12) The principle of adiabatics and the systems which do not admit angle coordinates

"Il principio delle adiabatiche ed i sistemi che non ammettono coordinate angolari,"
Nuovo Cimento **25**, *171-175, (1923)*

§ 1. - The importance of the Ehrenfest's principle of adiabatics for the determination of the selection rules for the stationary orbits of a system, in the Bohr theory, is well-known [1]. This principle, as we know, can be enunciated as follows: Let us assume that, in a mechanical system, the forces or the constraints are continuously modified with time but very slowly in comparison with the periods of the system, or, accordig to the Ehrenfest's expression, adiabatically; the principle of adiabatics states that, if the system initially is in a quantum preferred orbit, it will still be there at the end of the transformation.

Let us consider, for instance, a pendulum and imagine to shorten its string at a very low rate in comparison with the period of the pendulum itself. Frequency ν of the pendulum will then grow slowly, but it is easy to realize that energy u also will grow and just so that the ratio u/ν maintains constant. In this way, if this ratio was initially an integer multiple of Planck constant h, it will remain the same and then the state of the system will remain quantum preferred during the whole transformation. For further examples we refer to the Ehrenfest's memoir.

The formal basis for the principle of the adiabatics is provided by Burger's theorem [2]. Let us consider a system that in certain general coordinates $q_1, q_2, ..., q_f$ allows the separation of variables [3]. Then put

$$I_K = \oint p_K \, dq_K \qquad\qquad (K = 1, 2, ..., f) \qquad\qquad (1)$$

being p_K the canonically conjugate momentum to q_K and the integral extended, according to the rules of quantum theory, to a complete oscillation of coordinate q_K; in this way the conditions in order that the considered orbit of the system be quantum preferred are:

$$I_1 = n_1 h \; ; \; I_2 = n_2 h \; ; ...; \; I_f = n_f h \qquad\qquad (2)$$

being $n_1, n_2, ..., n_f$ integers. Let us suppose, now, to modify adiabatically our system, but in a way it allows the separation of the variables at any instant. Burger's theorem states that in this case integrals $I_1, I_2, ..., I_f$ do not change during the

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[1] Ehrenfest, Ann. d. Phys. **51**, 327 (1916).

[2] Burgers, Versl. Akad. van. Wetensch. - Amsterdam 1916, 1917; Ann. d. Phys. **52**, 195 (1917).

[3] For the validity of Burger's conclusions it is sufficient, more generally, that the system admits angle coordinates, i.e. it is possible to introduce in place of q_K, p_K new variables w_K, j_K such that the q_K's, expressed by means of the (w_K, j_K) are periodical with period 1 in variables w_K, and the energy, in the new coordinates, results a function of the j's only. Then, because of the Hamilton equations, the j's result to be constant and the w's linear functions of the time: the q's as functions of the time can be expanded in Fourier series with f indexes.

transformation, i.e. that they are adiabatic invariants. Therefore, if conditions (2) are satisfied at the onset of the transformation, they will be also satisfied at the end: then the principle of the adiabatics is satisfied.

In this Note I intend to show by means of a simple example that if a system adiabatically transforms into another system and the initial and final states both admit the separation of variables, but the intermediate states do not, the I_K are not adiabatic invariants. In this case the principle of adiabatics loses its basis.

§ 2. - Let us consider a mass point, moving on a plane inside a rectangle; we shall assume that no force acts on the point while it is inside the rectangle, but it bounces off the walls when it hits them. Consider sides AB and AC of the rectangle as coordinate axes x, y. Now, it is evident that our system admits the separation of variables in these coordinates. Calling a, b the lengths of sides AB, AC, coordinate x in fact oscillates between values $0, a$; coordinate y between values $0, b$.
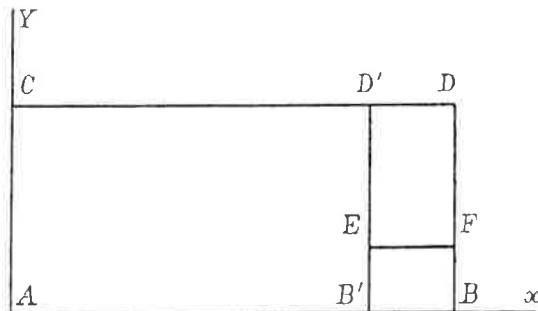
Moreover, if at a certain instant the components of the velocity are u, v, at an instant whatever they will be $\pm u$, $\pm v$, where one must choose sign $+$ or $-$ according to, whether the relative coordinate is increasing or decreasing at the considered instant. The conjugate momenta to x and y will be $\pm mu$, $\pm mv$, m is the mass of the point; then one will have

$$I_x = \oint (\pm mu)\, dx = \int_0^a mu\, dx + \int_a^0 (-mu)\, dx = 2\, mua \qquad (3)$$

and analogously

$$I_y = 2\, mvb \qquad (3')$$

Now we want to study how I_x and I_y change if we transform our system adiabatically. We just intend to transform rectangle ABDC into the other AB'D'C; we remark that such a transformation can be carried out in three ways:

(1) one parallelly shifts the segment BD until it reaches B'D';

(2) one parallelly shifts the segment BB' until it reaches DD', so that at an intermediate instant, the mass point can move inside concave polygon AB'EFDC;

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(3) one deforms anyway the broken line B'BDD until ~~to bring~~ it ~~to~~ coincide with
    segment B'D'.

Keeping out the last case, ~~really~~ somewhat complicated, from our considera-
tions, we shall limit ourselves to discuss the former two. As to the first one, we
remark that in this case at any instant the point can always move inside a rectangle,
therefore also in the intermediate instants it is always possible to have the separa-
tion of variables; according to Burger's theorem, in this case we must expect that
I_x and I_y remain invariant. This is obviously evident for I_x, since neither b, nor v
change during the transformation and then, due to (3'), nor I_y. As to I_x, instead,
a decreases during the transformation, being reduced from $a = AB$ to $a' = AB'$;
but at the same time u increases in consequence of the bounces on the moving wall
and an immediate consideration shows that things go just so that product au, and
then also I_x, remains constant [4], obviously on condition that the transformation
is realized slowly enough. If we pass on to consider case (2), it is easy to realize
that now things are different. As to I_x, in fact one immediately sees that the x
component of the velocity remains unchanged (except for the sign), since it could
change its absolute value only hitting a moving wall parallelly to x-axis, but the only
moving wall, EF, moves parallelly to y; instead a decreases from AB to AB'. In all,
therefore I_x reduces in the ratio a'/a and then does not remain constant. Likewise
also I_y does not remain constant; in fact b remains unchanged whereas v increases
due to the collisions on the moving wall EF. An immediate evaluation shows that
v, and then also I_y, increases in the ratio a/a'. From the above considerations we
can conclude that integrals I_K are adiabatic invariants only if in the intermediate
states the system always admits the separation of variables or at least, according to
Burger's theorems, always admits a system of angular coordinates. On the contrary,
at least in general, this is not true if the system does not always own a multiperiodic
motion. On the other hand, this fact is easily understandable also from the point
of view of quantum theory. In fact one knows, following Bohr, that a well defined
quantization is possible only if the motion of the system is multiperiodic. Then
one can realize that, if in the intermediate states the system cannot be quantized
rigorously, this ~~inexactitude~~ transmits to the final state.

Göttingen, February 1923.

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[4] In fact the number of knocks on the moving wall BD in time interval dt is obviously $\frac{u}{2a}dt$; on
the other hand, if V is the velocity of wall BD, the velocity of the point will experience an increase
of 2V at every knock; then the increase of u in time dt will be:

$$du = 2V\frac{u}{2a}dt = \frac{u}{a}Vdt = -\frac{u}{a}da$$

since, obviously, $-da = Vdt$. By integrating the preceding equation, we find exactly $ua = const.$,
as ~~said~~ above.

13) Some theorems of analytical mechanics of great importance for Quantum Theory

"Alcuni teoremi di Meccanica Analitica importanti per la Teoria dei Quanti,"
Nuovo Cimento 25, 271–285, (1923)

§ 1. - Ehrenfest's principle of adiabatics[1], as is known, states that, if a mechanical system is in a quantum orbit and its mechanism, forces or constraints, is changed in an infinitely slow way, the system remains in a quantum selected orbit during the whole transformation. In order that this principle have a definite sense, it is obviously necessary that the final orbit of the system only depends on the final mechanism and not on the one or another sequence of intermediate mechanisms followed during the transformation. Burgers[2] has shown that this is really the case, at least for that kind of systems which up to now has only been considered in quantum theory, i.e. for systems which, or admit a complete separation of variables, or at least can be represented by means of angular coordinates[3]. In this case, their motion can always be considered as resulting from periodic motions, generally having as many periods as the degrees of freedom are or, in case of degeneracy, with a lower number. But, just at this moment, the study of the simplest atomic structures having been accomplished, some problems which do not admit angular coordinates continually occur, first of all the three-body problem which occurs in the study of hydrogen molecule. As is known, all the efforts made up to now to reduce the study of these systems to that of systems with angular coordinates were in vain. Then it is to be desired to investigate whether and how far is it possible to attempt an extension of the principle of adiabatics to the general systems, hoping that it can give some information which can help in the search for rules suitable to determine the preferred orbits of these more general systems.

§ 2. - First of all we shall have better to fix a classification of the systems to be studied. Therefore we turn to the usual representation of the state of the system by means of a point of a 2f-dimensional space Γ, which has $q_1, q_2, ... q_f$ as the general coordinates of the system and $p_1, p_2, ... p_f$ as their conjugate momenta. We have, through each point of this space, a trajectory which corresponds to the motion of the system having its initial position and velocity determined by the point itself. We shall assume the forces and the constraints of the system being time-independent and the forces deriving from a potential so that an integral of the energy conservation does exist. We call E hypersurfaces the ipersurfaces energy=constant; through each point of Γ, one of the E's is passing on which (as provided by the energy integral)

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[1] P. Ehrenfest. Ann. d. Phys. 51, p. 327; 1916.

[2] Burgers. Versl. Akad. van Wetensch. Amsterdam, 25 November 1916. - Ann. d. Phys. 52, p. 195; 1917. - Phil. Mag. 33, p. 514; 1917.

[3] See for instance Sommerfeld. Atombau und Spektrallinen, III ed. Zusatz 7.

[4] They are the hydrogen atom and its various perturbations (Zeeman effect, Stark effect, and Feinstruktur) and the ion of the hydrogen molecule H_2^+, when nucleus rotations are not present.

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the trajectory through the point is located. The so called quasi-ergodic[5] mechanical systems enjoy the property that the trajectory generally passes infinitely close to every point of E, so to densely fill a $2f-1$ dimensional manifold. However, it may be that our system, besides the energy integral, admits some other uniform integral independent of time. In this case the manifold filled by the trajectory will obviously have a lower number of dimensions. Then let us assume that our system have on the whole m uniform first integrals independent of time,

$$\Phi_1(p,q) = c_1; \Phi_2 = c_2; ....; \Phi_m = c_m$$

being c_i arbitrary constants. We shall have, through each point of Γ, a $2f-m$ dimensional manifold G, intersection of the m hypersurfaces $\Phi_i = c_i$; and the trajectory passing through that point will be wholly contained in G. In general it will not be possible to find, within G, a submanifold which contains the whole trajectory; on the contrary, on the analogy of quasi-ergodic systems, we shall assume for our systems that in general the whole G be densely filled by the trajectory, i.e. that the trajectory passes infinitely close to all the points of G. In this way, the trajectory will come out characterized, at least in its statistical elements, by the only knowledge of the values $\Phi_1, \Phi_2, ..., \Phi_m$ corresponding to it. Therefore we call these values *characteristics of the trajectory*. Then a quasi-ergodic system has only one characteristic, its energy. A system with its energy independent of time, which admits the separation of variables, has in general as many characteristics as degrees of freedom, corresponding to the f a constants of the Jacobi's complete integral; a higher number can only occur in case of degeneracy, i.e. when linear relations with integer coefficients between the fundamental frequencies exist. Let us consider, for instance, the motion of a point in a plane acted on by a force proportional to the distance from two orthogonal straight lines. If the two attraction coefficients are not commensurate, the point describes an open Lissajous' curve in the plane. And in the four-dimensional space Γ the representative point densely fills a two-dimensional surface G. Therefore the system has two characteristics; for them we can take the energies of the projections of the motion on the two orthogonal straight lines. If instead the attraction coefficients are commensurate, the Lissajous' curve degenerates in a closed curve and G becomes one-dimensional; this corresponds to three characteristics.

§ 3. - Now we shall assume to be able to change arbitrarily the forces, or the constraints of the system, i.e. what on the whole, with a happy naming due to P. Hertz[6] we shall call the *mechanism* of the system. If we change the mechanism in an infinitely slow way, we have what is said an adiabatic transformation; and, in § 5, we shall easily find a system of differential equations which shows how the characteristics of the system change when the guiding parameter of the mechanism

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[5]The author recently demonstrated that the ordinary mechanical systems are, in general, quasi-ergodic, so that this is the most common case.

[6]P. Herz. Ann. d. Phys. 33, pp. 225, 537; 1910. Weber, Gans. Repertorium der Physik I, 2; 1916. We refer to these works for any explanations regarding the statistical part of the text.

μ, changes adiabatically. But, as we have already mentioned, one can ~~speak of application of~~ the Ehrenfest's principle to a definite system only if the values that its characteristics take at the end of an adiabatic transformation only depend on the final mechanism and not on the intermediate workings crossed during the transformation. To study this question, we shall assume afterwards that the mechanism, rather than depending on only one parameter, depend on two parameters λ and μ. The dependence of the characteristics on λ and μ, instead of being on a system of ordinary differential equations, will then be obviously expressed by a system of equations of total differentials; then the conditions for having the final values of the characteristics not depending on the path followed during the transformation in the λ, μ plane coincide with the integrability conditions for this system. We shall demonstrate that these conditions, for the quasi-ergodic system, are really satisfied. Instead, for the systems having more than one characteristic, in general they are not satisfied although important classes of exceptions exist.

