (three dimensional) oscillator with relative transition probabilities $\Gamma_1 = 1 - \varepsilon$, $\Gamma_2 = \Gamma_3 = \varepsilon/2$ (instead of $\Gamma_1 = 1$, $\Gamma_2 = \Gamma_3 = 0$; the common factor is ommited as irrelevant). Putting these values into (1) we obtain[4]

$$P_0' = \frac{9\varepsilon^2 - 12\varepsilon + 4}{3\varepsilon^2 - 4\varepsilon + 8}. \tag{2}$$

Thus $P_0' < 1/2$ for $\varepsilon > 0$.

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[2] The limiting value of the polarization of luminescence of an isotropic solution observed at right angle to the electric vector of plane polarized primary light when depolarizing factors (footnote (-)) are eliminated.

[3] This formula is given in a different but equivalent form in papers Jabłoński (1935) and (1936).

[4] This formula is equivalent to a formula derived by F. Perrin (1929) for a linear oscillator carrying out quick irregular oscillations about its mean orientation.

For an axially symmetrical flat oscillator the transition probabilities become (provided the distribution of γ for the symmetry axis perpendicular to the plane of the oscillator be axially symmetrical) $\Gamma_3 = \overline{\sin^2 \gamma} = \varepsilon$, $\Gamma_1 = \Gamma_2 = 1 - \frac{\varepsilon}{2}$ (instead of $\Gamma_1 = \Gamma_2 = 1$, $\Gamma_3 = 0$) and hence by means of (1)

$$P''_0 = \frac{9\varepsilon^2 - 12\varepsilon + 4}{3\varepsilon^2 - 4\varepsilon + 28}, \tag{3}$$

which shows that $P''_0 < 1/7$ for $\varepsilon > 0$.

We should like to postpone the publication of more general formulae to a later paper. For the time being we admit an approximate validity of (2) and (3) for particular cases discussed below and draw some conclusions from experimental data published by Perrin (1929) and by Feofilov (1947).

Assuming the virtual oscillator to be linear in the case of fluoresceine and resorufine and using the experimental value $P'_0 = 0{,}44$ of Perrin, we calculate ε by means of (2) We obtain $\varepsilon = 0{,}048$. Provided the whole „polarization deficiency" $P_0 - P'_0 = 0{,}5 - 0{,}44 = 0{,}06$ is due to the torsional vibrations of the above molecules, there results a standard deviation of the direction of the virtual oscillator from its equilibrium orientation equal to 10^0 for fluoresceine and resorufine solutions in glycerine at room temperature.

Using Feofilov's value $P''_0 = 1/14$ for the fluorescence of benzene solution in glycerine and assuming the oscillator in this case to be flat and symmetrical (the transition moment is known to be parallel to the plane of the benzene molecule for the band under consideration), we obtain by means of (3) $\varepsilon = 0{,}2$, which corresponds to a standard deviation of the sixfold symmetry axis of the benzene molecule equal to 26^0. This value seems to be somewhat to large. Possibly there were additional depolarising factors in Feofilov's experiments.

In general the distribution of γ depends on the principal moments o inertia, on intermolecular forces, and on temperature. The polarization deficiency depends apart from the above factors also on the anisotropy of the virtual oscillator and on its orientation with respect to the principal axes of inertia of the fluorescent molecule. Postponing the discussion of the general case to a later paper, we confine ourselves to a rough treatement of a simple case of a flat molecule having an at least threefold symmetry axis and a transition moment lying in the plane of the molecule, i. e. to the fluorescence of the benzene molecule in glycerine solution. In this case two of the three principal moments of inertia are equal. The third moment of inertia is irrelevant. We assume also the two relevant torsional eigenfrequencies to be equal. Then the angular frequency of this vibration is $\omega=\sqrt{\tau/I}$, where τ is the moment of torsion and I the moment of inertia. Assuming the eigenfunctions to be those of a two-dimensional symmetrical harmonic oscillator, we obtain the following formula for the mean square of γ

$$\overline{\gamma^2}=\frac{2\hbar}{I\omega}\left(\frac{1}{e^{\frac{\hbar\omega}{kT}}-1}+\frac{1}{2}\right);$$

for $kI \gg \hbar\omega$

$$\overline{\gamma^2}\approx\frac{\hbar}{I\omega}+\frac{2kT}{I\omega^2}. \tag{4}$$

Since $\varepsilon=\sin^2\gamma$ and $\sin^2\gamma\approx\gamma^2$ for $\gamma\ll 1$, we can easily calculate ω on ground of the values of ε deduced from experiment by means of (3), provided the moment of inertia of the molecule is known. Putting $I=1\cdot 4\cdot 10^{-38} g\cdot\mathrm{cm}^2$ and $T=263^0$ K, we obtain $\tilde{\nu}=\omega/2\pi c=26\ \mathrm{cm}^{-1}$ as order of magnitude of the frequency of torsional vibrations about axes lying in the plane of the benzene molecule for benzene solution in glycerine. Thus the frequency appears to be of the same order of magnitude as that deduced from the Raman spectra produced by torsional vibrations of different molecules in crystals (Rousset, 1947).

As can be easily seen ε does not vanish when the temperature of the luminescent solution tends to 0^0 K. At 0^0 K

$$\varepsilon=\frac{\hbar}{I\omega}=\frac{\hbar}{\sqrt{\tau I}}.$$

It seems probable that the investigation of the fundamental polarization and of its dependence on temperature can provide us in some cases with informations concerning intermolecular forces.

A fuller report is intended to be published shortly.

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THE PHENOMENA OF MOLECULAR ORIENTATION IN POLAR LIQUIDS AND THEIR SOLUTIONS. PART I. EXTENTION OF ONSAGER'S THEORY

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§ 1. The assumptions of Onsager's theory are summarized; the view that all molecules surrounding a given molecule may be considered as a continuous medium is rejected as inadmissible. § 2. Onsager's theory is generalized by treating the nearest molecules in the neighbourhood of the given molecule individually, whereas all those further away are considered as a continuous medium. The Onsager sphere separating the nearest neighbourhood of the molecule from the continuous medium has to be increased in size. § 3. Formula (36) is deduced and by means of this the molecular dipole polarization $P_2^{\rm dip}$ of a given polar substance, pure or dissolved, may be calculated. The ratio of this quantity to $P^{\rm dip}_{\rm gas} = \frac{4\pi N\mu^2}{9kT}$ is called the reduction factor R. The dependence of $P_2^{\rm dip}$ and R on the concentration of nitrobenzene dissolved in benzene is shown graphically (fig. 1). It is evident from Onsager's curves that for greater concentrations a new kind of coupling appears increasing the polarization. It consists probably in the coupling of molecules into ensembles greater than pairs. It is possible that antiparallel pairs are coupled in parallel (fig. 2c). § 4. Formulae (43) and (64) for the modified Kerr constant K^{m*} are deduced and applied to solutions of substances in non-polar solvents. Hence, the molar constant K_2^m of the dissolved substance may be calculated. The results for nitrobenzene are presented graphically (fig. 4). Here also Onsager's curve in contrast to Lorentz's curve rises for greater concentrations which seems to suggest, as in the case of polarization, a multiple coupling. § 5. The increase of the dielectric constant $\Delta\varepsilon$ under the influence of an external electric field is expressed by formula (84). The molar constant S^m of electric saturation is defined in (86). For dipolar substances dissolved in a non-polar solvent they may be determined from formula (85). Experimental data for the same nitrobenzene solutions are illustrated graphically in fig. 5. § 6. In the Cotton-Mouton effect the orientation of molecules is due to an external magnetic field. Owing to the extremely small magnetic permeability of organic liquids the external and the local fields are identical. For this reason Onsager's idea cannot produce any different results in this case. The Cotton-Mouton molar constant C^m as defined by (92) is expressed by (93) and (94). For liquids formula (96), expressing the additivity of the constant C^m, is applied. The molar constant C_2^m for nitrobenzene calculated by means of the latter formula is presented graphically in fig. 6. Its increase with increasing concentration suggests coupling of molecules in aggregates of two or more.

§ 1. The fields of Lorentz and Onsager. When in a dielectric medium there exists an electric field of intensity E, then each molecule is under the action of a field F, which is a little stronger than E, and is called molecular field. This is due to the fact that the field E is *ex definitione* a field acting inside a long and narrow tubular cavity cut in the medium along the lines of forces, while the molecules of this medium are subjected to an additional field due to the surrounding polarized molecules.

Lorentz has calculated the molecular field in a well-known way. He surrounds the molecule under consideration with a sphere from which all other molecules are removed, assuming that this does not alter the field F, nor the distribution of force lines inside the sphere. The field is given by the equation

$$F = E + \frac{4\pi}{3} J, \tag{1}$$

$4\pi J/3$ (J — the electric moment of 1 c. c. of the medium) is the additional field due to the electric charges of the polarized surface of the sphere. Since $J = (\varepsilon - 1)E/4\pi$

$$F = \frac{\varepsilon + 2}{3} E. \tag{1 a}$$

On the other hand $J = N'\alpha F$, where N' is the number of molecules per c. c. of the medium, and α — their polarizability. This leads to the famous Lorentz formula:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N'\alpha. \tag{2}$$

Since $N' = N\dfrac{d}{M}$ (N — Avogadro's number, M — molecular weight, d — density of the medium),

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{4\pi}{3} N\alpha. \tag{2 a}$$

The expression

$$P = \frac{4\pi}{3} N\alpha \tag{2 b}$$

is called molar or molecular polarization.

If the molecules are polar (dipole moment μ) then, according to Debye's theory, we have instead of α the expression

$$\alpha + \frac{\mu^2}{3kT}$$

and for the molar polarization the expression

$$P=\frac{4\pi}{3}N\left(\alpha+\frac{\mu^2}{3kT}\right). \tag{3}$$

The part of polarization due to dipoles

$$P^{\mathrm{dip}}=\frac{4\pi N\mu^2}{9kT} \tag{3 a}$$

is called „dipole polarization".

It is well known that the expression $\frac{\varepsilon-1}{\varepsilon+2}\frac{M}{d}$ for a polar liquid is much smaller than that for the vapour of the same substance at the same temperature. This fact is explained as a result of association or coupling of the molecules. Onsager (1936) tries to explain this fact in a different way. He supposes the existence of a cavity field different from the Lorentz field, and so he obtains for the polarization P a formula which is different from (2a).

Onsager imagines the molecule to be a spherical cavity of radius a equal to the radius of a molecule in a uniform and continuous medium. In the center of this sphere he localises the molecular momemt $\vec{m}$ (permanent plus induced). Inside this sphere there is a rather weak field

$$\vec{G}=\frac{3\varepsilon}{2\varepsilon+1}\vec{E}. \tag{4}$$

The moment $\vec{m}$, inducing on the surface of the sphere an electric charge, forms an additional „reaction field"

$$\vec{R}=\frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{\vec{m}}{a^3}, \tag{5}$$

so that the total internal field is

$$\vec{F}=\vec{G}+\vec{R}. \tag{6}$$

If we consider still that

$$\vec{m}=\alpha\vec{F}+\vec{\mu}, \tag{7}$$

where

$$\alpha=\frac{n_\infty^2-1}{n_\infty^2+2}a^3 \tag{8}$$

(n_∞ — refractive index of the medium for infinite wave-length), then we have cited all Onsager's assumptions leading to his equations.

I do not quote these formulae here, as they will be given in a more general form in the next paragraph. Further, Onsager's formula has a rather inconvenient form which makes it impossible to recognize the role of the parameters G, R and a in the phenomenon of dielectric polarization.

The rather serious defect of Lorentz's theory, namely that it does not take into account the action of the nearest molecules, is not removed by Onsager's theory, which treats the neighbourhood of each given molecule as a continuous medium, a procedure which, according to my opinion, is inadmissible. This is proved by many facts, especially by the behaviour of the electric saturation and the Cotton-Mouton phenomenon in liquids which will be considered in later parts of this work. Therefore, in a generalized Onsager's theory, the author surrounds the molecule under consideration with a larger sphere, containing several of the molecules in the immediate neighbourghood; the molecules outside this sphere are treated in Onsager's way but the few ones inside the sphere keep their individuality; they can be coupled in their own way causing an alteration in the observed phenomena.

§ 2. Foundation of Onsager's extended theory. According to Onsager's theory a polar molecule is placed in the center of a hollow sphere of radius a, equal to the radius of the molecule. This sphere is contained in the medium which is considered to be continuous; its surface is to be „smooth", which seems rather unreasonable if we consider that it is built up of molecules as large as the sphere itself. According to Onsager the given molecule induces charges on the surface of the sphere, producing a „reaction field" R. In consequence of this „smoothness" of the surface, the reaction field does not exert any directing action on the molecule, but only increases its permanent moment by an additional induced moment. We can say that the reaction field merely „stretches" the dipole, without rotating it. The dipole in its rotation would not have any position of minimum potential energy. Such a supposition seems to be very improbable and, as will be seen later, cannot be reconciled with several facts, especially with the behaviour of the Cotton-Mouton molecular constant in liquids.

Generalizing Onsager's theory, I assume that the sphere surrounding the molecule considered has a radius larger than a, and thus several molecules can now be found inside this sphere. If the radius of the sphere grows, the reaction field due to a centrally located molecule becomes weaker. But, since the molecules are distributed throughout the sphere, the average reaction field per molecule will be stronger than that of the central one, and will depend upon the properties of the molecules, and especially upon the position of the moment inside the molecule. In equation (5) there appears a factor k, which can be slightly larger, equal to or smaller than 1; its value will be chosen to satisfy the experimental data. Thus we shall write the equation (5) in the form

$$\vec{R} = r\frac{\vec{m}}{a^3}, \tag{9}$$

where

$$r = k\frac{2(\varepsilon-1)}{2\varepsilon+1}. \tag{9 a}$$

On the other hand formula (4) will remain unchanged. In order to give to the calculations and to the final formulae a clearer form, we shall write the formulae (4) and (8) in the following way

$$\vec{G} = g\vec{E}, \tag{10}$$

where

$$g = \frac{3\varepsilon}{2\varepsilon+1} \tag{10 a}$$

and

$$\alpha = pa^3, \tag{11}$$

where

$$p = \frac{n_\infty^2 - 1}{n_\infty^2 + 2}. \tag{11 a}$$

In the first part of this work we omit purposely the forces that couple together the molecule considered with its nearest neighbours inside Onsager's cavity, as well as the forces that couple it with the discontinuities of its walls. We shall introduce both couplings in the second part of this work. In this paper we deduce some equations disregarding the coupling; when comparing them with experiments we can find some information as to the kind of coupling forces characteristic of the investigated liquid.

According to these assumptions the total field acting on a molecule, expressed by the formula (6), is

$$\vec{F} = g\vec{E} + \frac{r\vec{m}}{a^3}. \tag{12}$$

Thus, using the formula (7), we obtain for the total moment of the molecule the expression

$$\vec{m} = \alpha\vec{F}^* + \vec{\mu}^*, \tag{13}$$

where $\vec{F}^*$ and $\vec{\mu}^*$ differ from $\vec{E}$ and $\vec{\mu}$ only by numerical coefficients, namely

$$\vec{F}^* = \frac{g}{1-rp}\vec{E} \tag{13 a}$$

and

$$\vec{\mu}^* = \frac{1}{1-rp}\vec{\mu}. \tag{13 b}$$

Combining (13) with (12), we obtain a more convenient equation for $\vec{F}$:

$$\vec{F} = \vec{F}^* + \frac{r}{a^3}\vec{\mu}^*. \tag{14}$$

Now we are able to calculate the moment of the forces acting on the dipole[1]

$$\vec{M} = \vec{F} \times \vec{\mu}^*, \tag{15}$$

or

$$M = \mu^* F^* \sin\theta, \tag{15 a}$$

where θ is the angle between the directions $\vec{E}$ and $\vec{\mu}$. Therefore, the potential energy of a dipole $W = \int M d\theta$ will be expressed by the formula

$$W = -\mu^* F^* \cos\theta. \tag{16}$$

§ 3. Dielectric polarization. (a) *Pure liquids.* In order to calculate the polarization, we must know the component of the moment of the molecules in the direction of the external field:

$$m_E = \alpha F^* + \mu^* \cos\theta. \tag{17}$$

The polarization of 1 c. c. of the medium is then

$$J = N'\overline{\overline{m_E}} = N'[\alpha F^* + \mu^* \overline{\overline{\cos\theta}}], \tag{18}$$

where the double line indicates the statistical mean and N' — the number of molecules in 1 c. c. $\overline{\overline{\cos\theta}}$ is to be calculated in the well known way from the Maxwell-Boltzmann theorem:

$$\overline{\overline{\cos\theta}} = \frac{\int\limits_0^\pi \cos\theta\, e^{-W/kT} 2\pi \sin\theta\, d\theta}{\int\limits_0^\pi e^{-W/kT} 2\pi \sin\theta\, d\theta} = L(x) = \frac{1}{3}x - \frac{1}{45}x^3 + \ldots, \tag{19}$$

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[1] Onsager calculates this moment in a different way; he puts namely

$$\vec{M} = \vec{G} \times \vec{m}$$

and obtains different equations. This method is not correct, because the directing field is not $\vec{G}$ but $\vec{F}$, and the dipole, rotating together with the molecule, is not $\vec{m}$ but $\vec{\mu}^*$. We have called attention to these facts with Prof. K. Zakrzewski in Nature (1939, b).

where $L(x)=\coth x-\frac{1}{x}$ is Langevin's function of the variable

$$x=\frac{\mu^{*}F^{*}}{kT}. \tag{19 a}$$

Taking into account only the first term of the development, i. e. neglecting the saturation effect, which appears in very strong fields, we obtain

$$J=N'\left(a+\frac{\mu^{*2}}{3kT}\right)F^{*}. \tag{20}$$

Since $J=(\varepsilon-1)E/4\pi$ we obtain the relation

$$\boxed{\frac{\varepsilon-1}{3g}=\frac{4\pi}{3}N'\left(a+\frac{\mu^{*2}}{3kT}\right)\frac{1}{1-rp}.} \tag{21}$$

If we apply this formula to non-polar liquids ($\mu=0$, $n^2_{\infty}=\varepsilon$) and suppose that $k=1$, we obtain the well-known equation of Lorentz.

For polar gases and vapours, where ε and n^2 are very nearly equal to unity, r and p are very nearly equal to 0 and $g\approx 1$; the equation (21) turns into Debye's formula:

$$\frac{\varepsilon-1}{3}=\frac{4\pi}{3}N'\left(a+\frac{\mu^{2}}{3kT}\right). \tag{22}$$

Thus we see that both theories: of Onsager and Debye (eq. (21)) and of Lorentz and Debye (eq. (22)) lead to identical results for gases and vapours. Both theories agree therefore upon the point that the moment determined by the method of measuring the dielectric constant of gas or vapour is the „real" moment of the molecule.

On the other hand, if we apply the Lorentz-Debye equation to dipole liquids we obtain generally a smaller value for μ. This diminution is attributed to association or coupling. Onsager's theory, however, suggests that it can also be applied to liquids without any further restrictions, and that equation (21), applied to liquids, should also give the real value of the dipole moment of the molecule. Prof. K. Zakrzewski and the author (1939, a) have already shown that this is not so.

