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1957

Physica XXIII
441–480

THE APPROACH TO EQUILIBRIUM IN QUANTUM STATISTICS

A PERTURBATION TREATMENT TO GENERAL ORDER

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Synopsis

The approach of a quantum system to statistical equilibrium under the influence of a perturbation is described by a well known transport equation, now often called master equation (see (1.1) hereunder). This equation holds only when the perturbation is taken into account to lowest non-vanishing order. It has been stressed in a recent paper that certain characteristic properties of the perturbation, easily seen to hold for actual systems (crystals, gases), play an essential role in determining the irreversible nature of the effects described by (1.1). On the basis of these properties it was possible to derive the lowest order master equation from the Schrödinger equation by making one assumption only, relative to the phases of the wave function at the initial time. In contrast with the usual derivation which assumes the phases to be random at all times, the method just mentioned is capable of extension to higher orders in the perturbation. This extension is carried out in the present paper. The essential results are the establishment of a generalized master equation valid to arbitrary order in the perturbation, and the proof that the long time behaviour of its solution corresponds to establishment of microcanonical equilibrium (the latter being taken for the total hamiltonian, perturbation included). The generalized master equation exhibits with its lowest order version the essential difference that it corresponds to a non-markovian process. The transition from the exact master equation to its lowest order approximation is discussed in detail. It illustrates the existence of two time scales, a short one and a long one, for very slow irreversible processes, as well as their overlapping in the case of faster processes.

1. *Introduction.* We have studied in a previous paper [1]), to be referred to hereafter as A, the transport equation describing the approach to statistical equilibrium of a quantum system under the influence of a small perturbation. This equation, the form of which is well known

$$\mathrm{d}P_\alpha/\mathrm{d}t = \Sigma_\beta(W_{\alpha\beta}P_\beta - W_{\beta\alpha}P_\alpha), \tag{1.1}$$

involves the probability distribution P_α of the system over groups of eigenstates of the unperturbed hamiltonian H and expresses its irreversible time evolution under the action of the perturbation. It holds only to lowest order in the perturbation. Following recent practice we shall call it the

master equation, thus avoiding possible confusion with transport equations of the Boltzmann type.

The first derivation of (1.1), given long ago by Pauli [2]), was based on the assumption that, when the total wave function is expanded in the eigenstates of H, the coefficients have *at all times* randomly distributed phases. As shown in A, this assumption, the unsatisfactory nature of which is obvious, can be avoided and replaced by an assumption on the wave function *at one initial time* (either randomness of phases or some other condition as stated in A) if one properly takes into account that the system has a very large number of degrees of freedom and that the perturbation satisfies certain special properties responsible for its irreversible effects and easily recognized on the systems met with in applications (gases, crystals, etc.). The formalism developed in A, while rather different from the one customary in quantum statistics, is better suited to the situation at hand because it gives a simple form to the relevant mathematical consequences of the facts just mentioned. With its help it was an elementary matter to derive the master equation from the Schrödinger equation under the conditions assumed for the initial value of the wave function.

While the assumption of random phases at all times can be used despite its unsatisfactory nature to derive the master equation to lowest order in the perturbation, it is strictly speaking incompatible with the Schrödinger equation itself, and would therefore be a completely erroneous starting point for an attempt at extending the master equation to higher order. The method used in A on the contrary, being rigorously correct, opens the possibility to solve this rather natural problem of deriving a generalized master equation valid to arbitrary order in the perturbation. Such a generalized master equation is obtained and analyzed in the present paper [3]).

A detailed description of the special properties of the hamiltonian, unperturbed part and perturbation, is given in the next section. Section 3 defines the quantity P, the time-dependence of which is to be expressed by the master equation, and discusses its physical significance for the time evolution of the quantum-mechanical system. The mathematical derivation of the master equation, eq. (4.31), is given in Section 4, to general order in perturbation. The following section shows how the general master equation reduces for small perturbations to the customary form (1.1). In Section 6 a detailed mathematical analysis is given for the asymptotic behaviour of the quantity P at long times. In Section 7, on the basis of proper assumptions on the symmetry of the transition rate matrix and the interconnection of states, it is established for finite but not too large perturbations that the long time limit of P is in accordance with the predictions of microcanonical ensemble theory, the microcanonical distribution being taken for the total hamiltonian, perturbation included.

The mathematical derivations carried out in Sections 4 to 7 are not simple.

Although we have relied more than once on earlier publications, the developments needed to derive the transport equation and to analyse its consequences are of considerable complication and length. In a number of places we have tried to alleviate their abstract character by inserting comments of a more physical nature. To help further the reader who likes to follow the general arguments by applying them to an example, we have considered briefly in the appendix, in its simplest form, a system composed of Bloch electrons and lattice vibrations (phonons) in a perfect crystal. Using the data of the appendix one can illustrate the various definitions and results of the general treatment.

2. *The hamiltonian and the basic representation.* We are interested in quantum-mechanical many-particle systems with a hamiltonian $H + \lambda V$ split into two parts. The first part, H, is assumed to give an essentially complete separation of variables and would therefore, taken alone, produce no approach to thermodynamical equilibrium. The perturbation λV (λ is a dimensionless parameter characterizing its size) mixes the many degrees of freedom left uncoupled by H and is entirely responsible for the irreversible behaviour. As examples we may quote non-conducting crystals (H contains then the harmonic part of the forces and λV is the potential of the anharmonic forces), the electron-phonon system in metals (H describes the free harmonic vibrations of the lattice and the conduction electrons in the periodic field of the ions at their equilibrium positions, the electron-phonon interaction is the perturbation), quantum gases (λV is here the potential of the intermolecular forces) etc.

In all such examples, considering the limiting case of a large system of given density (number of particles N and volume Ω tending to infinity with a constant ratio N/Ω), one finds a natural description of the unpertubed stationary states (eigenstates of H) in terms of elementary plane wave excitations. By the generic name excitation we understand phonons in crystals, phonons and electrons in metals, particles in gases, etc. Each of these excitations is characterized by a wave vector and possibly a polarization or spin index. The components of the wave vector vary by steps of order of magnitude $\Omega^{-\frac{1}{3}} \sim N^{-\frac{1}{3}}$ and behave consequently in the limit of a large system as continuous quantum numbers, while the unperturbed energy becomes a continuous function of them. Polarization or spin indices remain of course discrete.

This occurrence of continuous quantum numbers and the continuous nature of the unperturbed energies are the most important features through which the very large size of the system manifests itself in the properties of the unperturbed hamiltonian. We postulate them generally and simplify matters a little by leaving out of consideration all discrete quantum numbers like polarization or spin indices. The unperturbed hamiltonian is

thus assumed to have a complete set of eigenstates $|\alpha\rangle$, each of which is characterized by a collection α of quantum numbers (the quantum numbers of all excitations present) behaving as continuous variables in the limit of a large system. α may contain an infinity of such quantum numbers since an infinity of excitations may be simultaneously present. The corresponding eigenvalue $\varepsilon(\alpha)$, defined by

$$H\,|\alpha\rangle = |\alpha\rangle\,\varepsilon(\alpha) \tag{2.1}$$

is assumed to be continuous in all the quantum numbers in α. We further normalize $|\alpha\rangle$ in such a manner that $\langle\alpha \mid \alpha'\rangle$ becomes, in the limit of a large system, a product of δ-functions for all variables involved. We write accordingly

$$\langle\alpha \mid \alpha'\rangle = \delta(\alpha - \alpha'). \tag{2.2}$$

How this normalization must be carried out in practice can be found in the appendix.

As for the perturbation λV, the fact that it always extends over the whole system implies in the limit $N \to \infty$ *) remarkable analytical properties of its matrix elements in the $|\alpha\rangle$-representation. These properties are best recognized in practical examples by expressing V for large but finite systems in terms of emission and absorption operators of free excitations and going then over to an infinite system. We describe these properties hereunder in general terms. It is useful to check them in simple cases, e.g. by means of the equations in the appendix. In certain cases the first property holds only after parts of the diagonal matrix elements $\lambda\,\langle\alpha|\,V\,|\alpha\rangle$ have been incorporated in the unperturbed hamiltonian H.

Property (i): Take the matrix element $\langle\alpha \mid V| \alpha'\rangle$ for those states α and α' for which it is not identically zero (i.e. for α and α' differing by the few excitations absorbed or emitted by V) and consider it for those states as function of all distinct quantum numbers contained in α and α'. In the limit of a large system this function exhibits a δ-singularity. This singularity expresses overall conservation of momentum (or wave vector). It does not imply a δ-singularity in the difference $\varepsilon(\alpha) - \varepsilon(\alpha')$.

Property (ii): Take a higher order matrix element of the type $\langle\alpha\,|VA_1V\ldots A_nV|\,\alpha'\rangle$ where $A_1, \ldots A_n$ are diagonal operators in the $|\alpha\rangle$-representation

$$A_j\,|\alpha\rangle = |\alpha\rangle\,A_j(\alpha). \tag{2.3}$$

Assume each eigenvalue $A_j(\alpha)$ a smooth function of all quantum numbers involved in α. Consider this matrix element for those states α, α' for which it is not identically zero and regard it as function of all distinct quantum numbers in α and α'. In the limit of a large system, this function exhibits

*) By this limit we always understand $N \to \infty, \Omega \to \infty$ with finite density N/Ω.

singularities of δ-type originating from the singularities in $\langle\alpha''|V|\alpha'''\rangle$. In addition to the δ-factor expressing overall conversation of momentum (or wave vector) further δ-singularities may occur. They are caused by the fact that the number of intermediate states over which one has to sum when calculating (for a finite system) the expression

$$\langle\alpha|VA_1V\ldots A_nV|\alpha'\rangle = \sum_{\alpha_1\ldots\alpha_n}\langle\alpha|V|\alpha_1\rangle A(\alpha_1)\langle\alpha_1|V|\alpha_2\rangle\ldots A(\alpha_n)\langle\alpha_n|V|\alpha'\rangle$$

may be larger by one or more factors N (or Ω) when α is in a special relation to α' than otherwise. The number of such factors always turns out to be one third of the number of relations between quantum numbers in α and α'. Since each quantum number (being a momentum component of an excitation) varies with steps of order $N^{-\frac{1}{3}}$, one gets precisely a δ-singularity when the limit $N \to \infty$ is taken. Higher singularities are never obtained. An important point is now the following. Among all δ-singularities which are thus possible, none except one implies the equality of the unperturbed energies of initial and final states, i.e. implies a δ-singularity in the difference $\varepsilon(\alpha) - \varepsilon(\alpha')$. The only exception is the δ-singularity obtained when the state α and the state α' are identical, i.e. when α and α' have the same number of excitations present and these excitations all have the same quantum numbers. In other words, it is a singularity in $\delta(\alpha - \alpha')$. That such a singularity involves a $\delta[\varepsilon(\alpha) - \varepsilon(\alpha')]$-factor is obvious. This particular singularity plays a central role in the dynamics of the system and we split the matrix element $\langle\alpha|VA_1V\ldots A_nV|\alpha'\rangle$ in a term containing it and a rest term

$$\langle\alpha|VA_1V\ldots A_nV|\alpha'\rangle = \delta(\alpha - \alpha')F_1(\alpha) + F_2(\alpha, \alpha'). \tag{2.4}$$

The term $\delta(\alpha - \alpha')\,F_1(\alpha)$ is called the *diagonal part* of the matrix element, and we call diagonal part of the operator $VA_1V\ldots A_nV$ the operator $\{VA_1V\ldots A_nV\}_d$ defined by

$$\{VA_1V\ldots A_nV\}_d|\alpha\rangle = |\alpha\rangle F_1(\alpha). \tag{2.5}$$

The rest term $F_2(\alpha, \alpha')$ has no $\delta(\alpha - \alpha')$-singularity, nor has it any δ-singularity implying $\varepsilon(\alpha) = \varepsilon(\alpha')$.