§ 4. - Before ~~passing to~~ study the adiabatic transformations it is convenient to consider some formulae which are useful for calculating the probability that, at any instant, the representative point is in G. Then, for uniforming notations, differently from above we call $x_1, x_2, ..., x_{2f}$, the coordinates of Γ. Our problem can now be formulated in this way: calculate the probability that, at a certain instant, $x_1, x_2, ..., x_{2f-m}$ have values between x_1 and $x_1 + dx_1$, x_2 and $x_2 + dx_2, ... x_{2f-m}$ and $x_{2f-m} + dx_{2f-m}$, while the remaining m x's obviously take the values necessary to maintain the representative point in G. As we know, statistical mechanics, through the Liouville's theorem, states that the necessary condition for having a stationary distribution of the points in the Γ space is that their density in Γ should have a constant value on any G. A volume element of Γ can be written $dx_1, dx_2, ..., dx_{2f}$, but also, taking as new variables $x_1, x_2, ..., x_{2f-m}, \Phi_1, \Phi_2, ..., \Phi_m$ as $\frac{1}{D} dx_1, dx_2, ..., dx_{2f-m}, d\Phi_1, d\Phi_2, ..., d\Phi_m$, where D is the functional determinant $\frac{\partial(\Phi_1 ... \Phi_m)}{\partial(x_{2f-m+1}, ..., x_{2f})}$. And, since during the motion $d\Phi_1, d\Phi_2, ..., d\Phi_m$ obviously remain constant, the aforesaid volume element comes out to be proportional to $\frac{1}{D} dx_1, ..., dx_{2f-m}$. Therefore also the wanted probability is proportional to this expression; and since the total probability is obviously $= 1$, we finally find that the wanted probability is given by

$$\frac{\frac{d\sigma}{D}}{\int \frac{d\sigma}{D}} \tag{1}$$

where for short we put $d\sigma = dx_1, dx_2, ... dx_{2f-m}$ and the integral is extended to all values of $x_1, x_2, ..., x_{2f-m}$, corresponding to the points of G. Before leaving this subject, we also want to deduce a formula that will be useful in the case of quasi-ergodic systems. In this case G is a hypersurface, and we assume for the sake of simplicity it should be closed, and such to be intersected in only one point by the radii vectors coming out from a pole within it. This because a more general approach, even though it is not essentially different, would cause rather complicated calculations. We refer the space Γ to polar coordinates, by characterizing each

point by means of its radius vector and the intersection of this end with the unit hypersphere having the pole as center. We call H the only characteristic, i.e. the energy. In accordance with what said above, the probability that at a certain instant the representative point lie within an element of solid angle $d\omega$ is proportional to the hypervolume comprised between the two hypersurfaces $H(x_1, ... , x_{2f}) = H$, and $H(x_1, ... , x_{2f}) = H + dH$, and the solid angle $d\omega$. This volume, except for the constant factor dH, is evidently $\frac{r^{2f-1} d\omega}{H_r}$, where $H_r = \frac{\partial H}{\partial r}$. Since the total probability must be 1, we find that the wanted probability is given by

$$\frac{r^{2f-1} \frac{d\omega}{H_r}}{\int r^{2f-1} \frac{d\omega}{H_r}} \tag{2}$$

where the integral is extended to the whole unit sphere.

§ 5. - In this section we assume the mechanism of our system as a function of a parameter μ and we aim to study how the characteristics change when this parameter changes adiabatically. Since the mechanism depends on the parameter μ, in general also the characteristics $\Phi_1, \Phi_2, ... , \Phi_m$ will depend on μ, besides the p's and q's. Then, if at a certain instant the parameter μ changes of $d\mu$, characteristic Φ_i will correspondingly undergo the change $\frac{\partial \Phi_i}{\partial \mu} \partial \mu$. Since we are in presence of an adiabatic change, to have the effective change of Φ_i, we must consider the average of this expression which, according to the results of the previous section, will be

$$d\mu \frac{\int \frac{\partial \Phi_i}{\partial \mu} \frac{d\sigma}{D}}{\int \frac{d\sigma}{D}} \tag{3}$$

which results only to be a function of μ and $\Phi_1, ... , \Phi_m$. The dependence of the characteristics on μ in an adiabatic transformation will then be expressed by the system of ordinary differential equations:

$$\frac{d\Phi_1}{d\mu} = \frac{\int \frac{\partial \Phi_1}{\partial \mu} \frac{d\sigma}{D}}{\int \frac{d\sigma}{D}}; \frac{d\Phi_2}{d\mu} = \frac{\int \frac{\partial \Phi_2}{\partial \mu} \frac{d\sigma}{D}}{\int \frac{d\sigma}{D}}; ...; \frac{d\Phi_m}{d\mu} = \frac{\int \frac{\partial \Phi_m}{\partial \mu} \frac{d\sigma}{D}}{\int \frac{d\sigma}{D}} \tag{4}$$

If we know the values of the Φ's, for instance for $\mu = 0$, the integration of this system gives us their values for any μ. In the particular case of the quasi-ergodic systems, system (4) reduces to the only equation:

$$\frac{dH}{d\mu} = \frac{\int \frac{H_\mu}{H_r} r^{2f-1} d\omega}{\int \frac{d\omega}{H_r} r^{2f-1}} \tag{5}$$

where $H_\mu = \frac{\partial H}{\partial \mu}$.

§ 6. - Now we want to study in which cases the final values of the characteristics are independent of the way followed in passing adiabatically from the initial mechanism to the final one. Therefore we shall represent the mechanism of the system as a function of two parameters, λ and μ. If one alters adiabatically these two parameters, of $d\lambda$ and $d\mu$ respectively, the same conclusion of the preceding section shows that the corresponding change of the characteristic is:

$$d\Phi_i = \frac{\int \frac{\partial \Phi_i}{\partial \lambda} \frac{d\sigma}{D}}{\int \frac{d\sigma}{D}} d\lambda + \frac{\int \frac{\partial \Phi_i}{\partial \mu} \frac{d\sigma}{D}}{\int \frac{d\sigma}{D}} d\mu \qquad (i = 1, 2 ... , m) \tag{6}$$

The coefficients of $d\lambda$ and $d\mu$ are evidently functions of only λ and $\Phi_1, ... , \Phi_m$, then m equations (6) represent a system of equations of total differentials; if it will result unlimitedly integrable, the final values of Φ's will be effectively independent of the way followed during the transformation, or else it will not be so. We want to demonstrate that, in the case of quasi-ergodic systems, the condition of unlimited integrability is satisfied. In fact, for these systems, system (6) reduces to only an equation of total differentials analogous to (5)

$$dH = L d\lambda + M d\mu \tag{7}$$

where

$$L = \frac{\int \frac{r^{2f-1} H_\lambda d\omega}{H_r}}{\int \frac{r^{2f-1} d\omega}{H_r}}; \quad M = \frac{\int \frac{r^{2f-1} H_\mu d\omega}{H_r}}{\int \frac{r^{2f-1} d\omega}{H_r}} \tag{8}$$

and then L and M represent two functions of λ, μ and H. As we know, for obtaining the unlimited integrability of (7), it is necessary and sufficient that the total derivatives of L with respect to μ and of M with respect to λ be equal. Therefore it must be

$$\frac{\partial L}{\partial \mu} + M \frac{\partial L}{\partial H} = \frac{\partial M}{\partial \lambda} + L \frac{\partial M}{\partial H}. \tag{9}$$

To demonstrate that this equality is really satisfied, let us begin to calculate its first term. Therefore, let us ~~imagine to~~ give independent variations δH and $\delta\mu$ to H and μ, leaving λ unchanged; then we will have

$$\delta L = \frac{\partial L}{\partial H} \delta H + \frac{\partial L}{\delta \mu} \delta\mu. \tag{10}$$

On the other hand, from the first of (8), we remark that:

$$\delta L = \frac{1}{\left(\int \frac{r^{2f-1} d\omega}{H_r} \right)^2} \left\{ \left(\int \frac{r^{2f-1} d\omega}{H_r} \right) \delta \int \frac{r^{2f-1} H_\lambda d\omega}{H_r} \right.$$
$$\left. - \left(\int \frac{r^{2f-1} H_\lambda d\omega}{H_r} \right) \delta \int \frac{r^{2f-1} d\omega}{H_r^2} \right\}. \tag{11}$$

In the calculation of the two variations of the integrals within the curly brackets, we can of course interchange symbols δ and $\int$, as the limits of the integral do not change since it is extended to the whole unit hypersphere. Then we have:

$$\delta \int \frac{r^{2f-1} d\omega}{H_r} = (2f-1) \int \frac{r^{2f-2} \delta r d\omega}{H_r} - \int \frac{r^{2f-1} \delta H_r d\omega}{H_r^2}. \tag{12}$$

On the other hand, from the invariance on the unit sphere, one has:

$$\delta H = H_r \delta r + H_\mu \delta\mu$$

wherefrom

$$\delta r = \frac{\delta H}{H_r} - \frac{H_\mu}{H_r} \delta\mu$$

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and also

$$\delta H_r = H_{rr}\delta r + H_{r\mu}\delta\mu = \frac{H_{rr}}{H_r}\delta H + \left(H_{r\mu} - \frac{H_{rr}H_\mu}{H_r}\right)\delta\mu.$$

By substituting in (12) these expressions of δr, δH_r, one finds:

$$\delta\int\frac{r^{2f-1}d\omega}{H_r} = \delta H\left\{(2f-1)\int\frac{r^{2f-2}d\omega}{H_r^2} - \int\frac{r^{2f-1}H_{rr}d\omega}{H_r^3}\right\}$$
$$-\delta\mu\left\{(2f-1)\int\frac{r^{2f-2}H_\mu d\omega}{H_r^2} + \int\frac{r^{2f-1}d\omega}{H_r^2}\left(H_{\mu r} - \frac{H_\mu H_{rr}}{H_r}\right)\right\}.$$

In a similar way one finds:

$$\delta\int\frac{r^{2f-1}H_\lambda d\omega}{H_r} = \delta H\left\{(2f-1)\int\frac{r^{2f-2}H_\lambda d\omega}{H_r^2} + \int\frac{r^{2f-1}H_{\lambda r}d\omega}{H_r^2}\right.$$
$$\left.-\int\frac{r^{2f-1}H_\lambda H_{rr}}{H_r^3}d\omega\right\} + \delta\mu\left\{-(2f-1)\int\frac{r^{2f-2}H_\lambda H_\mu d\omega}{H_r^2}\right.$$
$$\left.+\int\frac{r^{2f-1}d\omega}{H_r}\left(H_{\lambda r} - \frac{H_{\lambda r}H_\mu}{H_r}\right) - \int\frac{r^{2f-1}H_\lambda d\omega}{H_r^2}\left(H_{\mu r} - \frac{H_\mu H_{rr}}{H_r}\right)\right\}.$$

By substituting in (11) these two last expressions, and comparing with (10), one finally finds:

$$\frac{\partial L}{\partial H} = \frac{1}{\left(\int\frac{r^{2f-1}d\omega}{H_r}\right)^2}\left[\left(\int\frac{r^{2f-1}d\omega}{H_r}\right)\left\{(2f-1)\int\frac{r^{2f-2}H_\lambda d\omega}{H_r^2} + \right.\right.$$
$$\left.+\int\frac{r^{2f-1}H_{\lambda r}d\omega}{H_r^2} - \int\frac{r^{2f-1}H_\lambda H_{rr}}{H_r^3}d\omega\right\}$$
$$\left.-\left(\int\frac{r^{2f-1}H_\lambda d\omega}{H_r}\right)\left\{(2f-1)\int\frac{r^{2f-2}d\omega}{H_r^2} - \int\frac{r^{2f-1}H_{rr}d\omega}{H_r^3}\right\}\right].$$

$$\frac{\partial L}{\partial\mu} = \frac{1}{\left(\int\frac{r^{2f-1}d\omega}{H_r}\right)^2}\left[\left(\int\frac{r^{2f-1}d\omega}{H_r}\right)\left\{-(2f-1)\int\frac{r^{2f-2}H_\lambda H_\mu d\omega}{H_r^2}\right.\right.$$
$$\left.+\int\frac{r^{2f-1}d\omega}{H_r}\left(H_{\lambda\mu} - \frac{H_{\lambda r}H_\mu}{H_r}\right) - \int\frac{r^{2f-1}H_\lambda d\omega}{H_r^2}\left(H_{\mu r} - \frac{H_\mu H_{rr}}{H_r}\right)\right\}$$
$$\left.-\int\frac{r^{2f-1}H_\lambda d\omega}{H_r}\left\{(2f-1)\int\frac{r^{2f-2}H_\mu d\omega}{H_r^2} + \int\frac{r^{2f-1}d\omega}{H_r^2}\left(H_{\mu r} - \frac{H_\mu H_{rr}}{H_r}\right)\right\}\right].$$

These two last equations, together with the second of (8), give us all the elements necessary to calculate the first term of (9). Once it has been calculated, it is immediate to recognize from its explicit expression that λ and μ appears symmetrically; then (9) is verified.

Therefore we can conclude that, for the quasi-ergodic systems, the value assumed by the energy at the end of an adiabatic transformation does not depend at all on the intermediate mechanisms of the transformation.

§ 7. - Come back now to ~~be interested in~~ the systems with more than one characteristic. In order that, also for these systems, the final characteristics were independent of the intermediate mechanisms of the transformation, the conditions of unlimited integrability of system (6) should be satisfied. But, if through a calculation, obviously more complicated than that performed in the preceding section but not essentially different from it, we effectively build up these conditions, we find that in general they are not satisfied. Rather than ~~to report~~ here this lengthy calculation, we prefer to show the argument through an example of a system with two characteristics. The example we choose is very similar to another one I have recently used in a note on the principle of adiabatics. From an origin O, we draw in a plane two orthogonal axes x, y. Then we take in the first quadrant two points P, Q and draw the perpendiculars from them to axes (PA, PB, QC, QD). We shall assume that P be internal to the rectangle OCQD. Now let us suppose that inside concave polygon APBDQCA a mass point is moving not acted on by forces and elastically bouncing off the walls of the polygon. Absolute values u, v of the components of the velocity of the point on axes x, y keep evidently constant during the motion, therefore the system has two characteristics. Let us suppose then to keep point Q (of coordinates a, b) fixed and to move point P (of coordinates λ, μ). In this way we shall have accomplished a mechanical system with two characteristics u, v and depending on two parameters λ, μ. By easy arguments, analogous to the ones carried out in the note quoted above, one finds that, changing adiabatically the position of point P, u and v change following the rule:

$$d \log u = \frac{2\mu \, d\lambda}{ab - \lambda\mu}; \quad d \log v = \frac{2\lambda \, d\mu}{ab - \lambda\mu}$$

Obviously none of these two equations is unlimitedly integrable; therefore the values that u and v take at the end of a transformation also depend on the path followed by point P. Then, in general, it is not possible to apply Ehrenfest's principle to systems with more characteristics.

§ 8. - However, some important classes of exceptions to this rule exist. We aim to study them in this section. The first one, and also the most important, is that of the systems with angular coordinates. Of these systems, according to Burgers' theorems, we not only know that Ehrenfest's principle can be applied (in the sense that it leads in any case to definite final conditions) but also that for them the aforesaid principle results to be *verified, by experience* as a logical consequence of Sommerfeld's conditions which are supported by all the theory and the experience made on the hydrogen atom. Another remarkable class of exceptions to the conclusions of § 7 is the following: Let us assume that of the m characteristics of our system only one, the energy, depends explicitly on parameters λ, μ of the mechanism. I say that for these systems, at the end of every adiabàtic transformation, the energy takes a value independent of the intermediate mechanisms, while the other characteristics even stay unchanged. The fact that all the characteristics, but the energy, stay unchanged comes out evident from the circumstance that, since they do not contain the parameters explicitly, stay unchanged in all the elementary processes of the

transformation: the same conclusion can be drawn from system (6) since, if Φ_i is one of these characteristics, one has by hypothesis $\frac{\partial \Phi_i}{\partial \lambda} = \frac{\partial \Phi_i}{\partial \mu} = 0$. For demonstrating that the final value of the energy does not depend on the path followed during the transformation in the plane λ, μ, one could put forward a consideration analogous to that of § 6. But it is easier to remark that, on the basis of the hypothesis, by means of a canonical transformation independent of the parameters, one can try to transform the characteristics independent of the parameters into coordinates of Γ. After this, the consideration of § 6 can be repeated word for word and the constant characteristics simply stand for constant parameter. Systems of this kind occur very frequently in applications; for instance, of this kind are all the systems which have, as only uniform integrals besides the energy (and not dependent on the energy), some integral of the conservation of momentum, or angular momentum, since the latter are always independent of the parameters of the mechanism.