(b) *Solutions.* We shall consider here solutions of a polar solute in a non-polar solvent. The equation (21) applied to such solutions changes into

$$\frac{\varepsilon_{12}-1}{3g_{12}}=\frac{4\pi}{3}N'_1 a_1\frac{1}{1-r_{12}p_1}+\frac{4\pi}{3}N'_2\left(a_2+\frac{\mu^{*2}}{3kT}\right)\frac{1}{1-r_{12}p_2}. \tag{23}$$

The indices 1, 2 and 12 refer, as usual, to the solvent, the solute and the solution. Attention must be called to the fact that the value of the moment μ^* depends not only on the properties of the molecule but also on those of the solution, namely on its dielectric constant, since

$$\mu^* = \frac{\mu}{1 - r_{12} p_2}, \tag{24}$$

where

$$r_{12} = k \frac{2(\varepsilon_{12} - 1)}{2\varepsilon_{12} + 1}. \tag{24 a}$$

N_1' and N_2' indicate the corresponding numbers of molecules of both components per 1 c. c. of the solution. If c_1 and c_2 indicate the weight concentrations of both components M_1 and M_2 their molecular weights, d_{12} the density of the solution and N — Avogadro's number, then

$$N_1' = \frac{N}{M_1} c_1 d_{12}, \quad N_2' = \frac{N}{M_2} c_2 d_{12}. \tag{25}$$

Sometimes instead of weight concentrations c_1 and c_2, it is more convenient to use the „molar fractions" of both components determined by the equations

$$f_1 = \frac{N_1'}{N_1' + N_2'}, \quad f_2 = \frac{N_2'}{N_1' + N_2'}; \tag{26}$$

then

$$c_1 = \frac{f_1 M_1}{M_{12}}, \quad c_2 = \frac{f_2 M_2}{M_{12}}, \tag{27}$$

where

$$M_{12} = f_1 M_1 + f_2 M_2. \tag{27a}$$

Using these equations, we obtain instead of (23)

$$\frac{\varepsilon_{12} - 1}{3 g_{12}} \frac{M_{12}}{d_{12}} = \frac{4\pi}{3} N \alpha_1 \frac{f_1}{1 - r_{12} p_1} + \frac{4\pi}{3} N \left(\alpha_2 + \frac{\mu^{*2}}{3kT} \right) \frac{f_2}{1 - r_{12} p_2}. \tag{28}$$

But Lorentz's equation applies to nonpolar liquids, and we may write it in the form

$$\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \frac{M_1}{d_1} = \frac{4\pi}{3} N \alpha_1 = P_1. \tag{29}$$

Besides this we introduce in (28) the expression (3) for molecular polarization of the solute:

$$P_2 = \frac{4\pi}{3} N \left(\alpha_2 + \frac{\mu^2}{3kT} \right). \tag{30}$$

For this purpose the polarization P_2 must be divided in two parts: the non-polar part

$$P_2^n = \frac{4\pi}{3} N a_2 \tag{31}$$

and the polar part

$$P_2^{\mathrm{dip}} = \frac{4\pi N \mu^2}{9kT}. \tag{32}$$

The first one is usually determined in the optical way from Lorentz's relation by extrapolating n_2 to infinite wavelengths

$$P_2^n = \frac{n_{2\infty}^2 - 1}{n_{2\infty}^2 + 2} \frac{M_2}{d_2}. \tag{33}$$

It can also be determined by measuring the dielectric constant ε_0 in condition in which the dipoles are immobilized, for instance in solidified substances

$$P_2^n = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \frac{M_2}{d_2}. \tag{34}$$

This method was applied by the author in his previous work (1933).

The polar part of the polarization, P_2^{dip}, is determined either in gases, according to a formula analogous to (22):

$$P_2 = P_2^n + P_2^{\mathrm{dip}} = \frac{\varepsilon - 1}{3} \frac{M}{d} = \frac{4\pi}{3} N \left(a + \frac{\mu^2}{3kT}\right), \tag{35}$$

or, more frequently, in solutions. According to Onsager's theory the formula (28) should be used for this purpose.

By using the equations (29), (31) and (32), we can simplify this formula and write

$$\boxed{\frac{\varepsilon_{12} - 1}{3g_{12}} \frac{M_{12}}{d_{12}} = P_1 \frac{f_1}{1 - r_{12} p_1} + \left(P_2^n + P_2^{\mathrm{dip}} \frac{1}{(1 - r_{12} p_2)^2}\right) \frac{f_2}{1 - r_{12} p_2}.} \tag{36}$$

This form will serve to determine the molecular polarization P_2^{dip} of the solute. The quantities p_1 and p_2 can be determined from the formulae (29) and (33):

$$p_1 = P_1 \frac{d_1}{M_1}, \quad p_2 = P_2^n \frac{d_2}{M_2}. \tag{36 a}$$

If we assume the molecular field to be the Lorentz field $F = (\varepsilon + 2)E/3$, then we must insert in the equation (36) the values $g_{12} = (\varepsilon_{12} + 1)/3$ and

$r_{12}=0$. It is then transformed into the formula derived from the Lorentz-Debye theory expressing the additivity of polarization:

$$P_{12}=P_1 f_1+P_2 f_2, \tag{37}$$

where:

$$P_{12}=\frac{\varepsilon_{12}-1}{\varepsilon_{12}+2}\,\frac{M_{12}}{d_{12}}. \tag{37 a}$$

Thus we see that in the Onsager-Debye theory the molar polarization does not fulfil the additivity relation.

(c) *Interpretation of experimental results.* The theories considered lead to different ways of calculating the molecular dipole polarization P_2^{dip}, but the theory of Onsager supplies different values for P_2^{dip} according to the choice of the reaction-field coefficient k. We shall make the calculations for mixtures of nitrobenzene and benzene, for which the dielectric constant, as well as the other effects of molecular orientation, have been carefully investigated. Thus we shall be able to apply the same mixture for the calculation of different molar constants of nitrobenzene, such as Kerr's constant and others.

For calculating P_2^{dip} the author has used the measurement of L. Kozłowski (1938). In table I are compiled the values of ε_{12} and d_{12}, interpolated for molar concentrations in round numbers, and P_2^{dip} calculated according to the theory of Lorentz (equation (37)) and Onsager (equation (36)) for $k=0,5$, 1, 1,5. For the non-polar part of the molecular polarization P_2^{n} the author has accepted the value 41 c. c. resulting from his measurements of the dielectric constant of solidified nitrobenzene (1933).

Table I. *Dipole part of molecular polarization of nitrobenzene as a function o concentration (solution nitrobenzene — benzene, temp. 20° C).*

				P_2^{dip} according to the theory of				R according to the theory of	
f_2	ε_{12}	d_{12}	$N'_2\times 10^{-21}$	Lorentz	Onsager $k=0,5$	Onsager $k=1$	Onsager $k=1,5$	Lorentz	Onsager $k=1$
0	2,282	0,8791	0	(c. 330)	(c. 520)	(c. 240)	(c. 20)	(c. 0,9)	(c. 0.66)
0,01	2,51	0,883	0,0678	300	472	214	37,7	0,820	0.584
0,02	2,75	0,887	0,130	294,5	412	212	82,4	0,804	0,579
0,05	3,40	0,899	0,338	247,4	325	180	82,6	0,676	0,492
0,10	4,56	0,9174	0,673	207,9	300	159	71,0	0,568	0,434
0,20	7,05	0,954	1,32	157,5	292	143	58,7	0,430	0,390
0,30	9,82	0,991	1,95	126,5	293	140	52,6	0,345	0,382
0,40	12,80	1,025	2,57	105,8	300	138	48,0	0,289	0,376
0,60	18,80	1,087	3,73	79,0	317	143	47,9	0,216	0,390
0,80	25,80	1,1467	4,85	63,2	343	151	49,1	0,173	0,412
1	34,33	1,2032	5,88	52,8	379	164	51,2	0,144	0,448

These results are illustrated by the curves in fig. 1. Contrary to the previsions of Onsager's theory, the polarization and also the value of the polar moment are not constant, and for a pure liquid the former is not equal to the polarization in the gaseous state (gas $P_2^{\text{dip}} = 366$ c. c. at $t = 20^0$ C). The value of μ, determined for the liquid state, will not be the true value (see C. J. Böttcher, 1938).

We see that both in Onsager's theory and in that of Lorentz we are obliged to assume a certain factor which alters the polar orientation. According to previous workers this factor was the association, i. e. the formation of a certain number of double molecules with a resultant moment equal to zero. According to Debye (1935) this factor is a quasi-crystalline coupling; we shall call it the type I coupling. But many facts have compelled the author (1937 a; 1939) to introduce a coupling of a second kind (type II coupling), differing from the association proper and consisting of a stronger or weaker coupling of each molecule with one of its nearest neighbours. Experimental facts convince us, that the type II coupling is very important, though the type I coupling is irreplaceable in some ways (see part II of this work).

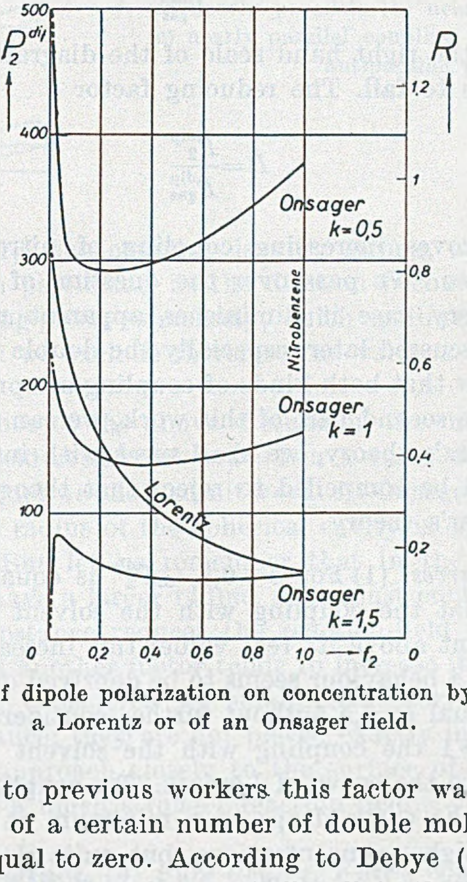

Fig. 1. Dependence of dipole polarization on concentration by the assumption of a Lorentz or of an Onsager field.

According to these opinions the interpretation of the results shown in fig. 1 would be approximately as follows:

Lorentz curve. This curve extrapolated for infinitely great dilution ($f_2 = 0$) gives the value ${}_{\infty}P_2^{\mathrm{dip}}$ equal to about 330 c. c. It is smaller than the value $P_{\mathrm{gas}}^{\mathrm{dip}}$ and indicates the existence of a coupling of nitrobenzene molecules with the solvent. The corresponding values of the reducing factor:

$$R = \frac{{}_{\infty}P_2^{\mathrm{dip}}}{P_{\mathrm{gas}}^{\mathrm{dip}}}$$

can be read on the right hand scale of the diagram. From this value the curve begins to fall. The reducing factor

$$R = \frac{P_2^{\mathrm{dip}}}{P_{\mathrm{gas}}^{\mathrm{dip}}} \qquad (38)$$

decreases. It proves increasing coupling of nitrobenzene molecules among themselves. We pass over the question of the nature of this coupling; in every case it diminishes apparent molecular moment. Results to be discussed later, especially the double refraction in a magnetic field, show that both kinds of coupling are present. Anticipating the results of the second part of this work, we can mention that if we adhere to Lorentz's theory, we shall meet with insurmountable difficulties. We shall be compelled to reject that theory and to adopt an extended Onsager's theory.

Onsager's curves. (1) For $k = 0{,}5$, ${}_{\infty}P_2^{\mathrm{dip}}$ is equal to about 500 c. c., which proves that the coupling with the solvent raises the average molecular moment above its real value; this increase grows as k gets smaller. As such a behaviour seems to be deprived of physical meaning, we exclude k equal to 0,5 without further consideration of the curve.

(2) For $k = 1$ the coupling with the solvent is a little stronger than according to the curve of Lorentz. The coupling grows with concentration and the curve drops to a minimum at f equal to 0,4. It rises again for higher concentrations, but quite slowly. This seems to indicate the existence of an additional coupling of a third kind (type III), depending on the formation of aggregates with increased moments. It is not supposed that they are quasi-parallel pairs (fig. 2 a), since nitrobenzene molecules show inclination to quasi-antiparallel coupling (fig. 2 b). We should rather suppose that they form a combination of two quasi-antiparallel pairs, coupled quasi-parallelly (fig. 2 c). Again, it should be mentioned that this opinion is strongly supported by the Cotton-Mouton effect in nitrobenzene solutions. We may

add that the above mentioned aggregates loose and transitory rather than rigid, and as such they will be considered in the theory of coupling in the second part of this work.

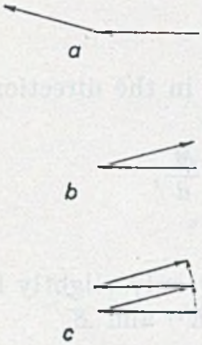

Fig. 2. Coupling of two dipoles: (a) nearly parallel, (b) nearly antiparallel, and (c) nearly parallel coupling between two nearly antiparallel pairs.

(3) For $k=1{,}5$ the coupling is very strong, as the curve P_2^{dip} runs very low. In particular, as the dilution becomes infinitely great ($f_2\to 0$), the coupling grows immensely, which again seems to be without physical meaning: we exclude therefore the value $k=1{,}5$ in Onsager's theory.

In consequence of the above discussion, the most suitable value for the reaction field coefficient is $k=1$ or a value very little different from it. In the sequel we shall admit $k=1$. In Onsager's original theory it means that the radius of the spherical cavity is equal to the radius of the molecule. But let us remember that in the extended theory the sphere must have a larger radius, as it must contain several molecules. This circumstance reduces the reaction-field coefficient k, but on the other hand another factor tends to increase it as the polar moments cannot be considered as small elementary moments acting from a great distance; they are not placed exactly in the center of the sphere and may approach closely to the surface of Onsager's cavity, and thus produce a much stronger reaction field.

§ 4. Kerr Effect. (a) *Pure liquids.* Kerr's constant is given by the formula

$$K=\frac{n_E-n_X}{n}\,\frac{1}{E^2},\tag{39}$$

where n is the refractive index of light and n_E and n_X are the refractive indices for light vibrations in the direction of the vector of external electric field E, and in the direction X normal to the latter respectively. It prooved to be convenient to introduce in connection with the Kerr effect in particular in solutions, the so called „molar Kerr constant“ K^m. Several authors give various formulae for this constant, differing by a numerical coefficient. The following definition seems to be most suitable

$$K^m = \frac{R_E - R_X}{F^2}, \tag{40}$$

where R_E and R_X are the molecular refractions in the directions of E and X,

$$R_E = \frac{n_E^2 - 1}{n_E^2 + 2}\,\frac{M}{d}, \quad R_X = \frac{n_X^2 - 1}{n_X^2 + 2}\,\frac{M}{d}, \tag{41}$$

and F is the intensity of the local field.

Taking into account that n_E and n_X differ only slightly from n, we come to the following formula connecting K^m and K

$$K^m = K\frac{6n^2}{(n^2+2)^2}\,\frac{M}{d}\left(\frac{E}{F}\right)^2. \tag{42}$$

If we assume that the Lorentz formula for the internal field (1a) is true, we get the well-known formula

$$K^m = K\frac{6n^2}{(n^2+2)^2}\,\frac{M}{d}\left(\frac{3}{\varepsilon+2}\right)^2. \tag{42 a}$$

On the other hand, in the case of Onsager's field we define the molar Kerr constant K^{m*} by replacing F by the local field which acts mainly in orientating the molecules, i. e. by putting $G = gE$ (cf. the formulae (10) and (10a)). Thus, we have

$$K^{m*} = \frac{R_E - R_X}{G^2} = K\frac{6n^2}{(n^2+2)^2}\,\frac{M}{d}\,\frac{1}{g^2}, \tag{43}$$

The Kerr constant may be also expressed by means of constants characterizing the molecule itself (and not the medium, as the constants ε, n, K). For this purpose we make use of the Lorentz — Lorenz function well known in optics:

$$R_E = \frac{4\pi}{3}N\overline{\overline{\gamma}}_E \quad \text{and} \quad R_X = \frac{4\pi}{3}N\overline{\overline{\gamma}}_X, \tag{41 a}$$

where $\overline{\overline{\gamma}}_E$ and $\overline{\overline{\gamma}}_X$ are statistical averages of the optical susceptibility of the molecule. Thus, for Onsager's field we get

$$K^{m*} = \frac{4\pi}{3}N\frac{\overline{\overline{\gamma}}_E - \overline{\overline{\gamma}}_X}{G^2}. \tag{44}$$

It remains now to calculate the susceptibilities and their statistical averages.