Property (iii): All what has just been said on the matrix element $\langle\alpha|VA_1\,V\ldots A_nV|\alpha'\rangle$ holds of course also for the partial matrix elements $\langle\alpha|VA_jVA_{j+1}V\ldots A_kV|\alpha'\rangle$ with $1 \leqslant j \leqslant k \leqslant n$. Since the latter are involved in the calculation of the former, one sees that the δ-singularities present in the latter will have to be taken into account when calculating the former by summation over intermediate states. In this summation (still for a finite system)

$$\langle\alpha|VA_1V\ldots A_nV|\alpha'\rangle = \sum_{\alpha_1\ldots\alpha_n}\langle\alpha|V|\alpha_1\rangle A(\alpha_1)\ldots\langle\alpha_n|V|\alpha'\rangle, \tag{2.6}$$

the singularities of $\langle\alpha_{j-1}|VA_jV\ldots A_kV|\alpha_{k+1}\rangle$ manifest themselves as follows (we assume $1 \leqslant j \leqslant k \leqslant n$, $k - j < n - 1$ and put $\alpha_0 = \alpha$, $\alpha_{n+1} = \alpha'$):

when the state α_{j-1} is taken in some special relation to the state α_{k+1}, the number of intermediate states α_j, α_{j+1} ... α_k becomes larger by a power of N compensating exactly the decrease in the number of possible choices of the pair α_{j-1}, α_{k+1}. We need not consider all possible situations of that kind. The only inportant ones for our purpose are those corresponding to the diagonal parts of partial matrices $\langle\alpha_{j-1}|VA_jV \ldots A_kV|\alpha_{k+1}\rangle$, i.e. to their $\delta(\alpha_{j-1} - \alpha_{k+1})$-singularities. Their effect in the summation (2.6) is simply that the partial sum obtained by putting $\alpha_{j-1} = \alpha_{k+1}$ gives even when $N \to \infty$ a contribution of the same order of magnitude as the remaining part of the sum. More generally, non-negligible contributions are obtained by simultaneous consideration of diagonal parts of several submatrices, i.e. from partial summations in (2.6) where several pairs of intermediate states are kept equal

$$\alpha_{j_1-1} = \alpha_{k_1+1}, \alpha_{j_2-1} = \alpha_{k_2+1}, \ldots (j_r \leqslant k_r, \quad r = 1, 2, \ldots). \tag{2.7}$$

A very important point is now that such a pairing of intermediate states only produces (for $N \to \infty$) a non-negligible contribution when no two pairs are interlocked, i.e. when no relation of the form

$$j_r - 1 < j_s - 1 < k_r + 1 < k_s + 1 \qquad (r, s = 1,2 \ldots) \tag{2.8}$$

holds. This is our property (iii). Just as the other properties it must be verified in all practical cases. The general reason for its validity can be stated as follows: the transitions contributing to the diagonal part of $\langle\alpha_{j-1}|VA_jV \ldots$ $\ldots A_kV|\alpha_{k+1}\rangle$ involve emission and reabsorption of excitations (or of holes in a sea of excitations) and one has to sum over a large number ($\sim N$) of states of these virtual excitations in order to get a non-vanishing contribution for $N \to \infty$. Therefore, in the case of interlocking diagonal parts as in (2.8), the state α_{k_r+1} cannot be kept identical to the state α_{j_r-1} because it involves the additional excitations (or holes) contributing to the diagonal part of $\langle\alpha_{j_s-1}|VA_{j_s}V \ldots A_{k_s}V|\alpha_{k_s+1}\rangle$. In order for simultaneous diagonal parts (2.7) to contribute, their relative positions have to be given by one of the equations

$$j_r - 1 < k_r + 1 \leqslant j_s - 1 < k_s + 1 \tag{2.9}$$

or

$$j_r - 1 < j_s - 1 < k_s + 1 < k_r + 1 \text{ *)} \tag{2.10}$$

We have described the special properties exhibited by the perturbation in the limit of a large system, as they can be verified in the actual examples and as they are needed for the development of the general theory. They essentially amount to the occurrence of diagonal parts in operator products $VA_1V \ldots A_nV$, as expressed in (2.4). The latter equation must be understood

*) The cases $j_r - 1 = j_s - 1 < k_s + 1 < k_r + 1$ and $j_r - 1 < j_s - 1 < k_s + 1 = k_r + 1$ reduce to the case (2.9) by a change of notation.

as expressing the relevant asymptotic properties of the matrix element $\langle \alpha | VA_1V \ldots A_nV | \alpha' \rangle$ for $N \to \infty$. The δ-function symbolizes the occurrence of a definite additional power of N in the value of the matrix element when α is identical to α'. One should always realize that both $F_1(\alpha)$ and $F_2(\alpha, \alpha')$ may still depend on N. In many applications these quantities actually have a complicated asymptotic behaviour for $N \to \infty$. As recently shown by Hugenholtz for systems near their groundstate, this behaviour is amenable to a thorough analysis leading to a neat separation of the effects of the perturbation in size-dependent and size-independent ones, in agreement with the physical expectations [4]). These questions, however, may be left out of consideration for our present purpose which is to establish to general order in λV a statistical equation for the approach to equilibrium. All we have to know concerning the asymptotic behaviour of matrix elements is expressed in (2.4).

As most readers will have observed, all what has been said until now on the hamiltonians of many-particle systems of quantum statistics applies as well to those of quantized fields in interaction. For this case diagonal parts of operators $VA_1V \ldots A_nV$ (V being the interaction between fields) correspond to the well known self-energy diagrams of the Feynman-Dyson theory, taken however not only for one-particle states but for general states (lower δ-singularities would correspond for example to vertex diagrams). The role played by the number of particles N or the volume Ω of the many-body system is taken over for fields by the volume of the large box in which one conventionally imagines them to the enclosed. We have shown in two previous papers [5]), to be referred to as I and II, how for fields the properties mentioned above imply the physical (self-energy and cloud) effects most characteristic of their interactions. While the occurrence of such effects has long been intuitively clear and the explicit calculation of self-energies is well known, most existing theoretical treatments circumvent the explicit consideration of cloud effects.

Despite the similarities between the hamiltonians, the many-particle systems of statistical mechanics have evidently a physical behaviour very different from interacting fields: the essential property we expect them to exhibit is a general tendency to approach thermodynamical equilibrium, i.e. an essentially dissipative type of motion, whereas nothing of that sort is to be found in the usual field-theoretical situations. The analogy between the hamiltonians is therefore not complete. One essential difference must be present, determining the dissipative or non-dissipative character of the motion under the influence of the perturbation. This difference has already been mentioned in I (section 4) and will be discussed at greater length hereafter. While I and II dealt with the non-dissipative case, the present paper is mainly concerned with the dissipative one.

A number of the results obtained in I, mainly those of Sections (I.2) and

(I. 3) *), will be used hereafter. They follow, as shown in I, from the properties of the hamiltonian listed above. Besides using the concept of diagonal part of a product $VA_1V \ldots A_nV$ (with $A_1, \ldots A_n$ diagonal in the $|\alpha\rangle$-representation), they rely on the concept of irreducible diagonal part. Its definition is the following. Consider the contribution to the matrix element (2.6) which is obtained when each submatrix $\langle\alpha_{j-1}|VA_jV \ldots A_kV|\alpha_{k+1}\rangle$, $(1 \leqslant j \leqslant k \leqslant n,\ k - j < n - 1, \alpha_0 = \alpha, \alpha_{n+1} = \alpha')$ is taken with neglection of its diagonal part, i.e. is taken for $\alpha_{j-1} \neq \alpha_{k+1}$. For $N \to \infty$ this contribution to (2.6), considered as function of α and α', can be separated in a part involving a $\delta(\alpha - \alpha')$-singularity and a part involving at most weaker singularities. Let us write this separation in analogy to (2.4),

$$\delta(\alpha - \alpha')F_1'(\alpha) + F_2'(\alpha, \alpha').$$

We call $\delta(\alpha - \alpha')\, F_1'(\alpha)$ the *irreducible diagonal part* of the matrix element $\langle\alpha|VA_1V \ldots A_nV|\alpha'\rangle$, and we define the irreducible diagonal part $\{VA_1V \ldots A_nV\}_{id}$ of the operator $VA_1V \ldots A_nV$ in analogy to (2.5) by

$$\{VA_1V \ldots A_nV\}_{id}|\alpha\rangle = |\alpha\rangle\, F_1'(\alpha).$$

It is also useful to define the *non-diagonal part* $\{VA_1\, V \ldots A_nV\}_{nd}$ of the operator $VA_1V \ldots A_nV$. It is the operator, the matrix elements of which are obtained by keeping in (2.6) *all states* $\alpha, \alpha_1, \ldots \alpha_n, \alpha'$ different from each other, the value of the matrix element for $\alpha = \alpha'$ being defined as the limit of its value for $\alpha \neq \alpha'$ when $\alpha' \to \alpha$.

The extension of these concepts to operators of the form $A_0VA_1V \ldots$ $\ldots A_nVA_{n+1}$ with all A's diagonal **), and to sums of such operators, is obvious and can be found in I, p. 907.