§ 9. - As regards a possible application of what said to the theory of quanta, we remark the following: On the basis of our conclusions, the possibility of an extension of Ehrenfest's principle is ruled out, save the mentioned exceptions. Instead, for quasi-ergodic systems, or the exceptions studied in § 8, such an application is not a priori ruled out, though obviously it is not possible now to foresee if the experience will confirm its results. All the same, one might try if, going on this way, some useful information on the rules for the determination of the quantum orbits of the systems without angular coordinates could be obtained. Of course, Ehrenfest's principle by itself, even if in case the experience should confirm it in this more general application, is not sufficient for the determination of such rules. It only allows us, when we know the selected orbits of a certain system, to deduce the orbits for all the systems which can be obtained from it by means of an adiabatic transformation. Therefore perhaps it might be useful, apart from the complexity of calculations, for finding the quantitative relations between the spark spectra, for instance of the alkaline metals, and the arc spectra of the noble gases. In fact, the systems which emit these spectra only differ in the charge of the nucleus and then can be easily transformed the one into the other.

Göttingen, April 1923.
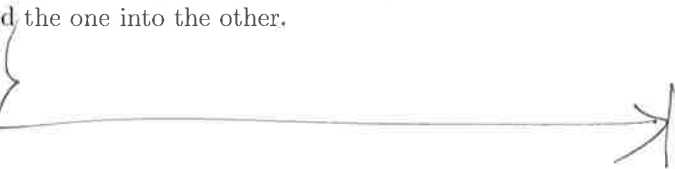
38b) A Theorem of Calculus of probability and Some Applications

"Un teorema di calcolo delle probabilitá ed alcune sue applicazioni,"
Teacher's Diploma Thesis of the Scuola Normale di Pisa.
Presented on June 20, 1922.

§ 1. The theorem we want to deal with concerns the properties of the sums of many incoherent addenda having a known statistical distribution. The fundamental theorem on these sums is due to Laplace[1]. We announce the theorem together with a short account of its demonstration from which we shall start for establishing a new theorem. Let n be a very great number and $y_1, y_2 \ldots y_n$ represent n unknowns, of which we know the statistical distribution; that is, we know that the probability that y_i has a value ranging between y_i and $y_i + dy_i$ is $\varphi_i(y_i)dy_i$, being φ_i a known function for which, obviously

$$\int_{-\infty}^{\infty} \varphi_i(y)dy = 1, \tag{1}$$

which means that y_i has certainly a value between $-\infty$ and $+\infty$. In addition we will assume that the statistical distribution of y_i is not affected by the values that the other y's can assume, that is, we assume the y_i's are completely incoherent among them. Then we take y_i having a vanishing average, that is:

$$\bar{y}_i = \int_{-\infty}^{\infty} y\varphi_i(y)dy = 0. \tag{2}$$

Finally the average of the squared y_i is put as

$$\bar{y}_i^2 = \int_{-\infty}^{\infty} y^2\varphi_i(y)dy = k_i^2 \tag{3}$$

and assume that, for any i, k_i^2 is negligible with respect to $\sum_1^n k_i^2$. Under these assumptions, the Laplace's theorem holds which says that: The probability that inequalities

$$x \leq \sum_1^n y_i \leq x + dx \tag{4}$$

hold at the same time is given by

$$F(x)dx = \frac{1}{\sqrt{2\pi \sum_1^n k_i^2}} e^{-\frac{x^2}{2\sum_1^n k_i^2}} dx. \tag{5}$$

To demonstrate it, we call r a number $\leq n$ and let $F(r, x)dx$ be the probability that inequalities

$$x \leq \sum_1^r y_i \leq x + dx \tag{6}$$

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[1]Théorie analytique des probabilités, Oeuvres, VII, p. 309.

hold true. Now, if p is any value, let us look for the probability that inequalities

$$\sum_1^{r-1} y_i < p < \sum_1^r y_i \qquad (7)$$

hold together, that is, that the addition of y_r to $\sum_1^{r-1} y_i$ does not exceed p. This probability is obviously given by

$$\int_0^\infty d\xi F(r-1, p-\xi) \int_\xi^\infty \varphi_r(y)dy.$$

Analogously, the probability that inequalities

$$\sum_1^{r-1} y_i > p > \sum_1^r y_i \qquad (8)$$

hold together is

$$\int_0^\infty d\xi F(r-1, p+\xi) \int_\xi^\infty \varphi_r(y)dy.$$

The difference of these two probabilities is obviously given by the difference between the probability that $\sum_1^r y_i > p$ and the probability that $\sum_1^{r-1} y_i > p$, that is by

$$\int_p^\infty F(r, x)dx - \int_p^\infty F(r-1, x)dx \quad .$$

Then we have

$$\int_p^\infty F(r, x)dx - \int_p^\infty F(r-1, x)dx = \int_0^\infty d\xi F(r-1, p-\xi) \int_\xi^\infty \varphi_r(y)dy$$

$$- \int_0^\infty d\xi F(r-1, p+\xi) \int_\xi^\infty \varphi_r(y)dy.$$

In the r.h.s. we can reverse the integrations by formulae

$$\int_0^\infty d\xi \int_\xi^\infty dy = \int_0^\infty dy \int_0^y d\xi \quad ; \quad \int_0^\infty d\xi \int_{-\infty}^{-\xi} dy = \int_{-\infty}^0 dy \int_0^{-y} d\xi$$

and it becomes, also changing in the second term ξ with $-\xi$

$$\int_{-\infty}^\infty \varphi_r(y)dy \int_0^y F(r-1, p-\xi)d\xi.$$

We put, as an approximation

$$F(r-1, p-\xi) = F(r-1, p) - \xi \frac{\partial F(r-1, p)}{\partial p}.$$

Thus the above expression becomes

$$F(r-1, p) \int_{-\infty}^\infty \varphi_r(y)dy \int_0^y d\xi - \frac{\partial F(r-1, p)}{\partial p} \int_{-\infty}^\infty \varphi_r(y)dy \int_0^y \xi d\xi$$

$$= F(r-1,p) \int_{-\infty}^{\infty} y\varphi_r(y)dy - \frac{1}{2}\frac{\partial F(r-1,p)}{\partial p} \int_{-\infty}^{\infty} y^2\varphi_r(y)dy$$

i.e., remembering (2) and (3):

$$-\frac{k_r^2}{2}\frac{\partial F(r-1,p)}{\partial p}.$$

In this way we obtain equality

$$\int_p^{\infty} F(r,x)dx - \int_p^{\infty} F(r-1,x)dx = -\frac{k_r^2}{2}\frac{\partial F(r-1,p)}{\partial p}. \tag{9}$$

Differentiating it with respect to p we obtain

$$-F(r,p) + F(r-1,p) = -\frac{k_r^2}{2}\frac{\partial^2 F(r-1,p)}{\partial p^2}. \tag{10}$$

Let us change in it $r-1$ with r, p with x, and, in our approximation, put

$$F(r+1,x) - F(r,x) = \frac{\partial}{\partial r}F(r,x).$$

Then (10) gives, for $F(r,x)$, differential equation

$$\frac{\partial}{\partial r}F(r,x) = -\frac{k_{r+1}^2}{2}\frac{\partial^2}{\partial x}F(r,x). \tag{11}$$

Changing r with the other variable

$$t = \int_0^{r+1} k_i^2 di \tag{12}$$

(11) becomes

$$\frac{\partial F}{\partial t} = \frac{1}{2}\frac{\partial^2 F}{\partial x^2}. \tag{13}$$

Then one has, obviously, the condition that, for any t

$$\int_{-\infty}^{\infty} F dx = 1 \tag{14}$$

and that, for $t=0$, F has a non vanishing value only when $|x|$ is infinitesimal. It is known that these conditions are more than sufficient to determine F. They are satisfied by putting

$$F = \frac{1}{\sqrt{2\pi t}}e^{-\frac{x^2}{2t}}.$$

By giving to t its value, which at our degree of approximation is $\sum_1^r k_i^2$, we find

$$F(r,x) = \frac{1}{\sqrt{2\pi \sum_1^r k_i^2}}e^{-\frac{x^2}{2\sum_1^r k_i^2}}. \tag{15}$$

Then one obviously has $F(x) = F(n,x)$, and then

$$F(x) = \frac{1}{\sqrt{2\pi \sum_1^n k_i^2}}e^{-\frac{x^2}{2\sum_1^n k_i^2}} \qquad \text{q.e.d.}$$

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§ 2. Let us mantain the notations and the assumptions made at the beginning of the previous section and in addition assume that all $\varphi_i(y)$ are equal (as a consequence we will cancel their index). Then let us indicate with a a positive value whatever. Thus we can state the following

Theorem 2.1. *The probability that at least one among the quantities*

$$y_1, y_1 + y_2, y_1 + y_2 + y_3, \ldots, \sum_1^n y_n$$

exceeds a is given by

$$\frac{2}{\sqrt{\pi}} \int_{\frac{a}{\sqrt{2nk^2}}}^{\infty} e^{-x^2} dx$$

provided that a is great enough with respect to k.

In particular, if n tends to infinity, such probability tends to 1, i.e., to certitude. To demonstrate it, let us indicate with $F(r,x)dx (x < a)$ the probability that the inequalities (6) are fulfilled and in addition all r quantities

$$y_1, y_1 + y_2, \ldots, \sum_1^r y_i \tag{16}$$

are lower than a. At the same time, the same arguments of the previous section show us that $F(r,x)$ [still] will satisfy the differential equation (11) which, in this case, can be written as

$$\frac{\partial F}{\partial r} = \frac{k^2}{2} \frac{\partial^2 F}{\partial x^2} \tag{17}$$

The boundary conditions will be changed instead. In fact, we observe that

$$\int_{-\infty}^{a} F(r,x)dx$$

gives the probability that none of quantities (16) exceeds a and then

$$-\int_{-\infty}^{a} F(r+1,x)dx + \int_{-\infty}^{a} F(r,x)dx$$

gives the proability that, because of the addition of y_{r+1}, $\sum_1^r y_i$ arrives at exceeding a. A calculation analogous to that performed in the previous section shows us that this probability is

$$\int_0^{\infty} F(r, a - \xi)d\xi \int_{\xi}^{\infty} \varphi(y)dy$$

i.e., at our degree of approximation, neglecting ξ with respect to a

$$F(r,a) \int_0^{\infty} d\xi \int_{\xi}^{\infty} \varphi(y)dy$$

that is, by reversing the quadratures

$$F(r,a)\int_0^\infty \varphi(y)dy \int_0^y d\xi = F(r,a)\int_0^\infty y\varphi(y)dy.$$

By putting now

$$h = \int_0^\infty y\varphi(y)dy \tag{18}$$

we find

$$\int_{-\infty}^a \{F(r+1,x) - F(r,x)\}\,dx = -hF(r,a).$$

But, at our usual degree of approximation, we can put

$$F(r+1,x) - F(r,x) = \frac{\partial F(r,x)}{\partial r}$$

and the previous equation becomes

$$\frac{\partial}{\partial r}\int_{-\infty}^a F(r,x)dx = -hF(r,a). \tag{19}$$

After all, our unknown function F must fulfill differential equation (17) in interval $-\infty, a$; fulfill equation (19) in extreme a; then it must vanish together with its derivatives in extreme $-\infty$ and, for $r = 0$, have a non-vanishing value only for $|x|$ very small, but with the condition that the area comprised between it and x-axis is 1. It is easy to prove that at least when h is positive, as in our case, these conditions are sufficient to determine F. Therefore, we observe that, by multiplying (17) by dx and integrating it between $-\infty$ and a, one finds

$$\frac{k^2}{2}\left(\frac{\partial F}{\partial x}\right)_a = \frac{\partial}{\partial r}\int_{-\infty}^a F(r,x)dx$$

as a consequence, (19) becomes

$$\frac{k^2}{2h}\left(\frac{\partial F(r,x)}{\partial x}\right)_a + F(r,a) = 0. \tag{19}$$

Then, for our purpose, it is evidently sufficient to prove that, if a function $\Phi(r,x)$ is 0 for $r = 0$ and fulfills equations

$$\frac{\partial \Phi}{\partial r} = \frac{k^2}{2}\frac{\partial^2 \Phi}{\partial x^2} \quad ; \quad \frac{k^2}{2h}\left(\frac{\partial \Phi}{\partial x}\right)_{x=a} + \phi(r,a) = 0 \tag{20}$$

and, for $x = -\infty$, it is always 0, it is certainly identically zero. In fact one has

$$\int_{-\infty}^a \left(\frac{\partial \Phi}{\partial x}\right)^2 dx = \int_{-\infty}^a \frac{\partial}{\partial x}\left(\Phi\frac{\partial \Phi}{\partial x}\right)dx - \int_{-\infty}^a \Phi\frac{\partial^2 \Phi}{\partial x^2}dx$$

that is, owing to (20)

$$\int_{-\infty}^a \left(\frac{\partial \Phi}{\partial x}\right)^2 dx = \left(\Phi\frac{\partial \Phi}{\partial x}\right)_{-\infty}^a - \frac{2}{k^2}\int_{-\infty}^a \Phi\frac{\partial \Phi}{\partial r}dx$$

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$$= \Phi(r,a)\left(\frac{\partial \Phi}{\partial x}\right)_{x=a} - \frac{1}{k^2}\frac{\partial}{\partial r}\int_{-\infty}^{a}\Phi^2 dx = -\frac{2h}{k^2}\Phi^2(r,a) - \frac{1}{k^2}\frac{\partial}{\partial r}\int_{-\infty}^{a}\Phi^2 dx$$

i.e.

$$\int_{-\infty}^{a}\left(\frac{\partial \Phi}{\partial x}\right)^2 dx + -\frac{2h}{k^2}\Phi^2(r,a) + \frac{1}{k^2}\frac{\partial}{\partial r}\int_{-\infty}^{a}\Phi^2(r,x)dx = 0 \ . \tag{21}$$

Let us now suppose that, for some value of r and x, Φ could be different from zero; then for some value $\bar{r}$ of r $\int_{-\infty}^{a}\Phi^2 dx$ would be certainly positive; in addition, since for $r = 0$ is $\phi = 0$, and then $\int_{-\infty}^{a}\Phi^2(0,x)dx = 0$, there will be certainly between zero and $\bar{r}$ some value of r for which $\frac{d}{dr}\int_{-\infty}^{a}\Phi^2(r,x)dx$ is positive. Now, the first two terms in (21) cannot be negative; the first one is, at least in some cases, positive and this is absurd. Then it will certainly be always $\phi(r,x) = 0$. q.e.d.