We shall denote by b_1, b_2, b_3, the components of the optical susceptibility of the molecule, referred to its main axes x, y, z. Let the external electric field E act in the direction of the Z-axis of another coordinate system X, Y, Z fixed in space (fig. 3). The angles between the molecule axes and the field E are a_1, a_2, a_3, and those between the molecule axes and the direction X are a_1', a_2', a_3'. We may consider two cases in which the electric field of the light wave E_0 is respectively parallel and perpendicular to E. In both cases an induced electric moment will arise in the molecule. The components of this moment along E and X respectively are (1)

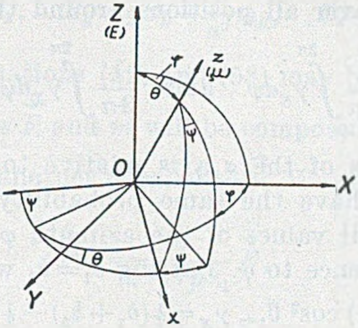

Fig. 3. Explanatory diagram for Kerr effect. X and Z — directions of vibrations of the light vector, Y — direction of the beam, Z — direction of the electric field, x, y, z — coordinate system connected with the molecule (z — axis of symmetry and of the electric moment), θ, φ, ψ — Euler's angles.

for $E_0 \| E$:

$$m_E = b_1 E_{0x} \cos a_1 + b_2 E_{0y} \cos a_2 + b_3 E_{0z} \cos a_3 = \gamma_E E_0, \tag{45}$$

where

$$\gamma_E = b_1 \cos^2 a_1 + b_2 \cos^2 a_2 + b_3 \cos^2 a_3; \tag{45 a}$$

(2) for $E_0 \perp E$:

$$m_X = b_1 E_{0x} \cos a_1' + b_2 E_{0y} \cos a_2' + b_3 E_{0z} \cos a_3' = \gamma_X E_0, \tag{46}$$

where

$$\gamma_X = b_1 \cos^2 a_1' + b_2 \cos^2 a_2' + b_3 \cos^2 a_3'. \tag{46 a}$$

Let θ, φ, ψ, be Euler's angles determining the position of the molecule in reference to the system XYZ (as shown in fig. 3); θ and φ correspond to geographical longitude and latitude, ψ is the angle of rotation around the z axis. We have

$$\left.\begin{array}{l} \cos a_1 = -\sin\theta\cos\psi, \quad \cos a_2 = \sin\theta\sin\psi, \quad \cos a_3 = \cos\theta, \\ \cos a_1' = \cos\theta\cos\varphi\cos\psi - \sin\varphi\sin\psi, \\ \cos a_2' = -\cos\theta\cos\varphi\sin\psi - \sin\varphi\cos\psi, \quad \cos a_3' = \sin\theta\cos\varphi. \end{array}\right| \tag{47}$$

We shall assume that the molecules are rotationally symmetrical and that z is their axis of symmetry. Thus, the rotation of the molecule around the z axis is completely free in spite of the external field E, and all possible values of ψ are equally probable. We may therefore by inserting the direction cosines (47) into (45a) and (46a) calculate the geometric mean over all positions around the axis z:

$$\frac{1}{2\pi}\int_0^{2\pi}\gamma_E d\psi \quad \text{and} \quad \frac{1}{2\pi}\int_0^{2\pi}\gamma_X d\psi.$$

However, all positions of the z axis relative to the direction of the electric field E also have the same probability. Thus, we calculate the mean value for all values of the azimuth φ by means of similar integrals, but in reference to φ. Putting $b_1=b_2$ we get

$$\gamma_E=b_1+(b_3-b_1)\cos^2\theta, \quad \gamma_X=\tfrac{1}{2}(b_1+b_3)-\tfrac{1}{2}(b_3-b_1)\cos^2\theta. \tag{48}$$

Finally, the statistical means of γ_E and γ_X should be calculated by calculating the statistical means of $\cos^2\theta$ over all possible positions of the axis of symmetry z, which now are obviously not equally probable,

$$\overline{\overline{\gamma_E}}=b_1+(b_3-b_1)\,\overline{\overline{\cos^2\theta}}, \quad \overline{\overline{\gamma_X}}=\tfrac{1}{2}(b_1+b_3)-\tfrac{1}{2}(b_3-b_1)\,\overline{\overline{\cos^2\theta}}. \tag{49}$$

Hence, thanks to (44), we have

$$K^{m*}=2\pi N\frac{b_3-b_1}{G^2}(\overline{\overline{\cos^2\theta}}-\tfrac{1}{3}). \tag{50}$$

Thus, we have reduced the problem to the calculation of $\overline{\overline{\cos^2\theta}}$. The Maxwell and Boltzmann theorem yields

$$\overline{\overline{\cos^2\theta}}=\frac{\int_0^{\pi}\cos^2\theta\cdot e^{-W/kT}\sin\theta d\theta}{\int_0^{\pi}e^{-W/kT}\sin\theta d\theta}. \tag{51}$$

To calculate this expression the potential energy W of the molecule must be calculated.

Let the components of the polarizability of the molecule in an external field be a_1, a_2, a_3; the molecule being symmetrical around the z axis, we have $a_1=a_2$, $\mu_1=\mu_2=0$ and $\mu_3=\mu$. If the field F acts on the molecule, the moment of the molecule will have the components

$$m_x=a_1F_x, \quad m_y=a_1F_y, \quad m_z=a_3F_2+\mu. \tag{52}$$

According to Onsager's theory, the molecule should be treated as if enclosed in an empty ellipsoidal space of identical dimensions with those of the molecule. In the modified form of this theory, however, we assume that several molecules are found in a spherical volume the radius of which greatly exceed that of the molecule. The internal field is expressed as before by (12):

$$F_x = gE_x + \frac{r}{a^3} m_x, \quad F_y = gE_y + \frac{r}{a^3} m_y, \quad F_z = gE_z + \frac{r}{a^3} m_z. \tag{53}$$

The solution of the equations (52) and (53) may be presented in vector form, where the vectors $\vec{F}$ and $\vec{m}$ will be composed of two components: one parallel to $\vec{E}$, and another parallel to $\vec{\mu}$. We shall use the following symbols

$$\vec{F}^* = \frac{g}{1 - rp\lambda_1} \vec{E}, \tag{54}$$

$$\vec{\mu}^* = \frac{1}{1 - rp\lambda_3} \vec{\mu}, \tag{55}$$

where

$$\lambda_1 = \frac{a_1}{a}, \quad \lambda_3 = \frac{a_3}{a} \quad \left(a = \frac{1}{3}(a_1 + a_2 + a_3)\right). \tag{56}$$

λ_1 and λ_2 give a measure of molecular anisotropy.

Further let us put

$$a_3^* = \varkappa a_3$$

with

$$\varkappa = \frac{1 - rp\lambda_1}{1 - rp\lambda_3}. \tag{57}$$

Finally, let $\vec{u}$ stand for a unit vector parallel to $\vec{\mu}$. The solution is as follows

$$\vec{F} = \vec{F}^* + \left[\frac{r}{a_3} \mu^* + (\gamma - 1) F^* \cos\theta\right] \vec{u}, \tag{58}$$

$$\vec{m} = a_1 \vec{F}^* + [\mu^* + (a_3^* - a_1) F^* \cos\theta] \vec{u}. \tag{59}$$

For isotropic molecules ($a_1 = a_2 = a_3 = a$) the above formulae become identical with our previous formulae (14) and (13).

The moment acting on the molecule is

$$\vec{M} = \vec{F} \times [\mu^* + (a_3^* - a_1) F^* \cos\theta] \vec{u}, \tag{60}$$

therefore

$$M = \mu^* F^* \sin\theta + (a_3^* - a_1) F^{*2} \cos\theta \sin\theta. \tag{60 a}$$

Hence the energy

$$W = -\int M d\theta = -\mu^* F^* \cos\theta - \frac{a_3^* - a_1}{2} F^{*2} \cos^2\theta. \tag{61}$$

For isotropic molecules this expression goes over into (16). The form of (61) is such that without the asterisks we obtain the same expression as with the Lorentz field; in this case F means of course $(\varepsilon+2)E/3$. We may now calculate $\overline{\overline{\cos^2\theta}}$ from (51). Expanding the exponential into a series and integrating term by term, we obtain

$$\overline{\overline{\cos^2\theta}}=\frac{1}{3}+\frac{2}{45}x^{*2}+\frac{4}{45}x_1^*, \tag{62}$$

where

$$x^*=\frac{\mu^*F^*}{kT},\quad x_1^*=\frac{a_3^*-a_1}{2kT}F^{*2}. \tag{63}$$

From the above and from (50) the final expression for Kerr's molar constant is obtained. We give it here in symbols which are connected with the theory of the Kerr effect based on the Lorentz field:

$$\boxed{K^{m*}=2\pi N[\theta_1^*+\theta_2^*]\frac{1}{(1-rp\lambda_1)^2},} \tag{64}$$

where

$$\left.\begin{aligned}\theta_1^*&=\frac{2}{45kT}(a_3^*-a_1)(b_3-b_1),\\ \theta_2^*&=\frac{2}{45k^2T^2}\mu^{*2}(b_3-b_1).\end{aligned}\right| \tag{65}$$

In the case of a Lorentz field, i. e. if we put $g=(\varepsilon+2)/3$ and $r=0$, the asterisks in the above expressions should be omitted and we obtain the well known formula

$$K^m=2\pi N(\theta_1+\theta_2), \tag{66}$$

in which the expressions

$$\theta_1=\frac{2}{45kT}(a_3-a_1)(b_3-b_1)$$

and

$$\theta_2=\frac{2}{45k^2T^2}\mu^2(b_3-b_1) \tag{67}$$

are a particular case of the expressions known from the theory of the Kerr effect, namely

$$\left.\begin{aligned}\theta_1&=\frac{1}{45kT}[(a_1-a_2)(b_1-b_2)+(a_2-a_3)(b_2-b_3)+(a_3-a_1)(b_3-b_1)]\\ &\text{and}\\ \theta_2&=\frac{1}{45k^2T^2}[(\mu_1^2-\mu_2^2)(b_1-b_2)+(\mu_2^2-\mu_3^2)(b_2-b_3)+(\mu_3^2-\mu_1^2)(b_3-b_1)].\end{aligned}\right| \tag{67 a}$$

(b) *Solutions*. Kerr's molar constant K^{m*} is calculated in the previous paragraphs on the one hand, by means of quantities characteristic of the medium (formula (43)) and on the other, by means of quantities characteristic of the molecule (formula (64)). In the latter formula, however, there appears the quantity r which is characteristic of the medium, that is the reason why the constant K^{m*} is not additive for solutions, in opposition to K^m which is based on the assumption of a Lorentz field. Nevertheless, we shall calculate K^{m*} for solutions. When taking the solution to be a continuous medium, we shall use formula (43) but, regarding it as a mixture of two kinds of molecules, we shall use formula (64).

We shall limit our reasoning to the case of a polar substance in a non-polar solvent, the anisotropic term θ_1 of the polar substance being so small in relation to the term θ_2 as to be negligible. A similar reasoning to that of § 3 (b) leads to the application of the formulae for K^{m*} to the case of one gram molecule of the mixture (M_{12} formula (27 a)). We obtain

$$K_{12}\frac{6n_{12}^2}{(n_{12}^2+2)^2}\frac{1}{g_{12}^2}\frac{M_{12}}{d_{12}}=\frac{2\pi N\theta_1^*}{(1-r_{12}p_1\lambda_1')^2}f_1+\frac{2\pi N\theta_2}{(1-r_{12}p_2\lambda_1'')^2(1-r_{12}p_2\lambda_3'')^2}f_2. \qquad (68)$$

As the first term on the right-hand side is a small fraction of the second for both big and small concentrations, we may put in its place the expression

$$\frac{2\pi N\theta_1}{(1-r_{12}p_1)^2}f_1.$$

Regarding

$$2\pi N\theta_1=K_1^m \qquad (69)$$

and

$$2\pi N\theta_2=K_2^m, \qquad (69\,\text{b})$$

as Kerr's molar constants of the dissolved substance and the solvent respectively, for a Lorentz field, the formula (68) may be written in a simplified form as follows

$$\boxed{K_{12}^{m*}=\frac{K_1^m}{(1-r_{12}p_1)^2}f_1+\frac{K_2^m}{(1-r_{12}p_2\lambda_1'')^2(1-r_{12}p_2\lambda_3'')^2}f_2,} \qquad (70)$$

where

$$K_{12}^{m*}=K_{12}\frac{6n_{12}^2}{(n_{12}^2+2)^2}\frac{1}{g_{12}^2}\frac{M_{12}}{d_{12}}, \qquad (70\,\text{a})$$

$$K_1^m=K_1\frac{6n_1^2}{(n_1^2+2)^2}\left(\frac{3}{\varepsilon_1+2}\right)^2\frac{M_1}{d^1}. \qquad (70\,\text{b})$$

By means of this formula we may calculate K_2^m, or $2\pi N\theta_2$. According to Onsager's idea this quantity (as well as the dipole moment) should be invariant for all concentrations and for vapour. We shall see that this is not so.

We notice that in the case of a Lorentz field, i. e. if we put $r_{12}=0$ and $g_{12}=(\varepsilon_{12}+2)/3$, formula (70) assumes the well-known form

$$K_{12}^m = K_1^m f_1 + K_2^m f_2, \tag{71}$$

by which the additivity of Kerr's molar constant is expressed.

(c) *Interpretation of experimental results.* We shall apply the above results to the case of a mixture of nitrobenzene and benzene. Nitrobenzene actually fulfils the condition assumed in (b), namely [2] $\theta_1^* \leqslant \theta_2^*$. Thus the formula (64) takes the form

$$K^{m*} = \frac{2\pi N\theta_2}{(1-rp\lambda_1)^2(1-rp\lambda_3)^2} = \frac{K^m}{(1-rp\lambda_1)^2(1-rp\lambda_3)^2}. \tag{72}$$

Hence, we may calculate Kerr's molar constant K^m for pure nitrobenzene. However, Kerr's molar constant of nitrobenzene determined from solutions is to be calculated (as K_2^m) from (70). In the case where $f_2=1$ this formula obviously takes the form (72).

We shall take numerical data from experiments of H. Friedrich (1937) performed at 23° C. Friedrich measured Kerr's constant K_{12} of nitrobenzene-benzene solutions and calculated the molar constant of the solution „$\mathfrak{K}_{12}$" from a formula which differs from our formula (42a) only by a factor of 9, namely $\mathfrak{K}_{12}=\frac{1}{9}K_{12}^m$. Accordingly, the constant K_{12}^{m*} appearing in (70) is calculated as follows: $K_{12}^{m*}=\mathfrak{K}_{12}(\varepsilon_{12}+2)^2/g_{12}^2$; its value is tabulated in the sixth column of Table II. Kerr's molar constant for pure benzene K_1^m is $9\mathfrak{K}_{12}$ for $f_2=0$ and amounts to $48{,}33\times10^{-12}$; p_1 and p_2 are calculated from (36a). For P_2^n we have assumed the polarisation of solid nitrobenzene, i. e. 41 c. c. Finally, we have evaluated λ_1'' and λ_3'' on the basis of b_1, b_2 and b_3 taken from Stuart's book quoted previously [3]. Table II contains the results of calculations of Kerr's

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[2] According to data from investigations of the Kerr effect in nitrobenzene vapour at 235,5° C, we have $\theta_1/\theta_2 = K_1/K_2 = 7/139 = 0{,}050$ (see H. Stuart *Molekülstruktur*, Berlin 1934, table 55, p. 211). At 23° C this ratio is 0,029. The ratio θ_1^*/θ_2^* is still smaller.

[3] In table 59, p. 222 we find $b_1=132{,}5\times10^{-25}$, $b_2=77{,}5\times10^{-25}$ and $b_3=177{,}6\times10^{-25}$. These are polarizabilities of the nitrobenzene molecule for visible light determined by means of the Kerr effect and the depolarization of light in nitrobenzene vapour. Assuming an approximate proportionality between a_1, a_2, a_3 and b_1, b_2, b_3, we calculate

$$\lambda_1'' = \frac{\frac{1}{2}(b_1+b_2)}{\frac{1}{3}(b_1+b_2+b_3)} = 0{,}813 \quad \text{and} \quad \lambda_3'' = \frac{b_3}{\frac{1}{3}(b_1+b_2+b_3)} = 1{,}374.$$

molar constant of nitrobenzene according to both the generalised theory of Onsager (for $k=1$) and to the theory of Lorentz. In the first place we see that the „constant" K_2^m is not constant as it should be according to Onsager's theory but depends in a rather queer way on the concentration. This dependence is represented by the diagram, fig. 4.

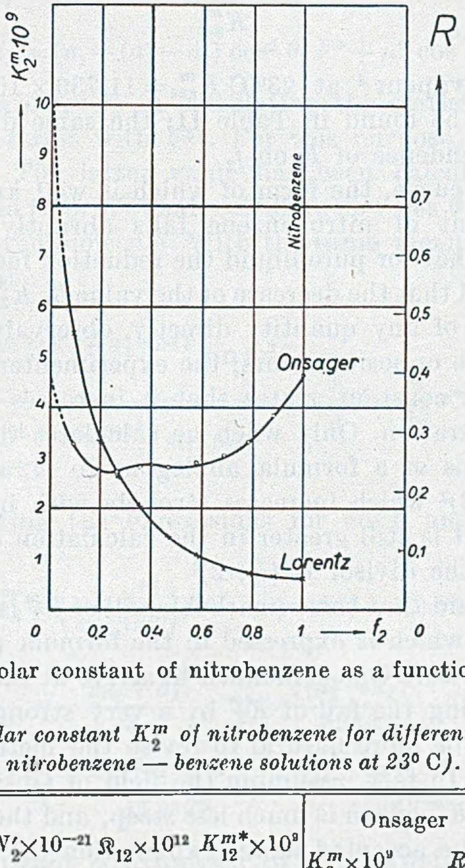

Fig. 4. Kerr's molar constant of nitrobenzene as a function of concentration.

Table II. *Kerr's molar constant K_2^m of nitrobenzene for different concentrations (from nitrobenzene — benzene solutions at 23° C).*

f_2	ε_{12}	d_{12}	$N'_2 \times 10^{-21}$	$\mathfrak{R}_{12} \times 10^{12}$	$K_{12}^{m*} \times 10^9$	Onsager $K_2^m \times 10^9$	Onsager R	Lorentz $K_2^m \times 10^9$ *	Lorentz R
0	2,26	0,8748	0	5,37	0,0646	(ca. 4,5)	(ca. 0,4)	(ca. 10)	(ca. 0,85)
0,0930	4,42	0,9097	0,62	61,5	1,395	3,27	0,28	5,48	0,47
0,1957	7,01	0,9468	1,29	77,0	3,190	2,75	0,24	3,34	0,29
0,2618	8,80	0,9701	1,70	80,7	4,687	2,73	0,23	2,64	0,23
0,3532	11,3	1,0014	2,27	84,2	7,210	2,83	0,24	2,06	0,18
0,4659	14,6	1,0387	2,95	78,5	10,28	2,82	0,24	1,46	0,12
0,5769	18,3	1,0743	3,59	72,7	14,05	2,93	0,25	1,10	0,094
0,6872	22,5	1,1083	4,21	65,0	18,12	3,07	0,26	0,83	0,071
0,7829	25,6	1,1369	4,73	65,8	23,15	3,32	0,28	0,74	0,063
0,8805	29,6	1,1654	5,25	67,1	30,80	3,84	0,33	0,68	0,058
1	34,5	1,1992	5,87	70,9	43,20	4,64	0,40	0,64	0,054

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* Friedrich's data multiplied by 9.

The reducing factor R is a measure of the diminution of the molar constant in comparison with the value for vapour. R is calculated as the ratio of the constant K_2^m determined from the solution or from the pure liquid to the molar constant K_{gas}^m of the same substance in gas or vapour form:

$$R = \frac{K_2^m}{K_{\text{gas}}^m}. \tag{73}$$

For nitrobenzene vapour[4] at 23° C $K_{\text{gas}}^m = 11{,}736 \times 10$. The calculated values of R may be found in Table II; the same diagrams on fig. 4 represent the dependence of R on f_2.

The Lorentz curve, the form of which is well known, shows that the molar constant of nitrobenzene falls abruptly with increasing concentration, so that for pure liquid the reduction factor is only 0,054. It might be noticed that the decrease of the value of K_2^m is not connected with the decrease of any quantity directly observable by the experimenter. Rather the opposite occurs; the experimenter when measuring the ordinary Kerr constant states that it increases remarkably with increasing concentration. Only when he calculates the molecular constant $\mathfrak{K}_{12}$ by means of a formula analogous to (42a) does he divide by the term $(\varepsilon+2)^2$ which increases strongly with increasing concentration. This effect is still greater in the calculation of electric saturation (§ 5), where the divisor is $(\varepsilon+2)^4$.

It might be said that this remarkable fall of K_2^m is due to the use of the Lorentz field, which is expressed in the formula (42a) in the form of a very large divisor. One is inclined to arrive at the conclusion that, instead of explaining the fall of K_2^m by a very strong coupling of molecules[5], it would be more natural to revise the method of calculating the internal field. In fact, assuming the field of Onsager, one obtains a fall of the curve K_2^m which is much less steep, and though some degree of coupling must be accepted as an explanation the coupling may be much weaker.

