

SUMMARY

PART I: THE STATISTICAL MECHANICS OF CONDENSING SYSTEMS.

by M. Born and K. Fuchs

The usual method of treating the equilibrium of two phases ON SOME PROBLEMS OF CONDENSATION, QUANTUM DYNAMICS for both phases AND THE STABILITY OF NUCLEI the coexistence of the two phases. The first successful attempt to derive the equilibrium of the gaseous and solid (or liquid) phase by a rigorous evaluation of the partition function taking KLAUS FUCHS all possible molecular arrangements - whether they are "solid-like" or "gas-like" - with their proper statistical weight has been made by Mayer and his collaborators.

The method used by Mayer is very involved and it is applicable only with certain simplifications which are not really essential. The main purpose of this paper is to put the theory of Mayer on a secure mathematical basis.

In the first section the partition function is written down and expanded in a series of "cluster" integrals

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The usual method of treating the equilibrium of two phases consists in approximating the equation of state for both phases and deriving the condition for the coexistence of the two phases. The first successful attempt to derive the equilibrium of the gaseous and solid (or liquid) phase by a rigorous evaluation of the partition function taking into account all possible molecular arrangements - whether they are "solid-like" or "gas-like" - with their proper statistical weight has been made by Mayer and his collaborators.

The method used by Mayer is very involved and it is applicable only with certain simplifications which are not really essential. The main purpose of this paper is to put the theory of Mayer on a secure mathematical basis.

In the first section the partition function is written down and expanded in a series of "cluster" integrals  $b_l$  in such a way that the integrand in each of these integrals is large only in those parts of phase space where  $l$  molecules are near each other. As is to be expected, such an expansion converges for large volumes (gaseous phase) for which the chance of  $l$  particles being near each other decreases rapidly with  $l$ . But it

diverges for smaller volumes. The idea of Mayer's theory is that the limit of the gaseous phase is determined by the limit of convergence of this expansion.

In section 2 the cluster integrals  $b_2$  are reduced to simpler "irreducible" integrals.

In section 3 the generating function of the partition function - as expanded in the first section - is found. With the help of this generating function the partition function can be represented by means of a complex integral, which can be evaluated by the method of steepest descent (with certain simplifications). The generating function introduces a new but simpler type of series and the next section is devoted to the connection of these series with the thermodynamical properties of the gas.

A more general type of generating functions is introduced in sections 5 (the H-functions). With the help of these the equation of state is expanded in a series of powers of the reciprocal volume and it is shown that the irreducible integrals are essentially the virial coefficients. In section 6 the complex integral for the partition function is evaluated rigorously by means of the H-functions. It is shown that the problem of finding the value of the partition function and the condensation point is reduced to determining the radii of convergence of certain series. The results of Mayer's theory are

rigorously proved without introducing any simplifications.

In section 7 the condition for the coexistence of more than two phases is derived.

## PART II: ON FLUCTUATIONS IN ELECTROMAGNETIC RADIATION.

by M. Born and K. Fuchs.

By means of general thermodynamical considerations and Plank's radiation formula an expression for the mean square fluctuation of electromagnetic radiation can be derived. On the other hand, the mean square fluctuation can be calculated explicitly from the field equations and the energy density of the electromagnetic field. The fluctuations in the latter case are due to the interference of the elementary waves. Any contradiction in the results obtained by the two methods would point to a defect in the theory.

The paper is preceded by a historical introduction to this problem, in which the important role it played in the early days of the quantum theory, is stressed. The classical theory of radiation (Maxwell equations) gives a result which does not agree with the result of the thermodynamical calculation. The contradiction was solved by quantum mechanics.

Later Heisenberg raised objections on the ground that divergent integrals had been neglected. The present

investigation was mainly prompted by these objections of Heisenberg, since we expected that these divergencies are connected with the limitations of the present quantum theory of radiation. But the results of the investigation forced us to reconsider the whole problem from the beginning.

It had generally been assumed that the thermodynamical consideration (given in the first section) should lead to exactly the same result as the interference calculation. In section 2 the two methods are compared with each other and it is pointed out that this is not to be expected. The two methods are concerned with two essentially different models and the zero energy plays quite a different role in the two cases. In order to compare the results derived by the two methods the formula obtained by thermodynamics must be supplemented by the addition of the fluctuation of the zero energy.

In the sections 3 to 5 the mean square fluctuation according to the quantum theory of radiation is calculated and it is shown that the result agrees with the thermodynamical formula if the latter is supplemented by the fluctuation of the zero energy. The error in the older quantum mechanical calculation is pointed out. This error led just to the suppression of the term representing the fluctuation of the zero energy. Heisenberg's objections are shown to be unjustified.

In order to obtain agreement (as far as can be expected) between the thermodynamical treatment and the interference calculation the zero energy is essential. But it is given by a divergent integral. In the last section the importance of this divergence with regard to the limitation of the present quantum theory of radiation is discussed in the light of the results of this paper.

### PART III: ON THE INVARIANCE OF QUANTIZED FIELD EQUATIONS.

by K. Fuchs.

The connection between the quantum theory and the general theory of relativity is as yet an unsolved problem. One of the difficulties is that in the quantum theory the time and energy play such a distinguished role. This is connected with the difficulty of writing the Hamiltonian equations in an invariant form.

The classical Hamiltonian equations for a field could easily be written in an invariant form; we need only introduce to each field variable four canonically conjugate variables. If the field variables form a tensor of rank  $n$ , these canonically conjugate variables form a tensor density of rank  $n+1$ . But in this form the Hamiltonian equations are not suitable for quantization. In order to formulate commutation relations which form - together with the field equations - a system free from contradictions we must introduce to

each field variable only one canonically conjugate variable. Therefore some of the components of the above mentioned tensor density must be distinguished from the others, which can only be done if one coordinate is given a special role.

PART IV: ON THE STABILITY OF NUCLEI AGAINST  $\beta$ -EMISSION.  
by K. Fuchs

The purpose of this paper is to show that the result of the process of quantization of a field is invariant against the choice of this special coordinate; the only restriction is that it should be of a time like character. If the energy of the nuclei were a smooth function of the number of neutrons and the number of protons, then for a given total number of particles there would be only one stable nucleus with that ratio of neutrons to protons for which the energy has a minimum. If we start from field equations which are invariant, the process of second quantization leads therefore again to invariant equations.

All other nuclei would emit electrons or positrons.

In section 2 the transformation formula for the conjugate field variables is derived and the field equations are written in the Hamiltonian form. In section 3 the quantization of the field according to the theory of Heisenberg and Pauli is carried through and some of the equations of those authors are repeated.

However, in view of the exchange character of the nuclear forces we obtain a two periodicity in the number of neutrons and the number of protons. Disregarding any further irregularities we obtain therefore four energy surfaces, each of which may be regarded as a smooth function of the number of neutrons and protons. One of them is applicable for even numbers of neutrons and protons, one for even number of neutrons and odd number of protons etc. In this way more than one minimum of the energy becomes possible.

The invariance of the commutation relations is proved in section 4. In the next section the transformation law of the Hamiltonian is determined from the condition that the field equations should be invariant. In section 6 this law of transformation is compared with the classical transformation. They differ by a complete differential, which - in the classical theory - has no influence on

The purpose of this paper is to explain this scheme, which can be done without recourse to any particular

the field equations. In the last section it is shown that also in the quantum theory the addition of a complete differential to the Hamiltonian does not change the equations of motion.

#### PART IV: ON THE STABILITY OF NUCLEI AGAINST $\beta$ -EMISSION.

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If the energy of the nuclei were a smooth function of the number of neutrons and the number of protons, then for a given total number of particles there would in general be only one stable nucleus with that ratio of neutrons to protons for which the energy has a minimum. All other nuclei would emit electrons or positrons.

However, in view of the exchange character of the nuclear forces we obtain a two periodicity in the number of neutrons and the number of protons. Disregarding any further irregularities we obtain therefore four energy surfaces, each of which may be regarded as a smooth function of the number of neutrons and protons. One of them is applicable for even numbers of neutrons and protons, one for even number of neutrons and odd number of protons etc. In this way more than one minimum of the energy becomes possible.

The general scheme of stable nuclei is determined by the relative position of these four energy surfaces. The purpose of this paper is to explain this scheme, which can be done without recourse to any particular



model of the nucleus, using only arguments which can be justified according to our general knowledge of the nuclear forces.

The paper starts with an outline of the explanation of the instability of nuclei with odd numbers of neutrons and protons given by Bethe and Bacher (section 2). In section 3 the general assumptions made are introduced and justified. They are mainly connected with the exchange character of the nuclear forces.

The conditions of stability and the general scheme of stable nuclei are developed in the next two sections. It is shown that there are a number of distinct regions - according to the number of surplus neutrons - which differ by the type of nuclei which are stable. The scheme obtained coincides with that found in nature.

The lightest nuclei make an exception from the general rules of stability. This is shortly discussed in section 6.

In section 7 the experimental values for the limits of the various regions of stability are discussed. An interesting correspondence with the frequency of the elements is found.

Sections 8 and 9 are concerned with the determination of the breadth of the various regions of stability. In general good agreement with the experimental values is obtained.

PART I

THE STATISTICAL MECHANICS OF CONDENSING  
SYSTEMS

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# The statistical mechanics of condensing systems

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*Edinburgh*

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## INTRODUCTION

J. E. Mayer (1937) has published, together with some collaborators, several papers under the same title as the present one.\* We consider these papers as a most important contribution to statistical mechanics, and this opinion was shared by the International Conference held in Amsterdam, 26 November 1937, in commemoration of Van der Waals' birth.

One of the present authors gave to this meeting a report on Mayer's work (published in *Physica*, 1937) which was followed by a vigorous discussion on the question as to whether Mayer's explanation of the phenomena of condensation is correct. Doubts about this point were raised by the referee, because it is difficult to comprehend how a method of approximation such as that of Mayer, starting from the gaseous state, can lead to the discontinuity of the density on an isothermal curve which corresponds to condensation. The usual methods for treating the equilibrium of two phases introduce the equation of state of both phases and derive the condition for their co-existence. Mayer's theory does nothing of this kind, but treats all possible molecular arrangements with their proper weight, as if there were only one phase. How can the gas molecules "know" when they have to coagulate to form a liquid or solid? Mayer's mathematical method is too involved to make this point quite clear.

We have devoted a considerable effort to control and clarify these calculations, making ample use of the theory of complex functions, and we believe that we have succeeded in showing rigorously, and in a somewhat simpler way than Mayer himself, that his statements are completely correct. And we have succeeded by our method in going a little farther, in so far as we can derive the conditions for co-existence of several phases (triple point). We have had the privilege of corresponding about these questions with Professor G. E. Uhlenbeck (Utrecht, Holland), to whom we

\* We have to thank Dr Mayer for sending us the manuscript of another paper (written in collaboration with S. F. Harrison) before publication; this article which has meanwhile appeared (1938) contains the most complete presentation of his theory.

owe several important hints for simplifying the proofs.\* We publish here the whole theory with complete proofs, so that the reader need not refer to other publications on this subject.

But we shall confine ourselves to presenting here the general theory as far as it can be developed with the minimum of arbitrary assumptions. The detailed discussion of phenomena in the neighbourhood of the critical point by Mayer and Harrison (1938), based on a special assumption about the irreducible integrals (defined in § 2), will therefore not be considered here.

### 1. THE PARTITION FUNCTION

We consider a system of equal particles (molecules) which act on one another with central forces.

If  $H(p, q) = T(p, q) + V(q)$  is the energy of the system,  $T$  and  $V$  being its kinetic and potential part, the thermodynamic properties can be derived from the partition function

$$Q = \frac{1}{N! h^{3N}} \iint \dots \int e^{-H(p, q)/kT} dp_1 \dots dq_{3N} = \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{Q_\tau}{N!}, \quad (1.1)$$

where 
$$Q_\tau = \iint \dots \int e^{-V(q)/kT} d\tau_1 \dots d\tau_N, \quad (d\tau_n = dx_n dy_n dz_n). \quad (1.2)$$

The assumption of central forces,  $V(q) = \sum_{1 \leq j < i \leq N} v(r_{ij})$ , leads to

$$Q_\tau = \iint \dots \int \prod_{N \geq i > j \geq 1} \{1 + f(r_{ij})\} d\tau_1 \dots d\tau_N, \quad (1.3)$$

where 
$$f_{ij} = f(r_{ij}) = e^{-v(r_{ij})/kT} - 1; \quad (1.4)$$

or 
$$Q_\tau = \iint \dots \int [1 + \sum_{i>j} f_{ij} + \sum f_{ij} f_{i'j'} + \dots] d\tau_1 \dots d\tau_N. \quad (1.5)$$

The usual procedure consists in evaluating the lowest terms of this series; the first sum corresponds to collisions of pairs of molecules, the second to triple encounters, etc. It is evident that this method is valid only for rarified gases and can never lead to a satisfactory theory of the condensed state.

\* After finishing this paper we have received a manuscript of Professor Uhlenbeck and Dr B. Kahn, "On the theory of condensation", which will be published in *Physica*. We have to thank the authors for sending us this paper which is supplementary to our own work, chiefly concerning the extension of the theory to quantum statistics.

Mayer's intention is a formula holding for any density. He uses, therefore, another principle, first adopted by Ursell (1927), for ordering the terms in (1.5). To illustrate his idea we write down any product of the  $f_{ij}$  as it appears in the terms of (1.5), for instance

$$f_{12}f_{23}f_{45}f_{67}f_{78}f_{68}.$$

As only those parts of the phase space contribute to the integral for which the distances of all pairs of molecules which appear in the term are small we can describe the contribution of this term by saying: it consists of *one* cluster of two molecules (4, 5), *two* of three (1, 2, 3 and 6, 7, 8), whereas *all other* molecules are "free", or form clusters of one molecule.

To each cluster of  $l$  molecules there belongs an integral

$$b_l = \frac{1}{l!} \int \dots \int \Sigma \Pi f_{ij} d\tau_1 \dots d\tau_{l-1}, \tag{1.6}$$

where the factor  $l!$  has been added for convenience and the integration is extended over the configuration volume of all but one of the  $l$  molecules, since evidently the integration over the last one yields simply the factor  $V$  (volume).

Each term of  $Q_\tau$  consists of  $m_1$  clusters of 1 molecule,  $m_2$  clusters of 2,  $m_3$  clusters of 3, etc., where

$$1m_1 + 2m_2 + 3m_3 + \dots = \Sigma lm_l = N$$

is the total number of molecules. As the  $l!$  permutations of the molecules in a cluster and the  $m_l!$  permutations of the  $m_l$  equal clusters of these molecules correspond to the same arrangement, the weight of this is

$$\frac{N!}{(1!)^{m_1}(2!)^{m_2} \dots m_1!m_2! \dots} = N! \prod_l \frac{1}{(l!)^{m_l} m_l!}.$$

Therefore we get 
$$\frac{Q_\tau}{N!} = \sum_{\Sigma lm_l = N} \prod_l \frac{(Vb_l)^{m_l}}{m_l!} = \sum_{m_l} \prod_l \frac{(Nvb_l)^{m_l}}{m_l!}, \tag{1.7}$$

where 
$$v = \frac{V}{N} \tag{1.8}$$

is the volume per molecule.

We shall consider first the integrals  $b_l$  and then evaluate the partition function  $Q_\tau$  by means of a complex integration.

## 2. THEOREM ON THE REDUCTION OF CLUSTER INTEGRALS\*

For a given cluster of size  $l$  there are a number of configurations, characterized by a product of the  $f_{ij}$ , such that this product cannot be split into two factors

$$F_{n_1 n_2 \dots p} F_{p m_1 m_2 \dots}$$

with *one* common index only. The sum of the corresponding integrals over the configuration space, divided by  $(l-1)!$  (for convenience) is defined as the *irreducible integral*  $\beta_{l-1}$ .

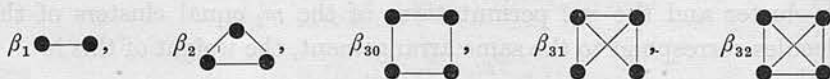
The simplest irreducible integrals are

$$\left. \begin{aligned} \beta_1 &= \int_0^\infty 4\pi r^2 f(r) d\tau, \\ \beta_2 &= \frac{1}{2} \iint f(r_{12}) f(r_{23}) f(r_{31}) d\tau_1 d\tau_2, \\ \beta_3 &= \frac{1}{2} (3\beta_{30} + 6\beta_{31} + \beta_{32}), \end{aligned} \right\} \quad (2.1)$$

where

$$\left. \begin{aligned} \beta_{30} &= \iiint f_{12} f_{23} f_{34} f_{41} d\tau_1 d\tau_2 d\tau_3, \\ \beta_{31} &= \iiint f_{12} f_{13} f_{14} f_{23} f_{34} d\tau_1 d\tau_2 d\tau_3, \\ \beta_{32} &= \iiint f_{12} f_{13} f_{14} f_{23} f_{24} f_{34} d\tau_1 d\tau_2 d\tau_3. \end{aligned} \right\} \quad (2.2)$$

They correspond evidently to the following figures of "bonds":



whereas figures as



belong to reducible integrals.

We shall say: an irreducible integral  $\beta_\nu$  belongs to an "irreducible cluster" (of size  $\nu+1$ ) with the index  $\nu$ . It is useful to consider  $\nu$  of the  $\nu+1$  molecules of the cluster as numbered (1, 2, ...,  $\nu$ ) and one unnumbered; this last one is then used for "connecting" the irreducible cluster to another one

\* This theorem has been found and proved by J. E. Mayer and Maria Goepfert-Mayer; but no complete proof has been published. We think that our proof is somewhat simpler than that which we tried to reconstruct from Mayer's indications.

by identifying it with a numbered particle of the other cluster. We define below such an aggregate of  $\nu$  numbered particles of an irreducible cluster of size  $\nu + 1$  as an "incomplete cluster".

Each cluster of the size  $l$  can be considered as composed of irreducible clusters of the indices  $\nu = 0, 1, 2, \dots, l - 1$ , where the irreducible cluster of index  $\nu$  may appear  $\mu_\nu$  times. Therefore we can write

$$l! b_l = \sum_{\mu_\nu} p_l(\mu_1, \mu_2, \dots) \prod_{\nu} (\nu! \beta_\nu)^{\mu_\nu}, \tag{2.3}$$

where the factors  $l!$  and  $\nu!$  are only a consequence of the definitions of the  $b_l$  and  $\beta_\nu$ .

Each term of (2.3) is the integral of a product of the  $f_{ij}$  of the form

$$F_{l_1 l_2 \dots p} F_{m_1 m_2 \dots q} F_{p q n_1 n_2 \dots r} F_{r s_1 s_2 \dots} \dots F_{y s_1 s_2 \dots z}, \tag{2.4}$$

multiplied with the number of possibilities  $p_l(\mu_1, \mu_2, \dots)$  of interchanging the particles without destroying the form of the integrand.

As integration over the  $\nu_1$  particles  $l_1 l_2 \dots$  makes the corresponding integral factor of (2.4) independent of  $p$ , we count  $p$  not to the first incomplete cluster, but in the example (2.4) to the third; in the same way we count the particle  $q$  to the third,  $r$  to the fourth, etc. Then in the last factor the last particle  $z$  plays a special role. We define the "incomplete clusters" which compose the given one, by the groups  $(l_1 l_2, \dots)$  of number  $\nu_1$ ,  $(m_1 m_2 \dots)$  of number  $\nu_2$  and so on, but for the last  $(y s_1 s_2 \dots z)$  of number  $\nu_a + 1$ . Then the number of possibilities of distributing the  $l$  particles over the incomplete clusters of  $\nu_1, \nu_2, \dots, \nu_a + 1$  particles is given by

$$\frac{l!}{\prod_{\nu} (\nu!)^{\mu_\nu}} \frac{1}{\prod_{\nu} (\mu_\nu)! \nu_a + 1}, \tag{2.5}$$

where we have split  $(\nu_a + 1)!$  into the factors  $\nu_a!(\nu_a + 1)$ . We remark here that any arbitrary cluster can be taken as the "last" one (with index  $\nu_a$ ).

$p_l(\mu_1, \mu_2, \dots)$  is therefore the factor (2.5) multiplied by the number  $\kappa$  of possibilities of connecting the incomplete clusters. We define  $q(\mu_1, \mu_2, \dots)$  as this number  $\kappa$  divided (for convenience) by  $\nu_a + 1$ . Then (2.3) can be written

$$b_l = \sum_{\mu_\nu} q(\mu_1, \mu_2, \dots) \prod_{\nu} \frac{(\beta_\nu)^{\mu_\nu}}{(\mu_\nu)!}, \quad q(\mu_1, \mu_2, \dots) = \frac{\kappa}{\nu_a + 1}. \tag{2.6}$$

In forming the factor (2.5) we have taken into account that two irreducible clusters of the same index can be exchanged, i.e. we have counted



as identical such distributions of the particles over the incomplete clusters which are obtained by exchanging all particles of two clusters of equal index. We must therefore now consider two possibilities of connecting the incomplete clusters, which are obtained by exchanging two clusters of the same index, as different. For this reason it is more convenient to introduce a different notation. We numerate the irreducible clusters in any order from 1 to  $m$ , where  $m$  is the total number of irreducible clusters, and characterize any configuration by the indices of the irreducible clusters  $\nu_1, \nu_2, \dots, \nu_m$ , where several  $\nu_i$  may be equal. Then

$$\sum_{i=1}^m \nu_i = l - 1, \quad (2.7)$$

and  $q$  is now to be considered as a function of the  $\nu_i$ :

$$q = q(\nu_1, \nu_2, \dots, \nu_m). \quad (2.8)$$

We assume now that the  $l$  particles are distributed over the incomplete clusters in a definite way. Each irreducible cluster—say of index  $\nu_i$ —contains  $\nu_i$  numbered particles (those of the incomplete cluster) and one unnumbered particle. (In the example (2.4)  $p$  is the unnumbered particle of the first cluster,  $q$  that of the second, and so on; only the  $\nu_a + 1$  particles of the “last” cluster are all numbered.) We “attach” one irreducible cluster  $\nu_i$  to another  $\nu_j$  by identifying the unnumbered particle of the irreducible cluster  $\nu_i$  with any numbered particle of the irreducible cluster  $\nu_j$ .

We consider first the simplest case of forming such attachments between the irreducible clusters in a simple chain. We start with the “last” cluster containing  $\nu_a + 1$  numbered particles and attach another cluster  $\nu_b$ , which can be done in  $\nu_a + 1$  different ways, since we can identify the unnumbered particle of the cluster  $\nu_b$  with any one of the  $\nu_a + 1$  particles of the last cluster. Correspondingly we obtain a factor  $\nu_b$ , when we attach a third cluster  $\nu_c$  to the second and so on (compare fig. 1a). The total number of possibilities of forming such a chain in any given order of the irreducible clusters is  $(\nu_a + 1) \prod_i \nu_i$ , ( $i \neq a$ ,  $i \neq x$ ), where  $\nu_x$  is the cluster attached last.

We obtain the same product  $(\nu_a + 1) \prod_i \nu_i$ , ( $i \neq a$ ,  $i \neq x$ ), if we exchange the  $m - 2$  clusters in the chain, keeping the clusters  $\nu_a$  and  $\nu_x$  fixed. Dividing by  $\nu_a + 1$  we obtain as contribution to  $q$

$$(m - 2)! \prod_{\substack{i \neq a \\ i \neq x}} \nu_i. \quad (2.9)$$

We take always the cluster  $\nu_a$  as the starting point for the process of attaching; but it is not necessary to attach just one cluster to  $\nu_a$ , we may attach two or more. If two clusters are attached to  $\nu_a$ —say  $\nu_b$  and  $\nu_c$ —one obtains a chain in which the cluster  $\nu_a$  is not at the end, as shown in fig. 1b.

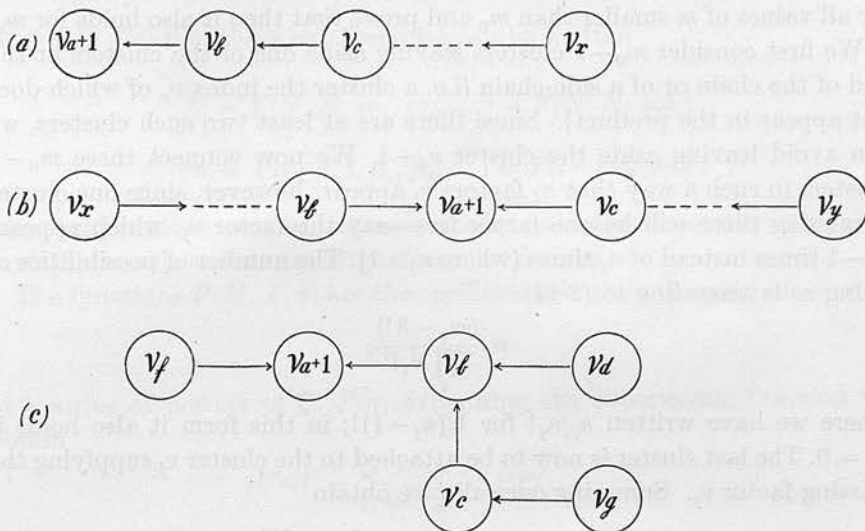


FIG. 1

In general we are not confined to attaching each cluster to the immediately previously attached cluster, but we can attach them to any one of the previously attached clusters, starting a “side-chain”. In this case the factor  $\nu_i$  may appear several times, though the total number of factors is always equal to  $m - 2$ , since after  $m - 1$  steps all clusters are attached and a factor  $\nu_a + 1$  always cancels. (In the case illustrated in fig. 1c, for example, we obtain  $(\nu_a + 1)\nu_b^2\nu_c$ .) It is to be noted that  $\nu_a + 1$  appears always instead of  $\nu_a$ ; the following formulae should be understood in this sense. Therefore,  $q$  can be written as the sum of such products

$$q(\nu_1, \nu_2, \dots, \nu_m) = \sum_{\substack{n_i \\ \sum n_i = m - 2}} f(m; n_1, n_2, \dots) \prod_i \nu_i^{n_i}. \tag{2.10}$$

$f(m; n_1, n_2, \dots)$  is here the number of possible arrangements in which  $n_1$  clusters are attached to the cluster  $\nu_1$ ,  $n_2$  to the cluster  $\nu_2$ , and so on, and  $n_a + 1$  to the cluster  $\nu_a + 1$  (since one factor  $\nu_a + 1$  is cancelled, cf. (2.6)).