Granted that, it will be enough for us to find a solution whatever fulfilling the imposed conditions for being sure it is the solution we were looking for. Let us try if our conditions can be satisfied by putting

$$F(r,x) = \frac{1}{k\sqrt{2\pi r}}e^{-\frac{x^2}{2rk^2}} - \frac{1}{k\sqrt{2\pi}}\int_{0}^{r}\frac{u(\rho)e^{-\frac{(a-x)^2}{2(r-\rho)k^2}}}{\sqrt{r-\rho}}d\rho \tag{22}$$

where being $u(\rho)$ a function to be determined. With this position, differential equation (17) and the limit conditions for $x = -\infty$ and $r = 0$ are certainly satisfied. Then it remains to determine $u(\rho)$ so that (19) is also satisfied too. Now, from (22) we have

$$F(r,a) = \frac{1}{k\sqrt{2\pi r}}e^{-\frac{a^2}{2rk^2}} - \frac{1}{k\sqrt{2\pi}}\int_{0}^{r}\frac{u(\rho)d\rho}{\sqrt{r-\rho}}$$

$$\int_{-\infty}^{a}F(r,x)dx = \frac{1}{k\sqrt{2\pi r}}\int_{-\infty}^{a}e^{-\frac{x^2}{2rk^2}}dx - \frac{1}{k\sqrt{2\pi}}\int_{0}^{r}\frac{u(\rho)d\rho}{\sqrt{r-\rho}}\int_{-\infty}^{a}e^{-\frac{(a-x)^2}{2(r-\rho)k^2}}dx$$

$$= \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\frac{a}{k\sqrt{2r}}}e^{-x^2}dx - \frac{1}{2}\int_{0}^{r}u(\rho)d\rho \tag{23}$$

and then

$$\frac{\partial}{\partial r}\int_{-\infty}^{a}F(r,x)dx = -\frac{ae^{-\frac{a^2}{2rk^2}}}{2k\sqrt{2\pi r^3}} - \frac{1}{2}u(r)$$

in this way (19) becomes

$$\frac{e^{-\frac{a^2}{2rk^2}}}{k\sqrt{2\pi r}}\left(h - \frac{a}{2r}\right) = \frac{h}{k\sqrt{2\pi}}\int_{0}^{r}\frac{u(\rho)d\rho}{\sqrt{r-\rho}} + \frac{u(r)}{2} \tag{24}$$

that is an integral equation of second kind for the unknown function $u(\rho)$. In spite of all our efforts, we have not succeeded to solve it exactly: we only have an approximate solution. We shall deal with this in a little while. We want to prove first, without approximations, that one has

$$\int_{0}^{\infty}u(r)dr = 1 \ .$$

Therefore, let ϑ be an arbitrary positive quantity and let us multiplicate both sides of (24) by $\sqrt{\theta}e^{-\theta r}dr$ and integrate then from $r = 0$ to $r = \infty$. One finds

$$\frac{\sqrt{\theta}h}{k\sqrt{2\pi}}\int_0^\infty \frac{e^{-\theta r - \frac{a^2}{2rk^2}}}{\sqrt{r}}dr - \frac{a\sqrt{\theta}}{2k\sqrt{2\pi}}\int_0^\infty \frac{e^{-\theta r - \frac{a^2}{2rk^2}}}{r^{3/2}}dr$$

$$= \frac{h\sqrt{\theta}}{k\sqrt{2\pi}}\int_0^\infty e^{-\theta r}dr\int_0^r \frac{u(\rho)d\rho}{\sqrt{r-\rho}} + \frac{\sqrt{\theta}}{2}\int_0^\infty e^{-\theta r}u(r)dr$$

$$= \frac{h\sqrt{\theta}}{k\sqrt{2\pi}}\int_0^\infty u(\rho)d\rho\int_\rho^\infty \frac{e^{-\theta r}dr}{\sqrt{r-\rho}} + \frac{\sqrt{\theta}}{2}\int_0^\infty e^{-\theta r}u(r)dr$$

$$= \frac{h}{k\sqrt{2}}\int_0^\infty e^{-\theta\rho}u(\rho)d\rho + \frac{\sqrt{\theta}}{2}\int_0^\infty e^{-\theta r}u(r)dr \; .$$

In addition one has

$$\sqrt{\theta}\int_0^\infty \frac{e^{-\theta r - \frac{a^2}{2rk^2}}}{\sqrt{r}}dr = 2\int_0^\infty e^{-x^2 - \frac{a^2\theta}{2k^2x^2}}dx = \sqrt{\pi}e^{-\frac{a\sqrt{2\theta}}{k}} \; .$$

Passing to the limit for $\theta = 0$ the above equation then becomes

$$\frac{h}{k\sqrt{2}} = \frac{h}{k\sqrt{2}}\int_0^\infty u(\rho)d\rho.$$

From which

$$\int_0^\infty u(\rho)d\rho = 1 \qquad\qquad (25)$$

q.e.d.

At this point we already obtain an interesting result. In fact, from (23) we have

$$\lim_{r=\infty}\int_{-\infty}^a F(r,x)dx = \lim_{r=\infty}\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\frac{a}{k\sqrt{2r}}} e^{-x^2}dx - \frac{1}{2}\int_0^\infty u(r)dr = 0 \; . \qquad (26)$$

If we remember the meaning of $F(r,x)$ this result can be read: The probability that at least one of the values (16) exceeds a is continual when r tends to infinity. We remark that this result holds true independently of the approximation we are going to make to solve (24). Let us pass now to the approximate solution of (24). For this we observe that, as one can immediately verify,

$$w(r) = \frac{ae^{-\frac{a^2}{2rk^2}}}{k\sqrt{2\pi r^3}} \qquad\qquad (27)$$

is a solution of the integral equation of the second kind

$$\frac{e^{-\frac{a^2}{2rk^2}}}{k\sqrt{2\pi r}}\left(h + \frac{a}{2r}\right) = \frac{h}{k\sqrt{2\pi}}\int_0^r \frac{w(\rho)d\rho}{\sqrt{r-\rho}} + \frac{1}{2}w(r) \qquad (28)$$

which differs from (24) only in the sign inside the bracket of the left-hand side. Now, owing to the assumptions we have made, whenever r is large enough so that

$e^{-\frac{a^2}{2rk^2}}$ is not too small $a/2r$ is negligible with respect to h and then we shall be allowed to assume $w(r)$ as an approximate solution of (24), by putting

$$u(r) = \frac{ae^{-\frac{a^2}{2rk^2}}}{k\sqrt{2\pi r^3}} \qquad (29)$$

It is easy to check that from (29) it is $\int_0^\infty u(r)dr = 1$. Now, from (23), we get

$$\int_{-\infty}^a F(r,x)dx = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\frac{a}{k\sqrt{2r}}} e^{-x^2}dx - \frac{1}{2}\frac{ae^{-\frac{a^2}{2\rho k^2}}}{k\sqrt{2\pi\rho^3}}d\rho =$$

$$= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\frac{a}{k\sqrt{2r}}} e^{-x^2}dx - \frac{1}{\sqrt{\pi}}\int_{\frac{a}{k\sqrt{2r}}}^\infty e^{-x^2}dx = 1 - \frac{2}{\sqrt{\pi}}\int_{\frac{a}{k\sqrt{2r}}}^\infty e^{-x^2}dx \; .$$

And then

$$1 - \int_{-\infty}^a F(r,x)dx = \frac{2}{\sqrt{\pi}}\int_{\frac{a}{k\sqrt{2r}}}^\infty e^{-x^2}dx \; . \qquad (30)$$

Remembering now the meaning of $F(r,x)$ one immediately realizes that

$$1 - \int_{-\infty}^a F(r,x)dx$$

represents the probability that at least one of the expressions (16) is greater than a. Therefore (30) completely demonstrates the theorem we have enunciated.

§ 3. The theorem just proved can immediately be applied to a famous theorem of calculus of probability: Peter and Paul make a game of chance. In each game each one has probability $1/2$ to win; the stake is always of k lire. Now Peter is infinitely rich, on the contrary Paul owns only a lire. If at a certain moment Peter is able to win all the money from Paul, the latter is ruined and is obliged to stop the game. So we are in the case considered in the above theorem and we can conclude that, after a sufficient number of games Peter will certainly ruin Paul; moreover, if a is much greater than k the probability that this happens in n games is

$$\frac{2}{\sqrt{\pi}}\int_{\frac{a}{k\sqrt{2n}}}^\infty e^{-x^2}dx$$

§ 4. We want now to apply the above theorem to an astronomic problem. Let us consider an elliptic comet which intersects Jupiter's orbit. The cometary orbit will be obviously perturbed by the action of Jupiter, and this particularly when Jupiter and the comet pass very close. Now it may happen that in these continuous transformations the comet's orbit ends by changing into a parabolic or hyperbolic

orbit; then the comet will go away forever escaping from the attraction of Jupiter and the Sun. I want to study what is the probability that this happens in a certain time. As far as I know the theory of the influence of Jupiter on the cometary orbits has never been studied from this point of view; people only dealt with this matter[2] looking for an explanation of the capture of comets with parabolic orbits when passing by chance close to Jupiter. We will make the following simplifying assumptions, the same of the restricted 3-body problem: The comet has a negligible mass, so that it does not perturb nor Jupiter neither the Sun. The mass of Jupiter (m) is negligible with respect to the mass of the Sun (M). In this way we are allowed to assume the Sun as fixed and to consider the orbit of the comet being appreciably perturbed only when passing in the close neighbourhood of Jupiter. Jupiter's orbit is circular. Comet's orbit is coplanar with Jupiter's orbit. We call u the velocity of Jupiter and V the velocity of the comet when it crosses Jupiter's orbit with respect to a reference frame moving along this orbit with velocity u; we indicate with θ the angle between the direction of V and Jupiter's orbit. If v is the absolute velocity of the comet, when it is crossing Jupiter's orbit one will have

$$v^2 = u^2 + V^2 + 2u\text{V}\cos\theta \tag{31}$$

Let us suppose that once, while the comet is crossing Jupiter's orbit, it passes very close this planet. Then it will be affected by a strong perturbation. Let b be the smallest distance between the two bodies if they were not attracted to one another. According to our assumptions, in order that the perturbation is considerable b must be very small if compared with the curvature radii of the two unperturbed orbits so that, during this "collision", the comet will appreciably describe a keplerian hyperbolic orbit during its motion around Jupiter.

§ 5. Thus, let us consider this relative motion, referring to polar coordinates (r, φ) having Jupiter as a pole and the polar axis parallel to the direction of the incoming comet. Since the motion is a Kepler motion, we have

$$\frac{1}{r} = \text{A} - \text{B}\cos(\varphi - \varphi_0) \tag{32}$$

being A, B, φ_0 constant. Moreover, for $\varphi = 0$, r must be infinite, that is

$$\text{A} - \text{B}\cos\varphi_0 = 0 \tag{33}$$

then it must be

$$b = \lim_{r=\infty} r\sin\varphi = \lim_{\varphi=0} \frac{\sin\varphi}{\text{A} - \text{B}\cos(\varphi - \varphi_0)} = -\frac{1}{\text{B}\sin\varphi_0} \tag{34}$$

The areas constant is then evidently Vb and owing to the well-known formulae of the Kepler motion one has

$$\text{A} = \frac{m}{\text{V}^2 b^2} \tag{35}$$

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[2]TISSERAND, ≪*Traité de mécanique céleste*≫, Tome IV, pp. 198-216; CALLANDREAU, ≪Ann. de l'observatoire≫ T. 22; A. NEWTON, ≪Mem. of the Nat. Acad. of Sci.≫, T. 6.

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From (33) and (34) we can now obtain the other two constants. One finds exactly

$$\tan\varphi_0 = -\frac{V^2 b}{m} \quad , \quad B = \frac{1}{b}\sqrt{1 + \frac{m^2}{b^2 V^4}} \qquad (36)$$

Now, let ψ be the angle between the direction of the comet when approaching and its direction when going away. Obviously one will have:

$$\psi = 2\varphi_0 - \pi$$

and then

$$\tan\frac{\psi}{2} = -\cot\varphi_0 = \frac{m}{V^2 b} \qquad (37)$$

We can conclude that the perturbation consists in keeping V unchanged and in altering θ of the angle ψ given by (37). Now it is convenient to calculate the averages of the squares of ψ. Therefore we observe that one has:

$$\psi = 2\arctan\frac{m}{V^2 b}$$

and then

$$\int_{-\infty}^{\infty} \psi^2 db = 4\int_{-\infty}^{\infty}\left(\arctan\frac{m}{V^2 b}\right)^2 db$$

$$= \frac{4m}{V^2}\int_{-\infty}^{\infty}\left(\arctan\frac{1}{x}\right)^2 dx = \frac{8m}{V^2}\int_{0}^{\infty}\left(\arctan\frac{1}{x}\right)^2 dx$$

by putting

$$h = \int_{0}^{\infty}\left(\arctan\frac{1}{x}\right)^2 dx \approx 2.5$$

then one has

$$\int_{-\infty}^{\infty}\psi^2 db = \frac{8mh}{V^2} \qquad (38)$$

Now, b being very small, the probability that its value is comprised between b and $b + db$ is obviously

$$\frac{db}{2\pi R \sin\theta}$$

R being the radius of Jupiter's orbit. The average of the squares of ψ therefore is

$$\bar{\psi}^2 = \int_{-\infty}^{\infty}\psi^2\frac{db}{2\pi R \sin\theta} = \frac{4mh}{\pi R\ V^2 \sin\theta} \qquad (39)$$

§ 6. In its motion around the Sun the energy constant of our comet is given by

$$\frac{v^2}{2} - \frac{M}{R} = W .$$

As it is well known, a Kepler orbit is elliptic, parabolic or hyperbolic according as the energy constant is negative, null or positive; now, remembering (31) we find for our comet:

$$W = \frac{1}{2}\left(u^2 + V^2 + 2uV\cos\theta - 2\frac{M}{R}\right)$$

but since for Jupiter we have the relation:

$$\frac{u^2}{R} = \frac{M}{R^2}$$

we can write

$$2W = V^2 + 2uV\cos\theta - \frac{M}{R} \ .$$

Since in the subsequent perturbations V is not changed and only θ changes, in order that the comet can become hyperbolic it is necessary that W, negative at present, can become positive in correspondence to suitable values of θ. Then it must be

$$V^2 + 2uV > \frac{M}{R}$$

but we remark that

$$u = \sqrt{\frac{M}{R}}$$

therefore the above inequality can be written:

$$\left(V + \sqrt{\frac{M}{R}}\right)^2 > \frac{2M}{R}$$

from which * and reduces at the end to

$$V > \left(\sqrt{2} - 1\right)\sqrt{\frac{M}{R}} = \left(\sqrt{2} - 1\right)u \ . \tag{40}$$

Then we will assume this inequality as certainly fulfilled. Moreover, for some values of θ, W must certainly be negative, otherwise the cometary orbit could not be elliptic; so it will be:

$$V^2 + 2uV < \frac{M}{R}$$

From which as above

$$V > \left(\sqrt{2} + 1\right)\sqrt{\frac{M}{R}} = \left(\sqrt{2} + 1\right)u \ . \tag{41}$$

Therefore let us assume that V fulfil (40) and (41) and indicate with θ_0 that particular value of θ for which the comet's orbit is hyperbolic, i.e. one has $W = 0$, that is

$$V^2 + 2uV\cos\theta_0 = \frac{M}{R}$$

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*Editor's Note: At this point, in the Fermi's manuscript there is a blank line which, obviously, would have contained the expansion of the square of the last formula.

and then

$$\cos\theta_0 = \frac{\frac{M}{R} - V^2}{2uV} = \frac{u^2 - V^2}{2uV}\,. \tag{42}$$

When θ is greater than θ_0, one has $W < 0$ and then the comet describes an elliptic orbit; on the contrary, when θ is less than θ_0 the orbit is hyperbolic.