Nevertheless the Onsager curve has a very remarkable form; it corresponds exactly to the variation of the molecular polarisation (fig. 1). At first the curve falls down, which is an argument for an increasing antiparallel coupling of the dipole molecules of nitrobenzene. For stronger concentrations there is an overwhelming influence of another type of coupling which, I am inclined to suppose, consists in a parallel coupling of antiparallel pairs (fig. 2).

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[4] According to Friedrich, this value is one ninth as large, i. e. $1{,}301 \times 10^{-9}$.

[5] As has been done by Debye (1935), Friedrich (1937) and the author (1939).

An interesting irregularity appears in the neighbourhood of $f=0{,}3-0{,}4$, which is connected with the attaining of a maximum by $\mathfrak{R}_{12}$, found experimentally.

§ 5. Electric Saturation. (a) *Pure Liquids.* The component of the moment of the molecule along E is given by the formula derived directly from (59):

$$m_E=[a_1+(a_1^*-a_1)\cos^2\theta]F^*+\mu^*\cos\theta\,. \tag{74}$$

Our problem consists in calculating the statistic mean value of $\overline{\overline{m_E}}$ retaining the terms with F^{3*}. For this purpose we shall calculate $\overline{\overline{\cos\theta}}$ and $\overline{\overline{\cos^2\theta}}$. The latter value has been calculated already and is given by (62) and (63). We shall calculate now $\overline{\overline{\cos\theta}}$ using formula (61) for the energy of the molecule. With the same meaning of the symbols as in (63), we have

$$\overline{\overline{\cos\theta}}=\frac{\int\limits_0^\pi \cos\theta\, e^{-x^*\cos\theta-x_1^*\cos^2\theta}\sin\theta\, d\theta}{\int\limits_0^\pi e^{-x^*\cos\theta-x_1^*\cos^2\theta}\sin\theta\, d\theta}=\frac{1}{3}x^*+\frac{4}{45}x^*x_1^*-\frac{1}{45}x^{*3}+\ldots \tag{75}$$

By substituting the expressions for $\overline{\overline{\cos\theta}}$ and $\overline{\overline{\cos^2\theta}}$ into (74) we get

$$\overline{\overline{m_E}}=\left(a+\frac{\mu^{*2}}{3kT}\right)F^*+(\theta_1^*+2\theta_2^*-\theta_3^*)F^{*3}, \tag{76}$$

where

$$a=\frac{2a_1+a_3^*}{3},\quad \theta_1^*=\frac{2(a_3^*-a_1)^2}{45kT},$$
$$\theta_2^*=\frac{2\mu^{*2}(a^*-a_1)}{45k^2T^2},\quad \theta_3^*=\frac{\mu^{*4}}{45k^3T^3}\,. \tag{77}$$

The dielectric constant is expressed by the formula

$$\varepsilon=1+4\pi N'\frac{\partial\overline{\overline{m_E}}}{\partial E}\,. \tag{78}$$

Differentiating (76) with regard to E and substituting into (78), we obtain an expression for the dielectric constant in a strong electric field:

$$\varepsilon=1+4\pi N'\left[a+\frac{\mu^2}{3kT}\frac{1}{(1-rp\lambda_3)^2}\right]\frac{g}{1-rp\lambda_1}$$
$$+12\pi N'(\theta_1^*+2\theta_2^*-\theta_3^*)\frac{g^3}{(1-rp\lambda_1)^3}E^2, \tag{79}$$

whereas in a very weak electric field we have

$$\varepsilon_0 = 1 + 4\pi N' \left[a_0 + \frac{\mu^2}{3kT} \frac{1}{(1 - r_0 p \lambda_3)^2} \right] \frac{g_0}{1 - r_0 p \lambda_1} \tag{80}$$

(the index $_0$ refering to the dielectric constant in a weak field). Under the influence of a strong applied field the dielectric constant is changed by $\Delta\varepsilon = \varepsilon - \varepsilon_0$. Using the definition

$$f(\varepsilon, \mu, T, \ldots) = 4\pi N' \left[a + \frac{\mu^2}{3kT} \frac{1}{(1 - r p \lambda_3)^2} \right] \frac{g}{1 - r p \lambda_1}, \tag{81}$$

we obtain by subtracting (80) from (79)

$$\Delta\varepsilon = f(\varepsilon, \ldots) - f(\varepsilon_0, \ldots) + 12\pi N' (\theta_1^* + 2\theta_2^* - \theta_3^*) \frac{g^3}{(1 - r p \lambda_1)^3} E^2.$$

For extremely small $\Delta\varepsilon$ (and only such are to be taken into account) we may write

$$f(\varepsilon, \ldots) - f(\varepsilon_0, \ldots) = \frac{\partial f}{\partial \varepsilon} \Delta\varepsilon,$$

hence

$$\Delta\varepsilon = \frac{1}{1 - \dfrac{\partial f}{\partial \varepsilon}} 12\pi N' (\theta_1^* + 2\theta_2^* - \theta_3^*) \frac{g^3}{(1 - r p \lambda_1)^3} E^2. \tag{82}$$

In the case of a Lorentz field ($g = (\varepsilon + 2)/3$, $r = 0$), the above formula takes the well-known form

$$\Delta\varepsilon = 12\pi N' (\theta_1 + 2\theta_2 - \theta_3) \left(\frac{\varepsilon + 2}{3} \right)^4 E^2, \tag{83}$$

where θ_1, θ_2 and θ_3 stand for expressions identical with (77) but without asterisks.

Formula (82) assumes a much simpler form for substances with a relatively big moment μ, for which a is small in comparison to the dipole part of the polarizability. For these substances the terms θ_1 and θ_2 may be neglected in comparison with θ_3 (in a still greater degree this applies to the expression with the asterisk). E. g., for nitrobenzene at 20° C we have $\theta_1 = 0{,}013 \times 10^{-72}$ and $\theta_2 = 0{,}44 \times 10^{-72}$, whereas $\theta_3 = 10{,}76 \times 10^{-72}$.

In these conditions

$$\boxed{\Delta\varepsilon = -\frac{12\pi N' \theta_3}{1 - \dfrac{\partial f}{\partial \varepsilon}} \frac{g^3}{(1 - r p \lambda_1)^3 (1 - r p \lambda_3)^4} E^2,} \tag{84}$$

where $\partial f / \partial \varepsilon$ is the derivative of (81).

If according to our assumption α is neglected, the formula for $\partial f/\partial\varepsilon$ becomes

$$\frac{\partial f}{\partial\varepsilon}=\frac{\varepsilon-1}{2\varepsilon+1}\left[\frac{1}{\varepsilon}+\left(\frac{\lambda_1}{1-rp\lambda_1}+\frac{2\lambda_3}{1-rp\lambda_3}\right)\right]\frac{6p}{2\varepsilon+1}. \tag{84 a}$$

(b) *Solutions.* We shall apply (84) together with (84a) to the solutions of nitrobenzene in benzene. The error introduced by the previously mentioned simplification does not exceed $10\,{}^0/_0$ for diluted solutions and decreases almost to $1\,{}^0/_0$ for concentrated solutions. More exact calculations are not needed as measurements of electric saturation are unusually difficult and their precision is limited. In the literature we find only few investigations concerning electric saturation. Besides Herweg's fundamental work we have the paper of Kautsch (1928) who measured $\Delta\varepsilon$ with great care and precision; his investigations, however, concern ether and chloroform only. More dipole liquids were investigated by Malsh (1928, *8*) and Gundermann (1930) but these authors did not take all the necessary precautions and their method gives only qualitative and relative results. Measurements of $\Delta\varepsilon$ for solutions of nitrobenzene in benzene and also in other solvents were made by the author together with B. Piekara (1936)[6]. The results of these measurements will be discussed here in connection with theory.

Formula (84) may be used here in a remarkably simple way, $\Delta\varepsilon$ for the pure solvent (benzene) being so small as to remain within the limits of experimental error; therefore we may write $\Delta\varepsilon=0$. Consequently, it is sufficient to replace N' by N'_2 from (25) to obtain the formula for mixtures:

$$\boxed{\frac{\Delta\varepsilon_{12}}{3g_{12}^3E^2}\,\frac{M}{c_2d_{12}}=\frac{S^m}{\left(1-\dfrac{\partial f}{\partial\varepsilon}\right)(1-r_{12}p\lambda_1)^3\,(1-r_{12}p\lambda_3)^4},} \tag{85}$$

where M, p, λ_1 and λ_3 refer to the nitrobenzene molecule and $\partial f/\partial\varepsilon$ is expressed by the same formula (84a) with the only difference that ε_{12} and r_{12} should take the place of ε and r respectively. The new symbol S^m appearing here is defined by the formula

$$S^m=-4\pi N\theta_3 \tag{86}$$

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[6] These investigations were continued in the following years and partly published (1937). The remaining notes were lost during the war. The measurements with pure nitrobenzene were repeated in 1939 by the author and A. Łempicki by means of a method different from that hitherto applied and using a cathode-ray oscillograph. The outbreak of the war interrupted this work and the apparatus has been destroyed.

and plays the same part as $K^m = 2\pi N \theta_2$ in the theory of the Kerr effect. We shall refer to it as „the molar constant of electric saturation".

It is easy to prove that if a Lorentz field is assumed and electrostriction is neglected S^m is the increase of molecular polarization per unit of external field F:

$$S^m = \frac{P_E - P_0}{F^2}; \tag{87}$$

P_E is the polarization in the field, P_0 — without a field:

$$P_E = \frac{\varepsilon - 1}{\varepsilon + 2}\frac{M}{d}, \quad P_0 = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\frac{M}{d}. \tag{88}$$

Assuming $\Delta\varepsilon = \varepsilon - \varepsilon_0$ to be small in comparison with ε and applying (83), we get

$$S^m = 4\pi N(\theta_1 + 2\theta_2 - \theta_3), \tag{89}$$

which for a particular case yields (86).

We shall calculate S^m for nitrobenzene. Putting $\mu = 4{,}23 \times 10^{-18}$, we obtain $\theta_3 = \mu^4/45k^3T^3 = 10{,}76 \times 10^{-22}$, hence $S^m = -81{,}4 \times 10^{-10}$. This value is obtained on the assumption of an absolute mutual independence of the molecules. It may be therefore applied only to gas or vapour; we shall use the symbol S^m_{gas} for it:

$$S^m_{\text{gas}} = -81{,}4 \times 10^{-10}.$$

If we insert this value into (85) and calculate $\Delta\varepsilon_{12}$, we get a result largely differing from the experimental values of $\Delta\varepsilon_{12}$. This shows directly that Onsager's theory cannot even approximately deal with the electric saturation in liquids (no more than with the dielectric polarization and the Kerr effect). This, however, is no reason to condemn Onsager's theory as false. We shall consider it as insufficient and we shall try to explain the discrepancies between theory and experimental results by the same coupling of molecules as in the case of the polarization and the Kerr effect.

We shall not calculate the values of $\Delta\varepsilon_{12}$ based on S^m_{gas}, but starting from experimental values of $\Delta\varepsilon_{12}$ we shall calculate the value of S^m by means of (85), and hence the reduction factor R_s of saturation:

$$R_s = \frac{S^m}{S^m_{\text{gas}}}. \tag{90}$$

The more the latter differs from unity, the greater is the part played by the coupling.

(c) *Interpretation of experimental results.* Table III contains the following experimental data: the weight concentration c_2 of nitrobenzene, the number of nitrobenzene molecules N'_2 per c. c. of the solution, the density and the dielectric constant of the solution, and the variation of the dielectric constant $\Delta\varepsilon_{12}$ under the influence of an electric field of 70 kV/cm. The last four columns contain the molar constant S^m of electric saturation of nitrobenzene and the reduction factor R_s calculated on the assumption of a Lorentz field

$$\Delta\varepsilon = 3\,\frac{d_{12}c_2}{M}\,S^m\left(\frac{\varepsilon+2}{3}\right)^4 E^2$$

as well as of an Onsager field (formula (85)).

The dependence of S^m and R_s on N'_2 based on the assumption of a Lorentz or an Onsager field is represented by diagrams in fig. 5. The Lorentz curve shows that the decrease of the molar constant of saturation with increasing concentration is here still more strongly

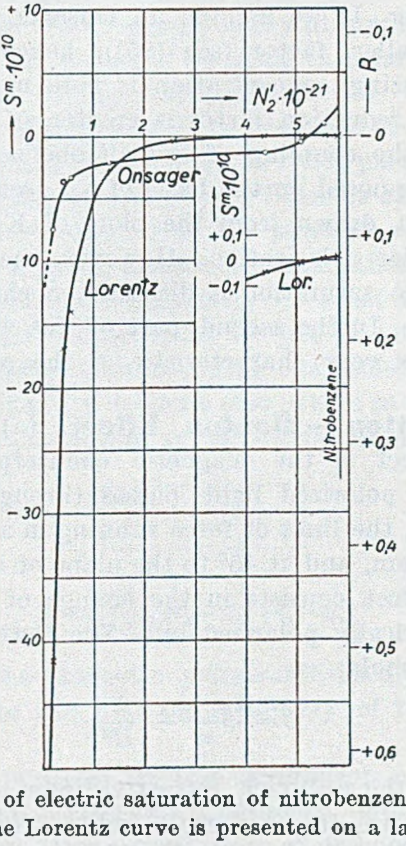

Fig. 5. Molar constant of electric saturation of nitrobenzene as a function of concentration. A part of the Lorentz curve is presented on a larger scale; the positive effect of saturation may be seen.

Table III. *Molar constant of electric saturation as a function of concentration (from solutions of nitrobenzene — benzene at 21° C and E=70kV/cm)*

c_2	$N'_2 \times 10^{-21}$	d_{12}	ε_{12}	$\Delta\varepsilon_{12} \times 10^4$	Lorentz		Onsager	
					$S^m \times 10^{10}$	R_s	$S^m \times 10^{10}$	R_s
0,0499	0,217	0,891	3,00	—1,89	—41,6	+0,51	—7,48	+0,092
0,0984	0,435	0,904	3,75	—2,71	—17,0	+0,21	—3,65	+0,045
0,1307	0,582	0,913	4,21	—4,06	—14,1	+0,17	—3,36	+0,041
0,2874	1,343	0,955	7,20	—9,47	—2,93	+0,036	—2,11	+0,026
0,522	2,63	1,028	13,05	—20,3	—0,45	+0,0055	—1,67	+0,0205
0,802	4,41	1,125	23,0	—32,7	—0,057	+0,00070	—1,35	+0,0165
0,902	5,14	1,164	28,3	—15,7	—0,0108	+0,00013	—0,53	+0,0065
0,972	5,57	1,192	32,5	+32,7	+0,0124	—0,00015	+0,99	—0,012
1	5,88	1,203	34,33	+75,4	+0,0220	—0,00027	+2,12	—0,026

marked than in the case of the Kerr effect (fig. 4). The decrease is so abrupt that the section corresponding to higher concentrations had to be drawn on a bigger scale. As has been previously mentioned in § 4 (c), this is caused by the fact that the ratio $F/E=(\varepsilon+2)/3$ enters to the fourth power. If we assume an Onsager field, there appears another, much smaller, factor (see (85)); hence the decrease of S^m and R_s with increasing concentration is here much less accentuated and in general the reduction factor is greater as shown by the curve of Onsager. Thus the coupling of the nitrobenzene molecules is not so strong as was supposed on the basis of a Lorentz field. This agrees with our conclusion drawn from the plots of Kerr's molar constant and of the molecular polarization. However, the final course of the curve of the electric saturation is different, S changing its sign from negative to positive. In the second part of this work we shall discuss this effect which is very characteristic of the second-kind coupling

§ 6 The Cotton — Mouton Effect. (a) *Pure liquids.* The Cotton-Mouton effect is the magnetic counterpart of the electric Kerr effect. Plane polarized light passes through the liquid placed in a magnetic field, the lines of force running in a direction perpendicular to the light beam, and at 45° to the plane of the vibrations of the light wave. The effect consists in the change of the plane polarized beam into an elliptically polarized one. The Cotton-Mouton constant is given by the formula

$$C=\frac{n_H-n_X}{n}\cdot\frac{1}{H^2}, \tag{91}$$

in which n means the ordinary refractive index for the given wavelenght, n_H and n_X are the refractive indices for vibrations parallel and perpendicular to the magnetic field respectively.

We shall define Cotton-Mouton molar constant, according to König (1938), as the difference between molecular refraction for parallel vibrations and that for vibrations perpendicular to a magnetic field of 1 oersted:

$$C^m = \frac{R_H - R_X}{H^2}, \tag{92}$$

where R_H and R_X are expressed by formulae similar to (41). In this case we do not make any distinction between the external and the internal field, as the magnetic permeability of most liquids is practically the same as that of the vacuum. The formula for C^m may be deduced from (42) directly, yielding

$$\boxed{C^m = C \frac{6n^2}{(n^2+2)^2} \frac{M}{d}.} \tag{93}$$

We see that in this case we are not concerned with the Lorentz or Onsager method of calculating the local field. Nevertheless, we shall consider the magnetic birefringence, as it will supply us with important information concerning molecular coupling in polar liquids (cf. part II of this work). The exceptional character of the Cotton-Mouton effect in contrast to the other effects discussed is connected with the fact that in this case the dipoles play no other part than that involved in the mutual coupling of molecules. There is no dipole orientation in an external field. Further, from the point of view of experimental methods, this effect is much more convenient than the preceding one, especially because electric conductivity does not intervene.

We shall express the constant C^m yet in another way, namely by means of parameters characterizing the molecule itself. We have a ready formula for it in § 4, formula (66), where in the case of magnetic dipoles we have to put $\theta_2 = 0$, as the dipole liquids are diamagnetic. Thus, we get

$$\boxed{C^m = 2\pi N \theta_1,} \tag{94}$$

where

$$\theta_1 = \frac{2}{45kT}(c_3 - c_1)(b_3 - b_1). \tag{95}$$

c_3 and c_1 are here the magnetic polarizabilities for directions parallel and perpendiculat to the axis od symmetry of the molecule respectively.

Formula (94) is based on the assumption of complete freedom of the molecules and is therefore applicable only to gases and those liquids in which there is no limitation of freedom of the molecules.

As we shall see, remarkable discrepancies will appear in cases in which coupling takes place.

(b) *Solutions.* As before, we shall limit ourselves to solutions of polar liquids (index 2) in a non-polar solvent (index 1).