We shall prove by induction that

$$f(m; n_1, n_2, \dots) = \frac{(m-2)!}{\prod_{i=1} n_i!}. \quad (2.11)$$

For  $m = 2$  or  $3$  this formula has already been proved; for in this case it reduces to the formula (2.9) for a simple chain. We, therefore, assume (2.11) is true for all values of  $m$  smaller than  $m_0$  and prove that then it also holds for  $m_0$ .

We first consider  $m_0 - 1$  clusters leaving aside one of the clusters at the end of the chain or of a side-chain (i.e. a cluster the index  $\nu_x$  of which does not appear in the product). Since there are at least two such clusters, we can avoid leaving aside the cluster  $\nu_x + 1$ . We now connect these  $m_0 - 1$  clusters in such a way that  $n_i$  factors  $\nu_i$  appear; however, since one cluster is missing there will be one factor less—say the factor  $\nu_j$ , which appears  $n_j - 1$  times instead of  $n_j$  times (where  $n_j \geq 1$ ). The number of possibilities of doing so is according to (2.11)

$$n_j \frac{(m_0 - 3)!}{\prod_i n_i!},$$

where we have written  $n_j/n_j!$  for  $1/(n_j - 1)!$ ; in this form it also holds if  $n_j = 0$ . The last cluster is now to be attached to the cluster  $\nu_j$  supplying the missing factor  $\nu_j$ . Summing over all  $j$  we obtain

$$f(m_0; n_1, n_2, \dots) = \sum_j n_j \frac{(m_0 - 3)!}{\prod_i n_i!}.$$

Since  $\sum_j n_j = m_0 - 2$  (compare (2.10)) we obtain formula (2.11), which thus is proved.

Inserting (2.11) in (2.10) we obtain

$$q(\nu_1, \nu_2, \dots, \nu_m) = \sum_{\sum n_i = m-2} (m-2)! \prod_i \frac{\nu_i^{n_i}}{n_i!} = (\sum_i \nu_i)^{m-2}.$$

Remembering that in each formula  $\nu_a$  must be replaced by  $\nu_a + 1$  this expression is according to (2.7)

$$q(\nu_1, \nu_2, \dots, \nu_m) = l^{m-2}.$$

Inserting this expression in (2.6) and observing that  $\sum \mu_\nu = m$ , we obtain finally the

**THEOREM:** *Each cluster integral can be split into a sum of products of irreducible integrals corresponding to the formula*

$$b_l = l^{-2} \sum_{\sum \nu \mu_\nu = l-1} \prod_{\nu} \frac{(l\beta_\nu)^{\mu_\nu}}{\mu_\nu!}. \quad (2.12)$$

3. INTEGRAL REPRESENTATION AND ASYMPTOTIC EXPRESSIONS

The formula (1.7) for  $Q_\tau$  and formula (2.12) for  $b_l$  are of the same type:

$$F(M, I, x_1, x_2, \dots) = \sum_{\substack{m_l \\ \sum l m_l = M}} \prod_l \frac{(Ix_l)^{m_l}}{m_l!} = F(M, I, x). \tag{3.1}$$

With this notation these two formulae can be written

$$\left. \begin{aligned} \frac{Q_\tau}{N!} &= F(N, N, vb_1, vb_2, \dots) = F(N, N, vb), \\ l^2 b_l &= F(l-1, l, \beta_1, \beta_2, \dots) = F(l-1, l, \beta). \end{aligned} \right\} \tag{3.2}$$

These expressions can be represented by complex integrals for which asymptotic expressions for large  $I$  can be derived.

The functions  $F(M, I, x)$  are the coefficients in the expansion of

$$\exp(I \sum x_\nu \xi^\nu)$$

in a series of powers of  $\xi$ . For, expanding the exponential function we obtain

$$\begin{aligned} e^{I \sum x_\nu \xi^\nu} &= \sum_m \frac{1}{m!} (\sum_\nu I x_\nu \xi^\nu)^m \\ &= \sum_m \frac{1}{m!} \sum_{\substack{\mu_\nu \\ \sum \mu_\nu = m}} m! \prod_\nu \frac{(Ix_\nu \xi^\nu)^{\mu_\nu}}{\mu_\nu!}. \end{aligned}$$

Here the second sum is to be taken over all sets of values of the  $\mu_\nu$  for which  $\sum \mu_\nu = m$ . Since the factor  $m!$  cancels  $m$  appears only in this restriction for the values of the  $\mu_\nu$ , and summing over all  $m$ , the restriction is removed. We can therefore write

$$e^{I \sum x_\nu \xi^\nu} = \sum_{\mu_\nu} \prod_\nu \frac{(Ix_\nu)^{\mu_\nu} \xi^{\nu \mu_\nu}}{\mu_\nu!} = \sum_{\mu_\nu} \xi^{\sum \nu \mu_\nu} \prod_\nu \frac{(Ix_\nu)^{\mu_\nu}}{\mu_\nu!}.$$

We now take together all sets of values  $\mu_\nu$ , for which  $\sum_\nu \mu_\nu = M$ ; we can then take  $\xi^{\sum \nu \mu_\nu} = \xi^M$  in front of the sum over  $\mu_\nu$ , and obtain

$$e^{I \sum x_\nu \xi^\nu} = \sum_M \xi^M \sum_{\substack{\mu_\nu \\ \sum \mu_\nu = M}} \prod_\nu \frac{(Ix_\nu)^{\mu_\nu}}{\mu_\nu!}.$$

Using the definitions

$$G_\lambda(\xi; x_1, x_2, \dots) = G_\lambda(\xi, x) = \sum_{\nu=1}^\infty x_\nu \xi^{\nu \lambda} \tag{3.3}$$

and (3.1) we may write

$$e^{I\Sigma x_\nu \xi^\nu} = e^{IG_0(\xi, x)} = \sum_M F(M, I, x) \xi^M. \quad (3.4)$$

Applying Cauchy's integral theorem,  $F$  can be expressed as the integral

$$F(M, I, x) = \frac{1}{2\pi i} \oint \frac{e^{IG_0(\xi, x)}}{\xi^{M+1}} d\xi. \quad (3.5)$$

We thus obtain the *integral representation for the*  $F(M, I, x)$

$$F(M, I, x) = \frac{1}{2\pi i} \oint e^{IG_0(\xi, x) - (M+1) \ln \xi} d\xi, \quad (3.6)$$

where the integration is to be extended over a path inside the region of regularity of  $\exp(IG_0(\xi, x))$  enclosing the point  $\xi = 0$ . It is obvious that the exponential function is regular inside the radius of convergence of  $G_0(\xi, x)$  with the exception of the point  $\xi = 0$ .

We shall now derive the asymptotic expressions for the integrals (3.6) by the *method of steepest descent*. We shall choose as path of integration a circle around the origin and therefore write

$$\begin{aligned} \xi &= Ze^{i\phi}, & d\xi &= iZe^{i\phi} d\phi, \\ \ln \xi &= i\phi + \ln Z. \end{aligned}$$

Substituting these expressions in (3.6) the integral can be written in the form

$$\left. \begin{aligned} F(M, I, x) &= \frac{1}{2\pi} \int_{-\pi}^{+\pi} e^{IG_0(Ze^{i\phi}, x) - (M+1) i\phi - (M+1) \ln Z} Ze^{i\phi} d\phi, \\ &= \frac{1}{2\pi} \int_{-\pi}^{+\pi} e^{f(Ze^{i\phi})} d\phi, \\ f(Ze^{i\phi}) &= IG_0(Ze^{i\phi}, x) - M \ln(Ze^{i\phi}). \end{aligned} \right\} \quad (3.7)$$

We now choose the radius of the circle of integration  $Z$  such that the function  $f(Ze^{i\phi})$  of  $\phi$  in the exponent has a maximum at the real axis (for  $\phi = 0$ ). Since according to (3.3)

$$\frac{\partial}{\partial \phi} [G_\lambda(Ze^{i\phi}, x)] = iG_{\lambda+1}(Ze^{i\phi}, x), \quad (3.8)$$

we obtain as equation for  $Z$

$$\left[ \frac{\partial}{\partial \phi} f(Ze^{i\phi}) \right]_{\phi=0} = i[IG_1(Z, x) - M] = 0,$$

or

$$G_1(Z, x) = \frac{M}{I}. \quad (3.9)$$

The point  $Z$  on the real axis is a saddle point of the function  $f(\xi)$ ;  $f(\xi)$  has a maximum perpendicular to the real axis and a minimum parallel to it.

The higher derivatives of  $f(\xi)$  at the saddle point with regard to  $\phi$  can easily be obtained, taking into account the relation (3.8); one finds

$$\left[ \frac{\partial^\nu}{\partial \phi^\nu} f(Ze^{i\phi}) \right]_{\phi=0} = I i^\nu G_\nu(Z, x),$$

and we can write (3.7)

$$F(M, I, x) = \frac{1}{2\pi} e^{f(Z)} \int_{-\pi}^{+\pi} \exp \left[ -IG_2(Z, x) \phi^2/2 + I \sum_{\nu=3}^{\infty} i^\nu G_\nu(Z, x) \phi^\nu/\nu! \right] d\phi.$$

Substituting  $\phi^2 = y^2 IG_2/2$  we obtain

$$F(M, I, x) = \frac{1}{2\pi} e^{f(Z)} \sqrt{\frac{2}{IG_2(Z, x)}} \times \int_{-\pi\sqrt{\frac{IG_2}{2}}}^{+\pi\sqrt{\frac{IG_2}{2}}} \exp \left[ -y^2 + I \sum_{\nu=3}^{\infty} i^\nu G_\nu(Z, x) y^\nu/\nu! (IG_2/2)^{\nu/2} \right] dy. \quad (3.10)$$

If  $I$  is large all terms in the exponential except  $y^2$  are negligible and the integral can be extended from  $-\infty$  to  $+\infty$  with negligible error. The integral is the well-known error function and yields a factor  $\sqrt{\pi}$ ;\* substituting according to (3.7) for  $f(Z)$  we obtain the asymptotic expression

$$F(M, I, x) = \frac{e^{IG_0(Z, x)}}{Z^M \sqrt{\{2\pi IG_2(Z, x)\}}}, \quad I \gg 1. \quad (3.11)$$

In neglecting all terms in the exponent of (3.10) except  $y^2$  we have assumed tacitly that the  $G_\nu$  are of smaller order than  $I$ . This need not be the case; in general we must add the condition

$$\frac{1}{\nu!} \frac{IG_\nu(Z, x)}{[IG_2(Z, x)/2]^{\nu/2}} \ll 1, \quad \nu \geq 3. \quad (3.12)$$

\* We have neglected here the possibility that other maxima might occur apart from the maximum at  $\phi = 0$ . However, if all  $x_\nu$  are positive it can be shown quite easily that these maxima will contribute negligible amounts. For the exponent of the integrand in (3.10) can be written:

$$f(Ze^{i\phi}) - f(Z) = I \Sigma x_\nu Z^\nu [(\cos \nu\phi - 1) + i \sin \nu\phi] - iM\phi.$$

The real part of this expression is negative and of the order  $I$ , except for  $\phi = 0$ .

Specializing for the two cases (3·2) we obtain from (3·11)

$$\frac{Q_\tau}{N!} = F(N, N, vb) = \frac{e^{NG_0(Z, vb)}}{Z^N \sqrt{[2\pi N G_2(Z, vb)]}}, \quad N \gg 1 \quad (3\cdot13)$$

$$l^2 b_l = F(l-1, l, \beta) = \frac{e^{lG_0(\rho, \beta)}}{\rho^{l-1} \sqrt{\{2\pi l G_2(\rho, \beta)\}}}, \quad l \gg 1 \quad (3\cdot14)$$

$$G_\lambda(Z, vb) = v \sum_{\nu=1}^{\infty} \nu^\lambda b_\nu Z^\nu, \quad (3\cdot15)$$

$$G_\lambda(\rho, \beta) = \sum_{\nu=1}^{\infty} \nu^\lambda \beta_\nu \rho^\nu, \quad (3\cdot16)$$

where  $Z$  and  $\rho$  are defined by the equations:

$$G_1(Z, vb) = 1, \quad (3\cdot17)$$

$$G_1(\rho, \beta) = 1. \quad (3\cdot18)$$

$\beta_\nu$  has the same dimension as  $b_\nu v$ , namely that of  $v^\nu$ ; it follows from (3·17), (3·18) that  $Z$  and  $\rho$  have the dimension of  $v^{-1}$  (or density).

We shall use the notation 
$$v_s = \frac{1}{\rho}. \quad (3\cdot19)$$

This volume, which depends on the temperature but not on the pressure, will play an important role in the theory of condensation.

The quantity  $Z$ , as given by (3·17), has also a simple physical meaning, which can be given only after deriving the thermodynamical properties of the system.

#### 4. THERMODYNAMICAL PROPERTIES OF THE GAS

The equation (3·13) enables us to express the thermodynamic potentials in terms of the series  $G_\lambda(Z, vb)$ . Neglecting all terms but those of the highest order in  $N$  one gets

$$\frac{1}{N} \ln \frac{Q_\tau}{N!} = G_0(Z, vb) - \ln Z, \quad G_1(Z, vb) = 1. \quad (4\cdot1)$$

The thermodynamical properties of the systems can be determined from the free energy  $A$  (as introduced by Helmholtz) which is connected with the partition function by the relation

$$A = -kT \ln Q. \quad (4\cdot2)$$

If we introduce here the values (1.1) and (4.1) we get with  $R = kN$

$$A = RT \left\{ \ln \left( \frac{h^2}{2\pi m k T} \right)^{\frac{3}{2}} - G_0(Z) + \ln Z \right\}. \quad (4.3)$$

The pressure is 
$$P = - \left( \frac{\partial A}{\partial V} \right)_T = \frac{RT}{V} v \frac{\partial}{\partial v} \{ G_0(Z) - \ln Z \}. \quad (4.4)$$

In the condensed state the  $b_\nu$  may depend on  $v$ ; but in the gaseous state we can assume them being independent of  $v$ . Then the differentiation in (4.4) can be easily performed; from (3.15) one has

$$Z \frac{d}{dZ} G_\lambda(Z) = G_{\lambda+1}(Z);$$

therefore for  $\lambda = 0$  
$$Z \frac{dG_0(Z)}{dZ} = G_1(Z) = 1. \quad (4.5)$$

Now we get

$$\begin{aligned} v \frac{\partial}{\partial v} \{ G_0(Z) - \ln Z \} &= v \frac{\partial}{\partial v} (v \sum_\nu b_\nu Z^\nu - \ln Z) \\ &= v \sum_\nu b_\nu Z^\nu + \frac{v}{Z} \left( Z \frac{\partial G_0(Z)}{\partial Z} - 1 \right) \frac{dv}{\partial Z}. \end{aligned}$$

The last bracket vanishes according to (4.5), and one gets

$$v \frac{\partial}{\partial v} \{ G_0(Z) - \ln Z \} = G_0(Z). \quad (4.6)$$

Introducing this in (4.4) one finds the *equation of state*

$$PV = RT G_0(Z). \quad (4.7)$$

Gibbs' thermodynamic potential is

$$F = A + PV = RT \left\{ \ln \left( \frac{h^2}{2\pi m k T} \right)^{\frac{3}{2}} + \ln Z \right\}. \quad (4.8)$$

From (4.7) one gets with (4.5)

$$V^2 \frac{dP}{dV} = RT G_1(Z) \frac{d \ln Z}{d \ln v} = RT \frac{d \ln Z}{d \ln v}. \quad (4.9)$$

The problem of finding the virial coefficients will be solved, if we can express  $G_0(Z)$  in terms of the volume. This will be done in the next paragraph.



## 5. DETERMINATION OF THE VIRIAL COEFFICIENTS

In order to find an expression of  $G_0(Z)$  in terms of the volume we consider the following functions

$$H_\lambda^m(z, x_1, x_2, \dots) = H_\lambda^m(z, x) = \sum_{N=1}^{\infty} \frac{F(N-m, N, x)}{N^\lambda} z^N \quad (5.1)$$

where  $F$  is defined by (3.1); we prove the following

## THEOREM

$$H_0^m(z, x) = \frac{\xi_0^m}{1 - G_1(\xi_0, x)} - \delta(m, 0) \quad (5.2)$$

$$\delta(m, 0) = \begin{cases} 1 & \text{for } m = 0 \\ 0 & \text{for } m \neq 0, \end{cases}$$

where  $\xi_0$  is defined by  $z = \xi_0 e^{-G_0(\xi_0, x)}$  (5.3)

and  $G_\lambda(\xi_0, x) = \sum_{\nu=1}^{\infty} \nu^\lambda x_\nu \xi_0^\nu$  (5.4)

so that  $\xi_0 \frac{d}{d\xi_0} G_\lambda(\xi_0, x) = G_{\lambda+1}(\xi_0, x)$ . (5.5)

We shall prove the theorem for small values of  $z$ ; it then follows that it is valid in general.

Inserting the complex integral (3.5) for the  $F$ -functions in (5.1) we obtain

$$H_0^m(z, x) = \frac{1}{2\pi i} \sum_{N=1}^{\infty} z^N \oint_{\xi^{N-m+1}} \frac{e^{NG_0(\xi, x)}}{\xi^{N-m+1}} d\xi, \quad (5.6)$$

where the path of integration must include the point  $\xi = 0$ . We choose the path in such a way that

$$\left| z \frac{e^{G_0(\xi)}}{\xi} \right| < 1. \quad (5.7)$$

This is possible for small values of  $z$  as shown below. We can now exchange integration and summation in (5.6) and obtain

$$H_0^m(z, x) = \frac{1}{2\pi i} \oint_{\xi} \frac{ze^{G_0(\xi)}}{\xi - ze^{G_0(\xi)}} \xi^{m-1} d\xi, \quad (5.8)$$

This integral has a singularity for a value  $\xi_0$  where (5.3) is satisfied. The residuum of the singularity is obtained by inserting the derivative of the

denominator in (5.8) in place of the denominator; with (5.5) and (5.3) we obtain for the residuum

$$\frac{ze^{G_0(\xi_0)}}{1 - ze^{G_0(\xi_0)}G_1(\xi_0)/\xi_0} \xi_0^{m-1} = \frac{\xi_0^m}{1 - G_1(\xi_0)}.$$

If  $m = 0$ , there is another singularity at  $\xi = 0$  with the residuum  $-1$ . Thus equation (5.2) is proved, provided there is one and only one point  $\xi_0$  inside the path of integration for which (5.3) is satisfied.

Now, the function  $e^{G_0(\xi)}/\xi$  (5.9)

has a pole of the first order at  $\xi = 0$ . This pole is surrounded by curves along which the absolute value of (5.9) is constant. Provided the absolute value is sufficiently high these curves are closed around  $\xi = 0$ ; therefore, if  $|z|$  is sufficiently small we can choose the path of integration according to (5.7) just outside the curve along which

$$\left| \frac{e^{G_0(\xi)}}{\xi} \right| = \frac{1}{|z|},$$

in such a way that there is only one such curve inside the path of integration. On this curve there is one and only one point for which (5.3) is satisfied.

From (5.3) we obtain with (5.5)

$$\frac{dz}{z} = \frac{d\xi_0}{\xi_0} [1 - G_1(\xi_0)]. \tag{5.10}$$

Multiplying (5.2) with (5.10) and integrating we find

$$\int_0^z H_0^m(z', x) \frac{dz'}{z'} = \int_0^{\xi_0} \left[ \xi^{m-1} - \delta(m, 0) \frac{1 - G_1(\xi)}{\xi} \right] d\xi.$$

The left-hand side yields the series  $H_1^m$  according to (5.1). The right-hand side gives for  $m > 0$

$$H_1^m(z, x) = \frac{\xi_0^m}{m}, \quad m > 0. \tag{5.11}$$

For  $m = 0$  the terms  $1/\xi$  cancel and we obtain with (5.5)

$$H_1^0(z, x) = G_0(\xi_0, x). \tag{5.12}$$

Repeating the integration in the same way, we obtain from (5.11)

$$H_2^m(z, x) = \frac{\xi_0^m}{m} \left[ \frac{1}{m} - G_{0,m}(\xi_0, x) \right], \quad m > 0 \tag{5.13}$$

$$G_{0,m}(\xi_0, x) = \sum_{\nu=1}^{\infty} \frac{\nu}{\nu+m} x_{\nu} \xi_0^{\nu}.$$

According to (3·2), (3·3) the series  $G_\lambda(z, vb)$  can be represented by  $H$ -functions:

$$G_\lambda(Z, vb) = vH_{\frac{1}{2}-\lambda}(Z, \beta). \quad (5\cdot14)$$

For  $\lambda = 0, 1$  we obtain with (5·11), (5·13) (with  $\xi_0 = y$ )

$$G_1(Z, vb) = vH_1^1(Z, \beta) = yv \quad (5\cdot15)$$

$$G_0(Z, vb) = vH_2^1(Z, \beta) = yv[1 - G_{0,1}(y, \beta)] = yv \left[ 1 - \sum_{\nu=1}^{\infty} \frac{\nu}{\nu+1} \beta_\nu y^\nu \right] \quad (5\cdot16)$$

where  $y$  is given by (5·3)  $Z = ye^{-G_0(y, \beta)}$ . (5·17)

The root of the equation  $G_1(Z, vb) = 1$  is, according to (5·15), given by (5·17) with

$$y = \frac{1}{v}. \quad (5\cdot18)$$

The equation of state can now be obtained by inserting (5·16) in (4·7)

$$PV = RTG_0(Z, vb) = RT \left[ 1 - \sum_{\nu=1}^{\infty} \frac{\nu}{\nu+1} \beta_\nu \frac{1}{v^\nu} \right]. \quad (5\cdot19)$$

Thus the virial coefficients are given by the irreducible integrals  $\beta_\nu$ , multiplied with  $-\nu/\nu+1$ .\*

## 6. CONDENSATION

The formulae of the last section can also be applied to the series

$$H_\lambda^0(r, vb) = \sum_{N=1}^{\infty} \frac{Q_{\tau, N} r^N}{N! N^\lambda}. \quad (6\cdot1)$$

For according to (3·2) these are again  $H$ -functions. We obtain from (5·2), (5·12) and (5·3) (replacing  $z$  by  $r$  and  $\xi_0$  by  $z$ ):

$$\sum_{N=1}^{\infty} \frac{Q_{\tau, N} r^N}{N!} = H_0^0(r, vb) = \frac{1}{1 - G_1(z, vb)} - 1, \quad (6\cdot2)$$

$$\sum_{N=1}^{\infty} \frac{Q_{\tau, N} r^N}{N! N} = H_1^0(r, vb) = G_0(z, vb), \quad (6\cdot3)$$

$$r = ze^{-G_0(z, vb)}; \quad \frac{dr}{r} = \frac{dz}{z} [1 - G_1(z, vb)], \quad (6\cdot4)$$

\* This theorem has been proved independently by Mayer and Harrison, Uhlenbeck and Kahn, and ourselves. The proof given here (which is, in fact, a special case of Lagrange's theorem) is essentially that of Uhlenbeck and Kahn; we are very grateful for being permitted to use this method which is simpler than the others.

whereas the corresponding expressions for the  $G_\lambda(z, vb)$  are, with (5.2), (5.15-5.17):

$$G_0(z, vb) = vH_2^1(z, \beta) = yv[1 - G_{0,1}(y, \beta)] = yv \left[ 1 - \sum_{\nu=1}^{\infty} \frac{\nu}{\nu+1} \beta_\nu y^\nu \right]. \quad (6.5)$$

$$G_1(z, vb) = vH_1^1(z, \beta) = yv, \quad (6.6)$$

$$G_2(z, vb) = vH_0^1(z, \beta) = \frac{yv}{1 - G_1(y, \beta)}, \quad (6.7)$$

$$z = ye^{-G_0(y, \beta)}; \quad \frac{dz}{z} = \frac{dy}{y} [1 - G_1(y, \beta)]. \quad (6.8)$$

We now use the fact that by definition (1.2) the  $Q_{r,N}$  are all positive. Professor G. E. Uhlenbeck has kindly communicated to us an idea due to Dr Kahn: The radius of convergence  $R$  of the power series in  $r$  (6.2) and (6.3) is determined by the theorem of Cauchy-Hadamard as

$$\frac{1}{R} = \lim_{N \rightarrow \infty} \left( \frac{Q_{r,N}}{N!} \right)^{1/N}.$$

This theorem supplies just the proper tool for handling the partition function. For, taking logarithms we find exactly the quantity which we need in order to obtain an expression for the free energy

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln \frac{Q_{r,N}}{N!} = -\ln R. \quad (6.9)$$

Let  $Z$  be the value corresponding to  $R$ ; we have with (6.4)

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln \frac{Q_{r,N}}{N!} = G_0(Z, vb) - \ln Z. \quad (6.10)$$

This equation is formally identical with (4.1). However  $Z$  is here defined in a different way.