Now we will suppose that initially the orbit is elliptic and very stretched, so that θ is very close to θ_0, and precisely slightly greater. We call θ^* this initial value. Whenever the comet goes beyond Jupiter's orbit, θ is changed of an amount ψ; the average of the squares of ψ depends indeed on θ, as (39) shows, but since we have supposed that θ remains always very close to θ_0 we can put

$$\bar{\psi^2} = \frac{4mh}{\pi R\,V^2\sin\theta_0} \tag{43}$$

if after a certain time θ became $< \theta_0$ the comet should become hyperbolic and should go away forever. Therefore we are in condition of being able to apply the theorem of §2. Then we must put $a = \theta^* - \theta_0$; $k^2 = \frac{4mh}{\pi R\,V^2\sin\theta_0}$. And the theorem we proved says that: The probability that the comet will be changed in hyperbolic after having crossed n times Jupiter's orbit is:

$$\frac{2}{\sqrt{\pi}}\int_{\frac{\theta^*-\theta_0}{\sqrt{\frac{8mhn}{\pi R\,V^2\sin\theta_0}}}}^{\infty} e^{-x^2}\,dx \tag{44}$$

and then tends to 1 when n tends to infinity. In the strict sense one could object that the above calculations would fail if the value of V were such that, when the orbit is parabolic, the comet took the same time as Jupiter to go from A to B, being A the point where the comet enters Jupiter's orbit, and B the point where it goes out. In Figure 14, S is the Sun, AJB Jupiter's orbit, AKB the orbit of the comet. But it is easy to realize that this case certainly cannot happen if the comet describes its trajectory with direct motion. In fact, if v is the absolute velocity in A of the comet in its parabolic orbit, one has

$$v^2 = u^2 + V^2 + 2uV\cos\theta_0$$

and then from (42)

$$v^2 = 2u^2$$

that is:

$$v > u\,. \tag{45}$$

Now, the velocity of the comet is not constant, but in the whole tract AKB it is always greater than in the extremes A and B, thus inequality (45) holds true with all the more reason in the whole tract AKB. On the other hand, if the motion is direct one has that arc AKB is shorter than arc AJB, and since it is covered with even higher velocity it is certain that the comet will arrive at B before Jupiter. If on the

contrary the motion of the comet were retrograde, and it described for instance the orbit AK'B' in the sense indicated by the arrow one would have

$$\text{arc AK'B'} > \text{arc AJB'}$$

and then, though (45) still holds, it is evident that for a particular value of the parameter of the cometary orbit it can happen that the two heavenly bodies take the same time to go from A to B; of course this can only happen for a particular value of V.

Fig. 1
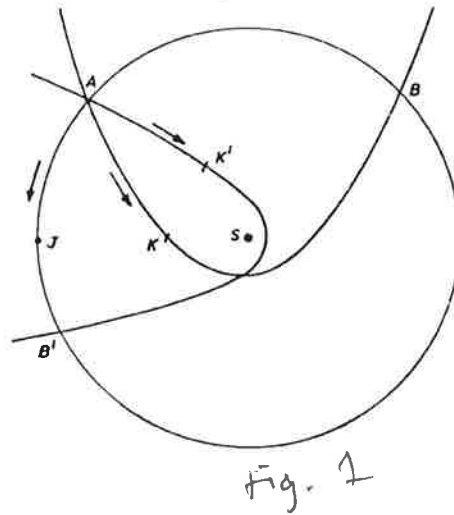
Now if this happened it could occur that the comet, elliptic at first, crossed Jupiter when passing through A and got changed in a parabolic one; but in this case it would meet Jupiter again when passing through B and could in case have a new perturbation which would change it in an elliptic comet again. For this reason we consider this particular value of V ruled out from our calculations.

§ 7. At last we want to consider the possibility that before being changed in hyperbolic the comet can crash into Jupiter and then be destroyed. What is the probability of this event? For this let us look first for the probability that the comet, crossing once Jupiter's orbit, collides with the planet. If we indicate with ρ the sum of the radii of Jupiter and the comet, to have the collision it is necessary that the perihelian distance of Jupiter from the comet, as calculated though the formulae of the Kepler motion is smaller than ρ. Call δ this perihelian distance; from the formulae of §5 it results in

$$\frac{1}{\delta} = A + B$$

and then from (35) and (36)

$$\frac{1}{\delta} = \frac{m}{V^2 b^2} + \frac{1}{b}\sqrt{1 + \frac{m}{V^4 b^2}}$$

If we want the collision occurs it must be $\delta < \rho$ and then

$$\frac{m}{V^2 b^2} + \frac{1}{b}\sqrt{1 + \frac{m}{V^4 b^2}} > \frac{1}{\rho}$$

by multiplying this inequality by the quantity, certainly positive

$$\rho\left(\frac{1}{b}\sqrt{1 + \frac{m}{V^4 b^2}} > \frac{1}{\rho} - \frac{m}{V^2 b^2}\right)$$

we find

$$\frac{\rho}{b^2}\frac{1}{b}\sqrt{1 + \frac{m}{V^4 b^2}} > \frac{1}{\rho} - \frac{m}{V^2 b^2}$$

and summing the last two inequalities

$$\left(\frac{2m}{V^2} + \rho\right)\frac{1}{b^2} > \frac{1}{\rho}$$

wherefrom finally

$$|b| < \sqrt{\rho^2 + \frac{2m\rho}{V^2}} \tag{46}$$

We recall now that the probability that the value of b is comprised between b and $b + db$ is $\frac{db}{2\pi R \sin\theta_0}$ and then probability p that the collision occurs in only one crossing of Jupiter's orbit is given by

$$p = \frac{1}{\pi R \sin\theta_0}\sqrt{\rho^2 + \frac{2m\rho}{V^2}} \tag{47}$$

We will assume p very small, and this obviously is equivalent to consider Jupiter's radius negligible if compared with the radius of its orbit. Let us now look for the probability that the collision occurs at the n-th time the comet crosses Jupiter's orbit. Therefore it is evidently necessary that the collision has not occurred before and the probability of this is obviously $(1 - p)^{n-1}$, that is in our approximation

$$e^{-pn} .$$

That the comet has not yet been changed in hyperbolic; and, having supposed p extremely small, remembering (44) and putting for the sake of brevity:

$$\frac{\theta^* - \theta_0}{\sqrt{\frac{8mh}{\pi R V^2 \sin\theta_0}}} = H$$

we can hold that the probability of this event is given by

$$1 - \frac{2}{\sqrt{\pi}}\int_{\frac{H}{\sqrt{n}}}^{\infty} e^{-x^2}\,dx = \frac{2}{\sqrt{\pi}}\int_0^{\frac{H}{\sqrt{n}}} e^{-x^2}\,dx .$$

And finally that the collision really occurs, for which we have the probability p. After all the probability that the collision occurs the n-th time is

$$\frac{2e^{-pn}p}{\sqrt{\pi}}\int_0^{\frac{H}{\sqrt{n}}} e^{-x^2}\,dx$$

and therefore the probability that the collision occurs ~~h time whatsoever~~ will be the sum of the above expression from $n = 1$ to $n = \infty$, or replacing the sum by an integral

$$\frac{2p}{\sqrt{\pi}} \int_0^\infty e^{-pn} dn \int_0^{\frac{H}{\sqrt{n}}} e^{-x^2} dx \ .$$

In this expression it is convenient to reverse the integration by the formula

$$\int_0^\infty dn \int_0^{\frac{H}{\sqrt{n}}} dx = \int_0^\infty dx \int_0^{\frac{H}{x^2}} dn$$

and in this way one finds for the wanted probability the expression:

$$\frac{2p}{\sqrt{\pi}} \int_0^\infty e^{-x^2} dx \int_0^{\frac{H}{x^2}} e^{-pn} dn = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x^2} \left(1 - e^{-\frac{pH}{x^2}} \right) dx =$$

$$= 1 - \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x^2 - \frac{pH}{x^2}} dx = 1 - e^{-2\sqrt{pH}} \ .$$

The probability that the collision never occurs is then

$$e^{-2\sqrt{pH}} \ .$$

7) Formation of Images with Röntgen Rays

"Formazione di immagini coi raggi Röntgen,"
Nuovo Cimento **25**, *63-68 (1923)*

Röntgen rays do not undergo reflections or refractions, at least in the usual sense of the word, since the reflection of diffraction occurs only under well defined incidence angles. As a consequence in the X-ray optics the problem of obtaining images cannot be solved, as in the ordinary optics, by means of spherical lenses or mirrors. Gouy[*] suggested theoretically a method for obtaining monochromatic images with X-rays, by means of a cylinder of mica. In a few words it is the following. Let us consider a circular cylinder of mica and suppose that in a point of its axis there is a source S of monochromatic Röntgen rays. They will be reflected on the mica in those points where Bragg's relation is fulfilled: these points obviously are on circular sections of the cylinder. And the rays reflected on one of these circles will gather in a point I on the axis, symmetric of S with respect to the plain of the reflecting circle, where one will have a real monochromatic image of S. If S were in the neighborhood of the axis, still an image of it will be formed in the neighborhood of the axis[†]. Suppose now to have, in the neighborhood of the axis, a planar figure from which points monochromatic X-rays come out, and to place a plate in the position where its image is formed. Let r be the mirror-object distance, R the radius of the cylinder of mica, θ the Bragg incidence angle, r' the image-mirror distance. If we project everything on a plane orthogonal to the axis of the cylinder of mica, the projections of r and r' will be $r\cos\theta$, $r'\cos\theta$; and then, according to the usual formulae of the spherical mirrors it will be

$$\frac{1}{r\cos\theta} + \frac{1}{r'\cos\theta} = \frac{2}{r} \ ,$$

from which

$$r' = \frac{Rr}{2r\cos\theta - R} \ .$$

The linear coefficient of enlargement of the segments orthogonal to r and the axis of the cylinder will be

$$\mu_1 = \frac{r'}{r} = \frac{R}{2r\cos\theta - R} \tag{1}$$

If the object is close to the axis we have approximately $\mu_1 = 1$. To calculate the enlargement of the segments parallel to the plane of the axis and of r, let us call φ and φ' the angles that the lines orthogonal to the plane of the object and of the plate form with r and r' respectively. Then one immediately sees that the looked for enlargement is

$$\mu_2 = \frac{\cos\varphi'}{\cos\varphi} \tag{2}$$

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[*]C. R. GOUY, ≪C. R.≫, 161, 176 (1915).

[†]Of course, provided that the cylinder is confined in a region small enough comprised between two generatrices.

Suppose now to photograph an aperture placed orthogonally to the plane of r and the axis by a flat plate of mica of length l. If h is the length of the aperture, the length of its image will be $2l + k$. If instead we bend the mica in order that the image is formed in the focus, the length will become h. The intensities of the two images will be obviously approximately in the inverse ratio of their lengths. Their ratio is then

$$\frac{2l + k}{h}.$$

If, for instance, $h = 1$ cm, $l = 4$ cm the ratio is 9. Then the intensity is almost decupled. I shall now describe the way in which I have actually succeeded in obtaining these images. The source of the rays consisted in a tube of the shape and size approximately indicated in Figure 1. I created the vacuum by a rotational pump Cacciari, type Gaede. Cathode K was concave, with a radius of 6 or 7 cm when one wanted to concentrate the rays on the anticathode as much as possible; if instead one wanted the whole surface of the anticathode be hit by the rays, the cathode was made with a smaller radius. The anticathode was generally of iron and sometimes was cut almost orthogonally to the cathode rays, in order to do without the slit. Instead, in other experiments it was cut as the spout of a flute, in order to present a large surface to the detecting instruments.
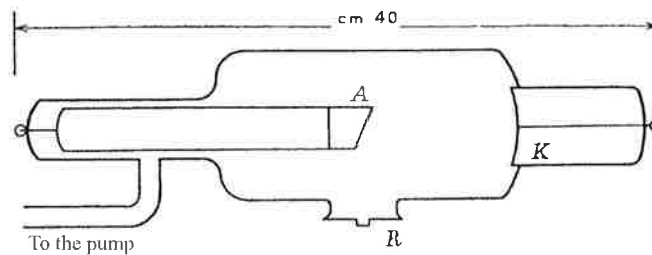

Fig. 1

Since the radiations typical of the iron are largely absorbed by the glass of the bulb, I thought it right to equip the tube with little window of aluminium R. During the work the tube was kept attached to the pump, so that after a short time, it assumed a running regular enough. The tube was driven by a big induction coil with a Wehnelt switch; in ordinary conditions the equivalent spark was 10 or 12 cm long. The tube was contained in a small wooden box sheathed by lead 6 mm thick on the side of the instruments and 3 mm thick on the other side. To obtain fairly precise images it was necessary the reflecting plate of mica be regular as much as possible. Therefore, it was carefully chosen among many samples; nevertheless we have never succeeded in finding plates that, in reflecting the light, were more regular than an ordinary windowpane. This is the cause of the irregularities and smudges we can observe in the reported images. The mica was bended by binding it fast

on a turned brass cylinder. Then a layer of sealing wax (little more than half a centimetre thick) was spread on the convex part. When the sealing wax had cooled, one could remove the fastenings and detach the mirror from the cylinder. In this way I succeeded in obtaining cylindrical mirrors relatively precise given the limit imposed by the natural irregularity of the plates used. They had mostly dimensions of 4×6 cm but usually their aperture was reduced to 4×2 cm^2 for making use of the less irregular parts, which were judged by trying the mirrors by the reflection of the ordinary light. The mirror was mounted on a graduate circle in order to be able to put it right. (The angle of which was turned for the study of the third order of the K_α of the iron was of $16°50'$). The detection of the rays was performed photographically. I carried out first a few experiments of orientation with planar crystals to verify the nature of the anticathode and the intensities of the reflections of the various orders. It resulted that the double K_α $K_{\alpha'}$ ($\lambda = 1.932; 1.928$), scarcely resolvable in the experimental conditions in which it was, the K_β ($\lambda = 1.748$) were emitted. The K_γ was scarcely visible due to the low intensity. The most intense orders were the first and the third. I preferred to work in the third in order not to be obliged to use incidence angles too much close to $90°$. Then I experienced the indicated method of obtain images first on the anticathode which was also working as an aperture. The distances anticathode crystal and crystal image varied from 18 to 22 cm. The exposure lasted about ten minutes.
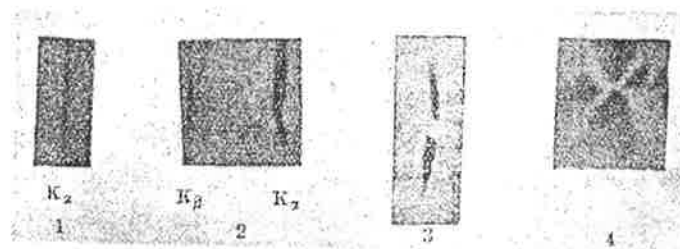