From § 4 (b) we shall take the formula

$$C_{12}^{m} = C_{1}^{m} f_{1} + C_{2}^{m} f_{2}, \tag{96}$$

where

$$C_{12}^{m} = C_{12} \frac{6n_{12}^{2}}{(n_{12}^{2}+2)^{2}} \cdot \frac{M_{12}}{d_{12}}$$

and

$$C_{1}^{m} = C_{1} \frac{6n_{1}^{2}}{(n_{1}^{2}+2)^{2}} \cdot \frac{M_{1}}{d_{1}}.$$

C_{2}^{m} should be determined from the equation (96) and compared with the value of the same constant for gas (C_{gas}^{m}). Therefore, we shall calculate the „reducing factor" R_{CM}:

$$R_{CM} = \frac{C_{2}^{m}}{C_{\text{gas}}^{m}}. \tag{97}$$

(c) *The interpretation of experimental results.* As far as we know, König (1938) was the first to calculate the Cotton-Mouton molar constant. His calculations were based on measurements with solutions of nitrobenzene in carbon tetrachloride performed by A. Goldet and the author with the large electromagnet at Bellevue in 1934. The results are presented in Table IV. The first column contains the weight concentrations, the second — the densities of the solutions extrapolated from measurements of N. N. Pal [7], the third — the number of nitrobenzene molecules N_{2}' per c. c., calculated from the preceding, the fourth — the Cotton-Mouton molar constant as given by König [8] and the fifth — the reducing factor R_{CM}. In order to calculate the latter, the value of the Cotton-Mouton molar constant for vapour is needed. König made an attempt to measure it, but found that the magnitude of the effect is within the range of experimental errors. For 20° C and 670 mm Hg he obtained

$$C_{\text{gas}}^{m} < 550 \times 10^{-17},$$

whereas for an infinitely diluted solution of nitrobenzene we obtain by extrapolation to $c_{2} = 0$

$$C_{\infty}^{m} = \text{ca. } 400 \times 10^{-17}$$

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[7] From *Landolt,Börnstein Tables*, vol. III, part 3, p. 1947 (1936).

[8] There is only a diagram in König's paper. The numerical values of the fourth column were obtained by careful measurement of the co-ordinates.

We shall use this value instead of C^m_{gas} for calculating R_{CM}, the obvious result being that $R_{CM}=1$ for $c_2=0$, which is equivalent to the assumption that the coupling of the nitrobenzene molecules with the solvent does not influence the constant C^m_2. In fact, as will be shown in Part 11 of this work, this influence is negligible.

Table IV. *Cotton-Mouton molar constant* C^m_2 *as a function of concentration (from nitrobenzene* — CCl_4 *solutions at* 20^0 *C)*

c_2	d_{12}	$N'_2 \times 10^{-21}$	$C^m_1 \times 10^{17}$	R_{CM}
0	1,5940	0	(ca. 400)	1
0,1217	1,5365	0,914	426	1,065
0,3084	1,4530	2.191	490	1,225
0,5461	1,3550	3,619	572	1,43
1	1,2035	5,885	700	1,75

As may be seen from (94) the Cotton-Mouton molar constant should really be independent of the concentration of the molecules, whereas, as shown in Table IV and graphically in fig. 6, C^m_2 increases rapidly with the concentration. The „reducing factor“ R_{CM} is in this case greater than unity, in contrast to the preceding effects. This unusual behaviour is caused by the type II coupling, and the effect

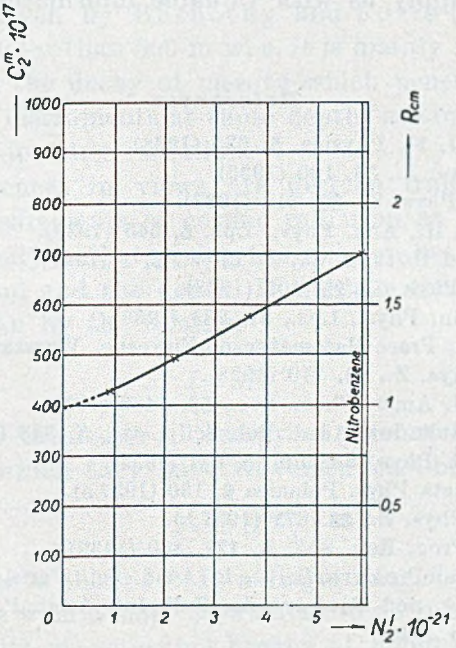

Fig. 6. Cotton-Mouton molar constant as a function of concentration.

is readily understood from the following exaggerated example. Let us suppose that the nitrobenezene molecules are so strongly coupled two by two that one may consider one gram molecule of the liquid as composed of $N/2$ associated pairs. The magnetic and optical polarizabilities of each pair are doubled (if we neglect mutual inductance influence). In consequence the expression θ_1 (95) is increased by a factor of four and therefore the molar constant C^m is doubled, hence $R_{EM}=2$. In reality for nitrobenzene $R_{CM}=1{,}75$, which means that the molecules are not associated in rigid pairs. The theory of the coupling (see Part II) gives for R_{CM} a value slightly smaller than 1,75 if we admit a coupling energy required by the three preceding effects on the assumption of a Lorentz field. To obtain the value $R_{CM}=1{,}75$ we must either admit a greater coupling energy, which would disagree with the trend of the preceding effects, or admit the possibility of a coupling of molecules in larger aggregates than in pairs. The latter possibility is in accord with the variation of the dielectric polarization and the Kerr effect, but only if the Onsager field is assumed. We see that although the local field does not appear directly in the Cotton-Mouton effect, the latter may supply us with valuable information on this subject.

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ON SOME PHOTON RADIATION OBSERVED BY MEASUREMENTS OF COSMIC RAYS AT GREAT DEPTHS

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The problem of great depths

As concerns the problem of cosmic radiation reaching great depths (some hundred metres water equivalent) it is assumed by most physicists that this radiation is a meson radiation (perhaps with some admixture of protons) accompanied by knock-on electrons and cascade showers started by these (Wilson 1943). Quite different views on this subject are given by Barnóthy and Forró (1948) who assume that at depths greater than 500 m w. e. it is mainly non-ionizing radiation produced by the decay of mesons which penetrates there. They consider that our instruments at those depths are operated by secondaries of that non-ionizing radiation.

These differences in views are derived from some anomalies observed by measurements of cosmic radiation at great depths. The best known anomaly is that giving the relation between the intensity of cosmic radiation and the depth. If we take the integral spectrum of mesons as given by the relation

$$I = cE^{-\gamma}$$

and we also take the losses of energy of mesons to be proportional to the depth H which they have traversed we obtain the relation

$$I = c'H^{-\gamma},$$

in which γ is equal to about 1,8. In a diagram log J vs. log H we should get a straight line with a slope γ, whereas if we take into account the experimental results, we get a line broken at about 300 m w. e. (Clay 1939). Up to 300 m w. e. we have a line with a slope of 1,8 and beyond this depth the slope changes from the value 1,8 to 2,8. Because of the fact that only mesons with energies higher than 10^{11} eV can penetrate to this depth, we might conclude that besides the normal loss of energy through ionization the particles concerned suffer an additional loss through some other mechanism. The other explanation might be that the spectrum of energy of mesons above energies of 10^{11} *eV* drops quicker than may be expected from the form $E^{-1,8}$.

Lyons (1941) considers an additional loss of energy ot very energetic mesons by radiation as a cause of this change of the dependence of intensity on depth. The mesons of high energies might radiate most of their energy in one collision and therefore we should get in the dependence of the intensity of cosmic rays vs. depth an additional exponential factor giving a quicker drop of the intensity with the depth. A closer analysis of this process proves that the losses of energy by radiation suffered by mesons of energies sufficient to penetrate such depths (10^{11} *eV*) are too small to explain this phenomenon.

There are now in the literature of the subject two opinions on this problem, based on similar assumptions of meson decay, given by J. Barnóthy and M. Forró (1948) and K. Greisen (1948). Barnothy had already considered this question in 1940.

The mean range of a meson in vacuum (because of the decay) is given by the formula

$$R = \tau_0 \cdot \frac{P}{\mu},$$

where τ_0 is the mean proper lifetime of the meson, P its momentum and μ its rest mass. In the spectrum of mesons we have a lack of particles of low energies, but in the spectrum of decay products we have a lack of particles of very high energies. This last phenomenon will be observed for those energies of mesons for which the mean range is equal to the height of production of mesons in the atmosphere. In the spectrum of decay products of mesons we have to add to the form $E^{-1,8}$ the factor E^{-1} for energies corresponding to the decay range equal to the height of the meson production layer. If we assume that at great depths we register the products of meson decay and that the losses of their energies are proportional to the depth they traverse, we get for sufficiently high energies a dependence of the intensity on the depth in the form $E^{-2,8}$.

The main difference between Barnóthy and Forró and Greisen is that Barnóthy and Forró assume that at great depths we observe neutral products of decay of normal mesons ($m \approx 200$); Greisen on the contrary introduces the decay of mesons of mass 300 with a much lower lifetime ($6,10^{-8}$ sec) and obtains in this way for the spectrum of energy a change of the form $E^{-1,8}$ to $E^{-2,8}$ for energies greater than 10^{11} *eV*. This is the energy necessary for a meson to traverse some hundred metres water equivalent. Thus, at great depths we observe normal mesons which themselves are already decay products.

For the evaluation of this critical energy, Greisen assumed to long a lifetime for the meson of mass 300, viz. 6.10^{-8} sec instead of about 8.10^{-9} sec, as it is now known. For the latter value for τ_0 the change of the exponent in the energy spectrum should occur at about 10^{12} *eV* rather than at 10^{11} *eV*. We might thus take the explanation of Greisen as quite satisfactory, because of the great inaccuracies in the data we have here at our disposal, and because of the neglect of the losses of energy due to radiation [1]).

Thus, we can assume that in cosmic rays at great depths we have to do with secondary particles produced by the same processes which are known from experiments at sea level.

But Barnóthy and Forró in the paper mentioned (1948) report among many interesting results also a phenomenon which they inerpret as an argument for the opinion that at great depths we have to do especially with neutral meson-decay products. This phenomenon mentioned already in 1939, was also communicated at the Cracow Cosmic-Ray Conference in Oct. 1947. They observed at the depth of 1000 m w. e. that the radiation there measured was able to give many times more double than threefold coincidences in the same telescope. The ratio of threefold to double coincidences in their measurements was 0,05. Barnóthy and Forró express the opinion that this phenomenon proves the existence at great depths of a scarcely ionizing component of cosmic radiation. For this component the probability of threefold coincidences ought to be decidedly smaller than that of double ones.

The aim of this work, of which we are giving provisional results in this paper, was to check this interesting phenomenon and investigate more closely the properties of the radiation which produces it.

Description of the aparatus

Our measurements were performed in the salt mine at Wieliczka near Cracow. The deepest level at our disposal was 282 m below ground. The layers above the telescope consisted of rock-salt, sandstone, gray

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[1] Since this paper was submitted for publication, we came across a paper of Satio Hayakawa and Sin-Itiro Tomonaga, Phys. Rev., **75**, 1958 (1949), in which these authors, considering the decay of mesons of mass from 287 to 217 with a lifetime of $1 \cdot 10^{-8}$ sec and taking into account the losses of energy due to radiation, have obtained a curve of the dependence of intensity vs. depth in accordance with experimental data.

silt and silt with grains of rock-salt, gypsum and anhydrite. The water equivalent was estimated from samples taken from different layers at different levels. The measurements were carried out in horizontal passages (about 2 m high) in the salt layers at two levels 660 and 540 m w. e. The work in the salt mine requires the apparatus to be built very thoroughly. Salt powder and moisture are deposited during the work and therefore the whole apparatus must be tightly closed. These difficulties may be easier overcome if we use all-metal counters with earthed cathodes. Because of the very large fluctuations of voltage in the mine, the apparatus had to be supplied with a stabilizer stabilizing the voltage within wide limits. The magnetic stabilizer [2]) which has been used was very helpful in this matter. The special conditions of work also needed some additional arrangements to make work continuous and safe (such as an automatic switch for too low voltage, a delayed switch for switching on the high tension for the register circuits, an electric clock set going by this delayed switch, etc.).

The measurements of the ratio of threefold to double coincidences were performed with an apparatus much improved in comparison with that of Barnóthy and Forró. The telescope consisted of three GM-counters 1, 2, 3 (Fig. 1). The middle counter 2 was of larger dimensions than the two others. The telescope was protected against side showers by 6 anticoincidence counters. The double coincidences D of the counters 1, 3, and the threefold coincidences T of the counters 1, 2, 3 were registered simultaneously by two separate P. O. registers. In this way we got a fairly small statistical error of the ratio T/D even for a not very great number of D coincidences. This is very important here because of the very low intensity of the cosmic radiation at the depths at which we have worked (the number of T coincidences at the lowest level is at the rate of about 1 per hour). In order to measure the double coincidences D the resolving time of our apparatus had

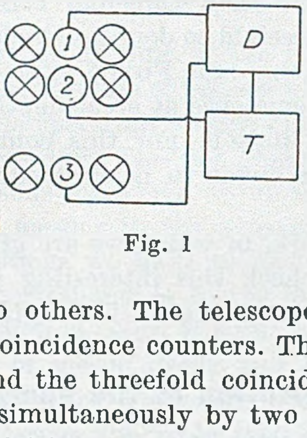

Fig. 1

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[2] The authors are greatly indebted for the design and the construction of this stabilizer to Mr. T. Czayka of the Cracow Mining Academy.

to be rather small. It was 2,6 μsec, which we achieved in such a way that the rectangular pulse coming from the counter amplifier was differentiated with a small time constant in the circuit of the grid of the Rossi valves (Mięsowicz 1947). The GM-counters we used were of the all-metal type filled with the usual argon-alcohol mixture. The dimensions of the counters were

$$\left.\begin{array}{ll}\text{Counters 1 and 2 . . . . .} & 4{,}3\times 65\ \text{cm}^2,\\ \text{Counter 3 and anticounters} & 5{,}2\times 70\ \text{cm}^2.\end{array}\right\}\ \text{Brass tubes 1 mm thick.}$$

The number of pulses per min. of these counters in the laboratory were about 650 for smaller and 900 for larger counters. The number of pulses per min. at the lowest level in the mine were about 70 and 100 respectively. The low background rates of the counters were very convenient for our measurements. After protecting the counters 1 and 2 by 5 cm Pb at the lowest level, the background dropped to 16 per min.

Measurements of the ratio of threefold to double and fourfold to threefold coincidences

In our preliminary measurements performed at two depths (660 m w. e. and 540 m w. e.) we found more double than threefold coincidences, proving in this way qualitatively even for those depths the existence of the effect found by Barnóthy and Forró at 1000 m w.e. We did not find however any difference between the number of threefold and fourfold coincidences. The results of the measurements are given in Tables I, II, and III. In all tables the numbers of D-coincidences are given after subtracting the accidental coincidences.

TABLE I

Vertical telescope at a depth of 660 m e. w.

	number of coincidences and time	average rate per hour
Threefold coinc. T	321	$1{,}34 \pm 0{,}05$
Double coinc. D	443	$1{,}86 \pm 0{,}06$
Time (in hours)	239,46	
Ratio of threefold to double coinc.	$\frac{T}{D} = (72{,}5 \pm 2{,}7)\ \%$	

TABLE II

Vertical telescope at a depth of 540 m w. e.

	number of coincidences and time	average rate per hour
Therefold coinc. T	454	$2{,}08 \pm 0{,}07$
Double coinc. D	660	$3{,}01 \pm 0{,}08$
Time (in hours)	218,6	
Ratio of threefold to double coinc.	$\frac{T}{D} = (69{,}0 \pm 2{,}2)\ \%$	

TABLE III

Vertical telescope at a depth of 540 m w. e.

	number of coinc. and time	average rate per hour
Fourfold coinc. F	354	$2{,}09 \pm 0{,}07$
Threefold coinc. T	356	$2{,}10 \pm 0{,}08$
Time (in hours)	169,3	
Ratio of fourfold to threefold coinc.	$\frac{F}{T} = 0{,}995 \pm 0{,}04$	

Investigation of the properties of the radiation causing the excess of double over threefold coincidences

Let us write the number of double, threefold and fourfold coincidences in the form (Clay 1942)

$$D = \lambda^2 N + J,$$
$$T = \lambda^3 N + J,$$
$$F = \lambda^4 N + J,$$

where J is the intensity of the ionizing component of the radiation going through the telescope for which we assume the efficiency of the GM-counter to be 1,0, N the intensity of the non-ionizing component and λ the efficiency of the GM-counter for this component. From our measurements of the ratio of F/T it follows that $\lambda^3 N \ll J$, in other words the number of threefold coincidences produced by the non-ionizing component is negligible in comparison with the number of threefold coincidences produced by the ionizing component. Then, we may consider T as the intensity J of the ionizing component and write

$$\frac{T}{D} = \frac{T}{\lambda^2 N + T} = \frac{T}{A + T},$$

where A gives the number of double coincidences due to the non-ionizing component. Table IV gives a comparison of the values of A and T for two depths.

TABLE IV

Depth	coincidences due to non-ionizing component A	coincidences due to ionizing component T
540 m w. e.	0,93/hour	2,08/hour
660 m w. e.	0,52 „	1,34 „

If A is considered as a measure of the intensity of the non-ionizing component of cosmic radiation, we should have a strong dependence on the depth and a high relative intensity. The ionizing component, however, shows that the intensity decreases with depth — in accordance with the measurements of other authors. For the exponent in the absorption formula we get from our figures the value 2,1, which taking into account our rather poor evaluation of the water equivalent, is quite consistent, within the limits of experimental errors, with the values given by other authors.

The other characteristics of the component A correspond in general to those found by Barnóthy and Forró for radiation recorded by double coincidences. For the investigation of the angular dependence of the component A, measurements of threefold and double coincidences in a horizontal position of the telescope have been carried out. The results are given in Table V.

From the figures given in it we can see that for a horizontal position of the telescope the number of threefold coincidences is negligible and the number of double coincidences has, within the limits of experimental errors, the same value as A. This is an evidence for the isotropic character of the component A.

TABLE V

The telescope in a horizontal position at 540 m w. e.

	number of coincidences and time	rate per hour
Threefold coincid. T	1	
Double coincid. D	109	0,90
Time (in hours)	120,5	

We have investigated also the influence of lead put between the counters on the ratio of T/D. The figures are given in Table VI.

TABLE VI

The telescope in a vertical position at 540 m w. e.

Thickness of lead in mm	T/D	A	$\frac{A}{A_{(0\text{ cm Pb})}}$
0	0,690	0,93	1,00
5	0,795	0,49	0,53
10	0,906	0,19	0,20
15	0,930	0,13	0,14
50	0,989	0,02	0,02

From these figures we can see that the component A is absorbed with an absorption coefficient of about 1,4 cm^{-1} Pb.

Efficiency of the counters for the component A

Barnóthy and Forró who evaluated the ratio T/D at 1000 m w. e. and found the value 0,05 interpret this figure as the efficiency of the counters for the radiation giving the coincidences. We think that this would be correct only if the telescope had not registered also a number of ionizing particles for which the efficiency of the GM-counters is equal to 1,0, and for which the numbers of double and threefold coincidences are the same. For the efficiency λ of the counter for radiation causing the excess of the double coincidences, we have $\lambda < T/D$. On the other hand, in these circumstances we cannot at all evaluate the specific ionization as it was done by Barnóthy and Forró, who gave the value of 0,04 ions/cm N. T. P. air for this radiation. It is not known a priori whether this radiation reacts on the counter by producing ions in the gas of the counter, or whether it gives secondaries in the walls of the counter which initiate the discharge. In the first case, the efficiency of the counter would depend on the specific ionization of the gas contained in it, but in the second case it would depend on the probability of emitting secondaries in the walls of the counter.