Let us now consider a region in the  $z$ -plane such that

( $\alpha$ ) The  $G_\lambda(z, vb)$  are regular;

( $\beta$ )  $G_1(z, vb) \neq 1$ .

Then (6.4) defines a conformal correspondence of the  $z$ -plane and the  $r$ -plane, and the series  $H_0^0(r, vb)$  is regular in the corresponding region of the  $r$ -plane. If  $H_0^0$  is singular, one of the conditions ( $\alpha$ ), ( $\beta$ ) must be violated.

The reverse also holds; if ( $\beta$ ) is violated, it is obvious from (6.2) that  $H_0^0$

has a pole. In order to show that  $H_0^0$  is singular if  $(\alpha)$  is violated, we consider the two equations (6.3), (6.4) which we may write

$$G_0(z, vb) = H_0^0(r, vb)$$

$$z = re^{H_1^0(r, vb)}; \quad \frac{dz}{z} = \frac{dr}{r} [1 + H_0^0(r, vb)].$$

In the same way as above we find that if  $G_0(z, vb)$  is singular, either  $H_0^0(r, vb)$  is singular, or

$$H_0^0(r, vb) = -1. \quad (6.11)$$

Since all coefficients of  $H_0^0(r, vb)$  are positive (compare (1.2)) (6.11) cannot be satisfied on the positive  $r$ -axis. For the same reason the singularity which determines the radius of convergence  $R$  is on the positive axis. We, therefore, can choose a region inside the radius of convergence  $R$ , including the positive axis from  $r = 0$  to  $r = R$ , in which there is no point for which (6.11) is satisfied.

We can now conclude that this region is conformally represented by a region in the  $z$ -plane, in which the  $G_\lambda(z, vb)$  are regular. In particular the positive  $r$ -axis is represented by the positive  $z$ -axis and to the point  $R$  there corresponds a point  $Z$  which we can now define as the smallest positive  $z$  for which one of the conditions  $(\alpha)$  and  $(\beta)$  is violated.

We now consider the equations (6.5)–(6.8); in the same way as above it follows that if  $G_0(z, vb)$  has a singularity, one of the following conditions must be violated:

(a) The  $G_\lambda(y, \beta)$  are regular;

(b)  $G_1(y, \beta) \neq 1$ .

The reverse argument is slightly different; we obtain from (6.6) and (6.7)

$$\left. \begin{aligned} G_1(y, \beta) &= 1 - \frac{G_1(z, vb)}{G_2(z, vb)}, \\ y &= \frac{1}{v} G_1(z, vb); \quad dy = v \frac{dz}{z} G_2(z, vb). \end{aligned} \right\} \quad (6.12)$$

If  $G_1(y, \beta)$  is singular, either  $G_1(z, vb)$  is singular or  $G_2(z, vb) = 0$ . If  $G_2(z, vb) = 0$ , it follows from (6.12) that  $G_1(y, \beta) = -\infty$ . In that case it follows from the equation (6.21) (which we shall prove later) that  $dP/dV$  tends to  $-\infty$ . We should have to deal with an incompressible body. We can exclude this case for physical reasons.

We can now argue as before that to the point  $\bar{Z}$  for which  $G_\lambda(z, vb)$  is

singular, there corresponds a point  $\bar{Y}$  which is the smallest positive  $y$  for which either condition (a) or condition (b) is violated.

Since the first coefficient of  $G_2(z, vb)$  is positive ( $b_1 = 1$ ) it follows that on the positive  $z$ -axis

$$G_2(z, vb) > 0 \quad \text{for } |Z| = Z. \tag{6.13}$$

*The equations for the gaseous phase*

We shall first consider the case ( $\beta$ ). Then  $Z$  is given by

$$G_1(Z, vb) = v \Sigma v b_\nu Z^\nu = 1. \tag{6.14}$$

Since  $b_1 = 1$ , there will always be a root of (6.14) inside the region of regularity for sufficiently large values of  $v$ . From (6.6) we conclude that the corresponding point  $Y$  is given by

$$Y = \frac{1}{v}. \tag{6.15}$$

With (6.14) the expression (6.10) for the partition function is identical with (4.1). We obtain, therefore, all the equations of the gaseous state derived in the preceding sections, which in this way are proved to be valid in general since we have made no assumptions about the  $b_l$  or  $\beta_\nu$ , provided we use the analytical continuations if the series in question diverge. (If some of the  $b_l$  or  $\beta_\nu$  are negative it is of course possible that the series diverge, but that the functions represented remain regular on the positive axis.)

*Condensation*

Let  $\bar{Z}$  be the smallest positive singular point of  $G_1(z, vb)$ , which tends to a finite limit as  $z$  approaches  $\bar{Z}$

$$\lim_{z \rightarrow \bar{Z}} G_1(z, vb) = \frac{v}{v_s}. \tag{6.16}$$

Since  $G_1(z, vb)$  increases monotonically according to (6.13) it follows that for  $v > v_s$  there exists a root of (6.14) and we are in the region of the gaseous phase. For  $v < v_s$ , however, there is no root of (6.14) inside the region of regularity and  $Z$  is given by  $\bar{Z}$ .

$$Z = \bar{Z}, \quad v < v_s. \tag{6.17}$$

With (6.10), (4.2) and (4.4), we find

$$PV = RT G_0(\bar{Z}, vb) = RT v \Sigma b_\nu \bar{Z}^\nu, \quad v < v_s. \tag{6.18}$$

Since  $\bar{Z}$  does not depend on the volume it follows that  $P$  remains constant.  $v_s$  therefore is the condensation volume.  $v_s$  can be obtained from (6.15)

$$\bar{Y} = \frac{1}{v_s} \quad (6.19)$$

where  $\bar{Y}$  is the point corresponding to  $\bar{Z}$ .

We now have to distinguish between two cases, corresponding to the two conditions (a) and (b). If the condition (b) is violated  $\bar{Y}$  is the smallest positive root of the equation

$$G_1(\bar{Y}, \beta) = 1. \quad (6.20)$$

In this case  $\bar{Y}$  is identical with the quantity  $\rho$  defined by (3.18). If no such root exists inside the region of regularity of  $G_1(y, \beta)$ ,  $\bar{Y}$  is the smallest singular positive point of  $G_1(y, \beta)$ .

In the two cases the gas shows a distinctly different behaviour as we approach the condensation volume. From (5.19) it follows that for the gaseous phase

$$V^2 \frac{dP}{dV} = RT[G_1(Y, \beta) - 1], \quad Y = \frac{1}{v}, \quad v > v_s. \quad (6.21)$$

If  $\bar{Y}$  is defined as the root of (6.20) it follows from that definition that  $dP/dV$  tends continuously towards zero as  $v$  approaches  $v_s$ .

If, however,  $\bar{Y}$  is a singular point, so that  $G_1(\bar{Y}, \beta) < 1$ ,  $dP/dV$  is discontinuous for  $v = v_s$ . In order to obtain agreement with the observed facts, we must assume that  $\bar{Y}$  is a singular point.

If the singularities  $\bar{Y}$  and  $\bar{Z}$  are situated on the circle of convergence of the series  $G_1(z, vb)$  and  $G_1(y, \beta)$ , the theory of condensation as presented here is in essence identical with Mayer's theory; we believe the above considerations show without doubt that his theory is correct in this case.

If, however, the singularities  $\bar{Y}$  and  $\bar{Z}$  are beyond the radii of convergence, the equations for the gas hold beyond these radii and we have to introduce the analytical continuations of these series.

The physical meaning of the quantities  $Y$ ,  $Z$  and  $R$  can now easily be seen. That of  $Y$  is clear from equations (6.15) and (6.19). The physical meaning of  $Z$  can be seen from (4.8); if we divide (4.8) by the number of molecules  $N$  and write  $R = Nk$ , we get

$$Z = \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} e^{\mu/kT}, \quad (6.22)$$

$$\mu = \frac{F}{N}.$$

Thus  $Z$  is connected with the thermodynamic potential per molecule,  $\mu$ , which is defined as the derivative with regard to  $N$  of the total energy  $E$  as function of  $N, V, S$

$$dE = \mu dN + TdS - PdV. \tag{6.23}$$

The function  $E$  is found from (4.8)

$$E = A + TS = F - PV + TS = \mu N - PV + TS. \tag{6.24}$$

The last expression can be interpreted as Euler's condition for  $E$  being homogeneous in  $N, V, S$ .

Following a remark of Professor R. H. Fowler one can introduce a thermodynamical potential for which  $\mu$  (or  $Z$ ),  $V, T$  are the natural independent variables, namely  $PV$ ; for, from (6.23) and (6.24) it follows that

$$d(PV) = PdV + SdT + Nd\mu. \tag{6.25}$$

For  $R$  finally we obtain a formula similar to (6.22). If we introduce the free energy per molecule  $a = A/N$ , then from (4.3) one gets with (6.4)

$$R = \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} e^{a/kT}, \tag{6.26}$$

$$a = A/N.$$

### 7. TRIPLE POINTS AND THE CRITICAL POINT

If the singularity  $\bar{Y}$  is on the circle of convergence of  $G_0(y, \beta)$ , we can apply the theorem of Cauchy and Hadamard; with (6.19) we have

$$\frac{1}{\bar{Y}} = v_s = \overline{\lim}_{\nu \rightarrow \infty} (|\beta_\nu|)^{1/\nu},$$

where  $\overline{\lim}$  denotes the upper limit of the limit points of the  $\beta_\nu$ . If there are several limit points we can relate to each of them a partial series  $\beta_{\nu_i}$  so that

$$\left. \begin{aligned} v_s &= 1/\bar{Y} = \max \beta_i \\ \beta_i &= \lim_{\nu_i \rightarrow \infty} (|\beta_{\nu_i}|)^{1/\nu_i}. \end{aligned} \right\} \tag{7.1}$$

Since  $d\beta_\nu/dT$  is continuous, it follows that in general  $dv_s/dT$  is continuous. A discontinuity will occur if a temperature  $T_3$  exists such that the greatest



$\beta_i$  is the limit of two different partial series above and below  $T_3$ . The vapour pressure can be obtained from (5.19):

$$P_s = \frac{kT}{v_s} \left[ 1 - \sum \frac{\nu}{\nu+1} \beta_{\nu} / v_s^{\nu} \right], \quad \bar{Y} = \frac{1}{v_s} \quad (7.2)$$

$dP_s/dT$  therefore is in general continuous except at the temperatures  $T_3$  which we may therefore identify with the triple points.

If  $\bar{Y}$  is not on the circle of convergence, we obtain similar formulae by applying the theorem of Cauchy and Hadamard to the series representing the analytical continuation of  $G_0(y, \beta)$ .

If at the triple point there are two crystal structures in equilibrium with the gaseous phase, (7.1) has a simple physical meaning. For the contributions to the integrals  $\beta_{\nu}$  for large values of  $\nu$  come mostly from parts of phase space in which the molecules have some ordered arrangement. It appears from (7.1) that the partial series  $\beta_{\nu_i}$  can directly be related to various crystal structures.

Finally we shall consider the critical temperature  $T_c$  where the condensation volume  $v_s$  itself is singular. It is obvious that this is impossible if  $v_s$  is determined by (7.1). We must assume that there is a temperature region below the critical temperature in which  $\bar{Y}$  is determined by (6.20).<sup>\*</sup> In this case  $v_s$  may be singular, if we assume that (6.20) has two roots on the positive axis which coincide for  $T = T_c$  and vanish into the complex plane for  $T > T_c$ . In this case we have

$$G_1(\bar{Y}, \beta) = 1, \quad G_2(\bar{Y}, \beta) = 0, \quad T = T_c \quad (7.3)$$

and therefore from (6.21)

$$\frac{dP}{dV} = 0, \quad \frac{d^2P}{dV^2} = 0, \quad T = T_c \quad (7.4)$$

The considerations about the critical point must however be taken with reserve, as is apparent if we consider the question of how the volume of the condensed phase may be defined in the present theory. One might be tempted to identify the second root of  $G_1(y, \beta) = 1$  with this volume. However, there is no justification for doing so. Indeed there is no possibility of defining the volume of the condensed phase in the present theory. We must assume that the condensed phase is in that region where the theory

\* Mayer and Harrison (1938) have identified this region with the region between the critical temperature and the temperature where the meniscus between the liquid and the solid phase disappears.

breaks down, i.e. where  $b_i$  and  $\beta_v$  are dependent on the volume.\* For this reason the equations for the critical temperature may need modification.

### CONCLUSIONS

We have shown that the exact evaluation of the partition function for a system of equal particles exerting central forces leads to the complete thermodynamics of a gas, including the phenomenon of condensation. One physical assumption had to be made from the beginning, namely that the coefficients of the partition function, which Mayer has introduced, the irreducible integrals  $\beta_v$ , do not depend on the volume. This is certainly true for large volumes, but not for the condensed phase. In spite of this fact the theory explains not only condensation but indicates even the possibility of the existence of different condensed phases. It appears, at first sight, astonishing that it is possible to obtain such far reaching results without knowing anything about the irreducible integrals  $\beta_v$ . We have, however, made full use of the fact that the partition function is positive, and this obviously imposes rather severe conditions on the  $\beta_v$ . As Mayer has discovered, the phenomenon of condensation is connected with the singularities of the series, which represent the thermodynamical properties, and as these series have coefficients depending on the  $\beta_v$ , the positivity condition mentioned is just sufficient to determine the singularity and thereby the condensation point.

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### NOTATION

- $Q$  partition function.  
 $Q_\tau$  factor of  $Q$  due to the potential energy multiplied with  $N!$   
 $A = E - TS$  Helmholtz' free energy.

\* Mayer and Harrison (1938) have developed the expressions which have to replace the functions  $G_\lambda(z, vb)$  in the case that the  $b_i$  depend on the volume. It should be investigated whether these formulae lead to a description of the condensed phase.

$F = A + PV$  Gibb's thermodynamic potential.

$v = V/N$  volume per molecule.

$b_i$  cluster integrals.

$\beta_\nu$  irreducible integrals.

$$F(M, I, x_1, x_2, \dots) = F(M, I, x) = \sum_{\substack{m_i \\ \sum m_i = M}} \prod_i \frac{(Ix_i)^{m_i}}{m_i!}.$$

$$G_\lambda(\xi, x_1, x_2, \dots) = G_\lambda(\xi, x) = \sum_{\nu=1}^{\infty} \nu^\lambda x_\nu \xi^\nu.$$

$$H_\lambda^m(r, x_1, x_2, \dots) = H_\lambda^m(r, x) = \sum_{N=1}^{\infty} \frac{F(N-m, N, x)}{N^\lambda} r^N.$$

The symbols  $r, z, y$  are reserved for the following series:

(a)  $H_\lambda^0(r, vb)$ .

(b)  $G_\lambda(z, vb)$ .

(c)  $G_\lambda(y, \beta)$ .

$R =$  radius of convergence of (a). ( $R$  is also used for the gas constant but there is no possibility of mistaking these two quantities.)

$Z, Y$  are quantities corresponding to  $R$ .

$\bar{Z} =$  nearest singularity of the series (b) on the positive axis.

$\bar{Y}$  is a quantity corresponding to  $\bar{Z}$ .

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INTRODUCTION

The question of fluctuations in electromagnetic radiation played an important role in the development of quantum theory. It was first considered by Planck in 1901 in connection with the derivation of his law of black-body radiation.

PART II

It is shown that the fluctuations in the energy of a radiation field are determined by the fluctuations in the number of photons. The fluctuations in the number of photons are determined by the fluctuations in the number of photons per unit volume.

ON FLUCTUATIONS IN ELECTROMAGNETIC RADIATION

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# ON FLUCTUATIONS IN ELECTROMAGNETIC RADIATION

by

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## INTRODUCTION

The question of fluctuations in electromagnetic radiation played an important role during the period of the development of quantum theory. After having introduced the conception of light quanta or photons in order to explain the observed phenomena of the photo-electric effect, Einstein(1905) considered the consequences of this idea for ~~the~~ other properties of the radiation.

Planck's formula for the energy density of radiation implies, by arguments of general thermodynamics and statistics, the following expression for the mean square fluctuation of the energy contained in a volume  $\nu$  in terms of the mean energy  $\bar{E}_\nu$ :

$$(0.1) \quad \overline{\Delta E_\nu^2} = \frac{\bar{E}_\nu^2}{z_\nu \nu} + h\nu \bar{E}_\nu,$$

where  $z_\nu = 8\pi\nu^2/c^3$  is the density of radiation oscillators in the  $\nu$ -scale. Some years later it was shown by Lorentz (1916) and by Ornstein and Zernicke (1919) that the first of the two terms can be accounted for by a classical calculation of the energy fluctuation in a radiation field as a consequence of the interference of the elementary waves. Einstein (1909) pointed out that the second term can be interpreted as showing the presence of photons. For it is well known that in an assembly of  $N$  independent particles the mean square fluctuations of the number in a small partial volume is equal to the

average number

$$(0.2) \quad \overline{\Delta n^2} = \bar{n}.$$

In the photon picture where each particle carries the energy  $h\nu$  one finds for the fluctuation of the total energy  $n h\nu = E_\nu$

$$(0.3) \quad \overline{\Delta E_\nu^2} = (h\nu)^2 \overline{\Delta n^2} = (h\nu)^2 \bar{n} = h\nu \overline{E_\nu}.$$

It was considered one of the greatest successes of quantum mechanics to be able to account for both terms (0.1) simultaneously. This attempt to derive (0.1) from the quantized laws of the electromagnetic field is contained in one of the first papers ~~xxx~~ on matrix mechanics by Born, Heisenberg and Jordan (1926); as a matter of fact, only a one-dimensional model was treated. Recently Heisenberg (1931) has raised objections against this proof because certain divergent integrals were neglected, and he has tried to remedy this defect by the assumption that the partial volume considered has no sharp boundaries.

We have been led to reconsider the problem in the hope of deriving some information from these divergent integrals about possible limits of our present radiation theory - similar to the information ~~xxxxxxxx~~ provided by the infinite zero-energy of the electron. The result of our study is rather surprising:

We find that Heisenberg's objections were not justified. On the other hand, we have discovered not only another serious

error in the old calculations, but convinced ourselves that the whole problem has not been clearly formulated by previous investigators and the numerous authors who have quoted their results in textbooks and lectures. It is not to be expected that the formula (0.1) derived by the methods of statistical mechanics should coincide exactly with the formula derived from the quantized electromagnetic field. The two methods are really concerned with different objects and, therefore, lead to different results. We shall give here the derivation of the correct formula for both cases and show that the difference can be interpreted physically. The result is that (in contradiction to Heisenberg's statement) no other infinities occur than that of the zero energy of the radiation field; if this is admitted the formula (0.1) is in full agreement with that derived from the ~~interference fluctuations of the quantized field~~ interference fluctuations of the quantized field. But the infinity of zero-energy is really disastrous to the whole argument. We shall discuss this difficulty in the last section in connection with the question of a future theory which avoids these infinities.

# 1. FLUCTUATIONS DERIVED FROM STATISTICAL MECHANICS.

The starting point of Einstein's considerations is the formula of statistical mechanics:

$$(1.1) \quad \overline{(\Delta E)^2} = - \frac{d\bar{E}}{d\beta} \quad , \quad \beta = \frac{1}{kT} \quad ,$$

which is easily proved for a system having a partition function

$$(1.2) \quad Z = \sum_n g_n e^{-\beta \epsilon_n}$$

For one has evidently (1)

$$(1.3) \quad \bar{E} = - \frac{Z'}{Z} \quad , \quad \overline{E^2} = \frac{Z''}{Z} \quad ,$$

hence

$$\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2 = \frac{Z''}{Z} - \frac{Z'^2}{Z^2} = \frac{d}{d\beta} \frac{Z'}{Z} \quad ,$$

which, on account of (1.3), proves (1.1). Fowler (Statistical Mechanics, 1936) has shown that (1.1) holds under the most general assumptions possible, including the Bose-Einstein and Fermi-Dirac statistics. If we apply (1.1) to the radiation energy as given by Plank's formula,

$$(1.4) \quad \bar{E}_\nu = z_\nu \nu \frac{h\nu}{e^{h\nu/\beta} - 1} \quad ,$$

we obtain, by eliminating  $\beta$ , Einstein's formula (D.1).

But (1.4) is not the total energy of radiation, but only the thermal part of it, the zero energy being omitted. If we are

(1) The dash means differentiation with regard to  $\beta$ .



now going to compare this formula with that derived from the quantized waves we have to consider that it is certainly not allowable to subtract the influence of the zero energy of the wave field on the mean square fluctuations; for these are interferences between zero waves and waves representing the motion of photons<sup>(1)</sup>. Therefore, in the statistical considerations we must also use the complete Plank formula with zero energy:

$$(1.5) \quad \bar{u}_\nu = \bar{E}_\nu + z_\nu \nu \frac{1}{2} h\nu = z_\nu \nu \left( \frac{h\nu}{e^{h\nu/\beta} - 1} + \frac{1}{2} h\nu \right)$$

Then we obtain from (0.1) by substitution, or by direct application of (1.1) to (1.5)

$$(1.6) \quad \overline{(\Delta u_\nu)^2} = \frac{\bar{u}_\nu^2}{z_\nu \nu} - z_\nu \nu \left( \frac{h\nu}{2} \right)^2.$$

This formula is, of course, identical with (0.1) but has a form proper for comparison with the result of the calculation of interferences.

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(1) This fact is not made clear in the old paper by Born, Heisenberg and Jordan.

## 2. COMPARISON OF THE STATISTICAL AND THE INTERFERENCE FLUCTUATIONS.

Following Einstein's idea we have to show that the mean square fluctuation of the energy contained in a partial volume  $\nu$  of a cavity filled with radiation, calculated from the interference of the quantized waves, satisfies (1.6). But can we really expect this?

We consider the limiting case of low temperatures; if we make  $T \rightarrow 0, \beta \rightarrow \infty$  we see from (1.5) that  $\bar{u}_\nu \rightarrow \frac{1}{2} z_\nu \nu h\nu$  therefore  $(\Delta u_\nu)^2 \rightarrow 0$ . This fact shows that in spite of adding the zero energy to Plank's formula, this zero vibration has no effect on the mean square fluctuation. And this is not surprising. For in deriving (1.6) we considered the radiation field of volume  $\nu$  as a total thermodynamical system in equilibrium with a bath of temperature  $T$ . If  $T=0$  the system is necessarily in its lowest quantum state, and no fluctuations of energy can be expected. Whether this lowest state is represented by 'no waves' (classical theory) or 'zero waves' (quantum theory) does not matter at all.

If we are now going to carry out Einstein's programme we have to consider a partial volume  $\nu$  and calculate the fluctuation of the energy contained in it. The source of these fluctuations is the interferences of the elementary waves, and these exist not only for waves proper which correspond to photons, but for zero waves as well. We shall, therefore, expect to find an additional term in the fluctuations

corresponding to the zero energy,  $z_\nu v (h\nu/2)^2$ . Indeed, we shall show that the wave calculation gives the result

$$(2.1) \quad \overline{(\Delta u_\nu)^2} = \frac{\bar{u}_\nu^2}{z_\nu v}$$

which differs from (1.6) by this term; expressed in terms of the 'thermal' energy  $\bar{E}_\nu$ , as given by (1.5), this becomes

$$(2.2) \quad \overline{(\Delta u_\nu)^2} = \frac{\bar{E}_\nu^2}{z_\nu v} + h\nu \bar{E}_\nu + z_\nu v \left( \frac{h\nu}{2} \right)^2$$

instead of (0.1).

In fact, we have to do with two essentially different models; (0.1) corresponds to a total system, (2.2) to a partial one. Einstein's argument in identifying these two models was apparently this: the partial volume filled with radiation should evidently behave in the same way as if the outer radiation were a bath of ~~temperature~~ constant temperature. This conclusion is quite right for higher temperatures, but if the temperature is so low that the thermal energy  $\bar{E}_\nu$  is of the same order or smaller than the zero energy the difference between the wave model and the total system becomes important: the zero waves in the partial volume continue to interfere and fluctuate, whereas the closed system comes to rest in its lowest quantum state.

We shall now proceed to prove (2.1) as a consequence of the wave theory.

### 3. QUANTUM FIELD AND ENERGY DENSITY.

We follow the presentation of the quantized electromagnetic field given by Heitler (1936) on p.43,44 of his book.