Fig. 2   1-4

I could immediately ascertain the very strong increase of intensity which can be obtained in this way. A rough idea of this is given by Fig. 2-1, and 2-2 which represent two photographs of the 3rd order of iron K_α obtained approximately in the same conditions of exposure and operation of the tube, the first one with flat mica and the second one with curved mica. The increase in intensity was indeed such that, particularly using mirrors of 6 cm of aperture, accustoming a few minutes the eyes to the darkness of the room, it was possible to see clearly the images on a screen of barium platinum cyanide. From Fig. 2-2 it is clearly visible that the emission intensity of the central part of the anticathode, where the cathode rays were concentrated, is considerably greater than that of the side parts. It is possible to see this because the method of images allows to observe the slit "Lockyer's art",

that is, to observe point by point what happens in the slit. To put this more in evidence I made the following experience: I placed before the window of aluminium a leaden thread of about 1 mm of diameter and shifted the photographic plate to carry it in the point where the image of the aluminium window was forming. Fig. 2-3 gives the result of this experiment: in the figure the gap in the image produced by the leaden thread is clearly visible. Finally Fig. 2-4 represents an attempt of obtaining an image of an object in two dimensions. The anticathode of iron was therefore cut as the spout of a flute and two cross shaped furrows were cut in it and inside them two copper wires were driven in order to form a sort of X. In Fig. 2-4, one can see the image of this X, obviously together with several irregularities due to the irregularity of the reflector.

This work was carried out at the Institute of Physics of the University of Pisa in Winter 1922.

30) On the Quantization of an Ideal Monatomic Gas

*"Sulla quantizzazione
del gas perfetto monoatomico,"*
Rend. Lincei 3, 145–149 (1926).

§ 1. – In classical thermodynamics one takes (referring to a single molecule) as specific heat at constant volume of an ideal monatomic gas $c = 3/2k$. However, it is clear that, if one wants to admit the validity of the Nerst principle also in the case of an ideal gas, one must think that the above expression of c is only an approximation valid at high temperatures and that, as a matter of fact, c tends to zero for $T = 0$, so that one can extend up to the absolute zero the integral expressing the value of entropy without the indeterminacy of the constant. And for realizing how such a variation of c can occur, it is necessary to admit that the motions of an ideal gas must be quantized as well. Then one realizes that such a quantization, besides the energy content of the gas, will influence the equation of state as well, thus giving rise to the socalled phenomena of degeneration of the ideal gas at low temperatures.

The purpose of this work is the exposition of a method for carrying out the quantization of an ideal gas which, in our opinion, is as much as possible independent of unjustified hypotheses on the statistical behaviour of the molecules of the gas.[*]

Recently various attempts have been made ~~for arriving~~ to establish an equation of state for the ideal gas.

The formulae given by the various authors differ from ours and from the classical equation of state only for very low temperatures and very high densities; unfortunately these are the same circumstances in which the deviations of the laws of ~~the~~ real gases from the ones of ideal gases are more important; and since, on conditions one can easily carry out experimentally, the deviations from the equation of state $pV = kT$ due to the degeneration of the gas, even if not negligible, are always considerably smaller than those due to the fact that the gas is real and not ideal, the former have been so far hidden by the latter. This does not exclude the possibility that, in a ~~more or less~~ near future, and with a more profound knowledge of the forces which act among the molecules of a real gas, one can pull the two deviations apart, thus arriving to choose experimentally among the different theories of the degeneration of the ideal gases.

§ 2. – ~~For being able~~ In order to be able to carry out the quantization of the motions of ~~the~~ molecules of an ideal gas, one must be ~~in such a condition to be~~ able to apply Sommerffield's rules to their motion; and this can be ~~made~~ done in an infinite number of ways ~~all of which, besides, lead to the same result.~~ One can, for instance, suppose the gas contained in a parallelepiped vessel with elastic walls, quantizing the three fold periodic motion

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[*]See for instance A. Einstein, *Sitzber. d. Pr. Akad. d. Wiss.* **22**, 261 (1924); **23**, 3, 18 (1925); M. Planck, *Sitzber. d. Pr. Akad. d. Wiss.* **23**, 49, (1925).

of the molecule bouncing off the six walls; or, more generally, one can subject the molecules to a system of forces such as their motion becomes periodic and then can be quantized. The hypothesis that the gas is ideal allow us in all these cases to neglect the forces acting among the molecules, so that the mechanical motion of each of them happens as if the other ones should not exist. Nevertheless one can recognize that the mere quantization, following Sommerfield's rules, of the motion of the molecules, considered mutually independent, is not sufficient for obtaining the correct outcomes; since, even if in this case the specific heat tends to zero for $T = 0$, yet his value, besides on temperature and density, comes to depend on the total quantity of gas as well, and tends, at any temperature, to the limit $3/2k$ when, even if the density remains constant, the quantity of gas tends to infinite. Then it appears necessary to admit that some complement to Sommerfield's rules is needed, when calculating systems which, as ours, contain elements indistinguishable between them.[†]

To have a hint on how to formulate the most plausible hypothesis, it is worth to consider how things go in other systems which, as our ideal gas, contain indistinguishable elements; and precisely we want to examine the behaviour of the atoms heavier than hydrogen which all contain more than an electron. If we consider the deep parts of a heavy atom, we are in such conditions that the forces acting among the electrons are very small in comparison with the ones exerted by the nucleus. In these circumstances the mere application of the Sommerfield's rules would lead to expect that, in the normal state of the atom, a considerable number of electrons should lie in an orbit of total quantum number 1. As a matter of fact, instead one sees that the ring K is already saturated when contains two electrons, and likewise the ring becomes saturated when contains 8 electrons, etc. This fact has been interpreted by Stoner,[‡] and in an even still more precise way by Pauli,[§] as follows: let us characterize an electronic orbit possible in a complex atom by means of 4 quantum numbers; n, k, j, m, which have respectively the meanings of total quantum, azimuthal quantum, internal quantum and magnetic quantum. Given the inequalities to which these 4 numbers must satisfy, one finds that, for $n = 1$, only two triplets of values exist of k, j, m: for $n = 2$, there are 8, etc. To realize the above fact, therefore it is sufficient to admit that in the atom two electrons whose orbits are characterized by the same quantum numbers cannot exist; in other words one must admit that an electronic orbit is already "occupied" when contains only one electron.

§ 3. – We Now intend to investigate if such hypothesis can give good outcomes in the problem of the quantization of the ideal gas as well: therefore we shall admit that in our gas almost a molecule whose motion is characterized by certain quantum numbers can exist, and we shall show that this hypothesis leads to a

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[†]E. Fermi, *N. Cimento* 1, 145 (1924).
[‡]E. C. Stoner, *Phil. Mag.* 48, 719 (1924).
[§]W. Pauli, *Zs. f. Phys.* 31, 765 (1925).

perfectly consequent theory of the quantization of the ideal gas, and in particular it gives reasons for the expected decrease of the specific heat at low temperatures, and leads to the exact value for the constant of entropy of the ideal gas.

Putting off the publication of the mathematical details of the present theory to a next occasion, in this Note we limit ourselves to expose the principles of the method we have followed and the results obtained.

First of all we must put our gas in such a condition that the motion of its molecules results to be quantizable. As we have seen, this can be made in an infinity of ways; but, since the result is independent of the particular way one adopts, we shall choose the most convenient for the calculation; and precisely we shall admit that our molecules are attracted by a fixed point O, with a force proportional to the distance r of the molecule from O; so that each molecule will be a spatial harmonic oscillator whose frequency we call ν. The orbit of the molecule will be characterized by three quantum numbers, s_1, s_2, s_3, which are linked to its energy through the relation

$$w = h\nu(s_1 + s_2 + s_3) = sh\nu . \tag{1}$$

Then the energy of a molecule can take all the values integer multiple of $h\nu$, and the value $sh\nu$ can be assumed $Q = \frac{1}{2}(s+1)(s+2)$ ways.

Therefore the zero energy can be realized in only one way, the energy $h\nu$ in 3 ways, the energy $2h\nu$ in 6 ways, etc. To realize the influence of our hypothesis, i.e. that to given quantum numbers can correspond only one molecule, let us consider the extreme case of N molecules to the absolute zero. At this temperature the gas must lie in the state of minimum energy. If we had no limitation to the number of molecules which can have a certain energy, all the molecules would lie in the state of zero energy, and all the three quantum numbers of each of them would be zero. On the contrary, as provided by our hypothesis, the existence of more than one molecule with all the three quantum numbers equal to zero is forbidden; therefore if $N = 1$, the only one molecule will occupy the place of zero energy; if instead $N = 4$, one of the molecules will occupy the place of zero energy, and the other three the place of energy $h\nu$; if $N = 10$, one of the molecules will occupy the place of zero energy, three of them the places of energy $h\nu$, and the remaining six the six places of energy $2h\nu$, etc. Now let us assume that we can distribute the total energy $W = Eh\nu$ ($E =$ integer) among our molecules; and call $N_s \leq Q_s$ the numbers of molecules of energy $sh\nu$. We find easily that the most probable values of N_s are

$$N_s = \frac{\alpha Q_s}{e^{\beta s} + \alpha} , \tag{2}$$

where α and β are constants depending on W and N. To find the relation between these constants and the temperature, we observe that, as a consequence of the attraction toward O, the density of our gas will be a function of r, which must tend to zero for $r = 8$. Accordingly, for $r = 8$ the phenomena of degeneration must cease, and in particular the distribution of velocities, easily deducible from

(2), must change into Maxwell law. Thus one finds that it must be

$$\beta = \frac{h\nu}{kT} \, . \tag{3}$$

Now we are able to deduce from (2) the function $n(L)dL$, which represents, for a given value of r, the density of the molecules of energy between L and $L+dL$ (analogous to the Maxwell law), and from this we can deduce the mean kinetic energy $\bar{L}$ of the molecules at distance r, which is a function, besides ~~of the~~ temperature, of the density n as well. One finds precisely

$$\bar{L} = \frac{3h^2 n^{2/3}}{4\pi m} P\left(\frac{2\pi mkT}{h^2 n^{2/3}}\right) \, . \tag{4}$$

In (4) we have called $P(x)$ a function, of a bit complicated analytic definition, which for values of x either very large or very small, can be calculated through the asymptotic formulae

$$P(x) = x\left(1 + \frac{1}{2^{5/2} x^{3/2}} + \dots\right) \, ;$$

$$P(x) = \frac{1}{5}\left(\frac{9\pi}{2}\right)^{1/3}\left[1 + \frac{5}{9}\left(\frac{4\pi^4}{3}\right)^{1/3} x^2 + \dots\right] \, . \tag{5}$$

To deduce from (4) the equation of state, we apply the virial relation. Then we find that the pressure is given by

$$p = \frac{2}{3} n\bar{L} = \frac{h^2 n^{5/3}}{2\pi m} P\left(\frac{2\pi mkT}{h^2 n^{2/3}}\right) \, . \tag{6}$$

At the limit for high temperatures, that is for small degeneration, the equation of state ~~takes then~~ the form

$$p = nkT\left[1 + \frac{1}{16}\frac{h^3 n}{(\pi mkT)^{3/2}} + \dots\right] \, . \tag{7}$$

Then the pressure result higher than the one coming from the classical equation of state. For an ideal gas having the atomic weight of the helium, at the temperature of absolute 5° and at pressure of 10 atmospheres, the difference would be 15%. From (4) and (5) one can also deduce the expression of the specific heat for low temperatures. One finds

$$c_v = \left(\frac{16\pi^8}{9}\right)^{1/3} \frac{mk^2}{h^2 n^{2/3}} + \dots \tag{8}$$

Likewise we can find the absolute value of entropy. Carrying out the calculations, at high temperatures one finds

$$S = \int_0^T \frac{1}{T} d\bar{L} = n\left[\frac{5}{2}\log T - \log p + \log\frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3}\right] \, , \tag{9}$$

which coincides with the value of entropy given by Tetrode and Stern.

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43) A Statistical Method for the Determination of Some Properties of the Atom (*)

"Un metodo statistico per la determinazione di alcune proprietà dell'atomo,"
*Rend. Lincei **6**, 602–607 (1927).*

The purpose of this work is to show some results about the distribution of electrons in a heavy atom which can be obtained dealing with these electrons, given their great number, using a statistical method; or in other words, considering them as a gas formed by electrons surrounding the nucleus.

Naturally this gas of electrons comes to find itself in a state of complete degeneracy, so much so that we cannot deal with it using classical statistics; on the contrary we must use the form of statistics proposed by the author (†) and based on the application of Pauli's exclusion principle to the theory of gas. This has the effect that the kinetic energy of the electrons, in the conditions in which they come to find themselves inside the atom, actually turns out to be bigger than it would have been according to the principle of equipartition of energy and practically independent of the temperature, at least as long as it does not go beyond certain limits.

In this Note we shall show first of all how the distribution of electrons around the nucleus can be calculated statistically; and based on this we shall then calculate the necessary energy to ionize completely the atom, that is to tear off all the electrons from it. The calculation of the distribution of electrons around the nucleus also allows the determination of the behavior of the potential at various distances from the nucleus and therefore to know the electric field in which the electrons of the atom come to find themselves. I hope to be able to show in a future work the application of this to the approximate calculation of the binding energies of single electrons and to some questions about the structure of the periodic system of elements.