3. *The transition probabilities.* We shall define in the present section the quantity P, the time evolution of which will later be expressed by means of a master equation to general order in the perturbation. Let us consider the wave function φ_0 of the system at an initial time $t = 0$ and let us expand it in the $|\alpha\rangle$-representation

$$\varphi_0 = \int |\alpha\rangle\, \mathrm{d}\alpha\, c(\alpha). \tag{3.1}$$

The expansion has been written for the limiting case $N \to \infty$, replacing summation over α by integration, since in this limit all quantum numbers are continuous. According to the orthonormalization equation (2.2) we have

$$\langle\varphi_0|\varphi_0\rangle = \int |c(\alpha)|^2\, \mathrm{d}\alpha. \tag{3.2}$$

We assume this expression to have the value unity.

*) This notation for the sections of I, as well as the notations (I. 1.1.) or (A.1.1) for equations of I or A, are self-explanatory.

**) From now on the expression *diagonal operator* will be used for operators diagonal in the $|\alpha\rangle$-representation.

Choosing the units so that $\hbar = 1$, the wave function at time t is given by

$$\varphi_t = U_t \varphi_0, \tag{3.3}$$

$$U_t = \exp\,[-\,i(H + \lambda V)t]. \tag{3.4}$$

We are interested in the occupation probabilities at time t of groups of states $|\alpha\rangle$ which for finite but large N contain many states but are still narrow enough to give a very small variation of the quantum numbers over the group. Since for $N \to \infty$ all quantum numbers become continuous, such a group corresponds in this limit to an infinitesimal volume element $\mathrm{d}\alpha$ in the space of the quantum numbers. The occupation probability of such a group can be written $p_t(\alpha)\,\mathrm{d}\alpha$, and the probability density $p_t(\alpha)$ is such that, for a diagonal operator A with

$$A\,|\alpha\rangle = |\alpha\rangle\, A(\alpha), \tag{3.5}$$

one has

$$\langle\varphi_t\,|A|\,\varphi_t\rangle = \int A(\alpha) p_t\,(\alpha)\,\mathrm{d}\alpha. \tag{3.6}$$

Inversely, the occupation probability density $p_t(\alpha)$ can be uniquely determined from a calculation of (3.6) for every diagonal A having as eigenvalue $A(\alpha)$ a smooth function of the quantum numbers in α. From (3.3) one has

$$\langle\varphi_t\,|A|\,\varphi_t\rangle = \langle\varphi_0\,|U_{-t}AU_t|\,\varphi_0\rangle. \tag{3.7}$$

If one expands U_t and U_{-t} in powers of the perturbation, the operator $U_{-t}AU_t$ becomes a sum of a diagonal operator and an infinity of products $A_0VA_1 \ldots VA_{n+1}$ with diagonal $A_0, \ldots A_{n+1}$. Consequently it has a diagonal part. We separate it out in the matrix element

$$\langle\alpha\,|U_{-t}AU_t|\,\alpha'\rangle = \delta(\alpha - \alpha')\, f_1(\alpha) + f_2(\alpha, \alpha'), \tag{3.8}$$

$f_2(\alpha, \alpha')$ having as usual only singularities weaker than $\delta(\alpha - \alpha')$. Obviously f_1 and f_2 depend linearly on the arbitrary diagonal operator A. These quantities are therefore linear functionals of the numerical function $A(\alpha'')$, in formulae

$$f_1(\alpha) = \int A(\alpha'')\,\mathrm{d}\alpha''\, P(t \mid \alpha''\alpha), \tag{3.9}$$

$$f_2(\alpha, \alpha') = \int A(\alpha'')\,\mathrm{d}\alpha''\, I(t \mid \alpha''\alpha\alpha'). \tag{3.10}$$

The functions $P(t \mid \alpha''\alpha)$ and $I(t \mid \alpha''\alpha\alpha')$ thus defined depend only on the system considered and on the variables indicated between brackets; they are independent of A. Inserting our equations in (3.7) we obtain

$$\begin{aligned}\langle\varphi_t\,|A|\,\varphi_t\rangle = {} & \int A(\alpha'')\,\mathrm{d}\alpha'' \int P(t \mid \alpha''\alpha)\,\mathrm{d}\alpha\, |c(\alpha)|^2 \\ & + \int A(\alpha'')\,\mathrm{d}\alpha'' \int I(t \mid \alpha''\alpha\alpha')\,\mathrm{d}\alpha\,\mathrm{d}\alpha'\, c^*(\alpha)\, c(\alpha')\end{aligned} \tag{3.11}$$

and for the occupation probability, by comparison with (3.6),

$$p_t(\alpha'') = \int P(t \mid \alpha''\alpha)\,\mathrm{d}\alpha\, |c(a)|^2 + \int I(t \mid \alpha''\alpha\alpha')\,\mathrm{d}\alpha\,\mathrm{d}\alpha'\, c^*(\alpha)\, c(\alpha'). \tag{3.12}$$

The equations just obtained exhibit a very important feature, the separate occurrence in the righthand sides of terms depending only on the absolute squares of the initial amplitudes $c(\alpha)$ and of terms depending on the relative phases of $c(\alpha)$ for various α (i.e. on the α-variation of the phase). The former involve only the initial occupation probabilities $|c(\alpha)|^2$, whereas the latter are of the nature of interference terms (whence the notations P and I). The fact just mentioned, which could also be described as a separation of the density matrix, is a direct consequence of the occurrence of diagonal parts, i.e. of the special properties of the hamiltonian described in the previous section.

The separation which thus appears between phase-independent and phase-dependent terms leads directly to the distinction between initial states φ_0 with "random" or "incoherent phases" and those with "special phases". Loosely speaking, an initial state with random or incoherent phases will be such as to give a negligibly small value to the interference term

$$\int I(t \mid \alpha''\alpha\alpha')\, \mathrm{d}\alpha\, \mathrm{d}\alpha'\, c^*(\alpha)\, c(\alpha') \tag{3.13}$$

for every t in the time interval of interest, whereas a φ_0 with special phases would give it a non-vanishing value. It is difficult to find for this distinction a formulation at the same time complete and general. Of course, if instead of one initial state we are willing to consider an ensemble of such states with prescribed $|c(\alpha)|$ and random (more exactly uniformly distributed) phases, the average value of (3.13) will be zero. One must however expect much more to be true. The integral (3.13), when taken for a single initial state selected in some sense at random, must be vanishingly small most of the time, at least if one limits oneself to the values of t in a finite interval $|t| \leqslant T$, where T can be chosen large compared to the time needed for the approach to statistical equilibrium *). For example, if the phase of $c(\alpha)$ varies very rapidly with α as compared to the phase of $\exp[i\varepsilon(\alpha)T]$, the expression (3.13) will certainly be very small, because the phases of $I(t \mid \alpha''\alpha\alpha')$ can certainly not vary fast compared to the expression mentioned. Since it seems reasonable to expect the phases of an initial state, when chosen at random, to vary rapidly most of the time, we may expect that (3.13) will be negligible for an overwhelming majority of initial states.

Further support for this view can also be drawn from an analogy with the quantum theory of collision processes. Let us take the simplest example of collision, elastic scattering of a particle by a target at rest. The hamiltonian can be written in the form $H + \lambda V$, H representing the kinetic energy of the

*) The latter time is here finite because we treat the perturbation as finite. In A on the contrary, the limiting case $\lambda \to 0$ was considered, T tending to infinity as λ^{-2}. This is the reason why we could neglect in A all interference effects even for initial states with slowly varying phases: all these effects took place in a time short compared to T. Such is not the case here. Both here and in A the Poincaré cycles are infinite because we deal with the limiting case of an infinite system.

particle and λV the interaction between particle and static target. The states $|\alpha\rangle$ are plane waves characterized by continuous quantum numbers, just as was the case until now. The number of these continuous parameters is now however limited to three, and the perturbation V is such that none of the singularities described in Section 2 occur in matrix elements $\langle\alpha|VA_1V \ldots A_nV|\alpha'\rangle$. The quantity P defined by (3.9) consequently reduces to

$$P(t \mid \alpha'\alpha) = \delta(\alpha' - \alpha),$$

giving for the occupation probability density at time t

$$P_t(\alpha'') = |c(\alpha'')|^2 + \int I(t \mid \alpha''\alpha\alpha')\, d\alpha\, d\alpha'\, c^*(\alpha)\, c(\alpha').$$

The time-dependence of p_t, i.e. the very occurrence of scattering, is here entirely determined by the interference term. It is in this case quite clear in which sense can be asserted that the interference term is negligible for most initial states. Unless the $c(\alpha)$'s have special singularities, the initial state (3.1) represents a wave packet, and random choice of the phases of this wave packet implies random choice of its location in space. The occurrence of scattering on the contrary requires proper aiming of the incoming particle at the target, i.e. a proper correlation between initial position and direction of motion. Consequently the interference term (3.13) can in this case safely be said to vanish most of the time for random choice of the phases of the amplitudes $c(\alpha)$.

This rather lengthy discussion was presented to support the view that the interference term in (3.11) and (3.12) will only contribute for a minority of "special" initial states, the occupation probability reducing for all other states to the simple expression

$$p_t(\alpha') = \int P(t \mid \alpha'\alpha)\, d\alpha\, |c(\alpha)|^2. \tag{3.14}$$

The latter equation is equivalent to

$$\langle\varphi_t|A|\varphi_t\rangle = \int A(\alpha')\, d\alpha' \int P(t \mid \alpha'\alpha)\, d\alpha\, |c(\alpha)|^2. \tag{3.15}$$

Our further analysis will be devoted to a study of the quantity $P(t \mid \alpha'\alpha)$. This quantity is entirely defined in terms of the hamiltonian and of the $|\alpha\rangle$-representation, and its study is a purely quantum-mechanical problem from the treatment of which all extraneous arguments, statistical or others must and will be barred. From (3.14), for most initial states, the quantity $P(t \mid \alpha'\alpha)$ directly expresses the occupation probabilities at time t in terms of the occupation probabilities $p_0(\alpha) = |c(\alpha)|^2$ at time zero. Clearly $P(t|\alpha'\alpha)$ is the *transition probability density* from α to α' in the time interval from 0 to t, assuming randomness of phases at time 0. Although the present paper will be entirely concerned with this transition probability, we do not mean to imply that the interference function $I(t \mid \alpha''\alpha\alpha')$ is deprived of interest, nor that its study would present abnormally high difficulties. The physical

importance of interference effects in dissipative systems can be illustrated by many examples. To quote only one, simultaneous excitation of two additional phonons in a crystal lattice in thermal equilibrium may give rise, for special configurations, to mutual scattering of the two phonons before they have covered their whole mean free parth and have vanished by dissipation. As for the quantum-mechanical study of $I(t \mid \alpha''\alpha\alpha')$, it can be tackled by the methods used hereafter and applied already in I and II where collision processes, i.e. interference effects, were extensively studied.