We consider the radiation contained in a cube of side  $L$  (Heitler puts  $L=1$ ). The vector potential is

$$(3.1) \quad \underline{A} = \sqrt{\left(\frac{4\pi c^2}{L^3}\right)} \sum_{\lambda} \sum_{\alpha} \underline{e}_{\lambda}^{\alpha} \left\{ q_{\lambda}^{\alpha} e^{i(\underline{k}_{\lambda}, \underline{r})} + q_{\lambda}^{\alpha*} e^{-i(\underline{k}_{\lambda}, \underline{r})} \right\}.$$

We assume that the field is periodic with the cube as basis<sup>(1)</sup>;

$\lambda$  denotes the different elementary waves with amplitudes

$$(3.2) \quad q_{\lambda}^{\alpha} = \dot{q}_{\lambda}^{\alpha} e^{-i\omega_{\lambda}t}, \quad \omega_{\lambda} = c/k_{\lambda} = 2\pi\nu_{\lambda}$$

and  $\alpha=1,2$  distinguishes the two directions of linear polarization, given by the unit vectors  $\underline{e}_{\lambda}^{\alpha}$ , which are perpendicular to one another and to  $\underline{k}_{\lambda}$ :

$$(3.3) \quad (\underline{e}_{\lambda}^{\alpha} \cdot \underline{k}_{\lambda}) = 0, \quad (\underline{e}_{\lambda}^{\alpha} \cdot \underline{e}_{\lambda}^{\beta}) = \delta_{\alpha\beta} \quad (\alpha, \beta = 1, 2);$$

therefore

$$(3.4) \quad \begin{aligned} c[\underline{k}_{\lambda} \times \underline{e}_{\lambda}^1] &= c/k_{\lambda} \underline{e}_{\lambda}^2 = \omega_{\lambda} \underline{e}_{\lambda}^2 \\ c[\underline{k}_{\lambda} \times \underline{e}_{\lambda}^2] &= -c/k_{\lambda} \underline{e}_{\lambda}^1 = -\omega_{\lambda} \underline{e}_{\lambda}^1 \end{aligned}$$

The amplitudes  $q_{\lambda}^{\alpha}$  satisfy the commutation relations (Heitler p.60):

$$(3.5) \quad [q_{\lambda}^{\alpha}, q_{\mu}^{\beta}] = 0, \quad [q_{\lambda}^{\alpha}, q_{\mu}^{\beta*}] = \frac{\hbar}{2\omega_{\lambda}} \delta_{\lambda\mu} \delta_{\alpha\beta}.$$

(1) We have convinced ourselves by a careful calculation that the assumption of reflecting walls (standing waves) gives exactly the same results.

The total energy, i.e. the Hamiltonian, is

$$(3.6) \quad H = \sum_{\alpha} \sum_{\lambda} H_{\lambda}^{\alpha}, \quad H_{\lambda}^{\alpha} = \omega_{\lambda}^2 (q_{\lambda}^{\alpha} q_{\lambda}^{\alpha+} + q_{\lambda}^{\alpha+} q_{\lambda}^{\alpha}).$$

The thermal energy (Heitler p.60) is

$$(3.7) \quad H' = \sum_{\alpha} \sum_{\lambda} H'_{\lambda}^{\alpha}, \quad H'_{\lambda}^{\alpha} = 2\omega_{\lambda}^2 q_{\lambda}^{\alpha+} q_{\lambda}^{\alpha};$$

it differs from the total energy by the zero energy  $\sum_{\lambda} \hbar \omega_{\lambda}$ .

The vectors of the electric and magnetic field are

$$(3.8) \quad \underline{\mathcal{E}} = -\frac{1}{c} \dot{\underline{A}} = \frac{i}{c} \sqrt{\left(\frac{4\pi c^2}{L^3}\right)} \sum_{\lambda} \sum_{\alpha} \underline{e}_{\lambda}^{\alpha} \omega_{\lambda} \left\{ q_{\lambda}^{\alpha} e^{i(\underline{k}_{\lambda}, \underline{r})} - q_{\lambda}^{\alpha+} e^{-i(\underline{k}_{\lambda}, \underline{r})} \right\},$$

$$\underline{\mathcal{H}} = \text{curl} \underline{A} = i \sqrt{\left(\frac{4\pi c^2}{L^3}\right)} \sum_{\lambda} \sum_{\alpha} [\underline{k}_{\lambda} \times \underline{e}_{\lambda}^{\alpha}] \left\{ q_{\lambda}^{\alpha} e^{i(\underline{k}_{\lambda}, \underline{r})} - q_{\lambda}^{\alpha+} e^{-i(\underline{k}_{\lambda}, \underline{r})} \right\}.$$

Squaring these expressions we see from (3.4) that we have in  $\mathcal{E}^2$  the factor

$$[\underline{k}_{\lambda} \times \underline{e}_{\lambda}^{\alpha}] \cdot [\underline{k}_{\mu} \times \underline{e}_{\mu}^{\beta}] = \pm \frac{1}{c^2} \omega_{\lambda} \omega_{\mu} (\underline{e}_{\lambda}^{\alpha} \cdot \underline{e}_{\mu}^{\beta})$$

the upper sign being taken for  $\alpha = \beta$ , and the lower if  $\alpha \neq \beta$ .

But in  $\mathcal{E}^2$  the corresponding factor is the same, but always with the + sign. Therefore, in  $\mathcal{E}^2 + \mathcal{H}^2$  all terms with  $\alpha \neq \beta$  cancel, and we get for the energy density

$$(3.9) \quad u = \frac{1}{8\pi} (\mathcal{E}^2 + \mathcal{H}^2) = \frac{1}{L^3} \sum_{\lambda, \mu} \sum_{\alpha} (\underline{e}_{\lambda}^{\alpha} \cdot \underline{e}_{\mu}^{\alpha}) \omega_{\lambda} \omega_{\mu} \left\{ (q_{\lambda}^{\alpha} q_{\mu}^{\alpha+} + q_{\mu}^{\alpha+} q_{\lambda}^{\alpha}) e^{i(\underline{k}_{\lambda} - \underline{k}_{\mu}, \underline{r})} - q_{\lambda}^{\alpha} q_{\mu}^{\alpha} e^{i(\underline{k}_{\lambda} + \underline{k}_{\mu}, \underline{r})} - q_{\lambda}^{\alpha+} q_{\mu}^{\alpha+} e^{-i(\underline{k}_{\lambda} + \underline{k}_{\mu}, \underline{r})} \right\}.$$

4. THE ENERGY IN A PARTIAL VOLUME AND ITS FLUCTUATIONS.

We consider a partial volume in the shape of a cube of side  $\ell$ . By integrating (3.9) over the cube we get the energy

$$(4.1) \quad U = \int u d\tau = U_1 + U_2$$

where

$$(4.2) \quad U_1 = \left(\frac{\ell}{L}\right)^3 \sum_{\lambda, \mu} \sum_{\alpha} (\underline{e}_{\lambda}^{\alpha} \cdot \underline{e}_{\mu}^{\alpha}) \omega_{\lambda} \omega_{\mu} (q_{\lambda}^{\alpha} q_{\mu}^{\alpha \dagger} + q_{\mu}^{\alpha \dagger} q_{\lambda}^{\alpha}) f(\underline{k}_{\lambda} - \underline{k}_{\mu}),$$

$$U_2 = -\left(\frac{\ell}{L}\right)^3 \sum_{\lambda, \mu} \sum_{\alpha} (\underline{e}_{\lambda}^{\alpha} \cdot \underline{e}_{\mu}^{\alpha}) \omega_{\lambda} \omega_{\mu} (q_{\lambda}^{\alpha} q_{\mu}^{\alpha} + q_{\lambda}^{\alpha \dagger} q_{\mu}^{\alpha \dagger}) f(\underline{k}_{\lambda} + \underline{k}_{\mu}),$$

with

$$(4.3) \quad f(\underline{k}) = \frac{\sin k_x \ell/2}{k_x \ell/2} \frac{\sin k_y \ell/2}{k_y \ell/2} \frac{\sin k_z \ell/2}{k_z \ell/2}.$$

We now average over the time, i.e. we take the diagonal elements of the matrices only. Then we get only contributions from the terms in  $U_1$  with  $\lambda = \mu$ ; with  $(\underline{e}_{\lambda}^{\alpha} \cdot \underline{e}_{\lambda}^{\alpha}) = 1$  and  $f(0) = 1$  we find for the mean energy in the partial volume  $\ell^3$

$$(4.4) \quad \bar{U} = \left(\frac{\ell}{L}\right)^3 \sum_{\lambda} \sum_{\alpha} \omega_{\lambda}^2 (q_{\lambda}^{\alpha} q_{\lambda}^{\alpha \dagger} + q_{\lambda}^{\alpha \dagger} q_{\lambda}^{\alpha})$$

in agreement with (3.6).

The fluctuation of the energy about this value  $\bar{U}$  is

$$(4.5) \quad \Delta U = U - \bar{U} = \Delta U_1 + \Delta U_2$$

where

$$\Delta u_1 = 2 \left(\frac{L}{L}\right)^3 \sum_{\lambda \neq \mu} \sum_a (e_{\lambda}^x \cdot e_{\mu}^x) \omega_{\lambda} \omega_{\mu} q_{\lambda}^x q_{\mu}^{x+} f(k_{\lambda} - k_{\mu})$$

(4.6)

$$\Delta u_2 = u_2$$

Here we have commuted  $q_{\mu}^{x+}$  and  $q_{\lambda}^x$  in  $\Delta u_1$ , which is permitted since  $\lambda \neq \mu$ .

The square of the fluctuation is:

$$(4.7) \quad (\Delta u)^2 = (\Delta u_1)^2 + (\Delta u_2)^2 + \Delta u_1 \cdot \Delta u_2 + \Delta u_2 \cdot \Delta u_1$$

with

$$\begin{aligned} (\Delta u_1)^2 &= 4 \left(\frac{L}{L}\right)^6 \sum_{\lambda \neq \mu} \sum_{\sigma, \rho} \sum_{\alpha, \beta} (e_{\lambda}^{\sigma} \cdot e_{\mu}^{\alpha}) (e_{\sigma}^{\beta} \cdot e_{\rho}^{\beta}) \omega_{\lambda} \omega_{\mu} \omega_{\sigma} \omega_{\rho} q_{\lambda}^{\sigma} q_{\mu}^{\alpha+} q_{\sigma}^{\beta} q_{\rho}^{\beta+} f(k_{\lambda} - k_{\mu}) f(k_{\sigma} - k_{\rho}), \\ (\Delta u_2)^2 &= \left(\frac{L}{L}\right)^6 \sum_{\lambda, \mu} \sum_{\sigma, \rho} \sum_{\alpha, \beta} (e_{\lambda}^{\sigma} \cdot e_{\mu}^{\alpha}) (e_{\sigma}^{\beta} \cdot e_{\rho}^{\beta}) \omega_{\lambda} \omega_{\mu} \omega_{\sigma} \omega_{\rho} (q_{\lambda}^{\sigma} q_{\mu}^{\alpha} + q_{\lambda}^{\sigma+} q_{\mu}^{\alpha+}) (q_{\sigma}^{\beta} q_{\rho}^{\beta} + q_{\sigma}^{\beta+} q_{\rho}^{\beta+}) \cdot \\ &\quad \cdot f(k_{\lambda} + k_{\mu}) f(k_{\sigma} + k_{\rho}), \end{aligned}$$

(4.8)

$$\begin{aligned} \Delta u_1 \cdot \Delta u_2 + \Delta u_2 \cdot \Delta u_1 &= 2 \left(\frac{L}{L}\right)^6 \sum_{\lambda \neq \mu} \sum_{\sigma, \rho} \sum_{\alpha, \beta} (e_{\lambda}^{\sigma} \cdot e_{\mu}^{\alpha}) (e_{\sigma}^{\beta} \cdot e_{\rho}^{\beta}) \omega_{\lambda} \omega_{\mu} \omega_{\sigma} \omega_{\rho} \cdot \\ &\quad \cdot \{q_{\lambda}^{\sigma} q_{\mu}^{\alpha+} (q_{\sigma}^{\beta} q_{\rho}^{\beta} + q_{\sigma}^{\beta+} q_{\rho}^{\beta+}) + (q_{\sigma}^{\beta} q_{\rho}^{\beta} + q_{\sigma}^{\beta+} q_{\rho}^{\beta+}) q_{\lambda}^{\sigma} q_{\mu}^{\alpha+}\} f(k_{\lambda} - k_{\mu}) f(k_{\sigma} + k_{\rho}). \end{aligned}$$

If we average these expressions over time all terms disappear

except those which contain the pairs  $q_{\lambda}^{\sigma}, q_{\lambda}^{\sigma+}$  and  $q_{\mu}^{\alpha}, q_{\mu}^{\alpha+}$

Therefore we get:

$$\overline{(\Delta u_1)^2} = 4 \left(\frac{L}{L}\right)^6 \sum_{\lambda \neq \mu} \sum_a (e_{\lambda}^x \cdot e_{\mu}^x)^2 \omega_{\lambda}^2 \omega_{\mu}^2 q_{\lambda}^x q_{\mu}^{x+} q_{\mu}^x q_{\lambda}^{x+} f^2(k_{\lambda} - k_{\mu}),$$

(4.9)

$$\begin{aligned} \overline{(\Delta u_2)^2} &= \left(\frac{L}{L}\right)^6 \sum_{\lambda, \mu} \sum_a (e_{\lambda}^x \cdot e_{\mu}^x)^2 \omega_{\lambda}^2 \omega_{\mu}^2 \{q_{\lambda}^x q_{\mu}^x q_{\lambda}^{x+} q_{\mu}^{x+} + q_{\lambda}^{x+} q_{\mu}^{x+} q_{\lambda}^x q_{\mu}^x + \\ &\quad + q_{\lambda}^x q_{\mu}^x q_{\lambda}^{x+} q_{\mu}^{x+} + q_{\lambda}^{x+} q_{\mu}^{x+} q_{\lambda}^x q_{\mu}^x\} f^2(k_{\lambda} + k_{\mu}), \end{aligned}$$

$$\overline{\Delta u_1 \cdot \Delta u_2 + \Delta u_2 \cdot \Delta u_1} = 0$$

Now we have to average over all directions of polarisation. Each term in the sum is a product of unit vectors belonging to two elementary waves  $(\underline{e}_\lambda^1, \underline{e}_\lambda^2, \underline{k}_\lambda)$  and  $(\underline{e}_\mu^1, \underline{e}_\mu^2, \underline{k}_\mu)$ . We can consider the first set of orthogonal vectors as fixed and coinciding with the coordinate axes, in the order  $(x, y, z)$ ; then

$$(\underline{e}_\lambda^1 \cdot \underline{e}_\mu^1) = e_{\mu x}^1, \quad (\underline{e}_\lambda^2 \cdot \underline{e}_\mu^2) = e_{\mu y}^2$$

are direction cosines, which can be expressed in terms of the Eulerian angles  $\varphi, \psi, \delta$ ; for instance

$$\cos \psi = e_{\mu x}^1 = \cos \varphi \cos \psi - \cos \delta \sin \varphi \sin \psi$$

where  $\delta$  is the angle between  $\underline{k}_\lambda$  and  $\underline{k}_\mu$ . This equation can at once be read from figure 1, which shows the intersections of the vectors in question with a sphere centred in the origin. Averaging over  $\varphi$  and  $\psi$  we find

$$(4.10) \quad (\overline{e_{\mu x}^1})^2 = \frac{1}{4} (1 + \cos^2 \delta) = \overline{(\underline{e}_\lambda^1 \cdot \underline{e}_\mu^1)^2} = \overline{(\underline{e}_\lambda^2 \cdot \underline{e}_\mu^2)^2}$$

In  $(\Delta u_1)^2$   $q_\lambda^{\alpha\tau}$  commutes with  $q_\mu^{\alpha\tau} q_\mu^\alpha$  since  $\lambda \neq \mu$ .

In  $(\Delta u_2)^2$   $q_\lambda^\alpha$  commutes with  $q_\mu^\alpha$  and  $q_\lambda^{\alpha\tau}$  with  $q_\mu^{\alpha\tau}$

Furthermore we shall show that we are allowed to commute  $q_\mu^\alpha$  with  $q_\lambda^{\alpha\tau}$  and  $q_\lambda^\alpha$  with  $q_\mu^{\alpha\tau}$ ; for, doing so and using (3.5) we get an additional term

$$R = \frac{1}{2} \left(\frac{\hbar}{L}\right)^6 \sum_{\lambda, \mu} \sum_{\alpha} (1 + \cos^2 \delta_{\lambda\mu}) \omega_\lambda^2 \omega_\mu^2 (q_\lambda^\alpha q_\mu^{\alpha\tau} - q_\lambda^{\alpha\tau} q_\mu^\alpha) \frac{\hbar}{2\omega_\lambda} \delta_{\lambda\mu} f^2(\underline{k}_\lambda, \underline{k}_\mu)$$



or

$$(4.11) \quad R = \frac{1}{2} \left(\frac{\ell}{L}\right)^6 \sum_{\lambda} \sum_{\alpha} \hbar \omega_{\lambda}^3 (q_{\lambda}^{\alpha} q_{\lambda}^{\alpha\dagger} - q_{\lambda}^{\alpha\dagger} q_{\lambda}^{\alpha}) f^2(2k_{\lambda}) = \left(\frac{\ell}{L}\right)^6 \sum_{\lambda} \sum_{\alpha} \left(\frac{\hbar \omega_{\lambda}}{2}\right)^2 f^2(2k_{\lambda})$$

which vanishes as we shall see later. Neglecting R, we get from (4.9), using (4.10):

$$(4.12) \quad \overline{(\Delta u_1)^2} = \left(\frac{\ell}{L}\right)^6 \sum_{\lambda \neq \mu} \sum_{\alpha} (1 + \cos^2 \delta_{\lambda\mu}) \omega_{\lambda}^2 \omega_{\mu}^2 q_{\lambda}^{\alpha} q_{\lambda}^{\alpha\dagger} q_{\mu}^{\alpha\dagger} q_{\mu}^{\alpha} f^2(k_{\lambda} - k_{\mu})$$

$$\overline{(\Delta u_2)^2} = \frac{1}{2} \left(\frac{\ell}{L}\right)^6 \sum_{\lambda \neq \mu} \sum_{\alpha} (1 + \cos^2 \delta_{\lambda\mu}) \omega_{\lambda}^2 \omega_{\mu}^2 \{ q_{\lambda}^{\alpha} q_{\lambda}^{\alpha\dagger} q_{\mu}^{\alpha} q_{\mu}^{\alpha\dagger} + q_{\lambda}^{\alpha\dagger} q_{\lambda}^{\alpha} q_{\mu}^{\alpha\dagger} q_{\mu}^{\alpha} \} f^2(k_{\lambda} + k_{\mu})$$

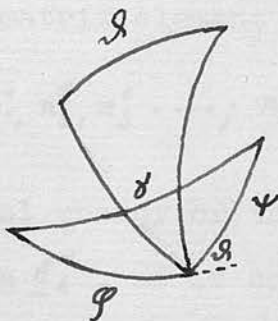


Figure 1.

5. MONOCHROMATIC FLUCTUATION.

If we introduce the matrices

$$(5.1) \quad A_{\lambda}^{\alpha} = 2\omega_{\lambda}^2 q_{\lambda}^{\alpha} q_{\lambda}^{\alpha \dagger}, \quad B_{\lambda}^{\alpha} = 2\omega_{\lambda}^2 q_{\lambda}^{\alpha \dagger} q_{\lambda}^{\alpha},$$

we can write the product  $4\omega_{\lambda}^2 \omega_{\mu}^2 q_{\lambda}^{\alpha} q_{\lambda}^{\alpha \dagger} q_{\mu}^{\alpha \dagger} q_{\mu}^{\alpha}$  appearing in the first equation (4.12) as

$$(5.2) \quad A_{\lambda}^{\alpha} \cdot B_{\mu}^{\alpha} = \mathcal{C}_{\lambda\mu}^{\alpha}$$

All three matrices  $A, B, \mathcal{C}$  commute and can be brought simultaneously into diagonal form. Each diagonal element corresponds to a state of the total radiation field which we characterise by the set of numbers  $n_{\lambda}^{\alpha}$  of photons present in the oscillator  $\lambda$  with direction of polarisation  $\underline{e}_{\lambda}^{\alpha}$ . The corresponding matrix element of  $A_{\lambda}^{\alpha}$  is denoted by

$$(5.3) \quad A_{\lambda}^{\alpha}(n) = A_{\lambda}^{\alpha}(n_1^{\alpha}, n_2^{\alpha}, n_3^{\alpha}, \dots; n_1^{\alpha}, n_2^{\alpha}, n_3^{\alpha}, \dots).$$

$B_{\lambda}^{\alpha}$  represents the thermal energy of the oscillator  $\lambda$  with direction of polarisation  $\underline{e}_{\lambda}^{\alpha}$ , as is seen from (3.7); and  $A_{\lambda}^{\alpha}$  represents the thermal energy plus twice the zero energy; therefore:

$$(5.4) \quad B_{\lambda}^{\alpha}(n) = n_{\lambda}^{\alpha} \hbar \omega_{\lambda}, \quad A_{\lambda}^{\alpha}(n) = (n_{\lambda}^{\alpha} + 1) \hbar \omega_{\lambda},$$

and

$$(5.5) \quad \mathcal{C}_{\lambda\mu}^{\alpha}(n) = (n_{\lambda}^{\alpha} + 1) n_{\mu}^{\alpha} \hbar^2 \omega_{\lambda} \omega_{\mu}.$$

Correspondingly, there appears in the second equation (4.12) the expression

$$(5.6) \quad \mathcal{D}_{\lambda\mu}^{\alpha} = A_{\lambda}^{\alpha} A_{\mu}^{\alpha} + B_{\lambda}^{\alpha} B_{\mu}^{\alpha}$$

with the diagonal element

$$(5.7) \quad \mathcal{D}_{\lambda\mu}^{\alpha}(n) = \left\{ (n_{\lambda}^{\alpha} + 1)(n_{\mu}^{\alpha} + 1) + n_{\lambda}^{\alpha} n_{\mu}^{\alpha} \right\} \hbar^2 \omega_{\lambda} \omega_{\mu}.$$

Substituting this in (4.12) we get

$$(5.8) \quad \overline{(\Delta u_1)^2} = \frac{1}{4} \left( \frac{\ell}{L} \right)^6 \sum_{\lambda \neq \mu} \sum_{\alpha} (1 + \cos^2 \vartheta_{\lambda\mu}) \hbar^2 \omega_{\lambda} \omega_{\mu} n_{\lambda}^{\alpha} (n_{\lambda}^{\alpha} + 1) f^2(\underline{k}_{\lambda} - \underline{k}_{\mu})$$

$$\overline{(\Delta u_2)^2} = \frac{1}{8} \left( \frac{\ell}{L} \right)^6 \sum_{\lambda, \mu} \sum_{\alpha} (1 + \cos^2 \vartheta_{\lambda\mu}) \hbar^2 \omega_{\lambda} \omega_{\mu} \left\{ (n_{\lambda}^{\alpha} + 1)(n_{\mu}^{\alpha} + 1) + n_{\lambda}^{\alpha} n_{\mu}^{\alpha} \right\} f^2(\underline{k}_{\lambda} + \underline{k}_{\mu}).$$

We now consider small regions in the  $\underline{k}$ -space, of the extension  $\Delta k$ , where

$$\frac{1}{L} \ll \Delta k \ll \frac{1}{\ell}.$$

so that each region contains a large number of oscillators and at the same time the factor  $(1 + \cos^2 \vartheta_{\lambda\mu}) \omega_{\lambda} \omega_{\mu} f^2(\underline{k}_{\lambda} \pm \underline{k}_{\mu})$  in the sums (5.8) does not change appreciably in one of the regions. This cannot be said about the factors depending on  $n_{\lambda}^{\alpha}, n_{\mu}^{\alpha}$ , for these numbers, of course, change at random as we pass from one oscillator to the next. We can now replace  $n_{\lambda}^{\alpha}, n_{\mu}^{\alpha}$  under the summation sign by their mean values over the small regions  $\Delta k$ , and we postulate that these mean values do not change appreciably in regions

whose extension is of the order

This is, of course, not the case for all matrix elements. If, however,  $\ell$  is sufficiently large our postulate is satisfied for those matrix elements which correspond to states of the radiation field for which a mean value  $\bar{n}_\lambda^\alpha d\underline{k}_\lambda$  of photons with wave vectors in  $(\underline{k}_\lambda, \underline{k}_\lambda + d\underline{k}_\lambda)$  and directions of polarisation  $\underline{e}_\lambda^\alpha$  can be defined. We restrict our considerations to such states, and all subsequent formulae hold only for matrix elements corresponding to such states<sup>(1)</sup>.