To determine the distribution of electrons, we must first of all search for the relation between their density and the electric potential at every point. If V is the potential, the energy of an electron will be $-eV$ and therefore according to classical statistics, the density of electrons would have to ~~then~~ be proportional to $e^{eV/kT}$. But, according to the new statistics, the relation between density and temperature is the following one:

$$n = \frac{(2\pi m k T)^{3/2}}{h^3} F(\alpha e^{eV/kT}) \tag{1}$$

where α is constant for the whole gas; the function F in our case (complete degeneracy), has the asymptotic expression

$$F(A) = \frac{4}{3\sqrt{\pi}} (\log A)^{3/2}. \tag{2}$$

Then in our case we find

$$n = \frac{2^{7/2}\,\pi m^{3/2}\, e^{3/2}}{3h^3} v^{3/2} \tag{3}$$

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where

$$v = V + \frac{kT}{e} \log \alpha \qquad (4)$$

represents the potential, apart from an additional constant. Now we observe that since in our case we are dealing with a gas of electrons, we must take into account the fact ($\ddagger$) that the statistical weight of the electron is 2 (corresponding to the two possibilities for the orientation of the spinning electron); and so for the density of electrons we must ~~actually~~ take a value equal to twice the value (3); namely we have:

$$n = \frac{2^{9/2}\,\pi m^{3/2}\,e^{3/2}}{3h^3} v^{3/2} \;. \qquad (5)$$

If in our case classical statistics were valid, we would have the average kinetic energy of the electrons $= \frac{3}{2}kT$. On the contrary according to the new statistics it turns out to be

$$L = \frac{3}{2}kT\,G(\alpha e^{eV/kT})/F(\alpha e^{eV/kT})$$

where G represents a function that, in the case of complete degeneracy, takes the asymptotic expression

$$F(A) = \frac{8}{15\sqrt{\pi}}(\log A)^{5/2}.$$

Therefore we find for our case

$$L = \frac{3}{5}\,ev \;. \qquad (6)$$

Now we observe that the electric density at a point is evidently given by $-ne$ so the potential v satisfies the equation

$$\Delta v = 4\,\pi\,ne = \frac{2^{13/2}\,\pi^2 m^{3/2}\,e^{5/2}}{3h^3} v^{3/2} \;. \qquad (7)$$

Since in our case it will then evidently be only a function of the distance r from the nucleus; then (7) can be written

$$\frac{d^2 v}{dr^2} + \frac{2}{r}\frac{dv}{dr} = \frac{2^{13/2}\,\pi^2 m^{3/2}\,e^{5/2}}{3h^3} v^{3/2} \;. \qquad (8)$$

If we indicate by Z the atomic number of our atom we shall evidently have

$$\lim_{r=0} rv = Ze \qquad (9)$$

$$\int n d\tau = 4\pi \int_0^\infty r^2 \, n dr = Z \qquad (d\tau = \text{volume element}) \;.$$

$\ddagger$ W. PAULI, *Zs. f. Phys.* **41**, 81 (1927).

This last equation, taking into account (5) can be written:

$$\frac{2^{13/2}\pi^2 m^{3/2} e^{5/2}}{3h^3} \int_0^\infty v^{3/2} r^2 dr \; = \; Ze \; . \tag{10}$$

So the potential v will be obtained searching for a function which satisfies Eq. (8) with the two conditions (9) and (10).

To simplify the search for v we change the variables r, v into two others x, ψ proportional to them, setting

$$r = \mu x \qquad , \qquad v = \gamma \psi \tag{11}$$

where we have

$$\mu = \frac{3^{2/3}\, h^2}{2^{13/3}\, \pi^{4/3}\, me^2\, Z^{1/3}} \qquad , \qquad \gamma = \frac{2^{13/3}\, \pi^{4/3}\, mZ^{4/3}\, e^3}{3^{2/3}\, h^2} \; . \tag{12}$$

Equations (8), (9) and (10) thus become

$$\begin{cases} \psi'' + \frac{2}{x}\, \psi' = \psi^{3/2} \\[2mm] \lim_{x=0} x\psi = 1 \\[2mm] \int_0^\infty \psi^{3/2} x^2 dx = 1 \; . \end{cases} \tag{13}$$

These equations simplify further by setting

$$\varphi = x\psi \; . \tag{14}$$

Indeed they become

$$\begin{cases} \varphi'' = \varphi^{3/2}/\sqrt{x} \\[2mm] \varphi(0) = 1 \\[2mm] \int_0^\infty \varphi^{3/2} \sqrt{x}dx = 1 \; . \end{cases} \tag{15}$$

It is easy to see that the last condition is certainly satisfied if φ goes to zero for $x = \infty$. So it remains only to search for a solution to the first of (15), with the conditions at its limits $\varphi(0) = 1$, $\varphi(\infty) = 0$.

Since I did not succeed in finding the general integral of the first of (15), I have solved it numerically. The graph in Figure 1 represents $\varphi(x)$; for x close to zero we have

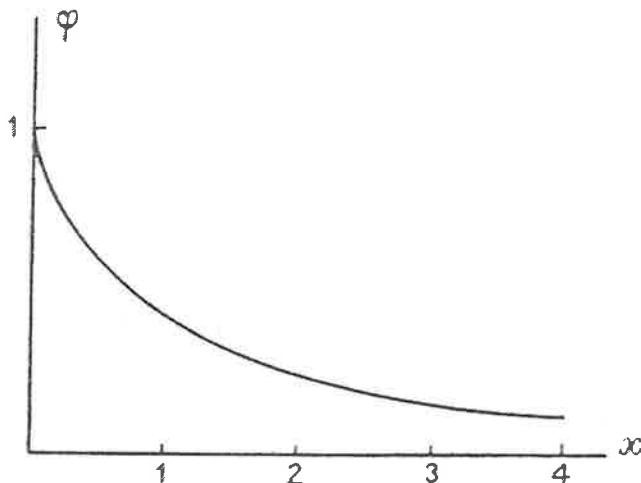$$\varphi(x) = 1 - 1.58\, x + \frac{4}{3}\, x^{3/2} + ... \tag{16}$$

Fig. 1

Thus the problem of the determination of the electric potential of the atom at a fixed distance from the nucleus is solved. Its result is given by

$$v = \gamma \frac{\varphi(x)}{x} = \frac{\gamma\mu}{r}\varphi(x) = \frac{Ze}{r}\varphi\left(\frac{r}{\mu}\right) \ . \tag{17}$$

So we can therefore say that the potential at every point is equal to that produced by an effective charge

$$Ze\,\varphi\left(\frac{r}{\mu}\right) \ .$$

Now we move on to calculate the total energy of the atom; this should be calculated as the sum of the kinetic energy of all the electrons and the potential energy of the nucleus and electrons. However, it is easier taking into account the fact that in an atom the total energy is equal, except for the sign, to the kinetic energy (which anyway in our case can be verified with an easy calculation). Thus we have

$$W = -\int L\,nd\tau$$

and taking into account (5), (6), (11), (12), (14) we find

$$W = -\frac{3}{5}\int_0^\infty r^2\,nv\,dr = -\frac{2^{13/3}3^{1/3}\pi^{4/3}me^4Z^{7/3}}{5h^2}\int_0^\infty \frac{\varphi^{5/2}}{\sqrt{x}}\,dx \ .$$

The last integral can be evaluated taking into account that φ satisfies (15) and (16); one finds

$$\int_0^\infty \frac{\varphi^{5/2}}{\sqrt{x}}\,dx = -\frac{5}{7}\left(\frac{d\varphi}{dx}\right)_{x=0} = \frac{5}{7}\,1.58$$

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and therefore we have

$$W = -1.58 \frac{2^{13/3}3^{1/3}\pi^{4/3}me^4 Z^{7/3}}{7h^2} = -1.58 \frac{2^{1/3}3^{1/3}}{7\pi^{2/3}} Rh \, Z^{7/3}$$

that is

$$W = -1.54 \, Rh Z^{7/3} \tag{18}$$

where by R we indicate Rydberg's number, so that $-Rh$ is the energy of the fundamental state of hydrogen.

(18) gives us the necessary energy to tear off from an atom all its electrons. Naturally given the statistical criteria which it has been deduced from, it begins to be valid only for considerable values of Z; in fact we find that for hydrogen (18) gives $W = -1.54 \, Rh$, while we actually have $W = -Rh$; the discrepancy is thus 54%. For helium the energy to produce complete ionization is obviously equal to the sum of the ionization energies of He and He$^+$; so we have

$$-W = (1.8 + 4) \, Rh = 5.8 \, Rh$$

but from the theory we obtain $1.54 \cdot 2^{7/3} = 7.8 \, Rh$; therefore the discrepancy in this case comes down to 35%. For the elements immediately following helium (Li, Be, B, C), nearly all of the atomic energy is due only to the two K electrons (for carbon about 86%) so the statistical method of course must still certainly give considerable discrepancies. For C in fact we still find a discrepancy close to 34%.

But we must expect that for elements of considerable atomic weight, the discrepancies between the statistical theory and empirical data are very much reduced; unfortunately the data is lacking for a precise comparison and we can base ourselves only on a rough valuation of the shield numbers for various orbits; such an evaluation, however, shows much better agreement.

80a) An Attempt at a Theory of β Rays

"Tentativo di un a teoria dei raggi β,"
Nuovo Cimento **11**, 1–19 (1934)

ABSTRACT

A quantitative theory of the emission of β rays is proposed in which the existence of the "neutrino" is assumed and the emission of electrons and neutrinos in β decay is treated in a way similar to the one followed in the theory of radiation for describing the emission of a quantum of light from an excited atom. We deduce the formulas for the lifetime and for the shape of the continuous spectrum of β rays and compare them with experimental data.

1. The fundamental hypotheses of the theory

In the attempt to construct a theory of the nuclear electrons and the emission of β rays, one encounters, as is known, two principal difficulties. The first depends on the fact that the primary β rays are emitted from nuclei with a continuous velocity distribution. If we do not want to abandon the energy conservation principle, we are obliged to admit that a fraction of the energy which is released in the process of β decay escapes our present possibilities of observation. According to Pauli's proposal one can for instance assume the existence of a new particle, the so-called "neutrino", having vanishing electric charge and mass on the order of magnitude of the electron mass or less. Thus we assume that in any β process are simultaneously emitted an electron, which is detected as a ray, and a neutrino which eludes the observation carrying a part of the energy away. In the present theory, we shall adopt the neutrino hypothesis.

A second difficulty for a theory of nuclear electrons depends on the fact that the present relativistic theories of the light particles (electrons or neutrinos) do not give a satisfactory explanation for the possibility that these particles are bound in orbits of nuclear size.

Consequently it seems more appropriate to agree with Heisenberg[*] and assume that all nuclei consist only of heavy particles, protons and neutrons. Then with the aim of understanding the possibility of emission of β rays, we will attempt to construct a theory of the emission of light particles from a nucleus in analogy with the theory of the emission of a quantum of light from an excited atom in the usual process of radiation. In the theory of radiation, the total number of the light quanta is not constant; the quanta are created when being emitted from an excited atom

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[*]W. HEISENBERG, *Zs. für Phys.* **77**, 1 (1932); E. MAJORANA, *Zs. für Phys.* **82**, 137 (1933).

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and disappear when absorbed. In analogy with that we will try to establish the theory of β rays on these assumptions:

(a) The total number of electrons and neutrinos is not necessarily constant. Electrons (or neutrinos) can be created or destroyed. On the other hand this possibility has no analogy with the possibility of the creation or destruction of an electron-positron pair; in fact if we interpret a positron as a Dirac "hole", we can simply consider this latter process as a quantum jump of an electron from a state of negative energy to a state of positive energy, conserving the total number (infinitely large) of the electrons.

(b) The heavy particles, neutron and proton, can be considered, following Heisenberg, as two different internal states of the heavy particle. We shall formulate this fact by introducing an internal coordinate ρ of the heavy particle, which can assume only two values: $\rho = + 1$, if the particle is a neutron; $\rho = - 1$, if the particle is a proton.

(c) The Hamiltonian function of the overall system, consisting of heavy and light particles, must be chosen so that every transition from neutron to proton be accompanied by the creation of an electron and a neutrino; and the inverse process, transformation of a proton into a neutron, be accompanied by the disappearance of an electron and a neutrino. It must be remarked that in this way the conservation of the electric charge is assured.

2. The operators of the theory

§ 2. A mathematical formalism which allows us to construct a theory in agreement with the three points of the preceding section can be easily constructed by using the method of Dirac-Jordan-Klein[†] called "the method of second quantization." Then we shall consider the probability amplitudes ψ and φ of the electrons and neutrinos in ordinary space, and their complex conjugates ψ^* and φ^* as operators; while for describing the heavy particles we shall use the usual representation in configuration space, in which obviously also ψ will be considered as a coordinate.

We introduce first two operators Q and Q^* which operate on the functions of the two-valued variable ρ as the linear substitutions

$$Q = \begin{vmatrix} 0 & 1 \\ 0 & 0 \end{vmatrix} \; ; \qquad Q^* = \begin{vmatrix} 0 & 0 \\ 1 & 0 \end{vmatrix} . \tag{1}$$

One immediately realizes that Q determines the transitions from proton to neutron, and Q^* the inverse transitions from neutron to proton.

[†]Cf. e.g. P. JORDAN and O. KLEIN, *Z. für Phys.* **45**, 751 (1927); W. HEISENBERG, *Ann. d. Phys.* **10**, 888 (1931).

The meaning of the probability amplitudes ψ and φ interpreted as operators is, as we know, the following. Let

$$\psi_1 \psi_2 \ldots \psi_s \ldots$$

be a system of individual quantum states of the electrons. Then put

$$\psi = \sum_s \psi_s a_s \; ; \qquad \psi^* = \sum_s \psi_s^* a_s^* \; . \tag{2}$$

The amplitudes a_s and the conjugate complex quantities a_s^* are operators which act on the functions of the occupation numbers $N_1, N_2, \ldots, N_s, \ldots$ of the individual quantum states. If the Pauli principle holds, each of the N_s can assume only one of the values 0, 1; and the operators a_s and a_s^* are defined as follows:

$$a_s \Psi \; (N_1, N_2, \ldots, N_s, \ldots)$$
$$= (-1)^{N_1 + N_2 + \ldots + N_{s-1}} \left(1 - N_s\right) \Psi \left(N_1, N_2, \ldots, 1 - N_s, \ldots\right) \tag{3}$$
$$a_s^* \Psi \; (N_1, N_2, \ldots, N_s, \ldots)$$
$$= (-1)^{N_1 + N_2 + \ldots + N_{s-1}} \left(1 - N_s\right) \Psi \left(N_1, N_2, \ldots, N_s, \ldots\right) \; .$$

The operator a_s^* determines the creation, while the operator a_s determines the disappearance of an electron in the quantum state s.

Corresponding to (2), for the neutrinos we shall set:

$$\varphi = \sum \varphi_\sigma b_\sigma \qquad ; \qquad \varphi^* = \sum \varphi_\sigma^* b_\sigma^* \; . \tag{4}$$

The conjugate complex operators b_σ and b_σ^* operate on the functions of the occupation numbers $M_1, M_2, \ldots, M_\sigma, \ldots$ of the individual quantum states $\varphi_1, \varphi_2, \ldots, \varphi_\sigma, \ldots$ of the neutrinos. If we assume that the Pauli principle also holds for these particles, the numbers M_σ can only assume the two values 0, 1; and one has

$$b_\sigma \; \Phi \; (M_1, M_2, \ldots, M_\sigma, \ldots)$$
$$= (-1)^{M_1 + M_2 + \ldots + M_{\sigma-1}} \left(1 - M_\sigma\right) \Phi \left(M_1, M_2, \ldots, 1 - M_\sigma, \ldots\right) \tag{5}$$
$$b_\sigma^* \; \Phi \; (M_1, M_2, \ldots, M_\sigma, \ldots)$$
$$= (-1)^{M_1 + M_2 + \ldots + M_{\sigma-1}} \left(1 - M_\sigma\right) \Phi \left(M_1, M_2, \ldots, M_\sigma, \ldots\right) \; .$$

The operators b_σ and b_σ^* determine the disappearance and the creation of a neutrino in the state σ, respectively.