In A the quantum-mechanical calculation of $P(t \mid \alpha'\alpha)$ was performed to lowest order in λ, more exactly in the limiting case $\lambda \to 0$, $t \to \infty$, $\lambda^2 t$ finite. Written in our present notation (which is more convenient than the notation of A for a study to general order in λ), the main result of A was that the transition probability density verifies the differential equation (see (A.6.11))

$$\begin{aligned} \mathrm{d}P(t \mid \alpha\alpha_0)/\mathrm{d}t = {} & 2\pi\lambda^2 \int \delta[\varepsilon(\alpha) - \varepsilon(\alpha')]\, W^{(0)}(\alpha\alpha')\, \mathrm{d}\alpha'\, P(t \mid \alpha'\alpha_0) \\ & - 2\pi\lambda^2 \int \mathrm{d}\alpha' \,.\, \delta[\varepsilon(\alpha') - \varepsilon(\alpha)]\, W^{(0)}(\alpha'\alpha) \,.\, P(t \mid \alpha\alpha_0). \end{aligned} \tag{3.16}$$

This equation is in more explicit form and in our notation the master equation (1.1). The kernel $W^{(0)}(\alpha'\alpha)$ is defined by the identity

$$\{VAV\}_d \,|\alpha\rangle = |\alpha\rangle \int A(\alpha')\, \mathrm{d}\alpha'\, W^{(0)}(\alpha'\alpha) \tag{3.17}$$

for arbitrary diagonal A with eigenvalues $A(\alpha')$. Equation (3.16), which holds for $t > 0$ but would apply to $t < 0$ after changing the sign of the righthand side, is characteristic of a stochastic process of Markov type, a feature which we will find not to hold to general order in the perturbation. The quantities $W^{(0)}$ play the role of transition rates, i.e. of transition probabilities per unit time. Eq. (3.16) must be supplemented by the initial condition

$$P(0 \mid \alpha\alpha_0) = \delta(\alpha - \alpha_0) \tag{3.18}$$

which follows immediately from the definition (3.8), (3.9) of P and is exact to all orders of the perturbation.

Two remarks will be made before we start in Section 4 the study of P. The first one concerns the dominant role played in all our considerations by the $|\alpha\rangle$-representation, despite the fact that it is of course not intrinsic to the many-particle system considered. In A, where the perturbation was assumed to be very small ($\lambda \to 0$), the use of the $|\alpha\rangle$-representation could be entirely motivated by the property that the $|\alpha\rangle$'s are the eigenstates of the hamiltonian in the limit $\lambda = 0$. Here however we assume the perturbation to be finite and the argument just mentioned consequently fails. The special significance of the $|\alpha\rangle$-representation for the many-particle systems of quantum statistics must be attributed to another fact, easily verified on all actual examples, to know: the simple relation of this representation to the physical quantities of greatest interest in irreversible processes. The latter

quantities have usually a simple mathematical expression in terms of one-particle operators, and these operators themselves have in crystals as well as in gases simple matrix elements in the $|\alpha\rangle$-representation *). It has often been remarked that the irreversible behaviour of a many-particle system is not truly an intrinsic property of the system but is partly determined by which class of properties of the system the observer is looking at. In other words, it is not for every operator 0 that one can expect the expectation value $\langle\varphi_t|0|\varphi_t\rangle$ to tend in the course of time (starting from most initial states) toward the average value $\langle 0\rangle_{eq}$ calculated from equilibrium statistical mechanics. From the experimental evidence we only know this property to hold for special physical quantities 0, and it is an easy matter to construct other operators for which it does not hold. On the basis of experience the representation $|\alpha\rangle$ seems to provide a natural way to characterize operators 0 for which $\langle\varphi_t|0|\varphi_t\rangle$ can be expected to tend toward $\langle 0\rangle_{eq}$. To state it loosely, these operators will be such as to have simple matrix elements in the $|\alpha\rangle$-representation, even in the limiting case of a very large system. A sharper formulation of this statement is of course required, but no attempt to find one has been made until now. The only operators 0 to be considered in the present paper are diagonal operators A, for which the approach of $\langle\varphi_t|A|\varphi_t\rangle$ toward $\langle A\rangle_{eq}$ for most initial states will indeed be established on the basis of Eq. (3.15) (see section 7). As seen from (3.15), all we need for achieving this goal is the asymptotic value of $P(t \mid \alpha'\alpha)$ for large times. An extension to other operators 0 would of course be desirable. It could in principle be carried out by essentially the same modification of the techniques used here as would be needed to incorporate into the theory discrete quantum numbers for polarization and spin.

Our second remark concerns the vanishing of the interference term (3.13) for a particular type of initial states φ_0: wave packets of very narrow extension in α:

$$\varphi_0 = \int_{\Delta\alpha} |\alpha\rangle \, d\alpha \, c(\alpha). \tag{3.19}$$

The integration extends over a very small domain $\Delta\alpha$ around a state α_0. Such a wave packet can be considered as an approximation to the unperturbed state $|\alpha_0\rangle$. Normalization requires.

$$\int_{\Delta\alpha} |c(\alpha)|^2 \, d\alpha = 1 \tag{3.20}$$

so that, from the Schwarz inequality,

$$\left|\int_{\Delta\alpha} c(\alpha) \, d\alpha\right| \leqslant \Delta\alpha^{\frac{1}{2}}. \tag{3.21}$$

For very small $\Delta\alpha$ the interference term (3.13) is negligible. As a matter of fact it can be written

$$I(t \mid \alpha''\alpha_0\alpha_0) \left|\int_{\Delta\alpha} c(\alpha) \, d\alpha\right|^2$$

*) This situation is radically different from what happens in field theory, where the unperturbed representation $|\alpha\rangle$ is formed by the unobservable bare particle states.

and from (3.21) it is seen to tend to zero for $\Delta\alpha \to 0$. The occupation probability (3.12) reduces in this limit to

$$p_t(\alpha) = P(t \mid \alpha\alpha_0). \tag{3.22}$$

This gives a new illustration of the physical significance of P as transition probability density.

4. *General properties of the system and master equation.* For the lowest order in the perturbation the transition probability $P(t \mid \alpha'\alpha)$ was calculated in A by taking the defining equations (3.8), (3.9) and carrying out a straight expansion of $U_{-t}AU_t$ in powers of λ, retaining the terms which do not vanish in the limit $\lambda \to 0$, $\lambda^2 t$ finite. The result obtained turned out to be the series expansion solution of the transport equation (3.16), i.e. the solution which would be derived from (3.16) and (3.18) by mere iteration. Besides its lack of elegance, such a method is very cumbersome to extend to higher orders in λ. The method to be followed presently is different and makes essential use of the resolvent

$$R_l = (H + \lambda V - l)^{-1}, \quad l \text{ complex number}, \tag{4.1}$$

an operator already applied in I and II to the study of non-dissipative systems.

The main properties of the resolvent for the type of hamiltonian here considered are the same for systems of statistical mechanics and for interacting fields; they have been derived in Section 3 of I. These properties concern the diagonal part D_l of the resolvent. Clearly, the study of the diagonal part of R_l on the basis of properties (i), (ii), (iii) of Section 2 presupposes that R_l can be expanded in powers of the perturbation, since this expansion is needed to bring R_l in the form of a sum of operators $A_0VA_1 \ldots$ $\ldots VA_{n+1}$ with diagonal A_j's. It is however only for l non-real that convergence of the expansion must be assumed. Furthermore, the formulation of the properties of D_l and the further development of the theory no longer use a complete expansion in powers of λ and thereby differ in an essential way from what ordinary perturbation calculus would give. One can say that all our equations differ from the corresponding results of ordinary perturbation theory through the fact that a number of partial summations have been carried out in closed form *). The possibility of such partial summations follows from the occurrence of diagonal parts, and our method seems to be well suited to take advantage of it. Still the summations explicitly carried out are only partial and we have to assume convergence for all remaining series.

Let us recall briefly the main properties of the resolvent for the limiting

*) Typical examples of these summations are found in I, section 3, Eq. (I.3.5) and (I.3.8).

case of a large system ($N \to \infty$, N/Ω finite). They have been derived in I under normal conditions of regularity of all functions involved, with due regard of course for the singularities implied by properties (ii), (iii) of section 2. The diagonal part D_l of R_l can be written in the form

$$D_l = (H - l - \lambda^2 G_l)^{-1} \tag{4.2}$$

where G_l is a diagonal operator satisfying the identity (see (I. 3.13))

$$G_l = \{VD_lV - \lambda VD_lVD_lV + \ldots\}_{id}. \tag{4.3}$$

This identity can be used to calculate G_l by successive approximations. The resolvent itself becomes, as stated in (I.3.15),

$$R_l = D_l - \lambda D_l \{V - \lambda VD_lV + \lambda^2 VD_lVD_lV - \ldots\}_{nd} D_l. \tag{4.4}$$

We denote by $G_l(\alpha)$ and $D_l(\alpha)$ the eigenvalues of G_l and D_l for the state $|\alpha\rangle$. From (4.2),

$$D_l(\alpha) = [\varepsilon(\alpha) - l - \lambda^2 G_l(\alpha)]. \tag{4.2 bis}$$

As a function of the complex variable l, $G_l(\alpha)$ is holomorphic in the whole complex plane except on a portion of the real axis *). It approaches zero as $|l|^{-1}$ when $l \to \infty$ **). It verifies

$$G_{l^*}(\alpha) = [G_l(\alpha)]^* \tag{4.5}$$

where the star denotes the complex conjugate. Furthermore

$$Im[G_l(\alpha)] > 0 \text{ for } Im(l) > 0, \text{ unless } G_l(\alpha) = 0 \quad \text{for all } l. \tag{4.5 bis}$$

For l approaching a point E of the real axis, $G_l(\alpha)$ approaches a finite limit

$$\lim_{0>\eta\to 0} G_{E\pm i\eta}(\alpha) = K_E(\alpha) \pm iJ_E(\alpha) \tag{4.6}$$

where $K_E(\alpha)$ is real and $J_E(\alpha)$ real non-negative. The latter quantity is positive on certain intervals of the E-axis and vanishes elsewhere; these intervals depend on α.