We now go to the limit  $L \rightarrow \infty$ . As  $k$  is the wave number per  $2\pi$  units of length we have to replace

$$\left(\frac{2\pi}{L}\right)^3 \quad \text{by} \quad \underline{dk};$$

then it follows from (5.8) that

$$\begin{aligned} (\overline{\Delta U_1})^2 &= \frac{1}{4} \left(\frac{\ell}{2\pi}\right)^6 \sum_{\alpha} \iint (1 + \cos^2 \vartheta_{\lambda\mu}) \hbar^2 \omega_\lambda \omega_\mu \bar{n}_\mu^\alpha (\bar{n}_\lambda^\alpha + 1) f^2(\underline{k}_\lambda - \underline{k}_\mu) d\underline{k}_\lambda d\underline{k}_\mu \\ (5.9) \quad (\overline{\Delta U_2})^2 &= \frac{1}{8} \left(\frac{\ell}{2\pi}\right)^6 \sum_{\alpha} \iint (1 + \cos^2 \vartheta_{\lambda\mu}) \hbar^2 \omega_\lambda \omega_\mu \{(\bar{n}_\lambda^\alpha + 1)(\bar{n}_\mu^\alpha + 1) + \bar{n}_\lambda^\alpha \bar{n}_\mu^\alpha\} f^2(\underline{k}_\lambda + \underline{k}_\mu) d\underline{k}_\lambda d\underline{k}_\mu \end{aligned}$$

Here all factors except  $f^2(\underline{k}_\lambda \pm \underline{k}_\mu)$  are practically constant over regions of the order  $1/\ell$ . Therefore we can apply

(1) This restriction which is obviously necessary for a thermodynamical interpretation of the fluctuation formula (as intended by Einstein) is not observed by Heisenberg in his critical paper (1931); he considers an example where only one photon is present. Furthermore the divergence which he finds (formula (15), p.6) is due to the additive term 1 in  $N_k(N_k+1)$ , i.e. to the zero energy, in contradiction to his statement. His objections are, therefore, not justified.

the formula

$$(5.10) \quad \int_{-\infty}^{+\infty} \left( \frac{\sin k l / 2}{k l / 2} \right)^2 F(k) dk = \frac{2\pi}{l} F(0)$$

and obtain

$$(5.11) \quad \overline{(\Delta U_1)^2} = \frac{1}{4} \left( \frac{l}{2\pi} \right)^3 \sum_{\alpha} \int 2 \hbar^2 \omega_{\lambda}^2 \bar{n}_{\lambda}^{\alpha} (\bar{n}_{\lambda}^{\alpha} + 1) d\underline{k}_{\lambda}$$

$$\overline{(\Delta U_2)^2} = \frac{1}{8} \left( \frac{l}{2\pi} \right)^3 \sum_{\alpha} \int 2 \hbar^2 \omega_{\lambda}^2 \{ (\bar{n}_{\lambda}^{\alpha} + 1)(\bar{n}_{-\lambda}^{\alpha} + 1) + \bar{n}_{\lambda}^{\alpha} \bar{n}_{-\lambda}^{\alpha} \} d\underline{k}_{\lambda}$$

In the same way we get from (4.11)

$$(5.12) \quad R = \frac{l^6}{(2\pi L)^3} \sum_{\alpha} \int \frac{\hbar^2 \omega_{\lambda}^2}{4} f^2(2\underline{k}_{\lambda}) d\underline{k}_{\lambda} = 0$$

since  $\omega_0 = 0$  (for  $k_0 = 0$ ); thus the neglect of R in (5.8), (5.9), and (5.11) is justified.

$\bar{n}_{\lambda}^{\alpha}$  and  $\bar{n}_{-\lambda}^{\alpha}$  are the numbers of photons of a definite direction of polarisation travelling in opposite directions. As we assumed periodicity in the cube  $L^3$  these numbers  $\bar{n}_{\lambda}^{\alpha}$  and  $\bar{n}_{-\lambda}^{\alpha}$  can be different; but if this model is to represent approximately a box with reflecting walls, we have to assume

$$(5.13) \quad \bar{n}_{\lambda}^{\alpha} = \bar{n}_{-\lambda}^{\alpha}$$

Then

$$(5.14) \quad \overline{(\Delta U)^2} = \overline{(\Delta U_1)^2} + \overline{(\Delta U_2)^2} = \left( \frac{l}{2\pi} \right)^3 \sum_{\alpha} \int \hbar^2 \omega_{\lambda}^2 \left( \bar{n}_{\lambda}^{\alpha} + \frac{1}{2} \right)^2 d\underline{k}_{\lambda}$$

We now assume that the radiation is isotropic and unpolarised,

i.e. that  $\bar{n}_\lambda^\alpha$  depends only on the frequency  $\omega$ , but not on the directions of propagation and polarisation. (This assumption is of course necessary<sup>(1)</sup> and is also made in the classical calculation because otherwise a comparison with a result of statistical mechanics would be meaningless).

If  $d\Omega$  is the element of solid angle we have

$$d\underline{k} = \frac{1}{c^3} d\Omega \omega^2 d\omega = \left(\frac{2\pi}{c}\right)^3 d\Omega \nu^2 d\nu$$

and we get by integrating over all angles and summing over the directions of polarisation

$$(5.15) \quad \overline{(\Delta U)^2} = \frac{\ell^3}{c^3} 8\pi \int h^2 \nu^4 \left(\bar{n}_\nu + \frac{1}{2}\right)^2 d\nu$$

The fluctuation in the frequency intervall  $d\nu$  is

$$(5.16) \quad \overline{(\Delta U_\nu)^2} d\nu \quad , \quad \text{where} \quad \overline{(\Delta U_\nu)^2} = 8\pi \nu^2 \frac{\ell^3}{c^3} \left(h\nu \left(\bar{n}_\nu + \frac{1}{2}\right)\right)^2$$

The density of radiation oscillators is

$$(5.17) \quad \bar{z}_\nu = \frac{8\pi \nu^2}{c^3}$$

Putting

$$(5.18) \quad \ell^3 = \nu \quad , \quad \nu \bar{z}_\nu h\nu \left(\bar{n}_\nu + \frac{1}{2}\right) = \bar{U}_\nu$$

we get finally

(1) If this assumption were not made one would have

$$\int (\bar{n}_\lambda^\alpha + \frac{1}{2})^2 d\Omega \neq 4\pi (\bar{n}_\nu^\alpha + \frac{1}{2})^2$$

$$\text{where } \bar{n}_\nu^\alpha = \frac{1}{4\pi}$$

$$\text{and } \sum_\alpha (\bar{n}_\nu^\alpha + \frac{1}{2})^2 \neq 2(\bar{n}_\nu + \frac{1}{2})^2$$

$$\text{where } \bar{n}_\nu = \frac{1}{2} \sum_\alpha \bar{n}_\nu^\alpha$$

$$(5.19) \quad \overline{(\Delta u_v)^2} = \frac{\overline{u_v^2}}{Z_v \nu}$$

as stated in (2.1). As the meaning of this result has already been discussed we have only to point out the errors in the older publications.

The error in the paper of Born, Jordan and Heisenberg<sup>(1)</sup> is in the evaluation of the term  $\Delta_1 \Delta_2 + \Delta_2 \Delta_1$  (compare formula (46'), p.612). On page 612 it is correctly stated that in the classical calculation the mean value of this quantity over all phases vanishes. This is also true in the quantum mechanical calculation as is apparent from formula (46'). At the end of page 614, however,  $\overline{\Delta_1 \Delta_2 + \Delta_2 \Delta_1}$  reappears again with a non-vanishing value and it is shown that it gives rise to an additional term by means of quite incomprehensible reasoning. It is just this term which transforms the correct formula (2.1) or (5.19) into the thermodynamical formula (1.6). But from the standpoint of wave theory this formula (1.6) is certainly wrong.

(1) As I am one of the three authors of the paper criticised here I ought to give an explanation of the mistake. But I can only apologise. Although the share of the three collaborators in the different sections of the paper is not equal, each of the signatories is, of course, responsible for the whole work. There is no other explanation than the enormous stress under which we worked in those exciting ~~days~~ first days of quantum mechanics. Max Born.

The error in the later paper of Heisenberg is in his statement that the integrals (corresponding here to (5.9)) diverge because of the factors  $\omega_\lambda, \omega_\mu$ , quite apart from the divergence of the zero-energy. This is certainly incorrect. As  $\beta^2 \leq 1$ ,  $1 + \cos^2 \frac{\beta}{\lambda\mu} \leq 2$ , one has the inequality

$$\overline{(\Delta U_1)^2} < \left(\frac{\ell}{2\pi}\right)^6 \iint \hbar^2 \omega_\lambda \omega_\mu \bar{n}_\mu (\bar{n}_\lambda + 1) d\underline{k}_\lambda d\underline{k}_\mu$$

or, resolving into factors,

$$\overline{(\Delta U_1)^2} < \left(\frac{\ell}{2\pi}\right)^6 \int \hbar \omega \bar{n}_\nu d\underline{k} \int \hbar \omega (\bar{n}_\nu + 1) d\underline{k}$$

which shows that the only infinity appearing comes from the 1 in the second integral, i.e. from the zero energy; and a similar consideration holds for  $\overline{(\Delta U_2)^2}$ .

It seems as if Heisenberg has overlooked the fact that  $\bar{n}_\nu$  depends on  $\nu$  in such a way that for all spectral distributions of radiation which could possibly be compared with black radiation (thermodynamical equilibrium) we have  $\bar{n}_\nu \rightarrow 0$  if  $\nu \rightarrow \infty$ .



## 6. FLUCTUATIONS AND RECIPROACITY.

The result that no other kind of infinity appears than that of the zero energy seems to indicate that the question of fluctuations has no deeper interest from the standpoint of the limits of our present theory. But that is not so. For in the case of the mean energy itself the zero energy is an infinite additive constant which can be omitted with some kind of justification. But in the case of fluctuations the zero energy is essential; this is evident from the form (2.2) of the correct wave formula, for the term  $h\nu \bar{E}_\nu$ , from which Einstein derived his photon interpretation of light has no other source than just the zero energy. It is impossible to treat the fluctuations of one frequency apart from the others; one has first to consider the fluctuations of the total energy in a partial volume ( and afterwards to resolve it into its spectral components); therefore one cannot avoid dealing with the divergent integral of the zero energy. We think that this fact is a strong argument for the view that the infinite zero energy of radiation is not a harmless imperfection of the present theory, but a very essential one. The only way of making the integral  $\int \frac{1}{2} h\nu z_\nu d\nu$  finite seems to be a modification of the function  $z_\nu$  in such a way that it vanishes sufficiently strongly for  $\nu \rightarrow \infty$ .

One of us (Born, 1938) has suggested, under the title

'postulate of reciprocity', a method of doing this. In our notation we have to replace  $\underline{dk}$  by  $\varphi(k)\underline{dk}$  with

$$(6.1) \quad \varphi(k) = \frac{1}{\sqrt{1 - \frac{\hbar^2 k^2}{b^2}}} = \frac{1}{\sqrt{1 - \tau^2 v^2}} = \psi(v)$$

where  $b$  is the 'absolute momentum', and  $\tau = \hbar/bc$ . We have therefore, for an isotropic distribution of particles

$$(6.2) \quad \underline{z}_v = \underline{z}_v^0 \psi(v)$$

where  $\underline{z}_v^0$  is the density function as used before.

We shall briefly investigate what changes occur in our formulae by using the distribution function (6.2) with any  $\psi(v)$  having properties similar to that given by (6.1).

In (5.10) we have to introduce under the integral the factor  $\varphi(k_\lambda) \varphi(k_\mu)$  and, therefore, in (5.11) and (5.14) the factor  $\varphi^2(k_\lambda)$ , and in (5.15)  $\psi^2(v)$ . In stead of (5.16) we have

$$(6.3) \quad \overline{(\Delta U_v)^2} = \psi^2(v) \frac{8\pi v^2}{c^3} \ell^3 \left( \hbar v \left( \bar{n}_v + \frac{1}{2} \right) \right)^2 \\ = \psi(v) \underline{z}_v v \left( \frac{\bar{u}_v}{\underline{z}_v v} \right)^2 = \psi(v) \frac{\bar{u}_v^2}{\underline{z}_v v}$$

On the other hand, the derivation of the fluctuation with the help of thermodynamics and statistical mechanics, as given in section 1, is independent of the form of the function  $\underline{z}_v$  and leads necessarily to (1.6); if we add

to this expression the fluctuation due to the zero energy the result differs from (6.3) by the factor  $\gamma_\nu$ . Now this factor deviates from 1 appreciably for high frequencies, and it seems very improbable that just in this region the radiation surrounding a partial volume should not behave as a bath of constant temperature. In this way we are led to the conclusion that something is wrong with the simple expedient of modifying the density function  $z_\nu$  by a factor  $\psi(\nu)$  so as to make the zero energy finite. Although Heisenberg's argument is invalid we have found some positive indications about the defects of the present theory. We hope to be able to follow this track a little further.

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## SUMMARY.

It is shown that all previous treatments of the fluctuation of radiation are inadequate. One cannot expect a complete coincidence of the formulae derived from statistical mechanics and from wave theory, as the zero energy plays a different role in these methods. The wave fluctuations are here recalculated for a quantized electromagnetic field, and it is shown that the result coincides with the statistical formula as far as can be expected, provided one overlooks the divergence of the zero energy. The importance of this infinity is discussed with regard to the question of the limitations and future improvement of the present radiation theory.

ON THE INVARIANCE OF QUANTIZED FIELD EQUATIONS

A. F. ...

1. INTRODUCTION

... and ...

PART III

(1)

where ... and

ON THE INVARIANCE OF QUANTIZED FIELD

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ON THE INVARIANCE OF QUANTIZED FIELD EQUATIONS.

by

K. Fuchs, Edinburgh

1. INTRODUCTION.

Heisenberg and Pauli (1929) developed a general scheme for the quantization of a field, if the field equations can be derived from a variation principle

$$(1) \quad \delta \int \mathcal{L}(z^\alpha, \dot{z}_i^\alpha) dx^1 dx^2 dx^3 dx^4 = 0$$

where  $z^\alpha$  denotes the field variables,  $\mathcal{L}$  is the Lagrangian and

$$(2) \quad \dot{z}_i^\alpha = \frac{dz^\alpha}{dx^i} \quad (i = 1, 2, 3, 4)$$

The scheme of Heisenberg and Pauli is known to be Lorentz invariant. It is the purpose of this paper to show that it is also invariant with regard to all coordinate transformations allowed by the general theory of relativity. The method adopted to prove this, is that used by Infeld (1937) and Pryce (1937) to prove the invariance of the "New Field Equations" against Lorentz transformations.

In order to formulate the quantum mechanical commutation brackets, it is necessary to define the canonically conjugate field variables. In the Lorentz invariant theory of Heisenberg and Pauli this can easily be done by the definition

$$(3) \quad P_{\alpha} = \frac{\partial \mathcal{L}}{\partial z_{\alpha}}$$

Here  $x^4=ct$  is the time coordinate. If now we use a general metric, the time coordinate can in general be separated only locally. There are now two alternatives. We may demand that the canonically conjugate variable has invariant significance. In that case we could proceed by defining the canonically conjugate variables at any given point in a local Lorentz system at that point. It is obvious that such a procedure would involve very cumbersome calculations, since we would have to consider a coordinate system which varies from point to point. The alternative is to assume that the canonically conjugate variable has no invariant significance.

We define similarly to (3) the tensor density

$$(3a) \quad P_{\alpha}^i = \frac{\partial \mathcal{L}}{\partial z_i}$$

Then the canonically conjugate variables do not form a tensor density but they are only part of the components of  $P_{\alpha}^i$ , namely the components  $P_{\alpha}^4$ . In this case the field equations can not be written as equations between tensors or tensor densities. For, if we change from one coordinate system to another, the canonically conjugate variables will in general be different components of the same tensor density  $P_{\alpha}^i$ . The field equations will, there-



fore, be only components of tensor or tensor-density equations. It is, of course, to be expected that the space or time like character of these equations should be preserved, so that in the limiting case the equations reduce to those of Pauli and Heisenberg. With this restriction the principle of general invariance demands that the various components of the field equations are equivalent.

A point of view, intermediate between the two alternatives, has recently been adopted by Weiss (1938)\*. He assumes a plane to be given and the normal to this plane gives a direction, independent of the coordinate system. Taking the component of  $P_{\alpha}^i$  (with respect to the index  $i$ ) along this direction, the canonically conjugate variables can be defined without reference to any particular coordinate system. The usual commutation relations are then adopted in this plane. However, this is not a complete proof of the invariance of quantum dynamics; if we adopt the commutation relations in one plane only, it is necessary to show that - as a consequence of the field equations - they also hold in any other plane. If we adopt the commutation relations in any arbitrary plane, the problem is overdetermined and it must be shown that the

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\* My thanks are due to Dr.P.Weiss for the privilege of seeing his paper before publication.

system of commutation relations plus field equations is not contradictory.

In this paper I shall adopt the second alternative.

$$(4) \quad L = \int d^3x \mathcal{L}$$

where  $L$  is a scalar function and  $g$  the metric determinant. The field variables  $\phi^a$  may be the components of a tensor of a tensor of any rank.

If we transform from one coordinate system to another

$$(5) \quad x^{\mu} = x^{\mu}(x^{\nu'})$$

the field variables transform according to an equation

$$(6) \quad \phi^a = A^a_b \phi^{b'}$$

where the coefficients  $A^a_b$  can be calculated from the coefficients  $\partial x^{\mu} / \partial x^{\nu'}$  of the transformation, if the type of the tensor  $\phi^a$  is known.

The derivatives of the  $\phi^a$ , at a point, do not form a tensor. They transform according to the law

$$(7a) \quad \partial_{\mu} \phi^a = A^a_b \frac{\partial x^{\nu'}}{\partial x^{\mu}} \partial_{\nu'} \phi^{b'} + \frac{\partial A^a_b}{\partial x^{\mu}} \frac{dx^{\nu'}}{dx^{\mu}} \phi^{b'}$$

We now define

$$(7b) \quad R^a_b = \frac{\partial A^a_b}{\partial x^{\mu}} \frac{dx^{\nu'}}{dx^{\mu}} \phi^{b'}$$

## 2. CANONICAL FORM OF THE FIELD EQUATIONS.

In the general theory of the Lagrangian function  $\mathcal{L}$  must be a scalar density

$$(4) \quad \mathcal{L} = \sqrt{-g} L$$

where  $L$  is a scalar function and  $g$  the metric determinant. The field variables  $z^\alpha$  may be the components of a tensor of a tensor of any rank.

If we transform from one coordinate to another

$$(5) \quad \bar{x}^i = \bar{x}^i(x^j)$$

the field variables transform according to an equation

$$(6) \quad \bar{z}^\alpha = A_\beta^\alpha z^\beta$$

where the coefficients  $A_\beta^\alpha$  can be calculated from the coefficients  $d\bar{x}^i/dx^j$  of the transformation, if the type of the tensor  $z^\alpha$  is known.

The derivatives of the  $z^\alpha$ , of course, do not form a tensor. They transform according to the law

$$(6a) \quad \bar{z}_i^\alpha = A_\beta^\alpha \frac{dx^j}{d\bar{x}^i} z_j^\beta + \frac{dA_\beta^\alpha}{dx^j} \frac{dx^j}{d\bar{x}^i} z^\beta$$

We now define

$$(7) \quad p_\alpha^i = \frac{\partial \mathcal{L}}{\partial z_i^\alpha}$$

The  $P_\alpha^i$  form the components of a tensor density, inspite of the fact that the  $z_i^\alpha$  are tensors for affine transformations only. This is the reason why it is possible to investigate the invariance of quantum dynamics not only against Lorentz transformations but also against the group of transformations allowed by the general theory of relativity without explicitly introducing the coefficients of affine connection.

The  $\bar{P}_\alpha^i$  in the new coordinate system are

$$\bar{P}_\alpha^i = \frac{\partial \bar{\mathcal{L}}}{\partial \bar{z}_i^\alpha} = \sqrt{\frac{-\bar{g}}{-g}} \frac{\partial \mathcal{L}}{\partial z_j^\beta} \frac{\partial z_j^\beta}{\partial \bar{z}_i^\alpha}$$

For, according to (4) we have  $\bar{\mathcal{L}} = \sqrt{-\bar{g}} \mathcal{L} / \sqrt{-g}$ . If we define  $B_\beta^\alpha$  by the equation

$$A_\beta^\alpha B_\gamma^\beta = \delta_\gamma^\alpha$$

then it follows from (6a) that

$$\frac{\partial z_j^\beta}{\partial \bar{z}_i^\alpha} = B_\alpha^\beta \frac{d\bar{x}^i}{dx^j}$$

and the transformed  $\bar{P}_\alpha^i$  are

$$(8) \quad \bar{P}_\alpha^i = \sqrt{\frac{-\bar{g}}{-g}} B_\alpha^\beta \frac{d\bar{x}^i}{dx^j} P_\beta^j$$

This equation shows that indeed the  $P_\alpha^i$  transform like a tensor density.

The field equations follow from the variation principle

(1) in the form of the Euler equations

$$(9) \quad \frac{\partial \mathcal{L}}{\partial z^\alpha} - \frac{d}{dx^i} \frac{\partial \mathcal{L}}{\partial z_i^\alpha} = 0$$

We now introduce the 4-components of the tensor density  $P_\alpha^i$  as canonically conjugate variables

$$(10) \quad P_\alpha \equiv P_\alpha^4 = \frac{\partial \mathcal{L}}{\partial z_4^\alpha}$$

If we define further the Hamiltonian by

$$(11) \quad \mathcal{H}(z^\alpha, z_r^\alpha, P_\alpha) = \mathcal{L} - P_\alpha z_4^\alpha \quad (r=1,2,3)$$

the field equations (9) can be written in the canonical form

$$(12) \quad \begin{aligned} \frac{\partial \mathcal{H}}{\partial z^\alpha} - \frac{d}{dx^r} \frac{\partial \mathcal{H}}{\partial z_r^\alpha} &= \frac{dP_\alpha}{dx^4} \\ \frac{\partial \mathcal{H}}{\partial P_\alpha} &= - \frac{dz^\alpha}{dx^4} \end{aligned}$$

(Throughout this paper indices  $r, s$  go from 1 to 3, indices  $i, j$  from 1 to 4, and indices  $\alpha, \beta$  go from 1 to  $4n$ , where  $n$  is the rank of the tensor  $z^\alpha$ ).

The simplest proof of (12) consists in showing that the following relations hold

$$(13) \quad \frac{\partial \mathcal{H}}{\partial z_r^\alpha} = \frac{\partial \mathcal{L}}{\partial z_r^\alpha} \quad ; \quad \frac{\partial \mathcal{H}}{\partial z^\alpha} = \frac{\partial \mathcal{L}}{\partial z^\alpha}$$

which we shall use later. They follow immediately from the definitions (10) and (11). For example:

$$\frac{\partial \mathcal{H}}{\partial z_r^\alpha} = \frac{\partial \mathcal{L}}{\partial z_r^\alpha} + \frac{\partial \mathcal{L}}{\partial z_4^\beta} \frac{\partial z_4^\beta}{\partial z_r^\alpha} - p_\beta \frac{\partial z_4^\beta}{\partial z_r^\alpha} = \frac{\partial \mathcal{L}}{\partial z_r^\alpha}$$

This proof depends on the commutability of the factors in the Lagrangian, since differentiation with regard to a dependent variable is not allowed, if the factors do not commute.

### 3. QUANTIZATION OF THE FIELD.

According to Heisenberg and Pauli the classical field equations are quantized by considering the field variables as non-commutable variables which satisfy the following commutation relations on a space section of constant time

$$\begin{aligned}
 & [P_\alpha(x), P_\beta(x')] = [z^\alpha(x), z^\beta(x')] = 0 \\
 (14) \quad & [P_\alpha(x), z^\beta(x')] = \delta_\alpha^\beta \delta(x^1-x'^1) \delta(x^2-x'^2) \delta(x^3-x'^3) \\
 & \qquad \qquad \qquad = \delta_\alpha^\beta \delta(x-x')
 \end{aligned}
 \left. \vphantom{\begin{aligned} & [P_\alpha(x), P_\beta(x')] = [z^\alpha(x), z^\beta(x')] = 0 \\ & [P_\alpha(x), z^\beta(x')] = \delta_\alpha^\beta \delta(x^1-x'^1) \delta(x^2-x'^2) \delta(x^3-x'^3) \\ & \qquad \qquad \qquad = \delta_\alpha^\beta \delta(x-x') \end{aligned}} \right\} x^4 = x'^4$$

Here the bracket symbol is defined by

$$[A, B] = \frac{i}{\hbar} (AB - BA)$$

We shall adopt the same commutation relations in the general case. Then we obtain of course all equations of the theory of Heisenberg and Pauli, some of which follow. By differentiating (14) we find

$$\begin{aligned}
 (15) \quad & [z^\alpha(x), z^\beta_r(x')] = 0 \\
 & [P_\alpha(x), z^\beta_r(x')] = -\delta_\alpha^\beta \frac{d}{dx^r} \delta(x-x')
 \end{aligned}$$

From (14) and (15) follows for a functional  $F$  of the field variables in the usual way

$$(16) \quad [z^\alpha, F] = -\frac{\partial F}{\partial P_\alpha} \quad ; \quad [P_\alpha, F] = \frac{\partial F}{\partial z^\alpha} - \frac{d}{dx^r} \frac{\partial F}{\partial z^\alpha_r}$$

$$F = \int \mathcal{F}(z^\alpha, z^\alpha_r, P_\alpha) dx^1 dx^2 dx^3.$$

The integration over  $x^1, x^2, x^3$  in (16) extended over

the whole of space has a meaning only if proper boundary conditions can be formulated. It is precisely for this reason that  $x^r$  must be space-like coordinates and  $x^4$  a time-like coordinate (cf. for example Weiss (1938)).