The Hamiltonian function

( )

[§ 3.] The energy of the overall system constituted by the heavy and the light particles is the sum of the energy H_{hea} of the heavy particles + the energy H_{lig} of the light particles + the interaction energy $\mathcal{H}$ between the light and heavy particles.

Limiting ourselves for the sake of simplicity to consider only the heavy particle, we shall write the first term in the form

$$H_{\mathrm{hea}} = \frac{1+\rho}{2}\mathcal{N} + \frac{1-\rho}{2}\mathcal{P} \tag{6}$$

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in which $\mathcal{N}$ and $\mathcal{P}$ are the operators which represent the energy of the neutron and the proton. We notice in fact that, for $\rho = +1$ (neutron), (6) reduces to $\mathcal{N}$; while for $\rho = -1$ (proton) it reduces to $\mathcal{P}$.

To write the energy H_{lig} in the simplest way, we shall consider the quantum states ψ_s and φ_σ of the electrons and neutrinos to be stationary states. For the electrons we shall take the eigenfunctions in the Coulomb field of the nucleus (conveniently shielded in order to take into account the action of the atomic electrons); for the neutrinos we simply shall take De Broglie plane waves, since possible forces acting on neutrinos are certainly very weak. Let $H_1, H_2, \ldots, H_s, \ldots$ and $K_1, K_2, \ldots, K_\sigma, \ldots$ be the energies of the stationary states of the electrons and the neutrinos; then we shall have

$$H_{\text{lig}} = \sum_s H_s N_s + \sum_\sigma K_\sigma M_\sigma \ . \tag{7}$$

There still remains to write the interaction energy. It consists first of the Coulomb energy between proton and electrons; however, in the case of heavy nuclei the attraction exercised by only a proton has no importance[‡] and in any case does not contribute in any way to the process of β decay. In order not to uselessly complicate the problem, we shall neglect this term. We must instead add a term to the Hamiltonian such that it satisfies the condition c) of § 1.

A term which necessarily joins the transformation of a neutron into a proton with the creation of an electron and a neutrino has, according with the results of § 2, the form

$$Q^* a_s^* b_\sigma^* \tag{8a}$$

while the conjugate complex operator

$$Q a_s b_\sigma \tag{8b}$$

joins together the inverse processes (transformation of a proton into a neutron and disappearance of an electron and a neutrino).

An interaction term satisfying the condition c) will then have the following form

$$\mathcal{H} = Q \sum_{s\sigma} c_{s\sigma} a_s b_\sigma + Q^* \sum_{s\sigma} c_{s\sigma}^* a_s^* b_\sigma^* \ , \tag{9}$$

where $c_{s\sigma}$ and $c_{s\sigma}^*$ are quantities which may depend on the coordinates, the momenta, etc. of the heavy particle.

A further determination of $\mathcal{H}$ must necessarily follow the principle of greatest simplicity; in any case the choices for $\mathcal{H}$ are restricted by the fact that $\mathcal{H}$ must be invariant with respect to a change of coordinates and moreover it must also satisfy momentum conservation.

If at first we neglect spin and relativistic effects, the simplest choice for (9) is the following

$$\mathcal{H} = g \left[Q \psi(x) \varphi(x) + Q^* \psi^*(x) \varphi^*(x) \right] \ , \tag{10}$$

[‡]The Coulomb attraction due to the many other protons must obviously be taken into account as a static field.

where g is a constant with dimensions $L^5 M T^{-2}$; x represents the coordinates of the heavy particle; ψ, φ, ψ^*, φ^* are given by (2) and (4) and must be evaluated at the position x, y, z of the heavy particle.

Obviously (10) is not the only possible choice for $\mathcal{H}$; any scalar expression as

$$L(p)\psi(x)M(p)\varphi(x)N(p) + \text{compl. conj.}$$

where $L(p)$, $M(p)$, $N(p)$, represent convenient functions of the momentum of the heavy particle, would have been admissible. On the other hand, since until now the consequences of (10) have been in agreement with experience, there is no need to resort to more complicated expressions.

On the contrary, it is essential to generalize (10) in such a way to be able to treat relativistically at least the light particles. Of course, ~~also~~ in this generalization, it does not seem possible to eliminate all arbitrariness. However, the most natural solution of the problem appears to be the following: Relativistically we have, in place of ψ and φ, two sets $\psi_1\psi_2\psi_3\psi_4$ and $\varphi_1\varphi_2\varphi_3\varphi_4$ of four Dirac functions. Let us consider the 16 independent bilinear combinations of $\psi_1\psi_2\psi_3\psi_4$ and $\varphi_1\varphi_2\varphi_3\varphi_4$. When the frame of reference undergoes a Lorentz transformation, the 16 bilinear combinations undergo a linear substitution which gives a representation of the Lorenz group. In particular the four bilinear combinations

$$
\begin{aligned}
A_0 &= -\psi_1\varphi_2 + \psi_2\varphi_1 + \psi_3\varphi_4 - \psi_4\varphi_3 \\
A_1 &= \psi_1\varphi_3 - \psi_2\varphi_4 - \psi_3\varphi_1 + \psi_4\varphi_2 \\
A_2 &= i\psi_1\varphi_3 + i\psi_2\varphi_4 - i\psi_3\varphi_1 - i\psi_4\varphi_2 \\
A_3 &= -\psi_1\varphi_4 - \psi_2\varphi_3 + \psi_3\varphi_2 + \psi_4\varphi_1
\end{aligned}
\tag{11}
$$

transform like the components of a four-vector, that is like the components of the electromagnetic four-potential. Then it is natural to introduce in the Hamiltonian of the heavy particle the four quantities

$$g\left(QA_i + Q^*A_i^*\right)$$

in a situation corresponding to that of the components of the four-potential. Here we run into a problem depending on the fact that we do not know a relativistic wave equation for the heavy particles. However, in the case in which the velocity of the heavy particle is small compared to c, one can limit oneself to the term corresponding to eV (V the scalar potential) and write

$$\mathcal{H} = g\left[Q\left(-\psi_1\varphi_2 + \psi_2\varphi_1 + \psi_3\varphi_4 - \psi_4\varphi_3\right) + Q^*\left(\psi_1^*\varphi_2^* + \psi_2^*\varphi_1^* + \psi_3^*\varphi_4^* - \psi_4^*\varphi_3^*\right)\right] .\tag{12}$$

To this term one must add other ones of the order of magnitude v/c. At the moment, however, we shall neglect these terms, since the velocities of the neutrons and protons inside the nuclei are in general small compared to c (Cf. § 9).

In matrix language, (12) can be written

$$\mathcal{H} = g\left[Q\bar{\psi}^*\delta\varphi + Q^*\bar{\psi}\delta\varphi^*\right] .\tag{13}$$

where ψ and φ are meant as matrices with one column and the symbol $\sim$ transforms a matrix into its transposed conjugate; and moreover

$$\delta = \begin{vmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{vmatrix} . \tag{14}$$

With this notation, one finds by comparing (12) with (9)

$$c_{s\sigma} = g\tilde{\psi}_s^* \delta\varphi_\sigma \; ; \qquad c_{s\sigma}^* = g\tilde{\psi}_s \delta\varphi_\sigma^* \; , \tag{15}$$

where ψ and φ represent the four-component normalized eigenfunctions of the states s of the electron and σ of the neutrino, considered as functions of the position x, y, z occupied by the heavy particle.

4. The perturbation matrix

With the Hamiltonian we have established one can develop a theory of β decay in complete analogy with the theory of radiation. In that theory, as is known, the Hamiltonian consists of the sum: Energy of the atom + Energy of the radiation field + Interaction between atom and radiation; the latter term is considered as a perturbation of the other two. Analogously we shall take

$$H_{\text{hea}} + H_{\text{lig}} \tag{16}$$

as the unperturbed Hamiltonian. The perturbation is represented by the interaction term (13).

The quantum states of the unperturbed system can be enumerated in the following way:

$$(\rho, n, N_1, N_2 \ldots N_s \ldots, M_1, M_2 \ldots M_\sigma \ldots) \; , \tag{17}$$

where the first number ρ takes one of the values ± 1 and indicates if the heavy particle is a neutron or a proton. The second number n indicates the quantum state of the neutron or the proton. For $\rho = +1$ (neutron) let the corresponding eigenfunction be

$$u_n(x) \; , \tag{18}$$

while for $\rho = -1$ (proton) let the eigenfunction be

$$v_n(x) \; . \tag{19}$$

The other numbers $N_1, N_2 \ldots N_s \ldots, M_1, M_2 \ldots M_\sigma \ldots$ can only take the values 0, 1 and indicate what states of the electrons and neutrinos are occupied.

By an examination of the general form (9) of the perturbation energy, one immediately realizes that it has nonvanishing matrix elements only for transitions in

which either the heavy particle passes from neutron to proton, while in the meantime one electron and one neutrino are created, or viceversa.

Through (1), (3), (5), (9), (18), (19) one easily finds that the corresponding matrix element is

$$\mathcal{H} \, {}^{1nN_1N_2...0_sM_1M_2...0_\sigma...}_{-1mN_1N_2...1_sM_1M_2...1_\sigma...} = \pm \int v_m^* c_{s\sigma}^* u_n d\tau \; , \tag{20}$$

where the integration must be extended over the entire configuration space of the heavy particle (with the exception of the coordinate ρ); the $\pm$ sign means more precisely

$$(-1)^{N_1+N_2+...+N_{s-1}+M_1+M_2+...M_{\sigma-1}}$$

and in any case does not enter into the calculations that will follow. To the inverse transition corresponds a matrix element which is the conjugate complex of (20).

Taking (15) into account, (20) becomes

$$\mathcal{H} \, {}^{1n0_s0_\sigma}_{-1m1_s1_\sigma} = \pm \int v_m^* u_n \tilde{\psi}_s \delta \varphi_\sigma^* d\tau \; , \tag{21}$$

where for the sake of brevity in the left-hand side we have omitted writing all the indexes which do not change.

5. Theory of β decay

A β decay consists of a process in which a nuclear neutron transforms into a proton, while at the same time, in the way we have described, an electron, which is observed as a β particle, and a neutrino are emitted. To calculate the probability of this process, we shall assume that, at the time $t = 0$, a neutron is in a nuclear state of eigenfunction $u_n(x)$, and furthermore the electron state s and the neutrino state σ are free, that is $N_s = M_\sigma = 0$. Then for $t = 0$ we shall put the probability amplitude of the state $(1, n, 0_s, 0_\sigma)$ equal to 1, that is

$$a_{1,n,0_s,0_\sigma} = 1 \; , \tag{22}$$

whereas we shall put the probability amplitude of the state $(-1, m, 1_s, 1_\sigma)$, in which the neutron has been transformed into a proton with eigenfunction $v_m(x)$ emitting an electron and a neutrino in the states s and σ initially equal to zero.

By applying the usual formulas of perturbation theory, for a time short enough to still consider (22) approximately valid one finds

$$\dot{a}_{-1,m,1_s,1_\sigma} = -\frac{2\pi i}{h} \mathcal{H} \, {}^{1n0_s0_\sigma}_{-1m1_s1_\sigma} e^{\frac{2\pi i}{h}(-W+H_s+K_\sigma)t} \; , \tag{23}$$

where W stands for the difference in energy between the neutron state and the proton state.

By integrating (23) we obtain (since for $t = 0$, $a_{-1m_1s_1\sigma} = 0$)

$$a_{-1m_1s_1\sigma} = -\mathcal{H}\,{}^{1n_0s_0\sigma}_{-1m_1s_1\sigma}\, \frac{e^{\frac{2\pi i}{h}(-W+H_s+K_\sigma)t} - 1}{-W + H_s + K_\sigma} \ . \tag{24}$$

The probability of the transition we consider is then

$$|a_{-1m_1s_1\sigma}|^2 = 4 \left| \mathcal{H}\,{}^{1n_0s_0\sigma}_{-1m_1s_1\sigma} \right|^2 \frac{\sin^2 \frac{\pi t}{h}(-W + H_s + K_\sigma)}{(-W + H_s + K_\sigma)^2} \ . \tag{25}$$

To calculate the lifetime of the neutron state u_n it is necessary to sum (25) with respect to all unoccupied states of the electrons and neutrinos. A strong reduction of this sum can be obtained by observing that the De Broglie wave length for electrons or neutrinos having energies of some millions of volts is much larger than the nuclear sizes. Thus one can, as a first approximation, consider the eigenfunctions ψ_s and φ_σ to be constants inside the nucleus. Thus (21) becomes

$$\mathcal{H}\,{}^{1n_0s_0\sigma}_{-1m_1s_1\sigma} = \pm g\tilde{\psi}_s \delta\varphi_\sigma^* \int v_m^* u_n d\tau \ , \tag{26}$$

where here and below ψ_s and φ_σ are meant to be taken in the nucleus (Cf. § 8). From (26) we draw:

$$\left| \mathcal{H}\,{}^{1n_0s_0\sigma}_{-1m_1s_1\sigma} \right|^2 = g^2 \left| \int v_m^* u_n d\tau \right|^2 \tilde{\psi}_s \delta\varphi_\sigma^* \tilde{\varphi}_\sigma^* \tilde{\delta}\psi_\sigma \ . \tag{27}$$

States σ of the neutrino are characterized by their momentum p_σ and by the spin direction. If, for the convenience of normalization, we quantize inside a volume Ω, whose size later on will be made to tend to infinity, the normalized neutrino eigenfunctions are Dirac plane waves having density $1/\Omega$. Then simple algebraic considerations allow us to perform in (27) an average with respect to all the orientations of p_σ and of the spin. (And in this only the states of positive energy must be considered; the negative energy states must be eliminated through a device like the Dirac hole theory.) One finds

$$\overline{\left| \mathcal{H}\,{}^{1n_0s_0\sigma}_{-1m_1s_1\sigma} \right|^2} = \frac{g^2}{4\Omega} \left| \int v_m^* u_n d\tau \right|^2 \left(\tilde{\psi}_s \psi_s - \frac{\mu c^2}{K_\sigma} \tilde{\psi}_s \beta \psi_s \right) \ , \tag{28}$$

where μ is the rest mass of the neutrino and β the Dirac matrix

$$\beta = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix} \tag{29}$$

By observing that the number of positive energy neutrino states with momentum between p_σ and $p_\sigma + dp_\sigma$ is $8\pi\Omega p_\sigma^2 dp_\sigma/h^3$, that furthermore $\partial K_\sigma/\partial p_\sigma$ is the neutrino velocity for the state σ, and finally that (25) has a strong maximum for the value of p_σ for which there is no variation of the unperturbed energy, that is

$$-W + H_s + K_\sigma = 0 \ , \tag{30}$$