The above properties imply that $D_l(\alpha)$ is holomorphic in l in the whole complex plane except on a portion of the real axis and that it approaches zero as $|l|^{-1}$ for $l \to \infty$. Further, from (4.5) and (4.5 bis),

$$D_{l^*}(\alpha) = [D_l(\alpha)]^*, \; Im\,[D_l(\alpha)] > 0 \text{ for } Im(l) > 0. \tag{4.7}$$

In contrast to the case of $G_l(\alpha)$, the behaviour of $D_l(\alpha)$ for l approaching the real axis may be of two different types. Clearly, the limit of $D_l(\alpha)$ for $l \to E$, E real, is finite whenever one or both of the inequalities

$$J_E(\alpha) > 0, \; \varepsilon(\alpha) - E - \lambda^2 K_E(\alpha) \neq 0$$

*) $G_l(\alpha)$ and $D_l(\alpha)$ often have analytical continuations accross the real axis, from above and from below. They will however play no part in our considerations.

**) Except possibly when l remains close to the real axis. This provision will always have to be made when we talk about the behaviour of analytic functions at infinity.

hold, but it becomes infinite when one has simultaneously

$$J_E(\alpha) = 0, \ \varepsilon(\alpha) - E - \lambda^2 K_E(\alpha) = 0. \tag{4.8}$$

In the latter case $D_l(\alpha)$ has a pole at $l = E$ *). The absence or presence of poles in $D_l(\alpha)$ is therefore determined by the absence or presence of common roots for the equations (4.8).

The two possibilities thus encountered correspond to the distinction between the state $|\alpha\rangle$ having a dissipative or a non-dissipative behaviour under the effect of the perturbation. This statement deserves some comments in addition to what was said in I, Section 4. What we mean by it can be described most simply as follows. Select as in (3.19) an initial state φ_0 forming a wave packet of very narrow extension $\Delta\alpha$ around α_0. A time t later the state has become φ_t, given by (3.3) and (3.4). Let us calculate in the limit of small $\Delta\alpha$ the probability $q_t(\alpha_0)$ to find back the system in its initial state φ_0. It is

$$q_t(\alpha_0) = \lim_{\Delta\alpha \to 0} |\langle \varphi_0 \mid \varphi_t \rangle|^2. \tag{4.9}$$

A calculation similar to the derivation of (3.22) shows that $\langle \varphi_0 \mid \varphi_t \rangle$ is, in the limit of small $\Delta\alpha$, identical to the eigenvalue for α_0 of the operator

$$\begin{aligned} \{U_t\}_a &= (i/2\pi) \{ \int_\gamma \exp(-ilt) \, R_l \, \mathrm{d}l \}_a \\ &= (i/2\pi) \int_\gamma \exp(-ilt) \, D_l \, \mathrm{d}l \end{aligned} \tag{4.10}$$

where γ is a contour in the complex plane encircling a sufficiently large portion of the real axis and is to be described counterclockwise. We have consequently

$$q_t(\alpha_0) = (2\pi)^{-2} \, | \int_\gamma \exp(-ilt) \, D_l(\alpha_0) \, \mathrm{d}l |^2. \tag{4.11}$$

This formula directly implies that $q_t(\alpha_0)$ tends to zero for $t \to \infty$ when $D_l(\alpha_0)$ has no pole, and tends to a positive limit when $D_l(\alpha_0)$ has one or more poles **).

In the first case it is natural to describe the behaviour of the state $|\alpha_0\rangle$ as *dissipative*, because under the influence of the perturbation this state (or more exactly the properly normalized state φ_0 for very small $\Delta\alpha$) is so deeply modified that, eventually, it gets completely spread out over the other states $|\alpha\rangle$ and contains its initial value only as a negligibly small component. One should note that such a radical effect does not in any way require the perturbation to be strong. On the contrary dissipative behaviour can occur for arbitrarily small perturbations, the vanishing of the probability $q_t(\alpha_0)$ demanding then correspondingly long times (of order λ^{-2}).

*) As established in (I.5.8), (I.5.9) such a pole of $D_l(\alpha)$ is always of order one. $D_l(\alpha)$ has never non-real poles.

**) See also loc. cit.[3]). We may remark that $|\langle \varphi_0 \mid \varphi_t \rangle|^2$ always tends to zero for $t \to \infty$ if the limit of small $\Delta\alpha$ is not taken. This effect, also present when there is no perturbation, is just the ordinary spreading of a wave packet and is of no interest to us.

In the case where $D_l(\alpha_0)$ has one or more poles, the state $|\alpha_0\rangle$ (more properly φ_0 in the limit of small $\Delta\alpha$), although of course affected by the perturbation, always retains a non-vanishing component identical to its initial value. This situation, which we call *non-dissipative*, would occur in a convergent field theory, where the bare particle states are present with non-vanishing probability in the corresponding dressed (i.e. observable) particle states. We may also remark that in the quantum theory of collision processes, already quoted for comparison in Section 3, the function $D_l(\alpha_0)$ reduces to its unperturbed value $[\varepsilon(\alpha_0) - l]^{-1}$, so that $q_t(\alpha_0)$ is unity at all times. This means that a true plane wave state (corresponding to the limit of small $\Delta\alpha$) is perturbed by a collision process only in a negligibly small fraction of its totality, as is physically obvious since the collision can only take place in a limited region of configuration space whereas the extension of the plane wave is of course infinite.

In I and II we gave a systematic study of what may be called *non-dissipative systems*, i.e. systems for which all states $|\alpha\rangle$ are non-dissipative. We made the slightly more restrictive assumption that for each α the equations (4.8) have one single common root $E(\alpha)$, in the neighbourhood of which $J_E(\alpha)$ vanishes identically. This is typically the situation which would occur in a convergent field theory with positive masses for all fields (neither infra-red nor ultra-violet divergences). Formally a system can have part of its states dissipative, part of them non-dissipative. For the many-particle systems of quantum statistics one should expect the quasi-totality of unperturbed states to be dissipative *). It seems reasonable to call them *dissipative systems* and our main interest goes to them in the present paper. It is for them that consideration of the transition probabilities $P(t \mid \alpha'\alpha)$ and of a master equation is of actual importance. In the present section the properties of $P(t \mid \alpha'\alpha)$ and the master equation will however be established in full generality, irrespective of the dissipative or non-dissipative character of the $|\alpha\rangle$'s. The algebraic form of the master equation is completely independent of this distinction, although of course the nature of the solutions will be radically different in the two cases. This situation is already familiar in the limiting case of small perturbations, where the lowest order master equation (3.16) is of true interest only when

$$\delta[\varepsilon(\alpha') - \varepsilon(\alpha)]\, W^{(0)}(\alpha'\alpha) \neq 0. \tag{4.12}$$

The validity of this inequality for some states $|\alpha'\rangle$ can easily be shown to characterize the state $|\alpha\rangle$ as dissipative in the approximation considered. The master equation (3.16) remains nevertheless valid when the lefthand side of (4.12) vanishes. In the field-theoretical case for example, where all

*) One cannot expect all states to be dissipative. For instance the ground state should be non-dissipative. It might perhaps also be a fairly general feature that very low lying excited states behave non-dissipatively, as is suggested by the phenomena of superfluidity and superconductivity.

unperturbed states are non-dissipative, this quantity vanishes for all α and α', so that (3.16) reduces to

$$dP(t \mid \alpha'\alpha)/dt = 0,$$

or, on account of (3.18),

$$P(t \mid \alpha'\alpha) = \delta(\alpha' - \alpha) \text{ for all } t.$$

In the approximation considered ($\lambda \to 0$) this result is correct but of course of little interest. Its extension to general order will be given at the end of Section 6.

We now go over to the investigation of $P(t \mid \alpha'\alpha)$ to general order in λ. We use as in (4.10) the representation of U_t by a contour integral over the resolvent and introduce it in the definition (3.8), (3.9) of $P(t \mid \alpha'\alpha)$. Clearly

$$U_{-t}AU_t = -(2\pi)^{-2}\int_\gamma dl \int_\gamma dl' \exp[i(l - l')t]\, R_l A R_{l'}, \tag{4.13}$$

γ being the same contour as in (4.10). Let us define the function $X_{ll'}(\alpha'\alpha)$ by the identity

$$\{R_l A R_{l'}\}_d \,|\alpha\rangle = |\alpha\rangle \int A(\alpha')\, d\alpha' X_{ll'}(\alpha'\alpha). \tag{4.14}$$

As usual A is an arbitrary diagonal operator of eigenvalues $A(\alpha')$. The quantity $X_{ll'}$ approaches zero as $|l|^{-1}$ for $l \to \infty$, as $|l'|^{-1}$ for $l' \to \infty$, as $|ll'|^{-1}$ when l and $l' \to \infty$. Introducing (4.14) into the diagonal part of (4.13) and comparing with (3.9) one finds

$$P(t \mid \alpha'\alpha) = -(2\pi)^{-2}\int_\gamma dl \int_\gamma dl' \exp[i(l - l')t]\, X_{ll'}(\alpha'\alpha). \tag{4.15}$$

We establish next a simple identity for $X_{ll'}(\alpha'\alpha)$. Define a new function $W_{ll'}(\alpha'\alpha)$ by the equation (A arbitrary diagonal operator)

$$\{(V - \lambda V D_l V + \ldots)\, A\, (V - \lambda V D_{l'} V + \ldots)\}_{id} \,|\alpha\rangle = |\alpha\rangle \int A(\alpha')\, d\alpha'\, W_{ll'}(\alpha'\alpha). \tag{4.16}$$

Comparison with (3.17) shows that

$$\lim_{\lambda \to 0} W_{ll'}(\alpha'\alpha) = W^{(0)}(\alpha'\alpha). \tag{4.17}$$

Furthermore, one has also from the definition

$$\lim_{l,l' \to \infty} W_{ll'}(\alpha'\alpha) = W^{(0)}(\alpha'\alpha). \tag{4.18}$$

The diagonal part in (4.14), after insertion of (4.4), can be reduced to irreducible diagonal parts, whereby property (iii) of Section 2 plays a central role: all simultaneous diagonal parts occurring in this particular reduction have the relative configuration (2.10). The result is an expression of X in terms of W,

$$X_{ll'}(\alpha\alpha_0) = D_l(\alpha)D_{l'}(\alpha)\,\delta(\alpha - \alpha_0) + \lambda^2 D_l(\alpha)D_{l'}(\alpha)[W_{ll'}(\alpha\alpha_0) + \\ + \lambda^2 \int W_{ll'}(\alpha\alpha_1)D_l(\alpha_1)D_{l'}(\alpha_1)\, d\alpha_1\, W_{ll'}(\alpha_1\alpha_0) + \ldots]\, D_l(\alpha_0)D_{l'}(\alpha_0). \tag{4.19}$$