We introduce further the momentum operators\*

$$(17) \quad \begin{aligned} \mathcal{H}_r &= -P_\alpha z_r^\alpha \\ \mathcal{H}_4 &\equiv \mathcal{H} \end{aligned} \quad H_i = \int \mathcal{H}_i dx^1 dx^2 dx^3$$

From (16) and the field equations (12) it then follows that

$$(18) \quad [P_\alpha, H_i] = \frac{dP_\alpha}{dx^i} \quad ; \quad [z_r^\alpha, H_i] = \frac{dz_r^\alpha}{dx^i}$$

By differentiating the second equation we find

$$(19) \quad [z_r^\alpha, H_i] = \frac{dz_r^\alpha}{dx^i}$$

From (18) and (19) follows as before for a function  $\mathcal{F}$  of the field variables

$$(20) \quad [\mathcal{F}, H_i] = \frac{d\mathcal{F}}{dx^i}$$

The equation (16) obviously remains correct if the function  $\mathcal{F}$  depends explicitly on the coordinates  $x^i$ . Equation (20) on the other hand does not hold in this case but must be replaced by

$$(21) \quad [\mathcal{F}, H_i] = \frac{d\mathcal{F}}{dx^i} - \frac{\partial \mathcal{F}}{\partial x^i}$$

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\* In the following I shall refer to  $\mathcal{H}$  as the Hamiltonian density and to  $H$  as the Hamiltonian.



#### 4. THE INVARIANCE OF THE COMMUTATION RELATIONS.

Consider now an arbitrary infinitesimal transformation

$$(22) \quad \bar{x}^i = x^i + \varepsilon \eta^i(x^j)$$

The field variables  $z^\alpha$  then transform according to an equation of the form

$$(23) \quad \bar{z}^\alpha - z^\alpha = \delta z^\alpha = \varepsilon a_\beta^\alpha z^\beta$$

where the  $a_\beta^\alpha$  can be obtained from the derivatives of the  $\eta^i$  which we shall denote by

$$(24) \quad \frac{d\eta^i}{dx^j} = \eta_j^i$$

The ratio of the metric determinants in the two systems can be obtained from the Jacobian

$$(25) \quad \sqrt{\frac{-\bar{g}}{-g}} = \left| \frac{dx^i}{d\bar{x}^j} \right| = \left| \delta_j^i - \varepsilon \eta_j^i \right| = 1 - \varepsilon \eta_i^i$$

With (8) the transformation of the conjugate variables  $P_\alpha$  is therefore given by

$$(26) \quad \bar{P}_\alpha - P_\alpha = \delta P_\alpha = -\varepsilon a_\alpha^\beta P_\beta + \varepsilon \eta_\alpha^4 P_\alpha - \varepsilon \eta_i^i P_\alpha$$

Heisenberg and Pauli pointed out that there is a certain ambiguity in the definition of the  $P_\alpha^r$ . According to (7) and (13) the following relation holds

$$p_{\alpha}^r = \frac{\partial \mathcal{L}}{\partial z_r^{\alpha}} = \frac{\partial \mathcal{H}}{\partial z_r^{\alpha}}$$

In quantum dynamics, as emphasized before, this relation is in general not correct. However this does not mean that we must restrict ourselves to those simple cases in which this relation holds. For there is a corresponding ambiguity in the transition from the Euler equations to the Hamiltonian equations and in the choice of the sequence of factors in the Hamiltonian. But once we have decided on a certain sequence of factors in one coordinate system the sequence in all other coordinate systems is determined. The ambiguity is reintroduced only, if we revert to the classical definition of the  $p_{\alpha}^r$  by means of the Lagrangian. In a consequent quantum theory we cannot return to the Euler equations and the Lagrangian. The correct definition to be used in quantum dynamics is that which uses the Hamiltonian density

$$(27) \quad p_{\alpha}^r = \frac{\partial \mathcal{H}}{\partial z_r^{\alpha}}$$

Consider now two points  $p(x^i)$  and  $p'(x'^i)$ , for which  $x^4 = x'^4$ . For these two points the commutation relations (14) hold in the old coordinate system. However we can not expect that they also hold in the new coordinate system for these two points, since they will in general not lie on the same plane of constant 'time' ( $\bar{x}^4 \neq x'^4$ ). But if

the commutation relations are invariant, they must hold in the new coordinate system for two different points  $\bar{p}, \bar{p}'$ ; which in the new system lie on a section  $\bar{x}^4 = \text{constant}$ . In particular they must hold for the two points which in the new system have the same coordinates  $x^i, x'^i$  as the points  $p, p'$  in the old system. According to (22) these two points have in the old coordinate system the coordinates

$$(28) \quad \bar{p}(x^i - \varepsilon \eta^i) \quad ; \quad \bar{p}'(x'^i - \varepsilon \eta'^i)$$

The condition that the commutation relations hold in the new coordinate system for the two points  $\bar{p}, \bar{p}'$  is obviously a **necessary and sufficient** condition for the invariance of the commutation relations.

We shall show that it is possible to find for any given value of  $x^4$  a transformation  $S$ , which transforms the field variables at the points  $p, p'$  in the old coordinate system into the field variables at the points  $\bar{p}, \bar{p}'$  in the new coordinate system according to the formula

$$(29) \quad (\bar{P}_\alpha)_{\bar{p}} = S (P_\alpha)_p S^{-1} \quad (\bar{Z}^\alpha)_{\bar{p}} = S (Z^\alpha)_p S^{-1}$$

where the transformation does not depend on the 'space' coordinates  $x^r$ . A transformation of this type does not change the value of the commutation brackets, since the  $\delta$ -functions are c-numbers. It follows therefore that, if the commutation relations hold in the old system for

for any section  $x^4 = \text{constant}$ , they also hold in the new coordinate system for a section  $\bar{x}^4 = \text{constant}$ . They are therefore invariant.

It remains to show that a transformation  $S$  exists, which satisfies (29). We may write this equation in the form

$$(30) \quad \begin{aligned} (\bar{P}_\alpha)_{\bar{p}} - (P_\alpha)_p &= \delta \bar{P}_\alpha = -\varepsilon [P_\alpha, T] \\ (\bar{z}^\alpha)_{\bar{p}} - (z^\alpha)_p &= \delta \bar{z}^\alpha = -\varepsilon [z^\alpha, T] \end{aligned}$$

where  $T$  is defined by the equation

$$(31) \quad S = 1 + \varepsilon T$$

The values of  $P_\alpha$ ,  $z^\alpha$  at the points  $\bar{p}$ ,  $\bar{p}'$  in the old coordinate system are given by (compare (28))

$$\begin{aligned} (P_\alpha)_{\bar{p}} &= (P_\alpha)_p - \varepsilon \frac{dP_\alpha}{dx^i} \eta^i \\ (z^\alpha)_{\bar{p}} &= (z^\alpha)_p - \varepsilon \frac{dz^\alpha}{dx^i} \eta^i \end{aligned}$$

If now we transform to the new coordinate system, the transformation formulae (23), (26) yield

$$(32) \quad \begin{aligned} \delta \bar{P}_\alpha &= -\varepsilon a_\alpha^\beta P_\beta - \varepsilon \frac{dP_\alpha}{dx^i} \eta^i + \varepsilon \eta_r^r P_\alpha - \varepsilon \eta_r^r P_\alpha \\ \delta \bar{z}^\alpha &= \varepsilon a_\beta^\alpha z^\beta - \varepsilon \frac{dz^\alpha}{dx^i} \eta^i \end{aligned}$$

Comparing (32) with (30) it follows that  $T$  must satisfy the relations

$$[z^\alpha, T] = -\dot{a}_\beta^\alpha z^\beta + \frac{dz^\alpha}{dx^i} \eta^i$$

$$(33) \quad [P_\alpha, T] = a_\alpha^\beta P_\beta + \frac{dP_\alpha}{dx^i} \eta^i - \eta_r^4 \frac{\partial \mathcal{H}}{\partial z_r^\alpha} + \eta_r^r P_\alpha$$

Here we have substituted for  $P_\alpha^r$  according to (27).

The following functional satisfies the equations (33)

$$T = \int \mathcal{T} dx^1 dx^2 dx^3$$

$$(34) \quad \mathcal{T} = P_\alpha a_\beta^\alpha z^\beta + \mathcal{H}_i \eta^i$$

Applying the equations (16) the first term in  $\mathcal{T}$  yields the first terms on the right hand side of (33). The second term in  $\mathcal{T}$  commuted with  $z^\alpha$  yields with the help of (18)

$$-\frac{\partial \mathcal{H}_i}{\partial P_\alpha} \eta^i = [z^\alpha, \mathcal{H}_i] \eta^i = \frac{dz^\alpha}{dx^i} \eta^i$$

The first equation (33) is thus satisfied. For the commutation of the second term in  $\mathcal{T}$  with  $P_\alpha$  equation (16) gives

$$\begin{aligned} \frac{\partial \mathcal{H}_i}{\partial z^\alpha} \eta^i - \frac{d}{dx^r} \left( \frac{\partial \mathcal{H}_i}{\partial z_r^\alpha} \eta^i \right) &= \left( \frac{\partial \mathcal{H}_i}{\partial z^\alpha} - \frac{d}{dx^r} \frac{\partial \mathcal{H}_i}{\partial z_r^\alpha} \right) \eta^i - \frac{\partial \mathcal{H}_i}{\partial z_r^\alpha} \eta_r^i \\ &= [P_\alpha, \mathcal{H}_i] \eta^i - \eta_r^4 \frac{\partial \mathcal{H}}{\partial z_r^\alpha} - \eta_r^5 \frac{\partial \mathcal{H}_5}{\partial z_r^\alpha} \end{aligned}$$

With (17) and (18) this reduces to

$$\frac{dP_\alpha}{dx^i} \eta^i - \eta_r^4 \frac{\partial \mathcal{H}}{\partial z_r^\alpha} + \eta_r^r P_\alpha$$

Therefore the second equation (33) is also proved.

### 5. THE TRANSFORMATION OF THE HAMILTONIAN.

The transformation S defined in the last paragraph can also be used to find a simple expression for the transformation of the Hamiltonian. We take the field equations in the form (18)

$$(35) \quad [P_\alpha, H] = \frac{dP_\alpha}{dx^4} \quad [z^\alpha, H] = \frac{dz^\alpha}{dx^4}.$$

Applying the transformation S we get

$$\begin{aligned} [SP_\alpha S^{-1}, SHS^{-1}] &= S \frac{dP_\alpha}{dx^4} S^{-1} \\ &= \frac{d}{dx^4} (SP_\alpha S^{-1}) - \frac{dS}{dx^4} P_\alpha S^{-1} - SP_\alpha \frac{dS^{-1}}{dx^4} \end{aligned}$$

and a corresponding formula for  $z^\alpha$ . According to (29)  $SP_\alpha S^{-1}$  is the field variable in the new coordinate system at the point  $\bar{p}$ . Putting  $S = 1 + \varepsilon T$  we thus find

$$[(\bar{P}_\alpha)_{\bar{p}}, H + \varepsilon [T, H]] = \frac{d}{dx^4} (\bar{P}_\alpha)_{\bar{p}} + \varepsilon [P_\alpha, \frac{dT}{dx^4}]$$

The value of  $[T, H]$  can be obtained by application of (21) after integrating this equation over the coordinates  $x^r$ , with the result

$$[(\bar{P}_\alpha)_{\bar{p}}, H + \varepsilon (\frac{dT}{dx^4} - \frac{\partial T}{\partial x^4})] = \frac{d}{dx^4} (\bar{P}_\alpha)_{\bar{p}} + \varepsilon [P_\alpha, \frac{dT}{dx^4}]$$

The terms containing  $dT/dx^4$  cancel to the first order, and the equations of motion in the new coordinates may, therefore, be written in the form

$$(36) \quad [(\bar{P}_\alpha)_{\bar{p}}, \bar{H}_{\bar{p}}] = \left( \frac{d\bar{P}_\alpha}{d\bar{x}^4} \right)_{\bar{p}} \quad [(\bar{z}^\alpha)_{\bar{p}}, \bar{H}_{\bar{p}}] = \left( \frac{d\bar{z}^\alpha}{d\bar{x}^4} \right)_{\bar{p}}$$

$$\bar{H}_{\bar{p}} = H - \varepsilon \frac{\partial T}{\partial x^4}$$

Here we have used the formula

$$(37) \quad \frac{d}{dx^4} (\bar{P}_\alpha)_{\bar{p}} = \left( \frac{d\bar{P}_\alpha}{d\bar{x}^4} \right)_{\bar{p}} \quad \frac{d}{dx^4} (\bar{z}^\alpha)_{\bar{p}} = \left( \frac{d\bar{z}^\alpha}{d\bar{x}^4} \right)_{\bar{p}}$$

The latter equation may also be written in the form

$$(37a) \quad (\bar{z}^\alpha)_{\bar{p}} - (z^\alpha)_p = \overline{\delta z^\alpha} = \frac{d}{dx^4} \left( (\bar{z}^\alpha)_{\bar{p}} - (z^\alpha)_p \right) = \frac{d}{dx^4} \overline{\delta z^\alpha}$$

(37) can easily be proved; for we have

$$\frac{d\bar{P}_\alpha}{d\bar{x}^4} = \frac{d\bar{P}_\alpha}{dx^4} - \varepsilon \frac{d\bar{P}_\alpha}{dx^i} \eta^i$$

Therefore the right hand side of (37) is to the first order

$$\begin{aligned} \left( \frac{d\bar{P}_\alpha}{d\bar{x}^4} \right)_{\bar{p}} &= \left( \frac{d\bar{P}_\alpha}{dx^4} \right)_p - \varepsilon \frac{d}{dx^i} \left( \frac{d\bar{P}_\alpha}{dx^4} \right) \eta^i \\ &= \frac{d\bar{P}_\alpha}{dx^4} - \varepsilon \frac{d\bar{P}_\alpha}{dx^i} \eta^i - \varepsilon \frac{d^2\bar{P}_\alpha}{dx^4 dx^i} \eta^i \\ &= \frac{d}{dx^4} \left( \bar{P}_\alpha - \varepsilon \frac{d\bar{P}_\alpha}{dx^i} \eta^i \right) = \frac{d}{dx^4} (\bar{P}_\alpha)_{\bar{p}} \end{aligned}$$

The equation (36) is exactly the same as the corresponding equation in classical mechanics (cf. for example Nordheim and Fues, 1927). It has been shown by Jordan (1926) that the equations (30) for the transformation of the field variables, can also be written in a form analogous to the corresponding classical equations. It is interesting that the analogy apparently also extends to the case, when the transformation  $S$  depends explicitly on the time.

## 6. CLASSICAL TRANSFORMATION OF THE HAMILTONIAN.

In the last paragraph we determined the transformation of the Hamiltonian in such a way that the equations of motion are invariant. The law of transformation found coincided with the classical law in the limiting case  $\hbar=0$ . If this were not so, the results of quantization would depend on the coordinate system in which the quantization has been carried out.

However, the transformation of the Hamiltonian is not completely determined by the argument of the last paragraph. In the classical theory any complete differential may be added to the Hamiltonian density.

Indeed, if we transform the Hamiltonian density explicitly, we find a result differing from (36) by a complete differential. This can easily be shown. The Hamiltonian in the classical theory is defined by

$$(38) \quad \mathcal{H} = \mathcal{L} - P_{\alpha} z_4^{\alpha}$$

where the Lagrangian  $\mathcal{L}$  is a scalar density. If we apply the transformation (22), the change in the Hamiltonian density is (compare (25))

$$\delta \mathcal{H} = -\varepsilon \eta_i^i \mathcal{L} - \delta P_{\alpha} z_4^{\alpha} - P_{\alpha} \delta z_4^{\alpha}$$

For the Hamiltonian density at the point  $\bar{p}$  we find



$$\delta \overline{\mathcal{H}} = \overline{\mathcal{H}}_p - \mathcal{H}_p = -\varepsilon \eta_i^i \mathcal{L} - \varepsilon \frac{\partial \mathcal{L}}{\partial x^i} \eta^i - \delta \overline{P}_\alpha z_4^\alpha - P_\alpha \delta z_4^\alpha$$

Reintroducing  $\mathcal{H}$  for  $\mathcal{L}$  this may be written in the form

$$\delta \overline{\mathcal{H}} = -\varepsilon \eta_i^i (\mathcal{H} + P_\alpha z_4^\alpha) - \varepsilon \frac{d}{dx^i} (\mathcal{H} + P_\alpha z_4^\alpha) \eta^i - \delta \overline{P}_\alpha z_4^\alpha - P_\alpha \delta z_4^\alpha$$

(37a) We introduce the values (32) for  $\delta \overline{P}_\alpha$  and  $\delta z_4^\alpha$ . A number of terms cancel and we get easily

$$\delta \overline{\mathcal{H}} = -\varepsilon \frac{d}{dx^i} (\eta^i \mathcal{H}) - \varepsilon \eta_i^4 P_\alpha^i z_4^\alpha - \varepsilon P_\alpha \frac{d a_\beta^\alpha}{dx^+} z^\beta + \varepsilon P_\alpha z_i^\alpha \eta^i$$

We now separate all terms with  $i=4$  and carry through the differentiation of  $\mathcal{H}$  with regard to  $x^4$

$$\begin{aligned} \delta \overline{\mathcal{H}} = & -\varepsilon \frac{\partial}{\partial x^+} (\eta^4 \mathcal{H} + P_\alpha a_\beta^\alpha z^\beta - P_\alpha z_r^\alpha \eta^r) - \varepsilon \frac{d}{dx^+} (\eta^r \mathcal{H}) \\ & - \varepsilon \eta^4 \left( \frac{\partial \mathcal{H}}{\partial z^\alpha} z_4^\alpha + \frac{\partial \mathcal{H}}{\partial z_r^\alpha} \frac{dz_r^\alpha}{dx^+} + \frac{\partial \mathcal{H}}{\partial P_\alpha} \frac{dP_\alpha}{dx^+} \right) - \varepsilon \eta_r^4 P_\alpha^r z_4^\alpha \end{aligned}$$

Applying the field equations (12) and the definition (17), we get the result

$$\begin{aligned} \delta \overline{\mathcal{H}} = & -\varepsilon \frac{\partial}{\partial x^+} (\eta^i \mathcal{H}_i + P_\alpha a_\beta^\alpha z^\beta) - \varepsilon \frac{d}{dx^+} (\eta^r \mathcal{H}) \\ & - \varepsilon \eta^4 \left( \frac{dP_\alpha^r}{dx^+} z_4^\alpha + P_\alpha^r \frac{dz_r^\alpha}{dx^+} \right) - \varepsilon \eta_r^4 P_\alpha^r z_4^\alpha \end{aligned}$$

or

$$(39) \quad \delta \overline{\mathcal{H}} = -\varepsilon \frac{\partial}{\partial x^+} (\eta^i \mathcal{H}_i + P_\alpha a_\beta^\alpha z^\beta) - \varepsilon \frac{d}{dx^+} (\eta^r \mathcal{H} + \eta^4 P_\alpha^r z_4^\alpha)$$

which is identical with the expression (36) apart from the last term.

7. THE COMPLETE DIFFERENTIAL IN THE HAMILTONIAN DENSITY.

If the boundary conditions of our problem are such that the Hamiltonian density vanishes sufficiently rapidly at the boundaries, the additional term in (39) does not matter. However in many applications it is more convenient to assume periodicity at the boundaries. Therefore it is of interest to show in general that the addition of a term of the form

$$(40) \quad \int \frac{d}{dx^r} \left\{ \mathcal{F}(z^\alpha, z^\alpha_{,r}, P_\alpha, x^i) \right\} d\tau \quad d\tau = dx^1 dx^2 dx^3$$

to the Hamiltonian does not change the field equations.

With other words:

$$(41) \quad [z^\alpha, \int \frac{d}{dx^r} \mathcal{F} d\tau] = 0 \quad , \quad [P_\alpha, \int \frac{d\mathcal{F}}{dx^r} d\tau] = 0$$

or with (21)

$$(42) \quad [z^\alpha, [F, H_r]] + [z^\alpha, \int \frac{\partial}{\partial x^r} \mathcal{F} d\tau] = 0$$

$$[P_\alpha, [F, H_r]] + [P_\alpha, \int \frac{\partial}{\partial x^r} \mathcal{F} d\tau] = 0$$

We use the equation

$$[A, [B, C]] = [B, [A, C]] + [[A, B], C]$$

and obtain for (42)

$$[F, [z^\alpha, H_r]] + [[z^\alpha, F], H_r] + [z^\alpha, \int \frac{\partial}{\partial x^r} \mathcal{F} d\tau] = 0$$

$$[F, [P_\alpha, H_r]] + [[P_\alpha, F], H_r] + [P_\alpha, \int \frac{\partial}{\partial x^r} \mathcal{F} d\tau] = 0$$

or with (16) and (18)

$$(43) \quad [F, Z_r^\alpha] - \left[ \frac{\partial F}{\partial P_\alpha}, H_r \right] - \frac{\partial}{\partial P_\alpha} \frac{\partial F}{\partial x^r} = 0$$

$$[F, \frac{dP_\alpha}{dx^r}] + \left[ \frac{\partial F}{\partial Z^\alpha} - \frac{d}{dx^s} \frac{\partial F}{\partial Z_s^\alpha}, H_r \right] + \frac{\partial}{\partial Z^\alpha} \frac{\partial F}{\partial x^r} - \frac{d}{dx^s} \frac{\partial}{\partial Z_s^\alpha} \frac{\partial F}{\partial x^r} = 0$$

We use the equation

$$[Z_r^\alpha, F] = - \frac{d}{dx^r} \frac{\partial F}{\partial P_\alpha} \quad \left[ \frac{dP_\alpha}{dx^r}, F \right] = \frac{d}{dx^r} \frac{\partial F}{\partial Z^\alpha} - \frac{d}{dx^r} \frac{d}{dx^s} \frac{\partial F}{\partial Z_s^\alpha}$$

which is easily proved by differentiating (16). Equation (43) yields therefore together with (21)

$$\frac{d}{dx^r} \frac{\partial F}{\partial P_\alpha} - \left( \frac{d}{dx^r} \frac{\partial F}{\partial P_\alpha} - \frac{\partial}{\partial x^r} \frac{\partial F}{\partial P_\alpha} \right) - \frac{\partial}{\partial P_\alpha} \frac{\partial F}{\partial x^r} = 0$$

$$- \frac{d}{dx^r} \frac{\partial F}{\partial Z^\alpha} + \frac{d}{dx^r} \frac{d}{dx^s} \frac{\partial F}{\partial Z_s^\alpha} + \left( \frac{d}{dx^r} - \frac{\partial}{\partial x^r} \right) \left( \frac{\partial F}{\partial Z^\alpha} - \frac{d}{dx^s} \frac{\partial F}{\partial Z_s^\alpha} \right) + \frac{\partial}{\partial Z^\alpha} \frac{\partial F}{\partial x^r} - \frac{d}{dx^s} \frac{\partial}{\partial Z_s^\alpha} \frac{\partial F}{\partial x^r} = 0$$

All partial differentiations can of course be exchanged, so that the first equation is an identity. The second reduces to

$$\frac{\partial}{\partial x^r} \frac{d}{dx^s} \frac{\partial F}{\partial Z_s^\alpha} - \frac{d}{dx^s} \frac{\partial}{\partial x^r} \frac{\partial F}{\partial Z_s^\alpha} = 0$$

We shall now show that  $d/dx^s$  and  $\partial/\partial x^r$  can also be exchanged.

The derivative of a function

$$f(Z^\alpha, Z_r^\alpha, P_\alpha, x^i) = f(Q_p, x^i)$$

( $Q_p$  stands for the field variables  $Z^\alpha$ ,  $P_\alpha$  and the derivatives  $Z_r^\alpha$ ) is defined by

$$\frac{d}{dx^s} f(Q_p, x^i) = \lim_{\lambda \rightarrow 0} \frac{f(Q_p + \lambda \frac{dQ_p}{dx^s}, x^i + \delta_s^i \lambda) - f(Q_p, x^i)}{\lambda}$$

Therefore

$$(44) \quad \frac{\partial}{\partial x^r} \frac{d}{dx^s} f = \lim_{\lambda, \lambda' \rightarrow 0} \frac{1}{\lambda \lambda'} \left\{ \begin{array}{l} f(Q_p + \lambda \frac{dQ_p}{dx^s} + \lambda \lambda' \frac{\partial}{\partial x^r} \frac{dQ_p}{dx^s}, x^i + \delta_s^i \lambda + \delta_r^i \lambda') \\ - f(Q_p, x^i + \delta_r^i \lambda') \\ - f(Q_p + \lambda \frac{dQ_p}{dx^s}, x^i + \delta_s^i \lambda) + f(Q_p, x^i) \end{array} \right\}$$

On the other hand

$$\frac{\partial}{\partial x^r} f = \lim_{\lambda' \rightarrow 0} \frac{f(Q_p, x^i + \delta_r^i \lambda') - f(Q_p, x^i)}{\lambda'}$$

and

$$(45) \quad \frac{d}{dx^s} \frac{\partial}{\partial x^r} f = \lim_{\lambda, \lambda' \rightarrow 0} \frac{1}{\lambda \lambda'} \left\{ \begin{array}{l} f(Q_p + \lambda \frac{dQ_p}{dx^s}, x^i + \delta_s^i \lambda + \delta_r^i \lambda') \\ - f(Q_p, x^i + \delta_r^i \lambda') \\ - f(Q_p + \lambda \frac{dQ_p}{dx^s}, x^i + \delta_s^i \lambda) + f(Q_p, x^i) \end{array} \right\}$$

This expression is identical with (44) provided

$$\frac{\partial}{\partial x^r} \frac{dQ_p}{dx^s} = 0$$

which is identical with the following three expressions

$$\frac{\partial}{\partial x^r} \frac{dz^a}{dx^s} = \frac{\partial}{\partial x^r} \frac{dz_t^a}{dx^s} = \frac{\partial}{\partial x^r} \frac{dP_a}{dx^s} = 0$$

These expressions follow immediately from (18) and (19)

by partial differentiation, since the left hand side of

these equations does not depend explicitly on the coordi-

ates  $x^i$ .