For getting at least a rough evaluation of the efficiency of the GM-counters for the radiation A, we compared the number of counts of a single counter caused by the radiation which is absorbed by 5 cm Pb with the number of double coincidences A. At 660 m w. e., for a counter of a length of $l = 65$ cm and a diameter of $a = 4{,}3$ cm, the number of counts without screening was 80/min., with a screen of 5 cm Pb from all sides it was 16/min., thus the number of counts due to the radiation absorbed in 5 cm Pb was 64/min. If we assume that this radiation is isotropic, we have a dependence between the number N of counts, the flux j of the radiation and the efficiency λ of the counters for this radiation of the form

$$N = \pi^2 al\left(1 + \frac{a}{2l}\right)\lambda j.$$

We get from it $\lambda j = 0{,}022/\text{sterad. cm}^2 \text{ min.}$

Let us now evaluate the probability of double coincidences due to this radiation, without any discussion of the particulars of the mechanism of this process. Let λ' be the efficiency of the telescope for double coincidences for this radiation, i. e., λ' is the probability that the particle or photon which discharges the first counter enters the second one and discharges it also. Assuming the radiation to be isotropic and paying due regard to the solid angle determined by the telescope, we get by simple integration for the number of double coincidences

$$A = 2\lambda\lambda' j a^2 \frac{l}{h} \operatorname{arc\,tang} \frac{l}{h},$$

where $h = 18$ cm is the mutual distance of the counters in the double coincidence telescope. From this equation, we get

$$\lambda' = 0{,}002,$$

a value 20 times smaller than that given by Barnóthy and Forró.

Conclusions

The results of this work therefore show the following properties of the radiation giving the excess of double over threefold coincidences:

1. It is scarcely ionizing.
2. It is isotropic.
3. It is absorbed by about 0,5 cm Pb to 50 %.

All these properties seem to prove the fact that this radiation is of photon character, and the absorption coefficient as well as the efficiency of the counters for this radiation also suggest that we may have here to do with some γ-radiation of about 1 *MeV* energy, originating perhaps from natural radioactive substances.

It remains to explain the mechanism of the coincidences given by such a radiation. It is not improbable that we are confronted here with an example of some compound Compton-effect. As a matter of fact, it might be possible that a photon entering the first counter and discharging it might enter afterwards the second counter and give off there another electron which discharges this second counter.

It may be seen from our evaluation of the efficiency of the counters for that radiation — assuming that the discharge in the counter is started by photons — that we get thus quite a reasonable figure for the efficiency for the double coincidences. Of course, in this case $\lambda' < \lambda$, because the loss of energy of the photons in the first counter causes a drop in the efficiency and the photons are dispersed producing in this way also an additional inefficiency.

We wish to thank the Science Department of the Ministry of education for financial aid which made it possible to carry out this work, and the Polish Academy of Science and Letters for supplying the laboratory at Wieliczka with lead. Our thanks are also due to the managers of the salt Mine of Wieliczka and all the miners for their kind co-operation, during our work at Wieliczka. We also thank Mr. S. Wojtów and Mr. A. Mikucki for their valuable help.

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PROPAGATION OF A CUT-OFF TRAIN OF DE BROGLIE WAVES

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The propagation of a cut-off train of monochromatic de Broglie waves has been investigated. Formulae have been developed describing completely the arrival of the wave front, the forerunner, and the main wave.

In the present paper we deal with the following problem of the propagation of a cut-off train of plane de Broglie waves. At the time $t=0$ we have at the negative x-axis a train of monochromatic de Broglie waves of frequency ν_0, that is

$$e^{i\alpha}\, e^{-2\pi i\nu_0\left(t-\frac{x}{u_0}\right)} \tag{1}$$

with a phase velocity u_0 given by

$$u_0=\frac{c}{\left(1-\left(\frac{\nu_1}{\nu_0}\right)^2\right)^{1/2}}, \tag{2}$$

where $\nu_1=m_0c^2/h$ is the frequency corresponding to the de Broglie wave length of a particle of rest mass m_0; α is an arbitrary phase constant. Our problem is to determine the propagation of these waves for $t>0$ and $x>0$.

This problem is formally a special case of Sommerfeld's (1914, cf. also L. Brillouin 1914) problem of the propagation of an electromagnetic cut-off wave train in a dispersive medium, namely the one dealing with free electrons without damping. This specialization enables us to obtain convergent series developments of the exact solution, whereas in Sommerfeld's general case it was only possible to discuss it approximately.

§ 1. Solution of the problem and its series developments. The integral

$$\varphi(t)=\frac{e^{i\alpha}}{2\pi i}\int\limits_{(U)} e^{-2\pi i\nu t}\,\frac{d\nu}{\nu-\nu_0}$$

taken in the upper half of the complex ν-plane along the path (U), fig. 1, from $+\infty$ to $-\infty$ of the real axis defines the function

$$\varphi(t)=\begin{cases}0 & \text{for } t<0,\\ e^{i\alpha}\,e^{-2\pi i\nu_0 t} & \text{for } t>0.\end{cases}$$

For $t<0$ we can namely deform the path (U) into the infinity of the upper half of the ν-plane where $\exp(-2\pi i\nu t)$ for $t<0$ vanishes exponentially. For $t>0$, however, we can deform (U) into the infinity of the lower half of the complex ν-plane, but in doing so, we must pass the pole at $\nu=\nu_0$, which gives a residue.

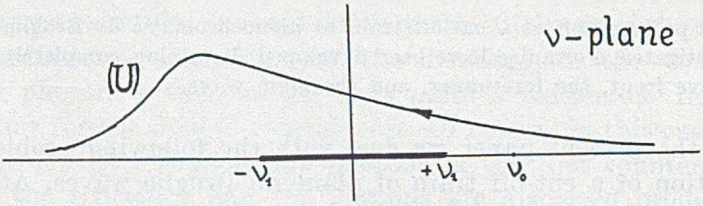

Fig. 1.

To a corpuscular wave of frequency ν corresponds a phase velocity u given by

$$\frac{1}{u}=\frac{1}{c}\left(1-\frac{\nu_1^2}{\nu^2}\right)^{1/2}. \tag{3}$$

We expect, therefore, the solution of our problem to be

$$f(t,x)=\frac{e^{i\alpha}}{2\pi i}\int\limits_{(U)} e^{w}\frac{d\nu}{\nu-\nu_0}, \tag{4}$$

where

$$w=-2\pi i\nu\left(t-\frac{x}{u}\right)=-2\pi i\left(\nu t-\frac{x}{c}\,(\nu^2-\nu_1^2)^{1/2}\right). \tag{5}$$

Owing to the fact that u in (3) is positive, we must give to the square root in (5) a positive sign for real ν-values $\nu>\nu_1$. The points $\nu=\pm\nu_1$ in (5) are branch points. In order to have to do with a definite branch of w, we place a branch cut on the real axis of the ν-plane between these two points.

First of all, we can show that $f(t,x)$ vanishes for $t<\frac{x}{c}$, that is for $\beta>1$, if

$$\beta=\frac{x}{ct}. \tag{6}$$

This means that the velocity of the wave front cannot be greater than the velocity of light. In the case $\beta > 1$ we can indeed deform the path of integration (U) into the infinity of the upper half-plane, because for large ν-values the function w, eq. (5), is given by $w = -2\pi i\nu\left(t - \frac{x}{c}\right)$. Hence,

$$f(t,x) = 0 \quad \text{for} \quad \beta > 1.$$

For $\beta < 1$, however, we can deform (U) into the infinity of the lower half-plane, where, in this case, w vanishes. But then there remains still a path of integration (U_1) surrounding the branch cut between $-\nu_1$ and $+\nu_1$ and the pole at $\nu = \nu_0$. For $\beta < 1$ we can therefore use instead of (U) the path of integration (U_1).

The meaning of β is as follows: according to (6), the value of $c\beta = x/t$ determines the velocity of a particle which would reach the point x at the time t starting from $x = 0$ at the time $t = 0$.

In order to obtain convergent developments for $f(t,x)$ in the case of $\beta < 1$, we deform (U_1) into a path of integration (E), fig. 2, on which

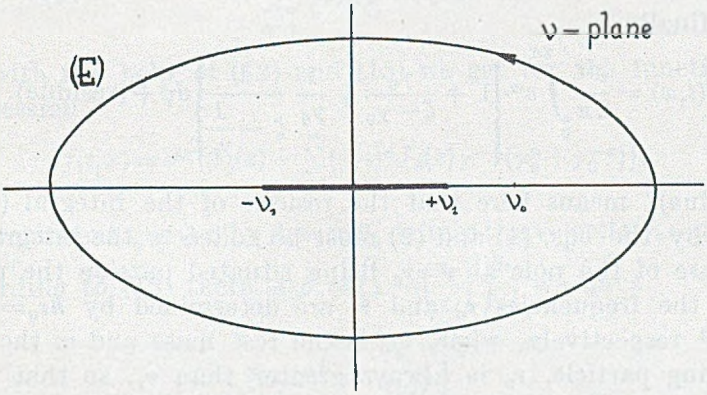

Fig. 2.

the real part of w, eq. (5), vanishes. (E) is an ellipse with its centre at $\nu = 0$ and with the principal semi-axes

$$a = \frac{\nu_1}{\sqrt{1-\beta^2}} \quad \text{and} \quad b = \frac{\nu_1 \beta}{\sqrt{1-\beta^2}}. \tag{7}$$

a and b are situated on the real and imaginary axes of the complex ν-plane respectively. (E) can therefore be represented by

$$\nu = \frac{\nu_1}{\sqrt{1-\beta^2}} (\cos\psi + i\beta \sin\psi) \qquad (0 \leqslant \psi \leqslant 2\pi).$$

Because on (E)

$$w = w_0 = -iz\cos\psi, \quad \text{where} \quad z = 2\pi\frac{x}{c}\nu_1\frac{\sqrt{1-\beta^2}}{\beta}, \tag{8}$$

we have

$$f(t,x) = \frac{e^{i\alpha}}{2\pi i}\int_0^{2\pi} e^{w_0}\frac{-\sin\psi + i\beta\cos\psi}{\cos\psi + i\beta\sin\psi - \frac{\nu_0}{\nu_1}\sqrt{1-\beta^2}}\,d\psi. \tag{9}$$

Putting

$$\zeta = \gamma e^{i\psi}, \quad \gamma = \sqrt{\frac{1+\beta}{1-\beta}}, \quad \gamma_0 = \frac{\nu_0}{\nu_1} + \sqrt{\left(\frac{\nu_0}{\nu_1}\right)^2 - 1}, \tag{10}$$

we obtain

$$\begin{aligned} \frac{-\sin\psi + i\beta\cos\psi}{\cos\psi + i\beta\sin\psi - \frac{\nu_0}{\nu_1}\sqrt{1-\beta^2}} &= i\,\frac{\zeta^2-1}{\zeta^2 - 2\frac{\nu_0}{\nu_1}\zeta + 1} \\ &= i\left(1 + \frac{\gamma_0}{\zeta-\gamma_0} + \frac{1}{\gamma_0}\,\frac{1}{\zeta - \frac{1}{\gamma_0}}\right), \end{aligned} \tag{11}$$

so that finally

$$f(t,x) = \frac{e^{i\alpha}}{2\pi}\int_0^{2\pi} e^{w_0}\left|1 + \frac{\gamma_0}{\zeta-\gamma_0} + \frac{1}{\gamma_0}\,\frac{1}{\zeta - \frac{1}{\gamma_0}}\right| d\psi + (\text{residue}). \tag{12}$$

„+(residue)" means here that the residue of the integral (4) which is given by the eqs. (1) and (2) must be added to the integral in (12) in the case of the pole at $\nu=\nu_0$ being situated outside the path (E).

As the frequencies ν_0 and ν_1 are determined by $h\nu_0 = mc^2$ and $h\nu_1 = m_0c^2$ respectively, where m_0 is the rest mass and m the mass of the moving particle, ν_0 is always greater than ν_1, so that the pole at $\nu=\nu_0$ lies outside of the branch cut. For $\beta\to 1$, according to (7), the semiaxes of (E) become infinite, and for $\beta\to 0$ the path (E) approaches the branch cut. If ν_0 is equal to the greater semiaxis a the path of integration (E) passes through the pole at $\nu=\nu_0$. Denoting the corresponding value of β by β_0, we get, according to (7),

$$\nu_0 = \frac{\nu_1}{\sqrt{1-\beta_0^2}}. \tag{13}$$

Inserting this into the eq. (10) for γ_0, we get

$$\gamma_0 = \sqrt{\frac{1+\beta_0}{1-\beta_0}}. \tag{14}$$

Using (12), we can now obtain representations for $f(t,x)$ by means of convergent series of Bessel functions

$$J_n(z)=\frac{i^n}{2\pi}\int_0^{2\pi} e^{-iz\cos\psi}e^{-in\psi}\,d\psi=\frac{i^n}{2\pi}\int_0^{2\pi} e^{-iz\cos\psi}e^{+in\psi}\,d\psi. \tag{15}$$

We deal with the case $1>\beta>\beta_0$ first. According to (10) and (14), we have then $+\infty>\gamma>\gamma_0$, so that owing to $\gamma=|\zeta|$

$$+\infty>|\zeta|>\gamma_0.$$

The path of intergration (E) contains in this case the pole at $\nu=\nu_0$ in its inside, so that there does not appear any residue in (12). According to $\nu_0>\nu_1$ and (10) we have $\gamma_0>1$. Under the supposition that $|\zeta|>\gamma_0$, we get have also $|\zeta|>\frac{1}{\gamma_0}$, so that the bracket expression under the sign of integration in (12) can be expanded into the power-series

$$1+\sum_{n=1}^{\infty}\frac{1}{\zeta^n}(\gamma_0^n+\gamma_0^{-n}).$$

Hence, with the help of (12) and (15) we get for the function $f(t,x)$ the expression

$$f(t,x)=e^{i\alpha}\{J_0(z)+\sum_{n=1}^{\infty}(-i)^nJ_n(z)\gamma^{-n}(\gamma_0^n+\gamma_0^{-n})\}. \tag{16}$$

The moment t_0 given by $\beta_0=x/ct_0$ defines the velocity $v_0=x/t_0=c\beta_0$. As, according to (13) there is $\beta_0=\left(1-\left(\frac{\nu_1}{\nu_0}\right)^2\right)^{1/2}$, we have

$$v_0=c\left(1-\left(\frac{\nu_1}{\nu_0}\right)^2\right)^{1/2},$$

and hence, using (2),

$$u_0v_0=c^2.$$

v_0 is therefore the group velocity corresponding to the phase velocity u_0. At the time t_0 there arrives at the point x that part of the wave train which travels with the group velocity v_0, i. e. with the velocity of the incident particles.

This means that the development (16) describes the events for a given point x from the arrival of the wave front to the arrival of the waves travelling with the particle velocity v_0. This development can be used also for times t greater than t_0, that is for $\beta_0>\beta>0$. But in this case the convergence is very slow.

For these β-values we get, however, a good convergent series by developing in (12) the expressions $\frac{\gamma_0}{\zeta-\gamma_0}$ and $\frac{1}{\gamma_0}\frac{1}{\zeta-(1/\gamma_0)}$ into power-series in ζ/γ_0 and $1/\zeta\gamma_0$ respectively. Taking into account that now the pole at $\nu=\nu_0$ lies outside of the path of integration (E) and therefore the residue must be added, we obtain

$$f(t,x)=e^{i\alpha}\left\{e^{-2\pi i\nu_0\left(t-\frac{x}{c}\left(1-\left(\frac{\nu_1}{\nu_0}\right)^2\right)^{1/2}\right)}-\sum_{n=1}^{\infty}(-i)^n J_n(z)\gamma_0^{-n}(\gamma^n-\gamma^{-n})\right\}. \tag{17}$$

(17) also can be used for all β-values in the interval $(0,1)$. From the equality of (16) and (17) we obtain a development of the incident wave given by (1) and (2) in a series of Bessel functions

$$e^{-2\pi i\nu_1\left(t-\frac{x}{c}\left(1-\left(\frac{\nu_1}{\nu_0}\right)^2\right)^{1/2}\right)}=J_0(z)+\sum_{n=1}^{\infty}(-i)^n J_n(z)\left(\left(\frac{\gamma_0}{\gamma}\right)^n+\left(\frac{\gamma}{\gamma_0}\right)^n\right).$$

This expansion follows also directly from the generating function of Bessel functions (Watson 1944)

$$e^{\frac{z}{2}(t-t^{-1})}=J_0(z)+\sum_{n=1}^{\infty}J_n(z)\,(t^n+(-t)^{-n})$$

if we put here $t=-i\gamma_0/\gamma$.

For large values of z we need an asymptotic expression for the wave function $f(t,x)$. We can get it by applying to (9) the principle of stationary phase. For large z-values the oscillations of e^{w_0} are very rapid in comparison with the changes of the remaining part of the integrand in (9). The phase w_0 has stationary values for $\psi=0$ and $\psi=\pi$. Using the approximations $\cos\psi=1-\frac{\psi^2}{2}$ and $\cos(\pi+\varphi)=-1+\frac{\varphi^2}{2}$ in the neighbourhood of these points, we get in the usual way

$$f(t,x)=\frac{e^{i\alpha}}{\sqrt{2\pi}}\frac{\nu_1\beta}{\sqrt{z}}\left(\frac{e^{-i\left(z-\frac{\pi}{4}\right)}}{\nu_1-\nu_0\sqrt{1-\beta^2}}+\frac{e^{+i\left(z-\frac{\pi}{4}\right)}}{\nu_1+\nu_0\sqrt{1-\beta^2}}\right)+\text{(residue)}. \tag{18}$$

Formula (18) can be used only if the path of integration (E) does not pass through the neighbourhood of the pole at ν_0, independently of the fact whether ν_0 lies inside or outside of (E). In the second case, that is for $\beta_0>\beta>0$, we must, however, take into account the residue at $\nu=\nu_0$.

Asymptotic expansions containing descendig powers of z and the expression (18) as the first term can be obtained by developing the product of $\exp\left[-iz\left((\cos\psi-\left(1-\frac{\psi^2}{2}\right)\right)\right]$ or $\exp\left[-iz\left(\cos(\pi+\varphi)+1-\frac{\varphi^2}{2}\right)\right]$ and the expression (11) in a series of ascending powers of ψ and φ respectively (an der Corput 1939). We can also get the expression (18) by the method of steepest descent.

§ 2. Discussion of the solution. In order to have an idea about the order of magnitude of z we introduce in (8) by

$$\Lambda=\frac{h}{m_0c}=\frac{c}{\nu_1} \tag{19}$$

the Compton wave length Λ of the incident particles. Thus we get

$$z=2\pi\frac{x}{\Lambda}\frac{\sqrt{1-\beta^2}}{\beta}. \tag{20}$$

For electrons, for example, is $\Lambda=2{,}4\ 10^{-10}$ cm, and therefore is z a large number for $x\neq 0$ and $\beta<1$.