On the other hand, the fundamental identity (4.3), taken for two values of l, gives by subtraction

$$G_l - G_{l'} = \{(V - \lambda V D_l V + \ldots)(D_l - D_{l'})(V - \lambda V D_{l'} V + \ldots)\}_{id}. \quad (4.20)$$

On account of (4.16) this is a simple identity for the function W:

$$G_l(\alpha) - G_{l'}(\alpha) = \int [D_l(\alpha') - D_{l'}(\alpha')]\, d\alpha'\, W_{ll'}(\alpha'\alpha). \quad (4.21)$$

It is convenient to introduce a new notation for the quantity under the integral

$$\tilde{W}_{ll'}(\alpha'\alpha) = i[D_l(\alpha') - D_{l'}(\alpha')]\, W_{ll'}(\alpha'\alpha). \quad (4.22)$$

Remark however that (4.2) gives

$$D_l - D_{l'} = [(l - l') + \lambda^2(G_l - G_{l'})]D_l D_{l'}. \quad (4.23)$$

Consequently the identity (4.21) can be written

$$(l - l')D_l(\alpha)D_{l'}(\alpha) = D_l(\alpha) - D_{l'}(\alpha) + i\lambda^2 \int d\alpha'\, \tilde{W}_{ll'}(\alpha'\alpha)D_l(\alpha)D_{l'}(\alpha). \quad (4.24)$$

It is then a simple matter to convert it into an identity for the function X. Multiplication of (4.19) by $l - l'$ and application of (4.24) gives

$$(l - l')\, X_{ll'}(\alpha\alpha_0) = [D_l(\alpha) - D_{l'}(\alpha)]\, \delta(\alpha - \alpha_0)$$
$$- i\lambda^2 \int \tilde{W}_{ll'}(\alpha\alpha')\, d\alpha'\, X_{ll'}(\alpha'\alpha_0) + i\lambda^2 \int d\alpha'\, \tilde{W}_{ll'}(\alpha'\alpha)\, X_{ll'}(\alpha\alpha_0). \quad (4.25)$$

The first part of the derivation is thereby ended. The only task left is to transform (4.25) into an equation for the time evolution of $P(t \mid \alpha\alpha_0)$. The form of the exponential in equation (4.15) shows that P depends only on an integral of $X_{ll'}$ over $l + l'$ for fixed difference $l - l'$. The identity (4.25) on the other hand refers to $X_{ll'}$ itself. As a consequence it was not found possible to derive an equation for the quantity P itself, but P could be written as an integral over another quantity $P_E(t \mid \alpha\alpha_0)$ for which (4.25) directly implies a master equation. The quantity $P_E(t \mid \alpha\alpha_0)$ is defined mathematically for $t \neq 0$ as

$$P_E(t \mid \alpha\alpha_0) = (2\pi^2)^{-1}\, s(t) \int_\gamma dl \exp(2ilt)\, X_{E+l,\, E-l}(\alpha\alpha_0), \quad (4.26)$$

E being real and γ being the same type of contour as before. The symbol $s(t)$, meaning sign of t, stands for $t^{-1}|t|$. We state that for $t \neq 0$ one has

$$P(t \mid \alpha\alpha_0) = \int_{-\infty}^{\infty} dE P_E(t \mid \alpha\alpha_0). \quad (4.27)$$

To establish this relation, replace in (4.26) the contour γ by two lines $l = E' \pm i\eta$ with $\eta > 0$ and very small. Only one of these lines (the one where $Re\,(ilt) > 0$) gives a non-vanishing contribution. After substitution of (4.26) into (4.27), transform the double integral obtained to the new variables $E \pm E'$. This is possible for $t \neq 0$ because the exponential factor involving t ensures convergence. The result is readily seen to be (4.15) with the contours taken as straight lines along the real axis.

On the other hand the time derivative of P_E contains according to (4.26) the combination $2l\, X_{E+l,\, E-l}$, which is the lefthand side of the identity (4.25) for the special suffices involved; we replace it by the righthand side. Let us now define

$$w_E(t \mid \alpha'\alpha) = (2\pi^2)^{-1} \int_\gamma \mathrm{d}l \exp(2ilt)\, \tilde{W}_{E+l,\, E-l}(\alpha'\alpha). \tag{4.28}$$

One easily establishes

$$s(t) \int_\gamma \mathrm{d}l \exp(2ilt)\, \tilde{W}_{E+l,\, E-l}(\alpha_3\alpha_2)\, X_{E+l,\, E-l}(\alpha_1\alpha_0) = 4\pi^3 \int_0^t \mathrm{d}t'\, w_E(t - t' \mid \alpha_3\alpha_2)\, P_E(t' \mid \alpha_1\alpha_0), \tag{4.29}$$

a result for which the vanishing of $\tilde{W}_{E+l,\, E-l}$ and $X_{E+l,\, E-l}$ for $l \to \infty$ is relevant. Introduce still the further definition

$$f_E(t \mid \alpha) = (2\pi^2)^{-1}\, is(t) \int_\gamma \mathrm{d}l \exp(2ilt)\, [D_{E+l}(\alpha) - D_{E-l}(\alpha)]. \tag{4.30}$$

With the help of (4.29) and (4.30) the time derivative of P_E finally takes the form we were aiming at:

$$\mathrm{d}P_E(t \mid \alpha\alpha_0)/\mathrm{d}t = \delta(\alpha - \alpha_0)\, f_E(t \mid \alpha) + 2\pi\lambda^2 \int_0^t \mathrm{d}t' \int w_E(t - t' \mid \alpha\alpha')\, \mathrm{d}\alpha' P_E(t' \mid \alpha'\alpha_0) - 2\pi\lambda^2 \int_0^t \mathrm{d}t' \int \mathrm{d}\alpha' w_E(t - t' \mid \alpha'\alpha)\, P_E(t' \mid \alpha\alpha_0). \tag{4.31}$$

The integro-differential equation (4.31) is the *master equation to general order in* λ. Its main structural differences with the lowest order equation (3.16) are apparent in the righthand side: they consist in the presence of an inhomogeneous term (the term in f_E) and in the time integration over the previous evolution of the system (non markovian nature of the process). Both features can be shown to be manifestations of the coherent phase relations present in the wave function φ_t at all times $t \neq 0$. We shall see in the next section how they become negligible in the limit of small perturbations.

The master equation (4.31) for P_E must be supplemented by an *initial condition* at $t = 0$. This condition is easily derived from the definition (4.26) of P_E. As we have seen, $X_{E-l,E+l}$ decreases as $|l|^{-2}$ for $l \to \infty$. Putting $t = 0$ in (4.26) and deforming the whole contour to infinity, one gets a vanishing result, so that

$$P_E(0 \mid \alpha\alpha_0) = 0. \tag{4.32}$$

With this initial condition the integro-differential equation (4.31) determines P_E uniquely for all times, positive or negative. One may wonder how (4.32) can be compatible with the fact, already noted in the previous section, Eq. (3.18), that the initial value of $P(t \mid \alpha\alpha_0)$ is $\delta(\alpha - \alpha_0)$. The reason is that (4.27) does not hold for $t = 0$. As stressed before, non-vanishing of t is necessary for P to be the integral of P_E over the energy E.

It must be noted that the quantities f_E, w_E and P_E are real for all values of their (real) arguments. For f_E the reality follows from (4.30) and the first

equation (4.7). For w_E one notices that, from (4.16), (4.7) and the hermiticity of V,

$$[W_{ll'}(\alpha'\alpha)]^* = W_{l'*l*}(\alpha'\alpha). \tag{4.33}$$

Reality of (4.28) then easily results. The reasoning for P_E is similar, using

$$[X_{ll'}(\alpha'\alpha)]^* = X_{l'*l*}(\alpha'\alpha). \tag{4.34}$$

In view of the importance of P_E, – it is this quantity rather than P itself which satisfies the general master equation –, it is good to get some insight into its physical significance. One may say loosely that P_E expresses how much of the transition probability P is contributed by the total energy shell $H + \lambda V = E$. This interpretation can be justified by the following considerations, which show at the same time how it has to be understood in more accurate terms. Let A be a diagonal operator and $F(H')$ an arbitrary function of the total hamiltonian $H' = H + \lambda V$. Define the symmetrized product $[AF]_s$ by expansion of F in powers of H' and application of the special rule

$$[AH'^n]_s = 2^{-n} \sum_{m=0}^{n} \binom{n}{m} H'^m A H'^{n-m} \tag{4.35}$$

which follows by induction from

$$[AH'^n]_s = \tfrac{1}{2}(H'[AH'^{n-1}]_s + [AH'^{n-1}]_s H').$$

Consider further, instead of (3.7), the expectation value $\langle \varphi_t \,|[AF]_s|\, \varphi_t\rangle$ for incoherent phases of the initial state φ_0. An easy calculation, similar to the derivation of (4.15) and (4.27), leads to

$$\langle \varphi_t \,|[AF]_s|\, \varphi_t\rangle = \int A(\alpha')\, \mathrm{d}\alpha'\, P'(t\,|\alpha'\alpha)\, \mathrm{d}\alpha\, |c(\alpha)|^2 \tag{4.36}$$

with

$$P'(t \mid \alpha'\alpha) = -(2\pi)^{-2} \int_\gamma \mathrm{d}l \int_\gamma \mathrm{d}l'\, F[\tfrac{1}{2}(l + l')]$$
$$\exp[i(l - l')t] X_{ll'}(\alpha'\alpha) = \int_{-\infty}^{\infty} \mathrm{d}E\, F(E)\, P_E(t \mid \alpha'\alpha). \tag{4.37}$$

Clearly, when F approximates a δ-function and thus picks out one energy shell, the quantity P' reduces to P_E. The relation of P_E to the total energy shell $H' = E$ will be confirmed later in the case of small perturbations (see eq. (5.9)) and, in the general case, by the long time expression of P_E for dissipative systems (see eq. (7.20) and the considerations thereafter).