Thus it is proved that the addition of a term of the form (40) does not change the equations of motion, and the proof of the invariance of the whole scheme of quantum dynamics is completed.

I wish to thank Professor M. Born for many stimulating discussions on the subject.

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(see particularly equation (5), p. 98).
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## SUMMARY

The invariance of quantum dynamics in the form developed by Heisenberg and Pauli (1929) against all transformations allowed by the general theory of relativity is proved.

1. Introduction.

If we disregard the question of whether or not, the stability of a nucleus depends on the number of protons or neutrons, there are a number of factors which determine the stability of nuclei. The most important of these are the number of protons and neutrons and an odd number of protons or neutrons, with a few exceptions. This rule has been established by various authors (1916, p. 102).

PART IV

ON THE STABILITY OF NUCLEI AGAINST

$\beta$ -EMISSION

In this paper we shall consider the stability of nuclei against  $\beta$ -emission. It will be shown that the stability of nuclei can be explained by a few simple principles, by means of the arguments of Bethe and Bacher (1936, p. 102). The stability of nuclei can be explained entirely in terms of the forces which are operative in nuclei, namely the strong forces, the electromagnetic forces, and the weak forces.

The main question is whether or not a nucleus is stable against  $\beta$ -emission. It is well known that the character of the forces which are operative in nuclei is such that they are practically independent of the number of nucleons in the nucleus.

Numerical calculations have been made of the various regions of stability against  $\beta$ -emission. These calculations are given in Section 2.

2. Bethe's



# ON THE STABILITY OF NUCLEI AGAINST $\beta$ -EMISSION.

by K. FUCHS, Edinburgh.

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## 1. Introduction.

If we disregard the lightest and heaviest nuclei, the stability of a nucleus depends only on whether it is  $\beta$ -radioactive or not. There are a number of striking rules about the stability of nuclei. The most striking rule is that nuclei with an odd number of neutrons and an odd number of protons are not stable, with a few exceptions. This rule has been explained qualitatively by Bethe and Bacher (1936, p.102).

In this paper I wish to show that the general scheme of stable nuclei can be explained in a very simple way, by making the arguments of Bethe and Bacher stricter. Furthermore the whole argument can be made entirely independent of any model of the nucleus, using only facts which are plausible according to present ideas about nuclear forces.

The main assumptions are the interaction energy between a pair of like particles in the same quantum state and the saturation character of the forces between unlike particles. These assumptions are practically sufficient to explain the whole scheme of stable nuclei qualitatively. (Sections 3 to 6).

Numerical calculations about the breadth of the various regions of stability seem to be in good agreement with the experimental values (Sections 7 and 8).

## 2. Bethe /

2. Bethe and Bacher's explanation of the instability of nuclei with odd neutron and proton numbers.

The explanation of the instability of nuclei with odd numbers of neutrons and protons by Bethe and Bacher is as follows: We start from a nucleus with even numbers of neutrons and protons and assume that there are definite energy levels for neutrons and for protons, which in general will be different. If we add now one particle, it will occupy the lowest empty state and, since each state can accommodate two particles, the next particle will occupy the same state. Both particles, which we add to the nucleus we started from, will therefore be either neutrons or protons, but it will never happen that one of them is a neutron and the other a proton. However, if this explanation is correct we would be led to the conclusion that the energy of the nucleus obtained by adding one neutron and one proton is always intermediate between the energies of the nuclei obtained by adding either two neutrons or two protons, as the dotted levels in figure 1 indicate. Experimentally, however, in many cases the former nucleus has a higher energy than either of the other two. This can readily be explained since there is an interaction between the two neutrons or protons in the same quantum state, which will depress the energy of the two nuclei with even number of neutrons or protons. This is shown by the full drawn out levels in figure 1. There will also, of course, be an interaction between the neutron and the proton in the nucleus with uneven neutrons /

neutrons and protons. But since the neutron proton force shows saturation, this interaction will be small, if the neutron and proton are in different quantum states; this happens when the number is larger than the number of protons. *total binding energy of neutrons*

nucleus with  $Z$  neutrons and  $Z$  protons. If we keep  $Z+N$  fixed, and vary the composition of the nucleus, the stable nuclei are near the maximum of  $B(Z, N)$  for which

$$(1) \quad F_Z - F_N = 0$$

should be maximum the second derivative must be negative

$$(2) \quad F_{ZZ} + F_{NN} < 0$$

Now  $F_Z$  and  $F_N$  are the energies gained by adding a neutron to the nucleus. (The  $E_1 + E_2$  true only if the second derivative

are small and therefore only if  $Z$  is larger than  $Z_0$ , see equation (5) below) Since the binding energy per nucleon is nearly the same for all nuclei, it follows from (2) that  $F_Z$  and  $F_N$  are both

constant along the line of maximum binding

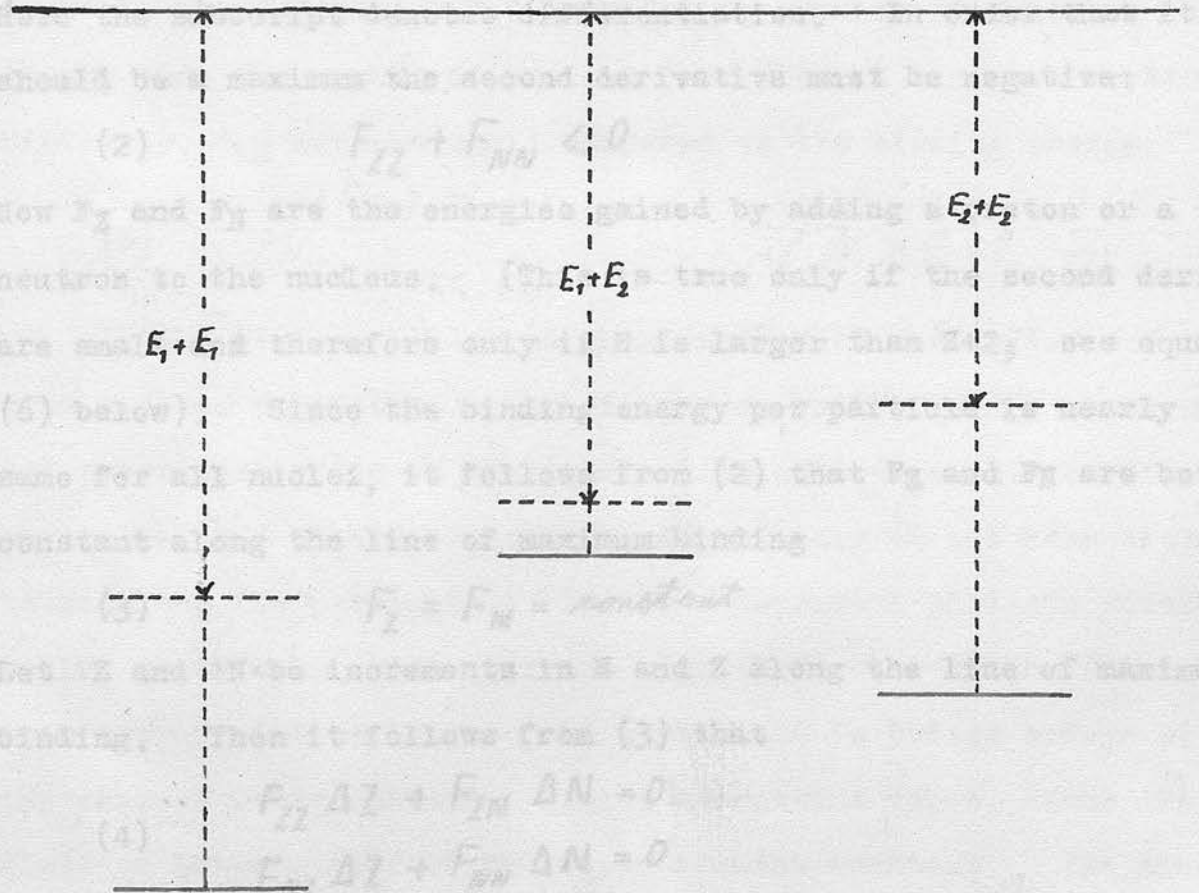
$$(3) \quad F_Z = F_N = \text{constant}$$

Let  $\Delta Z$  and  $\Delta N$  be increments in  $Z$  and  $N$  along the line of maximum binding. Then it follows from (3) that

$$(4) \quad \begin{aligned} F_{ZZ} \Delta Z + F_{ZN} \Delta N &= 0 \\ F_{NZ} \Delta Z + F_{NN} \Delta N &= 0 \end{aligned}$$

Since  $F_{ZZ} = F_{NN}$ , it follows from (4) that  $F_{ZZ}$  and  $F_{NN}$  are equal and therefore from (2) that  $F_{ZN}$  is negative.  $F_{ZN}$  according to (4)

Figure 1.



### 3. Assumptions about the nuclear forces.

In order to introduce the assumptions to be made, let us first consider the stability of nuclei in broad outline, disregarding the two-periodicity. Let  $F(N, Z)$  be the total binding energy of a nucleus with  $N$  neutrons and  $Z$  protons. If we keep  $N+Z$  fixed, and vary the composition of the nucleus, the stable nuclei must lie near the maximum of  $F(N, Z)$  for which

$$(1) \quad F_Z - F_N = 0$$

Here the subscript denotes differentiation. In order that it should be a maximum the second derivative must be negative:

$$(2) \quad F_{ZZ} + F_{NN} < 0$$

Now  $F_Z$  and  $F_N$  are the energies gained by adding a proton or a neutron to the nucleus. (This is true only if the second derivatives are small and therefore only if  $N$  is larger than  $Z+2$ ; see equation (6) below). Since the binding energy per particle is nearly the same for all nuclei, it follows from (2) that  $F_Z$  and  $F_N$  are both constant along the line of maximum binding

$$(3) \quad F_Z = F_N = \text{constant}$$

Let  $\Delta Z$  and  $\Delta N$  be increments in  $N$  and  $Z$  along the line of maximum binding. Then it follows from (3) that

$$(4) \quad \begin{aligned} F_{ZZ} \Delta Z + F_{ZN} \Delta N &= 0 \\ F_{NZ} \Delta Z + F_{NN} \Delta N &= 0 \end{aligned}$$

Since  $F_{NZ} = F_{ZN}$ , it follows from (4) that  $F_{ZZ}$  and  $F_{NN}$  <sup>sign</sup> are equal and therefore from (2) that they are negative.  $F_{ZN}$  according to (4) has /

has the opposite sign and is positive. Equations (4) and (5) hold

$$(5) \quad \begin{aligned} F_{ZZ} < 0 & \quad F_{NN} < 0 \\ F_{ZN} = F_{NZ} > 0 \end{aligned}$$

The equation (3) is simply an expression of the saturation character of the nuclear forces. This allows us to draw some conclusion about the order of magnitude of the second derivatives.  $F_{ZN}$  is the energy gained by the last proton, if another neutron is added. Owing to the saturation, this energy is small compared with the binding energy  $F_Z$ , provided the number of neutrons is larger than the number of protons (or rather  $N$  larger than  $Z+2$ ). Similarly,  $F_{NN}$  must be small compared to the binding energy:

$$(6) \quad \begin{aligned} |F_{NN}| &\ll F_N \\ F_{NZ} &\ll F_N \end{aligned} \quad \text{if } N > Z + 2$$

In the next paragraph we shall introduce the difference between even and odd particles. The difference in the energy of even and odd particles is due to the interaction between a pair of like particles, and should, therefore, depend only on the mean distance between the two particles. In the independent particle model we would, therefore, get a decrease with  $(N+Z)^{-1/3}$ . On the other hand, this energy will be largest, if a particle is paired always with the nearest other particle, giving a constant value, since the mean distance between nearest particles remains constant. The truth is probably somewhere between these two cases. The change in this energy with  $N$  and  $Z$  is, therefore, very small and can safely be neglected /

neglected. It follows then that the equations (4) and (6) hold for the energies of even particles as well as for the energies of odd particles.

The formulae of this paragraph are entirely independent of any particular model of the nucleus. They are only based on the saturation character of the nuclear forces.

#### 4. The conditions of stability.

In order to put the argument outlined in paragraph 2 into mathematical form, it will be most convenient to denote a given nucleus by the symbol  $(m, n, p)$ , where  $m$  is the number of proton pairs (or the number of  $\alpha$ -particles),  $n$  is the number of 'surplus neutrons' defined as the total number of neutrons minus  $2m$ , and  $p$  is correspondingly defined as the number of 'surplus protons'.  $p$  may have the values 0 or 1 only.  $n-p$  is the so-called isotopic number giving the difference between the number of neutrons and protons.

Consider now the energies gained by adding a neutron or a proton to a given nucleus. We assume an interaction between a pair of like particles and, therefore, must distinguish whether the particle to be added is an even particle or an odd particle. Furthermore the energies gained will in general depend on the nucleus from which we start. We thus define  $E_n(m, n, p)$  and  $E_p(m, n, p)$  as the energies gained by adding an even neutron or proton to the nucleus  $(m, n, p)$  and  $E'_n(m, n, p)$  and  $E'_p(m, n, p)$  as the corresponding energies for odd particles. These energies shall not include the Coulomb energy, which will be taken into account separately.

We shall consider for the time being only such states of the nucleus for which the total spin is zero if the total number of particles is even, or  $\frac{1}{2}$  if the total number of particles is odd; the complication introduced by the existence of other states will be /

be discussed later. Then it follows from the assumption of an interaction between pairs of like particles that

$$(7) \quad \begin{aligned} E_n(m, n, p) &> E'_n(m, n-1, p) \\ E_p(m, n, 1) &> E'_p(m, n, 0) \end{aligned}$$

For the Coulomb energy we shall assume the expression for a uniformly charged sphere of radius  $r_0 A^{-1/3}$ , where  $A$  is the total number of particles. If  $Z$  is the charge number, the expression for the Coulomb energy is

$$(8) \quad C \frac{Z^2}{A^{1/3}} = C \frac{(2m+p)^2}{(4m+n+p)^{1/3}} \quad C = \frac{3}{5r_0}$$

$r_0$  is a constant having the value  $2.05 \cdot 10^{-13}$  cm. (cf. Bethe, 1937, p.85). The particular expression (8) for the Coulomb energy is not important for our argument. Any expression having similar properties would do just as well.

Consider now the stability of a nucleus  $(m, n, 0)$  against  $\beta^+$ -emission. If  $E(m, n, p)$  denotes the binding energy of the nucleus  $(m, n, p)$ , the condition of stability for the nucleus  $(m, n, 0)$  is

$$(9) \quad E(m, n, 0) > E(m, n-1, 1) - \mu$$

where  $\mu$  is the rest mass of the electron. If (9) holds, the nucleus  $(m, n-1, 1)$  on the other hand is unstable and changes into the nucleus  $(m, n, 0)$  by emission of a positron or capture of a K-electron.

The condition (9) may be written in the form

$$C \frac{4m+1}{(4m+n)^{1/3}} + \mu > \begin{cases} E_2(m, n) & \text{if } n \text{ is odd} \\ E_4(m, n) & \text{if } n \text{ is even} \end{cases}$$

where /



where  $E_2$  and  $E_4$  are defined by

$$(10) \quad E_2(m, n) = E'_p(m, n-1, 0) - E'_n(m, n-1, 0)$$

$$(11) \quad E_4(m, n) = E'_p(m, n-1, 0) - E'_n(m, n-1, 0)$$

We define the numbers  $n_2$  and  $n_4$  by the equations

$$(11) \quad C \frac{4m+1}{(4m+n_2)^{1/3}} + \mu = E_2(m, n_2)$$

$$(11) \quad C \frac{4m+1}{(4m+n_4)^{1/3}} + \mu = E_4(m, n_4)$$

These equations correspond exactly to the equation (1), since the term on the left hand side (disregarding  $\mu$ ) is the contribution of the Coulomb forces to the energy of the proton. The change of this term with  $n$  is negligible.

In the last paragraph we found that the energy of the neutron decreases with  $N$  and, therefore, also with  $n$ , whereas the energy of the proton increases with  $n$  (cf. equation (5)). It follows from (10) that  $E_2$  and  $E_4$  increase with  $n$ . But according to (7)  $E_4$  is smaller than  $E_2$ . Therefore  $n_2$  must be smaller than  $n_4$ .

Thus we obtain three different regions according to the number  $n$  of surplus neutrons. If  $n$  is smaller than  $n_2$ , only nuclei of the form  $(m, n, 0)$  with an even number of protons exist. In the region between  $n_2$  and  $n_4$  nuclei with an even number of neutrons and no or one surplus proton exist, but no nuclei with an odd number of neutrons. If  $n$  is greater than  $n_4$  only nuclei with a surplus proton are stable. Putting  $n = 2\mathcal{V}$  if  $n$  is even and  $n = 2\mathcal{V}+1$  if  $n$  is odd, the types of stable nuclei are:

$$(12) \quad /$$

$$\begin{aligned}
 n < n_2 & \begin{cases} n=2\nu: & (m, 2\nu, 0) & - \\ n=2\nu+1: & (m, 2\nu+1, 0) & - \end{cases} \\
 n_2 < n < n_4 & \begin{cases} n=2\nu: & (m, 2\nu, 0) & - \\ n=2\nu+1: & - & (m, 2\nu, 1) \end{cases} \\
 n_4 < n & \begin{cases} n=2\nu: & - & (m, 2\nu-1, 1) \\ n=2\nu+1: & - & (m, 2\nu, 1) \end{cases}
 \end{aligned}
 \tag{12}$$

The stability of a nucleus  $(m, n-1, 1)$  against  $\beta^-$ -emission can be treated in the same way. The condition is

$$E(m, n-1, 1) > E(m+1, n-1, 0) - \mu$$

which leads to

$$c \frac{4m+3}{(4m+n)^{1/3}} + \mu > \begin{cases} E_p(m, n-2, 1) - E'_n(m, n-2, 1) & \text{if } n \text{ is even} \\ E_p(m, n-2, 1) - E_n(m, n-2, 1) & \text{if } n \text{ is odd} \end{cases}$$

Corresponding to (11) we define  $n_1$  and  $n_3$  by the equations

$$c \frac{4m+3}{(4m+n_1)^{1/3}} + \mu = E_1(m, n_1)$$

$$c \frac{4m+3}{(4m+n_3)^{1/3}} + \mu = E_3(m, n_3)$$

where

$$E_1(m, n) = E_p(m, n-2, 1) - E'_n(m, n-2, 1)$$

$$E_3(m, n) = E_p(m, n-2, 1) - E_n(m, n-2, 1)$$

and it follows in the same way as before that  $n_1$  is smaller than  $n_3$ .

We thus find again three regions with the following types of stable nuclei

$$\begin{aligned}
 n < n_1 & \begin{cases} n=2\nu: & (m, 2\nu-1, 1) & - \\ n=2\nu+1: & (m, 2\nu, 1) & - \end{cases} \\
 n_1 < n < n_3 & \begin{cases} n=2\nu: & - & (m+1, 2\nu-4, 0) \\ n=2\nu+1: & (m, 2\nu, 1) & - \end{cases} \\
 n_3 < n & \begin{cases} n=2\nu: & - & (m+1, 2\nu-4, 0) \\ n=2\nu+1: & - & (m+1, 2\nu-3, 0) \end{cases}
 \end{aligned}
 \tag{15}$$

### 5. The general scheme of stable nuclei.

In order to combine the two schemes (12) and (15), we must know which of the numbers  $n_1$  defined by (11) and (13) are larger. As pointed out at the end of paragraph 2, the change in the neutron and proton energies with  $n$  is the same whether the particle is even or odd. Furthermore, it is negative for neutrons and positive for protons. Therefore, we have

$$(16) \quad \begin{aligned} E_n(m, n, 0) - E_n(m, n+1, 0) &= E'_n(m, n-1, 0) - E'_n(m, n, 0) = \Delta_n(m, n) > 0 \\ E_p(m, n+1, 0) - E_p(m, n, 0) &= E'_p(m, n+1, 0) - E'_p(m, n, 0) = \Delta_p(m, n) > 0 \end{aligned}$$

Since it is immaterial whether we add first a neutron and then a proton or vice versa, the following relation between the neutron and proton energies holds

$$(17) \quad \begin{aligned} E_n(m, n, 0) + E'_p(m, n+1, 0) &= E'_p(m, n, 0) + E_n(m, n, 1) \\ E'_n(m, n, 0) + E'_p(m, n+1, 0) &= E'_p(m, n, 0) + E'_n(m, n, 1) \end{aligned}$$

These relations correspond to the relation (5) that  $F_{NZ} = F_{ZN}$ .

With the help of (17) we can eliminate  $E(m, n, 1)$  from the energies (14) and compare them with the energies (10). Using the definitions

$$(16) \text{ we get } \quad E_2(m, n) - E_3(m, n) = \begin{cases} [E_n(m, n, 0) - E'_n(m, n-1, 0)] - [E_p(m, n-2, 1) - E'_p(m, n-2, 0)] \\ + 2\Delta_p(m, n-2) + \Delta_n(m, n-2) + \Delta_n(m, n-1) \end{cases}$$

$$(18) \quad E_1(m, n) - E_2(m, n) = E_3(m, n) - E_4(m, n) = \begin{cases} E_p(m, n-2, 1) - E'_p(m, n-2, 0) \\ - 2\Delta_p(m, n-2) - \Delta_n(m, n-1) \end{cases}$$

Assuming that the energy between like particles is the same for neutrons and protons, the first two terms in the first equation (18) cancel /

cancel so that  $E_2$  is greater than  $E_3$  and  $n_2$  smaller than  $n_3$ . In the second equation (18) the first term is of the order of magnitude of the binding energy. In paragraph 2 we found that the change of the neutron and proton energy with  $n$  is much smaller than the binding energy. Therefore, the first term will be the most important and we conclude that  $E_1$  is larger than  $E_2$  and  $E_3$  larger than  $E_4$  so that  $n_1$  is smaller than  $n_2$  and  $n_3$  smaller than  $n_4$ . (The difference between  $4m+1$  and  $4m+3$  in (10) and (14) can be neglected).

We can now combine the two schemes (12) and (15) and find the following typical scheme for stable nuclei.

$$\begin{array}{l}
 n < n_1 \quad \left\{ \begin{array}{l} n = 2\nu: \quad (m, 2\nu, 0) \\ n = 2\nu+1: \quad (m, 2\nu+1, 0) \end{array} \right. \quad \begin{array}{l} - \\ - \end{array} \quad \begin{array}{l} - \\ - \end{array} \\
 n_1 < n < n_2 \quad \left\{ \begin{array}{l} n = 2\nu: \quad (m, 2\nu, 0) \\ n = 2\nu+1: \quad (m, 2\nu+1, 0) \end{array} \right. \quad \begin{array}{l} - \\ - \end{array} \quad \begin{array}{l} (m+1, 2\nu-4, 0) \\ - \end{array} \\
 (19) \quad n_2 < n < n_3 \quad \left\{ \begin{array}{l} n = 2\nu: \quad (m, 2\nu, 0) \\ n = 2\nu+1: \quad - \end{array} \right. \quad \begin{array}{l} - \\ (m, 2\nu, 1) \end{array} \quad \begin{array}{l} (m+1, 2\nu-4, 0) \\ - \end{array} \\
 n_3 < n < n_4 \quad \left\{ \begin{array}{l} n = 2\nu: \quad (m, 2\nu, 0) \\ n = 2\nu+1: \quad - \end{array} \right. \quad \begin{array}{l} - \\ - \end{array} \quad \begin{array}{l} (m+1, 2\nu-4, 0) \\ (m+1, 2\nu-3, 0) \end{array} \\
 n_4 < n \quad \left\{ \begin{array}{l} n = 2\nu: \quad - \\ n = 2\nu+1: \quad - \end{array} \right. \quad \begin{array}{l} - \\ - \end{array} \quad \begin{array}{l} (m+1, 2\nu-4, 0) \\ (m+1, 2\nu-3, 0) \end{array}
 \end{array}$$

Of course, it will not be necessary to compare the energies of nuclei differing by two units in the charge and both stable compared /

compared with the nucleus in between. They can disintegrate by a double process only, which is highly improbable. The scheme (19) is written in such a way that nuclei in the same row are isobars, and nuclei in the same column are isotopes. If we order the known stable nuclei in the same way, we obtain exactly this type of scheme (for the explanation of a few exceptions see Bethe and Bacher, 1936, p.198). Of course very often some of the various regions are so small that they vanish entirely. A more detailed comparison with the experiments will be made in the later paragraphs.