First of all, we consider the arrival of the wave front at a given point x. It comes at the instant determined by $\beta=1$, and hence by $z=0$ and $\gamma=\infty$. As $J_0(z)$ is the only Bessel function which does not disappear for $z=0$, it follows from (16) that for $\beta\sim 1$

$$f(t,x)=e^{i\alpha}J_0(z). \tag{21}$$

The intensity $|f(t,x)|^2$ of the arriving wave front is therefore of the order of magnitude of 1, that is of that of the incident wave. Moreover, (21) is independent of the frequency of the incident wave. We are hence compelled to assume that the events at the wave front are determined only by the process of the cutting off of the incident wave.

We ask now whether it is possible to assign a wave lenght λ and a frequency n to the front wave (21). The distances of two consecutive zero points of the Bessel functions $J_n(z)$ are of the order of magnitude of π. The variable z can therefore play the role of a phase. If z would be equal to $2\pi\left(\frac{t}{T}-\frac{x}{\lambda}\right)$, then the wave length λ and the frequency $n=1/T$ would be given by

$$\frac{1}{\lambda}=-\frac{1}{2\pi}\frac{dz}{dx} \quad \text{and} \quad n=\frac{1}{T}=\frac{1}{2\pi}\frac{dz}{dt}. \tag{22}$$

But following L. Brillouin (1914) we can use (22) as a formal definition of λ and n respectively. Using $\beta=x/ct$ we get then from (20) and (22)

$$\lambda=\Lambda\frac{\sqrt{1-\beta^2}}{\beta}, \quad n=\frac{\nu_1}{\sqrt{1-\beta^2}}. \tag{23}$$

λ is the de Broglie wave length of particles moving with the velocity $c\beta$, n is the frequency associated with λ by the de Broglie phase-velocity c/β. Owing to (19), we have $\lambda n = \Lambda \nu_1/\beta = c/\beta$ indeed. At the moment of the arrival of the wave front ($\beta = 1$) are $\lambda = 0$ and $n = \infty$; afterwards λ increases and n decreases.

The moment the wave front has passed the point x (that is for $\beta < 1$) the value of z increases so much that we can use the asymptotic expression (18), first for $\beta_0 < \beta < 1$ without the residue. This part of the wave $f(t,x)$ is called the forerunner or precursor. Owing to $\sqrt{z}$ in the denominator the function $f(t,x)$ decreases until β comes into the neighbourhood of β_0. Then, according to (13), the resonance denominator of the first term in brackets becomes very small, so that $f(t,x)$ increases again. But at the same time the asymptotic expression (18) ceases to be applicable, because the path of integration (E) passes through the neighbourhood of the pole at $\nu = \nu_0$. In this moment the „main wave" given by the residue arrives. Subsequently, the contribution of the first term in the brackets, which at $\nu = \nu_0$ has changed its sign, becomes less important. With the advance of time ($\beta \to 0$) the value of $\sqrt{z}$ approaches infinity, so that practically only the main wave remains.

The expressions (23) for λ and n are valid also for the first term in the asymptotic approximation (18). With decreasing β, the wave length λ increases, until at the moment ($\beta = \beta_0$) of the arrival of the main wave it becomes equal to the de Broglie wave length of the main wave. After this moment λ increases further.

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COMPARISON METHOD OF MEASURING THE ANGULAR CORRELATION OF GAMMA-RAYS

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(received October 30, 1949)

From theoretical considerations (Hamilton 1940, Goertzel 1946) it follows that when two γ-quanta are emitted in cascade in the process of nuclear de-excitation the relative probability that the second quantum will be emitted at an angle Θ with the first is

$$W(\Theta)=1+\sum_{l=1}^{l} A_l \cos^{2l}\Theta,$$

where $2l$ is the highest multipole order occuring.

Up to now, the investigations of the angular correlation of γ-rays (Beringer 1943, Boehm 1949, Brady 1947, Good 1946, Kikuchi 1942) were carried out by observing the coincidences between a counter A, fixed with respect to the sample P, and a movable counter B (Fig. 1). As these measurements extend as a rule over long periods of time, they require a far reaching stability of the working conditions of the counters and an exact reproducibility of the geometrical configuration. If the effects of the angular correlation are small (as is to be expected in the majority of cases) a very slight instability of the experimental conditions may spoil the measurements to such an extent as to make them wholly unreliable.

Fig. 1

In this note a comparison method of determining the angular correlation is suggested which is more or less insensitive to the instability of the working conditions of the counters and of their spatial disposition. During the whole course of a series of measurements two counters A and B (Fig. 2) are fixed, while a third one C is placed in position 1 during the first part of the series and afterwards in position 2. The first part of the measurements consists in the simultaneous counting of the (A, C_1)- and (B, C_1)-coincidences (counter C in position 1). The numbers of these coincidences are given by

$$(A, C_1) = N_1 \omega_A \omega_{C_1} \varepsilon_A \varepsilon_C V_{AC} W(90^0), \quad (B, C_1) = N_1 \omega_B \omega_{C_1} \varepsilon_B \varepsilon_C V_{BC} W(180^0),$$

where N_1 is the number of decays during the measurements, ω are the respective solid angles, ε the efficiencies of the respective counters, V are the respective losses of coincidences, and $W(\Theta)$ is the relative probability of emission of two successive quanta at an angle Θ. The ratio of the above numbers is given by

$$\frac{(A, C_1)}{(B, C_1)} = \frac{\omega_A \varepsilon_A V_{AC}}{\omega_B \varepsilon_B V_{BC}} \, \frac{W(90^0)}{W(180^0)}. \tag{1}$$

Similarly, the second part of the measurements with counter C in position 2 gives

$$(A, C_2) = N_2 \omega_A \omega_{C_2} \varepsilon_A \varepsilon_C V_{AC} W(180^0), \quad (B_1, C_2) = N_2 \omega_B \omega_{C_2} \varepsilon_B \varepsilon_C V_{BC} W(90^0),$$

and their ratio

$$\frac{(A, C_2)}{(B, C_2)} = \frac{\omega_A \varepsilon_A V_{AC}}{\omega_B \varepsilon_B V_{BC}} \, \frac{W(180^0)}{W(90^0)}. \tag{2}$$

From (1) and (2) we get

$$\sqrt{\frac{(A, C_1)}{(B, C_1)} \Big/ \frac{(A, C_2)}{(B, C_2)}} = \frac{W(90^0)}{W(180^0)}, \tag{3}$$

a quantity which is independent in a high degree of the fortuitously changing working conditions of the whole coincidence apparatus.

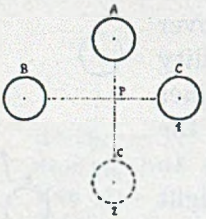

Fig. 2

In Fig. 2, the counters are shown in position for a measurement of the ratio of the probabilities at 90⁰ and 180⁰, but it is easily seen that this ratio may be measured for any other two angles by an appropriate change in the angular setting of the counters A, B, and C.

Of course, the same method may be also used for angular correlation measurements of (β, γ)- and (β, β)-processes. The errors introduced by the absorption of the β-particles in the sample may be avoided by a steady rotation of the sample around its axis.

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DIPOLE MOMENT OF CARBONYL CYANIDE

By M. PUCHALIK, Institute of Physics of the L. Waryński Silesian Academy of Medicine, Rokitnica

(Received March 16, 1950)

The dipole moment of carbonyl cyanide has been investigated. This compound, for the first time obtained by Prof. Małachowski and collaborators (1937) has an analogous structure to phosgene. It has been ascertained that in carbonyl cyanide, just as in phosgene, there appears a compensation of dipole moments of two strongly polar groups.

The investigations of the polar properties of phosgene by Smyth and Mc Alpine (1934) and Le Fèvre and Le Fèvre (1935) led to the following conclusions: (1) The molecule of phosgene forms a dipole with an electric moment$=1{,}18$ D (1934) or $1{,}099$ D (1935). (2) The dipole moment of $COCl_2$ may be calculated from the values of the moments of the two groups $=$CO and -C-Cl. (3) The relatively low dipole moment of phosgene in spite of the presence of strongly polar groups is due to mutual compensation of both their moments.

It seemed interesting to investigate the polar properties of carbonyl cyanide, as this compound has an analogous chemical structure to phosgene. Carbonyl cyanide was synthesized for the first time by Prof. R. Małachowski and coll. (1937). This remarkable substance shows great chemical activity, e. g., it reacts violently with water giving CO_2 and HCN. As hydrogen cyanide shows a rather high dipole moment ($\mu = 2{,}5$ D) all precautions were to be taken to avoid humidity of the substance as well as of the apparatus. Even small amounts of water would strongly influence the results of the dipole-moment measurements. A special capacitor was used which made it possible to protect the examined substance from any influence of humidity. The construction of this capacitor is shown schematically in fig. 1. In principle, it is a capacitor with two dielectrics: glass and the investigated substance. Before use the capacitor was always carefully dried with a current of air passing through H_2SO_4, $CaCl_2$ and P_2O_5.

The capacity of such a capacitor when connected to the measuring circuit is given by the formula

$$C=\frac{A\varepsilon}{B\varepsilon+D}, \tag{1}$$

where A, B and D are constants ($A=BD$), C_0 is the capacity of the connecting wires, and ε the dielectric constant of the examined substance. C_0 is very small in comparison with C. From (1) we get

$$\varepsilon=\frac{D(C-C_0)}{A-B(C-C_0)}. \tag{2}$$

Let ε_1 and ε_{12} denote the dielectric constants of the solvent and the dilute solution respectively. As the difference ΔC of the capacities for $\varepsilon=\varepsilon_{12}$ and $\varepsilon=\varepsilon_1$ is small, we may write

$$\varepsilon_{12}-\varepsilon_1=\frac{B\varepsilon_1^2}{(C_1-C_0)^2}\Delta C$$

or, neglecting higher powers of C_0/C,

$$\varepsilon_{12}=\varepsilon_1+\frac{B\varepsilon_1^2}{C^2(1-2C_0/C)}\Delta C.$$

The dielectric constants of the two non-polar solvents used (CCl_4 and C_6H_6, $\varepsilon_{25^\circ}=2,245$ and $2,278$ respectively) differed only slightly

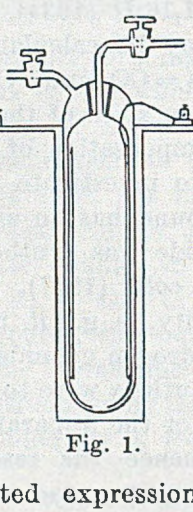

Fig. 1.

and, therefore, the bracketed expressions in the denominator may be considered as a constant, say H/B, yielding finally

$$\varepsilon_{12}=\varepsilon_1+H\frac{\varepsilon_1^2}{C_1^2}\Delta C, \tag{3}$$

where H is a constant to be determined by experiment. This was done by calibrating the capacitor with benzene, carbon tetrachloride, and hexane.

The determination of the dipole moment of $CO(CN)_2$ was performed by the method of dilute solutions; those of the dielectric constant by means of the bridge method at audio frequency. A general scheme of the experimental arrangement may be seen from fig. 2.

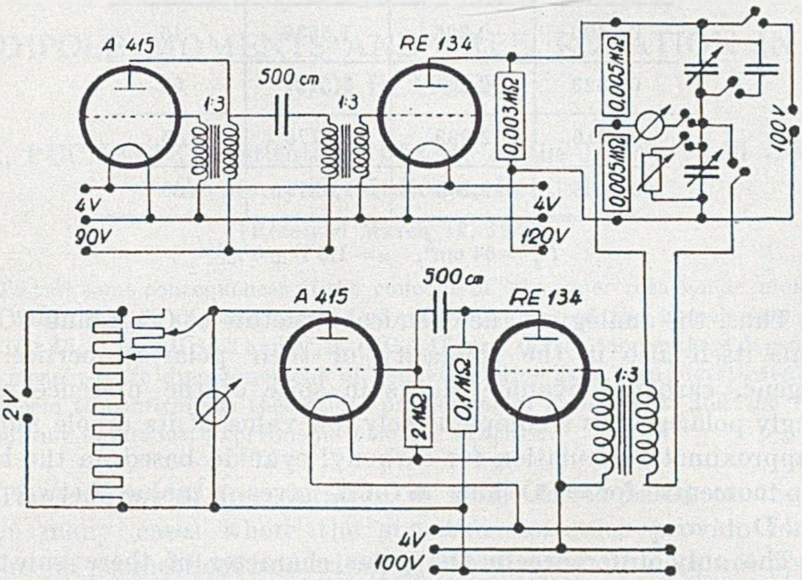

Fig. 2.

The results of the measurements are shown in the following tables [1], where f_2 is the mulecular concentration of the carbonyl cyanide, ϵ_{12} and d_{12} are respectively the dielectric constant and the density of the solution, and P_2 is the molecular polarization of carbonyl cyanide.

Table I

$CO(CN)_2$ in C_6H_6, $T = 25^0$ C, $R = 16{,}93$ cm³

f_2	ε_{12}	d_{12} g/cm³	P_2 cm³
0,1149	2,444	0,8927	45
0,0548	2,391	0,8823	50
0,0276	2,339	0,8768	60
0,0184	2,320	0,8756	61

$P_2^{\infty} = 64\ \mathrm{cm}^3, \quad \mu = 1{,}5\ \mathrm{D} \pm 5\%$

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[1] Preliminary results were communicated at the IX Meeting of Polish Physicists at Wilno, October 1938.

Table II

$CO(CN)_2$ in CCl_4, $T = 25^0$ C

f_2	ε_{12}	d_{12} g/cm³	P_2 cm³
0,0490	2,306	1,5638	45
0,0323	2,291	1,5727	50
0,0216	2,283	1,5775	55
0,0108	2,263	1,5819	60

$P_2^{\infty} = 64$ cm³, $\mu = 1{,}5$ D ± 5%

Thus, the analogy of the chemical structure of $COCl_2$ and $CO(CN)_2$ reveals itself also in the similarity of their polar properties. Like phosgene, carbonyl cyanide shows in spite of the presence of two strongly polar groups a comparatively low value of its dipole moment. An approximate calculation for carbonyl cyanide based on the known group-moments for $=CO$ and $\equiv C\text{-}CN$ gives a value between 1 D and 2 D.

The only difference in the polar character of these substances consists in the fact that the moment of the carbonyl group is greater in the case of phosgene and smaller in the case of carbonyl cyanide than the geometrical sum of the moments of the C-Cl snd the C-CN groups respectively.

These investigations were carried out in the Institute of Experimental Physics of the University, Lwów, in 1938—1939. By comparison of their results with modern litterature the author has got the impression that their value remains unchanged.

The author wishes to express his gratitude to Professor S. Loria for his most valuable advice in the course of this work.

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DIPOLE MOMENTS AND FREE ROTATION IN MOLECULES

By M. PUCHALIK, Institute of Physics of the L. Waryński Silesian Academy of Medicine, Rokitnica

(Received March 16, 1950).

To test some consequences of the concept of free inner rotation in molecules (*a*) the mean square dipole-moments of some members of the homologous series $C_5H_9(CH_2)_nCl$, $C_6H_5(CH_2)_nCl$ and $C_6H_{11}(CH_2)_nCl$, and (*b*) the temperature dependence of the mean square dipole-moment of benzyl chloride have been investigated. The results seem to confirm the theoretical predictions of Zahn (1932) and the results of some, not numerous, experiments of other authors.

The concept of free rotation in molecules is based on the fact that in many cases where the structure formulas provide for the existence of geometrical isomerism, such an isomerism does not appear. It is obvious that in polar molecules the freedom of rotation cannot be complete; the mutual repulsion of the polar groups makes the *trans* configuration of the molecule the most probable one, as this configuration is connected with a minimum of potential energy. According to known chemical facts one must assume that the difference between the minimum and the maximum potential energy is small and the energy of the molecular motion is sufficient to be able to change the *trans* configuration into the *cis* configuration and vice versa.

It may be inferred on theoretical grounds that the mean square dipole-moment of molecules which form a stable system with an axis of completely free rotation is given by the following simple formula (Zahn 1932)

$$\overline{\mu^2} = \mu_0^2 + \sum_k \mu_k^2, \qquad (1)$$

where μ_0 is the geometrical sum of the rigid group-moments and the components of the rotating group-moments in the direction of the axis of free rotation. It is evident that during the rotation these components keep their magnitude and their direction constant. μ_k are the components of the rotating polar groups perpendicular to the axis of rotation.

In the general case in which the single axis of rotation can rotate freely, the value of $\overline{\mu^2}$ may be calculated by successive application of formula (1).

The determination of the degree of the freedom of rotation may be of great assistance in solving different problems connected with the chemical structure of molecules. It may be performed by means of the following considerations: The values of the mean square dipole-moment of a chemical compound with an incompletely free inner rotation depends on the temperature as well as on the mutual distance of the rotating polar groups. The increase of both these factors makes the freedom of rotation more and more complete and at the same time the mean square dipole-moment tends towards a limiting value given by formula (1). For rigid molecules and for molecules with a complete freedom of rotation the mean square dipole-moment is independent of the temperature.

In the case of a homologous series having polar groups at both ends of a carbon chain the lengthening of the carbon chain increases the distance of the polar groups, so that the higher members of such a series ought to show nearly constant values of their dipole moments, which corresponds to a practically completely free rotation. This was confirmed by the investigation of Riedinger (1938) on the members of the homologous series $Br(CH_2)_nBr$ and $C_6H_5(CH_2)_nC_6H_5$.

More extensive systematic researches on this matter seemed to be advisable, and so the author decided to verify the validity of the above mentioned considerations on the inner rotations in molecules by experimental investigation of some members of other homologous series. The determination of $\overline{\mu^2}$ were carried out by the method of dilute solutions, benzene and carbon tetrachloride being used as non-polar solvents. The dielectric constant was measured by means of a bridge method described in a previous paper (Puchalik 1950).

The members of the following homologous series were investigated: (1) $C_5H_9(CH_2)_nCl$, $(n=0,1,2)$, (2) $C_6H_5(CH_2)_nCl$ $(n=0,1,2)$, (3) $C_6H_{11}(CH_2)_nCl$ $(n=0)$.

The mean square dipole-moments of the following chemical compounds belonging to the above series were determined for the first time: (1) Cyclo-penthyl chloride, cyclopenthyl-methyl chloride, cyclopenthyl-ethyl chloride, (2) β-phenyl-ethyl chloride; for chlorobenzene and benzyl chloride the results obtained are in good agreement with previous determinations of other authors, (3) Cyclohexyl chloride; the mean square dipole-moment of 2-p-cymenomethyl chloride has also been measured.

The results of the measurements are shown in the following four tables, where f_2 is the molecular concentration of the dissolved polar substance and R is the molecular refraction.