5. *The limiting case of small perturbations.* The object of this section is to show how the general master equation (4.31) reduces to the familiar form (3.16) when the perturbation is very small. We note first that the time variation of the functions $w_E(t \mid \alpha'\alpha)$ and $f_E(t \mid \alpha')$, – more exactly of integrals over α' involving them –, takes place over time intervals, the order of magnitude T_0 of which does not change when $\lambda \to 0$. This can best be seen by studying the definitions (4.28) and (4.30) for small λ. Even in this limiting

case both functions converge to zero in the mean for t large compared to a finite time T_0. As a consequence a distinction must be made, in the righthand side of the master equation (4.31), between the inhomogeneous term containing f_E and the two homogeneous terms. The former is only present for times of the order of T_0 whereas the latter, in the case of dissipative systems, keep varying during all the time needed to reach statistical equilibrium. The order of magnitude T_1 of the latter time is $\lambda^{-2}\, w^{-1}$, where the energy w gives the order of magnitude of the quantity $W^{(0)}$.

In contrast with T_0, T_1 increases as λ^{-2} when $\lambda \to 0$. For very small perturbations we may therefore distinguish between two time scales, a short one of order T_0, essentially independent of λ, and a long one of order T_1, proportional to λ^{-2}. The inhomogeneous term of (4.31) is effective only when t is of the order of the short time scale T_0; it then completely dominates the homogeneous terms, the contribution of which is smaller by a factor λ^2. The equation can thus be written

$$\mathrm{d}P_E(t \mid \alpha\alpha_0)/\mathrm{d}t = \delta(\alpha - \alpha_0)\, f_E(t \mid \alpha) \qquad \text{for } |t| \sim T_0 \tag{5.1}$$

with neglection of terms of order λ^2. On the other hand, when $|t|$ exceeds the short time scale and becomes of order T_1, the situation is reversed. The inhomogeneous term becomes negligibly small, the whole time-dependence of P_E is determined by the homogeneous terms alone and it is consequently very slow:

$$\mathrm{d}P_E/\mathrm{d}t \sim P_E/T_1 \sim \lambda^2 w P_E.$$

This slow time variation implies a further simplification, because in the time integrals of the form

$$\int_0^t \mathrm{d}t' w_E(t - t' \mid \alpha'\alpha)\, P_E(t' \mid \alpha_0'\alpha_0) = \int_0^t \mathrm{d}t_1 w_E(t_1 \mid \alpha'\alpha)\, P_E(t - t_1 \mid \alpha_0'\alpha_0) \tag{5.2}$$

the integration in t_1 extends over the short time scale, $t_1 \sim T_0$, i.e. over an interval in which P_E varies very little. We may therefore approximate (5.2) by

$$\int_0^t \mathrm{d}t' w_E(t - t' \mid \alpha'\alpha)\, P_E(t' \mid \alpha_0'\alpha_0) = P_E(t \mid \alpha_0'\alpha_0) \int_0^\infty \mathrm{d}t_1 w_E(t_1 \mid \alpha'\alpha) = \\ = (2\pi)^{-1}\, P_E(t \mid \alpha_0'\alpha_0)\, \tilde{W}_{E-i0,\, E+i0}(\alpha'\alpha).$$

The last step, carried out under the assumption $t > 0$, follows from (4.28) through integration over t; the notation $E \pm i0$ is used for $E \pm i\eta$ with $\eta > 0$ very small. The master equation on the long time scale now becomes

$$\mathrm{d}P_E(t \mid \alpha\alpha_0)/\mathrm{d}t = \lambda^2 \int \tilde{W}_{E-i0,E+i0}(\alpha\alpha')\, \mathrm{d}\alpha'\, P_E(t \mid \alpha'\alpha_0) \\ - \lambda^2 \int \mathrm{d}\alpha'\, \tilde{W}_{E-i0,E+i0}(\alpha'\alpha)\, P_E(t \mid \alpha\alpha_0) \qquad \text{for } t \sim T_1. \tag{5.3}$$

It holds for positive t. The corresponding equation for negative times is obtained by interchanging the two indices of $\tilde{W}$.

The equations (5.1) and (5.3) have been derived under the assumption

$T_0 \ll T_1$ and they neglect corrections of relative order $T_0/T_1 \sim \lambda^2$. Consistency therefore requires that the functions f and $\tilde{W}$ which they contain should be taken to order λ only. To this order, as shown by (4.2), the operator D_l reduces to its unperturbed expression $(H - l)^{-1}$ and by substitution in (4.30) one finds

$$f_E(t \mid \alpha) = 2\pi^{-1} \cos [2(\varepsilon(\alpha) - E)t].$$

Integration of (5.1) for the short time scale is then elementary and gives

$$P_E(t \mid \alpha\alpha_0) = \pi^{-1}[\varepsilon(\alpha) - E]^{-1} \sin [2(\varepsilon(\alpha) - E)t]\, \delta(\alpha - \alpha_0) \quad \text{for } t \sim T_0. \tag{5.4}$$

At the upper end of the short time scale this expression approaches in the mean a limit which is obviously

$$P_E(t \mid \alpha\alpha_0) = \delta[\varepsilon(\alpha) - E]\, \delta(\alpha - \alpha_0) \quad \text{for} \quad T_0 \ll t \ll T_1. \tag{5.5}$$

The latter expression can now be used as initial value for the equation (5.3) relative to the long time scale. As we have seen, $\tilde{W}$ must be taken to first order in λ. Substituting $(H - l)^{-1}$ for D_l in (4.22) we find

$$\tilde{W}_{E-i0,E+i0}(\alpha'\alpha) = 2\pi\delta\,[\varepsilon(\alpha') - E]\, W^{(1)}_{E-i0,\,E+i0}\,(\alpha'\alpha)$$

where $W^{(1)}_{ll'}$ is the first order approximation of the function $W_{ll'}$ defined in (4.16). The master equation on the long time scale becomes

$$\mathrm{d}P_E(t \mid \alpha\alpha_0)/\mathrm{d}t = 2\pi\lambda^2 \int \delta[\varepsilon(\alpha) - E]\, W^{(1)}_{E-i0,E+i0}(\alpha\alpha')\, \mathrm{d}\alpha'$$

$$P_E(t \mid \alpha'\alpha_0) - 2\pi\lambda^2 \int \mathrm{d}\alpha'\, \delta[\varepsilon(\alpha') - E]\, W^{(1)}_{E-i0,E+i0}(\alpha'\alpha) P_E(t \mid \alpha\alpha_0). \tag{5.6}$$

It must be integrated with the initial condition (5.5). Clearly, from the occurrence of the δ-functions in the equation and the initial condition, the solution has the form

$$P_E(t \mid \alpha\alpha_0) = \delta[\varepsilon(\alpha) - E]\, \delta[\varepsilon(\alpha_0) - E]\, p(t \mid \alpha\alpha_0). \tag{5.7}$$

Substitution of this relation into (4.27) shows that

$$P(t \mid \alpha\alpha_0) = \delta[\varepsilon(\alpha) - \varepsilon(\alpha_0)]\, p(t \mid \alpha\alpha_0). \tag{5.8}$$

Consequently, to first order in λ, the transition probability $P(t \mid \alpha\alpha_0)$ contains a factor $\delta[\varepsilon(\alpha) - \varepsilon(\alpha_0)]$ implying conservation of the unperturbed energy. We note further from (5.7) and (5.8) that

$$P_E(t \mid \alpha\alpha_0) = \delta[\varepsilon(\alpha) - E]\, P(t \mid \alpha\alpha_0). \tag{5.9}$$

Substitution of this last expression into (5.6) gives, after eliminating a δ-factor,

$$\mathrm{d}P(t \mid \alpha\alpha_0)/\mathrm{d}t = 2\pi\lambda^2 \int \delta[\varepsilon(\alpha) - \varepsilon(\alpha')]\, \overline{W}^{(1)}(\alpha\alpha')\, \mathrm{d}\alpha'\, P(t \mid \alpha'\alpha_0)$$

$$- 2\pi\lambda^2 \int \mathrm{d}\alpha'\, \delta[\varepsilon(\alpha') - \varepsilon(\alpha)]\, \overline{W}^{(1)}(\alpha'\alpha)\, P(t \mid \alpha\alpha_0), \tag{5.10}$$

with the abbreviation

$$\overline{W}^{(1)}(\alpha\alpha') = W^{(1)}_{E-i0.E+i0}(\alpha\alpha') \quad \text{for} \quad E = \varepsilon(\alpha). \tag{5.11}$$

Equation (5.10) is the master equation on the long time scale, neglecting corrections of relative order λ^2. In contrast to the exact equation (4.31), it involves the transition probability P itself. It must be supplemented by the initial condition

$$P(t \mid \alpha\alpha_0) = \delta(\alpha - \alpha_0) \quad \text{for} \quad |t| \ll T_1 \tag{5.12}$$

directly obtained by comparison of (5.5) and (5.9). It should be noted that (5.12) holds for all times short compared to T_1, in particular for t of order T_0. Thus, to first order in λ, P is constant on the short time scale, whereas P_E has there a marked variation, given by (5.4).

Eq. (5.10) differs from the familiar lowest order equation (3.16) only by the fact that the transition rates $\overline{W}^{(1)}$ are correct to first order in λ, while (3.16) contains the zero order expression of these rates *). Our reduction of the general master equation to its well known lowest order form is thus complete. The interest of this reduction is of course not so much that it provides a new derivation for the familiar master equation. It lies rather in the clear and explicit picture obtained for the role of the two time scales, T_0 and T_1, and for the manner in which they remain completely separated if and only if all corrections of order $T_0/T_1 \sim \lambda^2$ are neglected. To be sure, the existence of a short time scale T_0 for all systems to which the familiar master equation applies has always been recognized. Still it seems to us quite instructive to have a more complete equation covering also the events on the short time scale and describing how the motions on the two time scales mix when T_0 and T_1 become of comparable order of magnitude.

6. *The long time behaviour of the transition probabilities.* Returning to the study of our system to general order in the perturbation, we want to investigate the asymptotic behaviour of the function $P_E(t \mid \alpha\alpha_0)$ and of the transition probability $P(t \mid \alpha\alpha_0)$ for very large times, $t \to \pm\infty$. From the identity

$$\int \mathrm{d}\alpha\, P(t \mid \alpha\alpha_0) = 1 \tag{6.1}$$

(an obvious consequence of the definition of P), it follows that P and consequently P_E must have non-vanishing asymptotic expressions for $t \to \infty$. Our problem is to study them.