As an example the stable nuclei with mass numbers between  $A=124$  and  $A=139$  are given in the following table. The first row gives the number  $m$ , the second the charge number. The first column gives the mass number  $A$  and the numbers in the table give the values of  $n$ .

Stable nuclei with masses between 124 and 139

$m$	$28$	$29$	$30$	$31$					
$A$	$Z$	$52$	$53$	$54$	$55$	$56$	$57$	$58$	$59$
124		20		16					
125		21							
126		22		18					
127			22						
128		24		20					
129				21					
130		26		22		18			
131				23					
132				24		20			
133					24				
134				26		22			
135						23			
136		$(m, 0, 0)$		28		24		$(m, 0, 0)$	20
137		$(m, 1, 0)$				25		$(m, 1, 0)$	
138				$(m, 1, 1)$		26		$(m, 2, 0)$	22
139				$(m, 2, 1)$			26		$(m, 2, 1)$

## 6. The light nuclei.

The general scheme (19) does not hold for the lightest nuclei. If the Coulomb energy is very small, there will be no solution at all for the numbers  $n_i$ ; in other words,  $n$  is always greater than  $n_4$  and the nuclei  $(m-1, n-4, 0)$  are always stable compared with the nuclei  $(m, n, 0)$  and  $(m, n-1, 1)$ , provided  $n$  is greater than 4. We need only consider the stability of nuclei with less than 4 surplus particles, where the scheme (12) applies. It would follow from this scheme that only nuclei of the form  $(m, n-1, 1)$  exist. However, we had assumed that if a proton is added, there would already be a surplus neutron present with which it could interact strongly. If this is not the case, neutron and proton are equally favoured apart from the Coulomb energy. Therefore the first particle to be added will be a neutron, followed by a proton. Then, for the same reason, another neutron will be added and finally another proton. This scheme extends from  $\text{He}_2^4$  to  $\text{N}_7^{15}$ . The only exceptions are that  $\text{He}_2^5$  and  $\text{Be}_4^8$  are not stable. This, however, is due to the emission of heavy particles.

The first deviation from this scheme will occur when a solution of  $n_4$  larger than 2 exists. For in this case it follows from the scheme (12) that the nucleus  $(m, 1, 1)$  is not stable, but changes into the nucleus  $(m, 2, 0)$  by emission of a positron. Thus the first two schemes are:

$$\begin{array}{rcc}
 \begin{pmatrix} m, 0, 0 \\ m, 1, 0 \\ - \\ - \end{pmatrix} & \begin{array}{c} - \\ - \\ (m, 1, 1) \\ (m, 2, 1) \end{array} & \begin{pmatrix} m, 0, 0 \\ m, 1, 0 \\ m, 2, 0 \\ - \end{pmatrix} & \begin{array}{c} - \\ - \\ - \\ (m, 2, 1) \end{array}
 \end{array}$$

The second scheme extends without exception from  $O_8^{16}$  to  $P_{15}^{31}$ .

An alternative interpretation of these 'periods' by means of a shell model has been proposed by Elsaesser (1936).

In this way, of course, only within two units, and for this reason it is not possible to separate  $n_1$  from  $n_2$  and  $n_3$  and  $n_4$  for light and for heavy nuclei. The result is shown in Figure 2, showing the values of  $n_1$  as functions of  $n$ .

An interesting phenomenon are the dips in the curves for  $n$  about 13, 19, 28. They correspond to the maxima in the frequency of the elements for  $Fa_{16}$ ,  $Sm_{32}$  and  $Ra_{80}$ . As a consequence, therefore, to a sudden increase in  $n_1$ , which is not accompanied by a gradual decrease, which is also found in the frequency curves (cf. for example Weizsaecker, 1935, p. 105).

From the  $n$ -curves we can find the corresponding  $n_1$  curves  $E_1$  by means of the equations (4) and (5). The differences between the four  $E_1$  curves is so small that only one curve has been drawn in figure 3. The reason for this is that the Coulomb energy changes very slowly with  $n$ . The energies  $E_1$  obtained from these values of  $n_1$  range from about 5 MeV to 12 MeV. They are of the order of magnitude of the binding energy as is to be expected.

### 7. The experimental n-curves.

The limits  $n_1$  of the different regions of stability can be obtained from the known stable nuclei. They are determined in this way, of course, only within two units, and for this reason it is not possible to separate  $n_1$  from  $n_2$  and  $n_3$  and  $n_4$  for light and for heavy nuclei. The result is shown in figure 2, showing the values of  $n_1$  as functions of  $m$ .

An interesting phenomenon are the dips in the n-curves for  $m$  about 13, 19, 28. They correspond to the maxima in the frequency of the elements for  $\text{Fe}_{26}$ ,  $\text{Sr}_{38}$  and  $\text{Ba}_{56}$ . They correspond, therefore, to a sudden increase in  $E_p$ , which makes the n-values smaller. It is interesting to note that there is a sudden increase followed by a gradual decrease, which is also found in the frequency curves (cf. for example Weizsaecker, 1937, p.164).

From the n-curves we can find the corresponding energies  $E_i$  by means of the equations (4) and (6). The difference between the four  $E_i$  curves is so small that only one curve has been drawn in figure 3. The reason for this is that the Coulomb energy changes very slowly with  $n$ . The energies  $E_i$  obtained from these values of  $n_1$  range from about 5 MeV to 12 MeV. They are of the order of magnitude of the binding energy as is to be expected.



Experimental values for  $n_i$  can in general only be obtained for values of  $m$  greater than 8. But for  $n_4$  it can be obtained for  $m$  greater or equal to 3, which is the limit of the first "period" of the lightest nuclei. The corresponding energy can easily be extrapolated to  $m=0$ , giving a value of about 1.5 MeV.

The corresponding energy is the difference in the energy  $E'_p$  of an odd proton and the energy  $E_n$  of an even neutron. In the limit  $m \rightarrow 0$  these energies should tend against the interaction energy between one neutron and one proton and the energy between a pair of neutrons in a nucleus. ( For larger values of  $m$  both energies are of course larger, owing to the additional interaction with other particles.)

If we use the values of Bethe and Bacher (1936, p.145, formula (128)), we obtain the following result: The constants in the expressions for the force between unlike and like particles respectively are 30.7 MeV and 21.0 MeV. The ratio of the energy difference  $E'_p - E_n$  to the energy of the  $\alpha$ -particle with four bonds between unlike particles and two between like particles is therefore  $(30.7 - 21.0)/(4 \times 30.7 + 2 \times 21.0)$ . With 28 MeV for the energy of the  $\alpha$ -particle, we obtain 1.6 MeV for  $E'_p - E_n$  in the limit  $m=0$ , in good agreement with the above result.

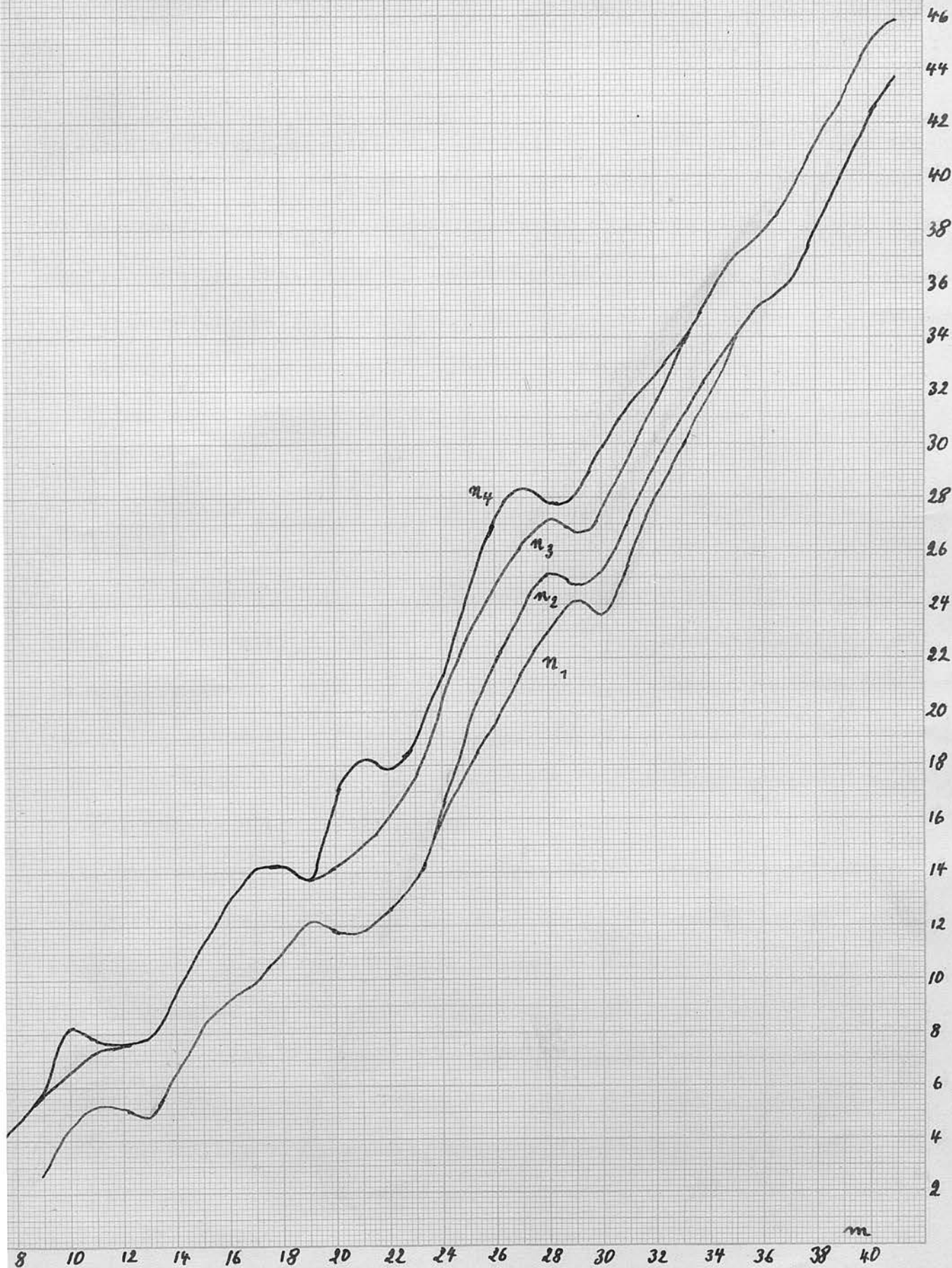


Figure 2

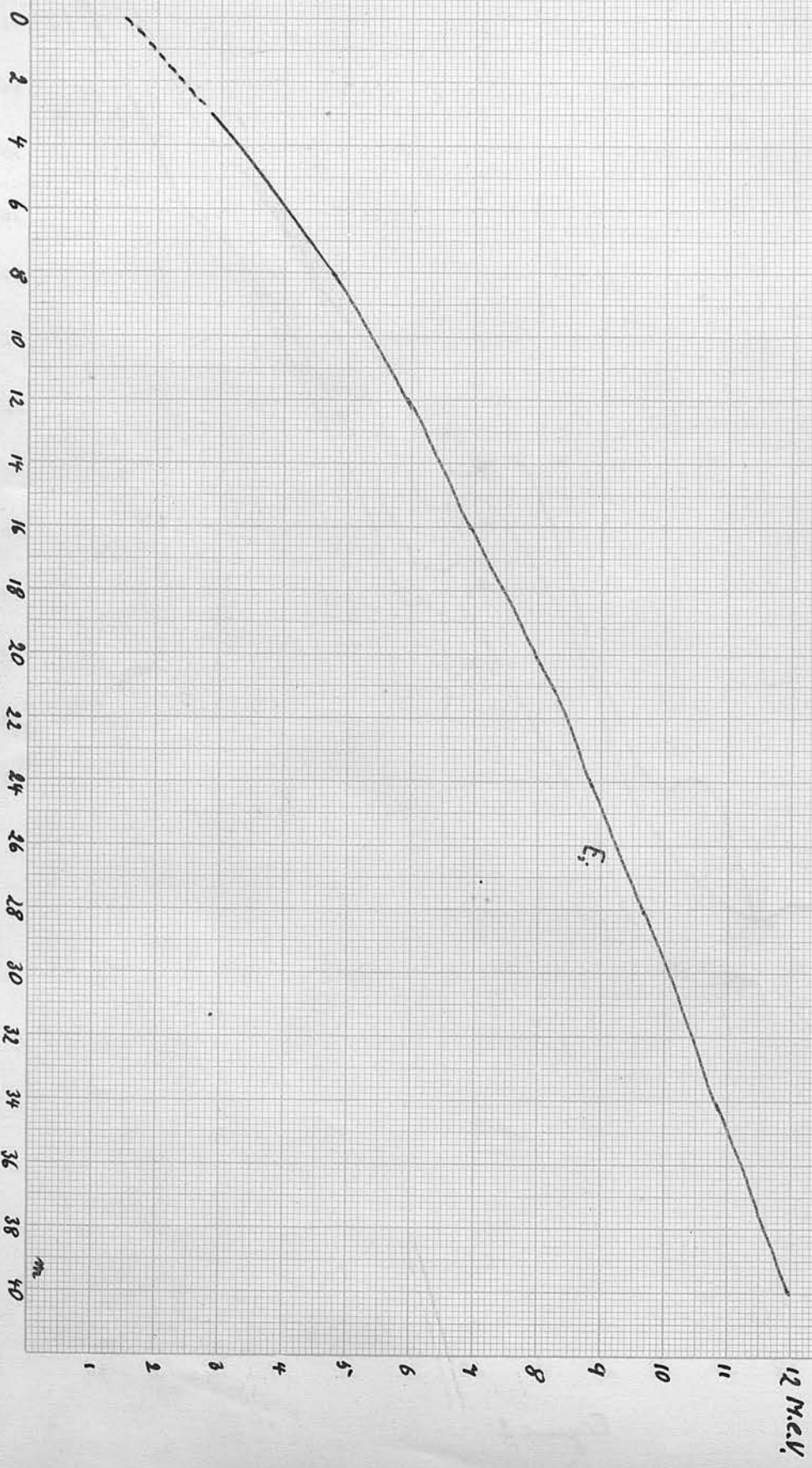


Figure 3.

8. The isotropic breadth of nuclei with odd number of protons.

The isotropic breadth for odd charge number is directly given by the difference  $n_3 - n_2$ , as is apparent from the scheme (19). We shall now show that  $E_2(m, n)$  is nearly equal to  $E_3(m, n+2)$ . Since the change in the Coulomb energy is entirely negligible if  $n$  changes by two units, this shows that  $n_3 - n_2$  is equal to two.

The statement follows at once from the definitions (11), (13) and the equations (16), (17). Analogous to (18) we find

$$(20) \quad E_2(m, n) - E_3(m, n+2) = \Delta_p(m, n) - \Delta_p(m, n-1)$$

As pointed out before,  $\Delta_p(m, n)$  is a small quantity and the change of this quantity with  $n$ , which occurs on the right hand side of (20), is smaller still. It can therefore be neglected. (If we use the estimates given in the next section, it can easily be shown that the right hand side of (20) influences the difference  $n_3 - n_2$  only by the fraction of a unit).

The values of  $n_2$  and  $n_3$  are determined by the comparison of energies of nuclei with an odd number of particles, and either an even number of protons and odd number of neutrons or vice versa. But we have so far compared only the states with spin  $\frac{1}{2}$ . Very often these states are not the lowest states and, therefore, the actual energy curves of the lowest state will be somewhat lower. Now, the nuclei with an odd number of protons have in general the higher spin value. We conclude that their energies are depressed rather /

rather more than those of the nuclei with odd number of neutrons and they will, therefore, be stable beyond the limits  $n_2$  and  $n_3$ , obtained by comparing only the energy of states with spin  $\frac{1}{2}$ . Thus the true values of the isotropic breadth  $n_3 - n_2$  should be rather larger than two units. Experimentally it lies between 2 and 4, for the number of stable isotopes with odd charge number is always equal to one or two.

If we neglect the change in the binding energy of the nucleus from  $n_2$  to  $n_3$ , we have

$$(22) \quad E_1(n_2) - E_1(n_3) = E_2(n_2) - E_2(n_3)$$

neglecting higher derivatives. From (21) it follows that

$$\frac{dE_1(n)}{dn} = \frac{dE_2(n)}{dn} = E_2(n) - E_1(n)$$

according to the definition (11), if we neglect higher derivatives. Substituting this result in (22) we get

$$E_2(n_2) - E_1(n_2) = E_2(n_3) - E_1(n_3)$$

or with (21), we obtain  $E_2(n_2) - E_1(n_2) = E_2(n_3) - E_1(n_3)$

$$E_2(n_2) - E_1(n_2) = E_2(n_3) - E_1(n_3)$$

If the same way we find

$$E_2(n_2) - E_1(n_2) = E_2(n_3) - E_1(n_3)$$

Since /

9. The isobaric region.

The region between  $n_4$  and  $n_1$  is the region in which stable isobars can exist. Corresponding to the equations (18), the difference between  $E_1$  and  $E_4$  is given by

$$(21) \quad \begin{aligned} E_1(m, n) - E_4(m, n) \\ = E_n(m, n-1, 0) - E'_n(m, n-2, 0) + E_p(m, n-2, 1) - E'_p(m, n-2, 0) - 2\Delta_p(m, n-2) \end{aligned}$$

If we neglect the change in the Coulomb energy, if  $n$  changes from  $n_2$  to  $n_4$ , we have

$$(22) \quad E_1(m, n_1) - E_4(m, n_4) = E_4(m, n_1) + (n_4 - n_1) \frac{dE_4(m, n)}{dn}$$

neglecting higher derivatives. From (11) it follows that

$$\frac{dE_4(m, n)}{dn} = \frac{dE_p}{dn} - \frac{dE_n}{dn} = \Delta_p + \Delta_n$$

according to the definitions (16), if again we neglect higher derivatives. Inserting this value in (22)  $n_4 - n_1$  is given by

$$n_4 - n_1 = \frac{E_1(m, n_1) - E_4(m, n_1)}{\Delta_p + \Delta_n}$$

or with (21), putting  $E_n - E'_n = E_p - E'_p$

$$n_4 - n_1 = 2 \frac{E_n - E'_n - \Delta_p}{\Delta_p + \Delta_n}$$

In the same way we find

$$n_4 - n_3 = n_2 - n_1 = \frac{E_n - E'_n - 2\Delta_p - \Delta_n}{\Delta_p + \Delta_n}$$

Since /

Since we neglect higher order derivatives we can identify  $-\Delta_n$  and  $+\Delta_p$  with the derivatives  $F_{NN}$  and  $F_{ZN}$ , defined in paragraph 3.

The above equations can then be written in the form

$$(23) \quad n_4 - n_1 = 2 \frac{E_n - E'_n - F_{ZN}}{F_{ZN} - F_{NN}}$$

$$n_4 - n_3 = n_2 - n_1 = \frac{E_n - E'_n - 2F_{ZN} + F_{NN}}{F_{ZN} - F_{NN}}$$

According to (4) and (5) the ratio  $-F_{ZN}/F_{NN}$  is equal to the ratio of the increments in the number of neutrons and the number of protons along the line of stable nuclei, which is about 1.5

$$(24) \quad -\frac{F_{ZN}}{F_{NN}} = \frac{\Delta N}{\Delta Z} = 1.5$$

If we can estimate the interaction energy between like particles  $E_n - E'_n$  and the change of  $E_n$  with  $n$ , we can, therefore, calculate

$n_4 - n_1$ . (23) yields the following values

$E_n - E'_n$  is known to be about 5 MeV for nuclei below Argon (cf. Livingstone and Bethe, 1937, p.381). For nuclei above Argon there is now sufficient experimental evidence, but as pointed out before, the change cannot be very big. We, therefore, use the value of 5 MeV.

The change of  $E_n$  with  $n$  can unfortunately be estimated from experimental values only with great difficulty. In a few cases the masses of sufficient isotopes are known (for example for Krypton) but the accuracy allows us only to say that the change seems to be smaller than 1 MeV per unit. Further evidence can be obtained

from /

from the energies of emitted  $\beta$ -particles. This energy gives the energy difference  $F_Z - F_N$  between a proton and a neutron and its change with  $n$  is therefore equal to  $F_{ZN} - F_{NN}$ . But this evidence is not very reliable in view of the well-known difficulty in finding the true upper limit of the  $\beta$ -ray spectrum. But the experimental values seem to be consistent with a value of about 0.5 to 1 MeV for  $F_{NN}$ .

Rather indirect evidence can be obtained from Weizsäcker's semi-empirical formula for the binding energy of nuclei (1937, p.50). The value obtained from this formula varies inversely to the total number of particles from 2 MeV for Argon to 0.4 MeV for Mercury. The particular dependence on the number of particles, however, is due to the function which he uses.

We assume, therefore, for  $-F_{NN}$  a value of about +0.5 to +1 MeV. Then (23) yields the following values

$$(25) \quad \begin{aligned} n_4 - n_1 &\approx 3 - 7 \\ n_4 - n_3 &= n_2 - n_1 \approx 0.5 - 2.5 \end{aligned}$$

These values agree well with the experimental values shown in figure 2.

The relation  $n_4 - n_3 = n_2 - n_1$  is satisfied exactly within the limits of error, except for  $m=10$  and  $m=20, 21$ . This relation follows from (18), if we neglect the change of  $\Delta_n$  and  $\Delta_p$  and of  $E_n - E'_n$  with  $n$ . It should, therefore, be satisfied also if states with higher spin values are taken into account, as long as the value of the spin does not change between  $n_1$  and  $n_4$ .

Let /



Let us finally consider the dependence of  $n_4 - n_1$  on the number  $m$ . Inserting (24) in (23) we find that  $n_4 - n_1$  depends only on the ratio  $E_n - E'_n / F_{ZN}$ .

$$(26) \quad n_4 - n_1 = 1.2 \left( \frac{E_n - E'_n}{F_{ZN}} - 1 \right)$$

$E_n - E'_n$  should be expected to decrease slightly with  $m$  owing to the volume effect as discussed in paragraph 3. But so would  $F_{ZN}$ , which is the energy gained by a proton when we add a neutron. But  $F_{ZN}$  would decrease furthermore with the isotopic number owing to the saturation effect. We conclude that  $F_{ZN}$  decreases more rapidly than  $E_n - E'_n$  so that  $n_4 - n_1$  should increase with  $m$ . This is actually the case up to  $m=30$ .

Beyond  $m=30$ , however,  $n_4 - n_1$  decreases again. There seems to be no plausible explanation of this effect. It could be thought that the decrease is due to the possible emission of heavy particles. However  $RaE$ , which determines  $n_4$  for  $m=40$ , does not emit heavy particles but electrons, showing that the numbers  $n_1$  are determined by  $\beta$ -radioactivity even for the heaviest stable nuclei. The effect could, perhaps, be connected with the spin of the lowest state being large.  $n_4$  and  $n_1$  are obtained by comparing energies of nuclei with even number of particles and either even numbers of neutrons and protons or odd numbers of neutrons and protons. Below  $n_4$  the nucleus  $(m, 2\nu, 0)$  is stable compared with  $(m, 2\nu-1, 1)$ ; above  $n_4$  it is not stable and changes into the nucleus  $(m, 2\nu-1, 1)$ , which itself changes /

changes into  $(m+1, 2\nu-4, 0)$ . The spins of the even nuclei are, of course, always zero, but for those with odd numbers of neutrons and protons the state with spin Zero might not be the lowest state. The energy of the lowest state would then be lower and, therefore,  $n_4$  would be smaller. Correspondingly  $n_1$  would become bigger.

However, this explanation does not agree with the normal life times of RaD and RaE. For, if the explanation were correct, RaD - being an even nucleus - should have a lower energy than the state of RaE with a high spin value. It should, therefore, have an abnormally large life time. Indeed, since the energy of the emitted electrons is very small, it should for all practical purposes be stable. Correspondingly, RaE could either disintegrate with a normal life time into a state of Polonium with high spin, which would emit  $\gamma$ -rays, or it could disintegrate with a high life time into the normal state of Polonium.

I wish to thank Professor M. Born for the interest he has taken in the progress of this paper.

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SUMMARY.

By means of purely qualitative arguments which do not depend on any particular model the general scheme of stable nuclei and the isotopic breadth of nuclei with odd charge number has been explained.

The breadth of the isobaric region, can only be obtained if the numerical values of certain energies are known. Though these can be estimated only very roughly, the values for the breadth of the isobaric region obtained in this way are in good agreement with the experimental values. The increase in the breadth of the isobaric region from light nuclei to heavier nuclei can be explained, but no plausible explanation has been found for the fact that for the heaviest nuclei it decreases again.