Table I

Homologous series $C_5H_9(CH_2)_nCl$

A. Cyclopenthyl chloride in CCl_4

$t = 25^0$ C, $n_D = 1{,}4488$ $d = 0{,}99458$ g/cm³ $R = 28{,}15$ cm³

f_2	ε_{12}	d_{12}	P_2 cm³
0,1454	3,079	1,4977	109
0,0850	2,726	1,5289	115
0,5574	2,526	1,5499	110
0,0324	2,393	1,5635	107

$$\sqrt{\overline{\mu^2}} = 1{,}98\ \mathrm{D} \pm 5\%$$

B. Cyclopenthyl-methyl chloride in CCl_4

$t = 25^0$ C, $R = 32{,}78$ cm³

f_2	ε_{12}	d_{12} g/cm³	P_2 cm³
0,0683	2,749	1,5297	148
0,0493	2,627	1,5502	154
0,0323	2,438	1,5585	142
0,0192	2,377	1,5718	147

$$\sqrt{\overline{\mu^2}} = 2{,}35\ \mathrm{D} \pm 5\%$$

C. Cyclopenthyl-ethyl chloride in CCl_4

$t = 25^0$ C, $R = 37{,}39$ cm³

f_2	ε_{12}	d_{12}	P_2 cm³
0,0780	2,823	1,5223	150
0,0473	2,567	1,5469	157
0,0285	2,453	1,5611	157
0,0179	2,363	1,5672	156

$$\sqrt{\overline{\mu^2}} = 2{,}38\ \mathrm{D} \pm 5\%$$

Table II

Homologous series $C_6H_5(CH_2)_nCl$

A. Benzene chloride in benzene

$t = 25^0$ C, $n_D = 1{,}5219$, $d = 1{,}0952$ g/cm³, $R = 31{,}26$ cm³

f_2	ε_{12}	d_{12} g/cm³	P_2 cm³
0,2601	3,163	0,9295	65
0,1593	2,838	0,9138	77
0,1021	2,649	0,8993	82
0,0647	2,363	0,8875	84

$P_2^\infty = 84$ cm³, $\sqrt{\overline{\mu^2}} = 1{,}58$ D $\pm 5^0/_0$

B. Benzyl chloride in benzene

$t = 25^0$ C, $n_D = 1{,}5362$, $d = 1{,}09259$ g/cm³, $R = 36{,}12$ cm³

f_2	ε_{12}	d_{12} g/cm³	P_2 cm³
0,2506	3,374	0,9408	85
0,1455	2,852	0,9118	89
0,0826	2,606	0,8961	91
0,0436	2,482	0,8857	105

$\sqrt{\overline{\mu^2}} = 1{,}86$ D $\pm 5^0/_0$

C. β-phenyl-ethyl chloride in CCl_4

$t = 25^0$ C $\varepsilon = 5{,}43$ $n_D = 1{,}5280$ $d = 1{,}0655$ g/cm³ $R = 37{,}73$ cm³

Surface tension $\sigma = 42{,}7$ dyn/cm Viscosity $\mu = 0{,}0192$ cm¹ g/sek¹

f_2	ε_{12}	d_{12} g/cm³	P_2 cm³
0,2310	3,530	1,4492	108
0,1345	2,988	1,4997	115
0,0742	2,636	1,5559	121
0,0449	2,456	1,5537	111

$\sqrt{\overline{\mu^2}} = 1{,}92$ D $\pm 5^0/_0$

Table III

Cyclohexyl chloride CCl_4

$t = 25^0$ C, $n_D = 1{,}4606$, $d = 0{,}9910\ \mathrm{g/cm^3}$ $R = 32{,}80\ \mathrm{cm^3}$

f_2	ε_{12}	$d_{12}\ \mathrm{g/cm^3}$	$P_2\ \mathrm{cm^3}$
0,0973	2,888	1,5170	130
0,0847	2,810	1,5155	136
0,0509	2,560	1,5463	128
0,0289	2,440	1,5618	130

$$\sqrt{\overline{\mu^2}} = 2{,}2\ \mathrm{D} \pm 5^0/_0$$

Table IV

Karvakryl chloride in CCl_4

$t = 25^0$ C, $n_D = 1{,}5233$, $d = 1{,}0104\ \mathrm{g/cm^3}$ $R = 51{,}29\ \mathrm{cm^3}$

f_2	ε_{12}	$d_{12}\ \mathrm{g/cm^3}$	$P_2\ \mathrm{cm^3}$
0,0861	2,690	1,4905	145
0,0325	2,364	1,5097	142
0,0138	2,260	1,5309	134

$$\sqrt{\overline{\mu^2}} = 2{,}1\ D \pm 5^0/_0$$

These experimental results show that: (a) In good agreement with the above mentioned theoretical considerations, the change of the mean square dipole-moment for the two first homologous series becomes small with increasing n, which means that the freedom of rotation becomes soon practically complete. For the second series the limiting value of the mean square dipole-moment can be calculated and one gets the value 1,9 D, possessed already by β-phenyl-ethyl-chloride. (b) The mean square dipole-moment of benzyl chloride is less than of cyclohexyl chloride and cyclopenthyl chloride. The change of the benzene ring to an alicyclic ring produces thus an increase of the mean square dipole-moment. Unfortunately, the number of the investigated members of each series was rather small.

These investigations were performed in the Institute of Experimental Physics of the University, Lwów, but were interrupted in 1941 by the outbreak of war between the Soviet Union and Germany. By comparing their results with modern literature, it has been ascertained that they have retained their value up to now, as the state of the experimental knowledge of the dependence of the mean square dipole-moments on the freedom of rotation seems to have advanced but little during these last years.

It would be interesting to be able to verify the above mentioned conclusions by means of measurements of further members of the homologous series investigated in Lwów; unfortunately, it is now very difficult to obtain the catalyzers needed for the synthesis of these compounds.

As the increase of the temperature has a similar effect upon the mean square dipole-moment of the molecules with an incomplete freedom of rotation as the increase of the carbon-chain length, the author has decided to investigate the dependence on temperature of the mean square dipole-moment of benzyl chloride. These researches have been carried out in the Institute of Medical Physics of the Silesian Medical Academy. The determination of the mean square dipole-moment in the temperature intervall from 20° C to 80° C have been performed by the method of dilute solutions, refined petroleum being used as non-polar solvent. The polarization of benzyl chloride has been calculated by means of the formula (Müller 1933)

$$P_2=\frac{1}{n_2}\left(\frac{\varepsilon_{12}-1}{\varepsilon_{12}+2}V_{12}-\frac{\varepsilon_1-1}{\varepsilon_1+2}V_1\right), \tag{2}$$

where n_2 is the number of gram molecules of the dissolved polar substance, and V_{12} are respectively the dielectric constant and the volume of the solution, and V_1 are the same quantities for the non-polar solvent.

The dielectric constant has been measured by means of the bridge method, a measuring capacitor being used as in the previous work of the author (Puchalik 1950). The measuring apparatus produced by the establishments „Duo“ at Gliwice is similar to the one previously used. Its schematic diagram is shown in Fig. 1. Modern vacuum tubes and feeding from alternating current network has been used. The accuracy of the determination of the mean square dipole-moment was about 3 per cent. The whole arrangement was tested by means of a solution of benzyl chloride in benzene.

The results of the measurements are shown in the following tables.

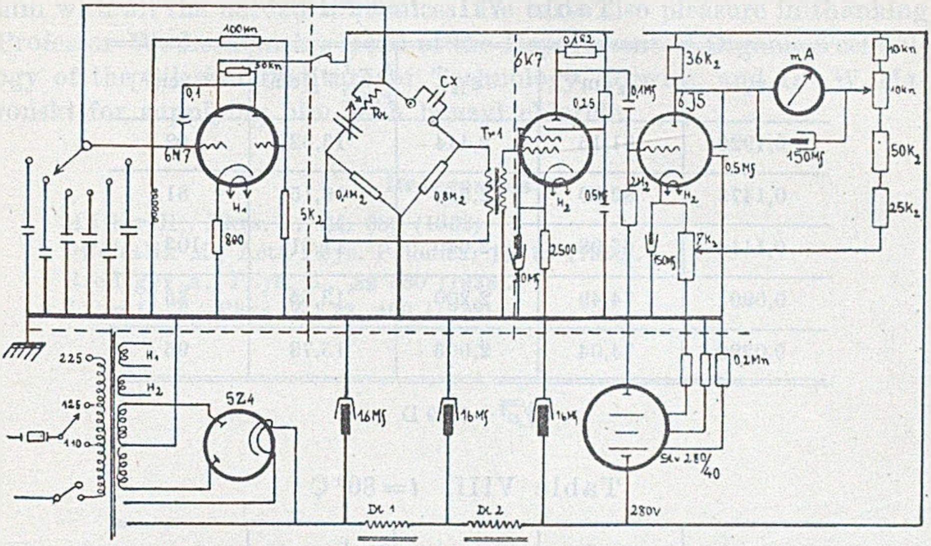

Fig. 1.

Table V. $t = 20^0$ C

n_2	V_{12} cm³	ε_{12}	$\frac{\varepsilon_1-1}{\varepsilon_1+2}V_1$[cm³]	P_2 [cm³]
0,1920	77,83	2,310	13,02	55,36
0,1478	79,05	2,632	16,15	79
0,1114	62,30	2,740	11,51	102
0,0901	71,40	2,342	13,55	94
0,0290	71,11	2,053	15,73	93

$\sqrt{\overline{\mu^2}} = 1{,}69$ D

Table VI. $t = 40^0$ C

n_2	V_{12} cm³	ε_{12}	$\frac{\varepsilon_1-1}{\varepsilon_1+2}V_1$[cm³]	P_2 [cm³]
0,1920	79,32	2,446	13,02	66
0,1478	80,60	2,585	16,15	78
0,1114	63,52	2,650	11,51	99
0,0901	72,90	2,230	13,55	85
0,0290	72,52	2,020	15,73	92

$\sqrt{\overline{\mu^2}} = 1{,}71$ D

Table VII. $t = 60^0$C

n_2	V_{12} cm^3	ε_{12}	$\frac{\varepsilon_1-1}{\varepsilon_1+2}V_1$ [cm^3]	P_2 [cm^3]
0,1920	81,15	2,444	13,02	69
0,1478	82,50	2,556	16,15	81
0,1114	65,08	2,640	11,51	103
0,0901	74,49	2,200	13,55	86
0,0290	74,04	2,006	15,73	95

$\sqrt{\overline{\mu^2}} = 1{,}79$ D

Table VIII. $t = 80^0$ C

n_2	V_{12} cm^3	ε_{12}	$\frac{\varepsilon_1-1}{\varepsilon_1+2}V_1$ [cm^3]	P_2 [cm^3]
0,1920	82,86	2,360	13,02	62
0,1478	84,10	2,526	16,15	82
0,1114	66,34	2,583	11,51	102
0,0901	76,01	2,114	13,55	98
0,0290	75,68	1,994	15,73	104

$\sqrt{\overline{\mu^2}} = 1{,}85$ D

These experimental results show that:

(1) In the case of petroleum as non-polar solvent one obtains for the mean square dipole-moment of benzyl chloride a somewhat smaller value than by using benzene as solvent.

(2) The mean square dipole-moment of benzyl chloride varies very little with temperature.

(3) Thus, one is drawn to the conclusion that the freedom of rotation in the benzyl chloride molecule is not yet complete.

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LETTERS TO THE EDITOR

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On the Theory of Non-Local Fields

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Recently Yukawa[1] initiated a relativistic theory of particles with finite radius based on Born's ideas of non-localizability and reciprocity. The non-local field operator U satisfies the following commutation relations

$$[d_\mu,[d_\mu,U]]=\varkappa^2 U, \quad [x_\mu,[x_\mu,U]]=\lambda^2 U, \quad [d_\mu,[x_\mu,U]]=0, \tag{1}$$

where d_μ is the displacement operator

$$[x_\mu, d_\nu]=\delta_{\mu\nu}. \tag{2}$$

In the representation where x_μ are diagonal U is a matrix $\langle x'|U|x''\rangle$ which may be regarded also as a function $U(X,r)$ with

$$X_\mu=1/2(x'_\mu+x''_\mu), \quad r_\mu=(x'_\mu-x''_\mu). \tag{3}$$

$U(X,r)$ satisfies the equations

$$\left[\left(\frac{\partial}{\partial X}\cdot\frac{\partial}{\partial X}\right)-\varkappa^2\right]U(X,r)=0, \tag{4'}$$

$$[(r\cdot r)-\lambda^2]U(X,r)=0, \quad \left(r\cdot\frac{\partial U}{\partial X}\right)=0. \tag{4''}$$

Equations (4″) may be treated as supplementary conditions. The general solution of (4) is

$$U(X,r)=\sum_k \left(u_k(r)e^{i(k\cdot X)}+w_k^*(r)e^{-i(k\cdot X)}\right)\delta((k\cdot r))\,\delta((r\cdot r)-\lambda^2) \tag{5}$$

with $(k\cdot k)=-\varkappa^2$.

If the scalar $U(X,r)$ shall describe spinless particles, then no direction can be priviledged except k_μ so that $u_k(r)$, $w_k(r)$ may depend only on $(r\cdot r)$ and $(r\cdot k)$, which means that they do not depend on r_ν at all, due to the supplementary conditions. Thus, for spin zero we may write in (5) u_k, w_k instead of $u_k(r)$, $w_k(r)$.

We may establish a correspondence between a local quantity a and a non-local A in the following way

$$a(X)\rightarrow\int d^4r\,\langle x'|A|x''\rangle. \tag{6}$$

If A itself is local, then it is of the form

$$\langle x' | A | x'' \rangle = a(x')\,\delta(x' - x'') = a(X)\,\delta(r)$$

and the correspondence becomes an identity. From (6), there is a correspondence between the traditional local field function $\psi(X)$ and the non-local $U(X,r)$:

$$\psi(X) \rightarrow \int d^4 r\, U(X,r) \tag{7}$$

or

$$\sum_k (a_k e^{i(k\cdot X)} + b_k^* e^{-i(k\cdot X)}) \rightarrow \sum_k (u_k e^{i(k\cdot X)} + u_k^* e^{-i(k\cdot X)})\, S_k, \tag{7'}$$

where S_k is the surface of the ellipsoid

$$S_k = \int d^4 r\, \delta((k\cdot r))\, \delta((r\cdot r) - \lambda^2). \tag{8}$$

(7′) enables us to write immediately the commutation relations for $U(X,r)$. We see that $u_k S_k$ must satisfy the same commutation relations as a_k. Hence, we may put

$$U(X,r) = \sum_k \frac{1}{S_k} (a_k e^{i(k\cdot X)} + b_k^* e^{-i(k\cdot X)})\, \delta((k\cdot r))\, \delta((r\cdot r) - \lambda^2), \tag{9}$$

where a_k, b_k are the well-known matrices satisfying the commutation relations

$$[a_k, a_l^*] = [b_k, b_l^*] = \frac{\hbar}{2\sqrt{k^2 + \varkappa^2}} \cdot \frac{\delta_{kl}}{V} \tag{10}$$

while all other commutators vanish.

In order to have a complete theory we must find the important bilinear expressions for the Hamiltonian energy density, charge density etc. To do so we have to replace the products of ψ, ψ^* and their derivatives by corresponding expressions in terms of U and U^*. The correspondence rule (6) yields

$$\psi^*(X)\,\psi(X) \rightarrow \int d^4 r \langle x' | U^* U | x' \rangle = \int d^4 r \int d^4 x''' \langle x' | U^* | x''' \rangle \langle x''' | U | x'' \rangle. \tag{11}$$

With the aid of the notations

$$\begin{gathered} X = \frac{x' + x''}{2}, \quad X' = \frac{x' + x'''}{2}, \quad X'' = \frac{x' + x'''}{2} \\ r = x' - x'', \quad r' = x' - x''', \quad r'' = x'' - x''' \end{gathered} \tag{12}$$

(11) becomes

$$\begin{aligned} \psi^*(X)\,\psi(X) &\rightarrow \int d^4 r \int d^4 x''' U^*(X', r')\, U(X'', r'') \\ &= \int d^4 r' \int d^4 r'' U^*(X + r''/2, r')\, U(X + r'/2, r''). \end{aligned} \tag{13}$$

By rewritting the traditional Hamiltonian for a scalar local field by means of (13) and using (9) and (10), we easily find that the new Hamiltonian has the same eigenvalues as the former and yields the correct field equations (4) in the operator form. The traditional expression for the charge density, rewritten with the aid of (13), yields also, if integrated, the correct eigenvalues for the total charge. Thus, the theory of spinless non-local fields in vacuo yields the same results as the local field formalism.

Interaction between two spinless fields. Let us consider the simplest possible type of interaction between a complex and a real scalar field:

$$H'(x)=g\psi^*(x)\,\varphi(x)\,\psi(x). \tag{14}$$

This interaction energy density is subject to the well-known inconsistencies inherent in any local field theory. To take into account the non-localizability we have again to apply the rule (6). We limit ourselves to two special cases:

(1) φ local, ψ non-local. In this case the correspondence rule (6) yields

$$H'(X)=g\int d^4r'\int d^4r''\,U^*(X+r''/2,r')\,\varphi\left(X-\frac{r'+r''}{2}\right)U(X+r'/2,r''). \tag{15}$$

(2) ψ local, φ non-local. In this case we find

$$H'(X)=g\int d^4r\,\psi^*(X-r/2)\,V(X,r)\,\psi(X+r/2), \tag{16}$$

where $V(X,r)$ is the non-local neutral field. The interaction appears suitably spread out over the ellipsoids representing the non-local particles.

Les us calculate from (16) the self-energy of a neutral non-local particle at rest:

$$H_{self}=\sum_{\vec{p}}\frac{H'_{0\vec{p}}\,H'_{\vec{p}0}}{E_0-E_p}. \tag{17}$$

Here, the initial state, denoted by 0, represents one neutral particle at rest and the intermediate state, denoted by $\vec{p}$, represents a pair of charged particles with momenta $\vec{p}$ and $-\vec{p}$. The matrix element $H'_{\vec{p}0}$ differs from the usual one by a factor α:

$$\alpha=\frac{1}{S_0}\,d^4r\,e^{-i[(p\cdot r)-(q\cdot r)]/2}\,\delta(\varkappa r_0)\,\delta((r\cdot r)-\lambda^2) \tag{18}$$

with

$$p_\mu=(\vec{p}\,|\sqrt{p^2+M^2}),\quad q_\mu=(-\vec{p}\,|\sqrt{p^2+M^3}).$$

S_0 is now simply the surface of a sphere with radius λ. Performing the integration, we get

$$\alpha=\frac{\sin\lambda p}{\lambda p}. \tag{19}$$

Thus, instead of a divergent integral over dp we get a convergent one with the „damping factor" α^2 in the integrand.

We have shown that the non-local field may be treated by the usual Hamiltonian method. Contrary to the opinion expressed by Yukawa[1] it is neither necessary to reject the Schrödinger equation not to replace the Hamiltonian formalism by the S-matrix scheme. We hope that the well-known convergence difficulties may well be overcome in terms of this new formalism. Moreover, this theory may be able to put the problem of elementary particles with higher spin in an entirely new light.

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[1] Yukawa H., Phys. Rev., **77**, 219 (1950).

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