To find the asymptotic behaviour of P_E, which in turn implies through (4.27) the behaviour of P, one must according to (4.26) determine the singularities of $X_{E+l,E-l}$ as a function of the complex variable l. These singularities are located on the real axis. They can be either points where the function has a finite discontinuity for l crossing the real axis, or points in the neighbourhood of which the function becomes infinite. The former singular points fill continuous intervals of the real axis. Only the latter ones, which are

*) One should however say that in practice $\overline{W}^{(1)}$ is often identical with $W^{(0)}$, the difference $W_{ll'} - W^{(0)}$ being of order λ^2.

isolated and will be called hereafter *pseudopoles*, give any contribution to P_E in the limit of long times, as is readily seen from (4.26) by deforming the contour γ into lines $l = E' \pm i\eta$ with η very small. The name pseudopole is used because near such a singularity the function, while becoming infinite as in a pole, usually has in addition a finite discontinuity in every neighbouring point of the real axis. More precisely, the pseudopoles to be found for $X_{E+l,E-l}$ will be points E_0 such that the function

$$(l - E_0)\, X_{E+l,\,E-l}$$

has around E_0, as only singularities, finite discontinuities accross the real axis. Such pseudopoles may be called of degree one. Typical examples are given at $l = 0$ by the simple functions

$$l^{-1} \int_{-1}^{1} (x - l)^{-1}\, \mathrm{d}x,\ l^{-1} + \int_{-1}^{1} (x - l)^{-1}\, \mathrm{d}x.$$

We attempt to obtain information on the pseudopoles of $X_{E+l,E-l}$ from a discussion of the expansion (4.19). The function $W_{E+l,E-l}$, on account of its definition (4.16), has no pseudopoles. Its only singularities are finite discontinuities accross the real axis. Pseudopoles of $X_{E+l,E-l}$ may result in two ways from poles of the functions $D_{E\pm l}$ occurring in the expansion (4.19), i.e. from the presence of non-dissipative states in this expansion. Firstly pseudopoles may originate from the products

$$D_{E+l}(\alpha) D_{E-l}(\alpha), \quad D_{E+l}(\alpha_0) D_{E-l}(\alpha_0) \tag{6.2}$$

which occur as factors in each term of the expansion. For example, if the function $D_{l'}(\alpha)$ has a pole at $l' = E(\alpha)$ (the state $|\alpha\rangle$ being then non-dissipative), the first product (6.2) gives rise to two pseudopoles of degree one at

$$l = \pm\, [E(\alpha) - E]. \tag{6.3}$$

In the asymptotic expression of $P_E(t \mid \alpha\alpha_0)$ for large times such a pair of pseudopoles produces an oscillatory term involving

$$[E(\alpha) - E]^{-1} \sin\, [2(E(\alpha) - E)t].$$

This term would however disappear for large t in any integrated expression of the form

$$\int A(\alpha)\, \mathrm{d}\alpha\, P_E(t \mid \alpha\alpha_0) \tag{6.4}$$

under the condition that $E(\alpha)$ remains different from E in the integration. Since in practice integrations of the type (6.4) over α and similar integrations over α_0 (compare (3.15)) are usually taken, this sort of pseudopole is of little interest except in the case where the integral (6.4) includes points where $E(\alpha) = E$, i.e. when the poles (6.3) of the two factors in the product (6.2) become coincident, and in a similar case for an integration over α_0.

The latter circumstances are but examples of the second way in which

poles of the functions $D_{E\pm l}$ give rise to pseudopoles of $X_{E+l,E-l}$. Generally any integral of the form

$$\int F(\alpha')D_{E+l}(\alpha')D_{E-l}(\alpha')\,\mathrm{d}\alpha' \tag{6.5}$$

where $F(\alpha')$ is some function of α', will now be shown to have a pseudopole of degree one at $l = 0$ when the two functions $D_{E\pm l}$ have poles which become coincident in the domain of integration. Integrals as (6.5) occur in the expansion (4.19) of $X_{E+l,\,E-l}$ as a result of the integrations over intermediate states; they occur also when integrations like (6.4) are performed over the states α or α_0. To prove our assertion we let $E(\alpha')$ be a pole of $D_{l'}(\alpha')$. The quantity $J_E(\alpha')$ may be taken to vanish for E around $E(\alpha')$ and the function $G_{l'}(\alpha')$ is then holomorphic in this point. In its neighbourhood we may write

$$D_{l'}(\alpha') = N(\alpha')[E(\alpha') - l']^{-1} \tag{6.6}$$

with the notation, already introduced in (I. 5.8),

$$[N(\alpha')]^{-1} = 1 + \lambda^2\,[\partial G_l(\alpha')/\partial l]_{l=E(\alpha')}. \tag{6.7}$$

In those parts of the domain of integration in (6.5) where $E(\alpha') \neq E$ the two factors D have their poles at different l-values, the integrand has only poles of degree one, producing after integration finite discontinuities across the real axis. Consider now the case that the domain of integration contains a manifold where $E(\alpha') = E$. For α' in its immediate neighbourhood the poles of $D_{E\pm l}(\alpha')$ may be studied by means of the approximate expression (6.6), which gives in the integral

$$\int F(\alpha')[N(\alpha')]^2(E(\alpha') - E - l)^{-1}(E(\alpha') - E + l)^{-1}\,\mathrm{d}\alpha' =$$

$$= (2l)^{-1}\int F(\alpha')[N(\alpha')]^2\,[(E(\alpha') - E - l)^{-1} - (E(\alpha') - E + l)^{-1}]\,\mathrm{d}\alpha'. \tag{6.8}$$

In this form the occurrence of a pseudopole of degree one at $l = 0$ is obvious.

Since the expansion (4.19) contains terms with simultaneous integrations over several states and since, as we have just seen, each such integration may give rise to a pseudopole of degree one at $l = 0$, it might look as if more complicated singularities will result from superposition of pseudopoles of degree one. It will now be shown that such complications never occur. For this purpose we need considerations very similar to those of I, Section 4. We have there defined for each state $|\alpha\rangle$ the family x_α composed of the states $|\alpha'\rangle$ which play an effective part as intermediate state in the righthand side of the equation (see (4.3))

$$|\alpha\rangle\, G_l(\alpha) = \{VD_lV - \lambda VD_lVD_lV + \ldots\}_{id}\,|\alpha\rangle.$$

We can here formulate this definition more simply in terms of the function $W_{ll'}(\alpha'\alpha)$ introduced by (4.16). The family x_α is composed of the states $|\alpha'\rangle$ for which the function $W_{ll'}(\alpha'\alpha)$ of the complex variables l, l' is not identically zero. This family can in practice always be pictured as a set of continuous

manifolds in the space of the quantum numbers characterizing the states $|\alpha'\rangle$. In Section 4 of I another set of states was also defined, the family y_α obtained by taking together all states of x_α, all states belonging to the families $x_{\alpha'}$ associated with the latter states, and so on. On account of (4.19) an alternative definition of y_α is the following: y_α is composed of the states $|\alpha'\rangle$ for which the function $X_{ll'}(\alpha'\alpha)$ of the variables l, l' does not vanish identically. The physical interpretation of the family y_α was given in I for the special case of non-dissipative systems. This interpretation is valid for a state $|\alpha\rangle$ as soon as it is itself non-dissipative, irrespectively of the properties of the other states. Another interpretation holds more generally, also when $|\alpha\rangle$ is dissipative; y_α is simply the set of all states $|\alpha'\rangle$ which get involved in the time evolution of a wave packet initially concentrated very narrowly around $|\alpha\rangle$. The family x_α has no special physical significance; in practice it is always found to coincide with y_α.

The property of the family y_α which we have to use presently is the following. Whenever $D_l(\alpha)$ has a pole at $l = E(\alpha)$, the functions $D_l(\alpha')$ belonging to all states $|\alpha'\rangle$ of y_α are regular around $l = E(\alpha)$ and those belonging to states $|\alpha'\rangle$ such that $|\alpha\rangle$ is in $y_{\alpha'}$ have a finite discontinuity for l crossing the real axis at $l = E(\alpha)$. As was shown in Section (I. 4), this property is a direct consequence of the identity (I. 3.13) or (4.3). Consider now the general term of the expansion (4.19) of $X_{E+l,E-l}$. It reads

$$\lambda^{2(n+1)} D_{E+l}(\alpha) D_{E-l}(\alpha) \int W_{E+l,E-l}(\alpha\alpha_n) D_{E+l}(\alpha_n) D_{E-l}(\alpha_n)\, \mathrm{d}\alpha_n \ldots$$
$$\ldots \mathrm{d}\alpha_1\, W_{E+l,E-l}(\alpha_1\alpha_0) D_{E+l}(\alpha_0) D_{E-l}(\alpha_0). \tag{6.9}$$

Take any sequence of states α, α_n, ... α_1, α_0 for which the integrand does not vanish. The family y belonging to any element of the sequence contains all elements of the sequence situated more to the left. From the property just mentioned it follows then immediately that if in (6.9) the two factors of a product

$$D_{E+l}(\alpha_j) D_{E-l}(\alpha_j) \tag{6.10}$$

have coincident poles at $l = 0$ no other such product appearing in (6.9) can have the same singularity.

The singularities of $X_{E+l,E-l}(\alpha\alpha_0)$ which are produced by poles of D_l-functions are thereby completely described: except for finite discontinuities accross the real axis and uninteresting pseudopoles which disappear when integrations are carried out over α and α_0, the only possible singularity is a pseudopole of degree one at $l = 0$. It is remarkable that the latter type of singularity also occurs when none of the D_l-functions involved in the expansion of X has a pole at $l' = E$ in the domain of integration. This is best seen on the basis of the simple equation

$$D_{E+l}(\alpha_0) - D_{E-l}(\alpha_0) = 2l \int \mathrm{d}\alpha\, X_{E+l,\,E-l}(\alpha\alpha_0) \tag{6.11}$$

which is easily derived by taking the diagonal part of the well known identity

$$R_l - R_{l'} = (l - l')\, R_l R_{l'}$$

and applying the definition (4.14) of X. Obviously, whenever $D_{l'}(\alpha_0)$ has a finite discontinuity for l' crossing the real axis at the point E (i.e. whenever $J_E(\alpha_0) \neq 0$) the integral in the righthand side of (6.11) has a pseudopole of degree one at $l = 0$. Consequently the function $X_{E+l,\, E-l}\,(\alpha\alpha_0)$ must then have the same singularity, at least for some range of values of α. This pseudopole must occur irrespectively of the presence or absence of poles in the D-functions involved in X. We also note that it cannot reduce to a true pole, because for non-vanishing $J_E(\alpha_0)$ the limit of the whole expression (6.11) for $l \to 0$ is different depending on the sign of $Im(l)$.

When, in the expansion (4.19) taken for $X_{E+l,E-l}$, none of the $D_{l'}$-functions involved has a pole at $l' = E$, the individual terms of the expansion have no singularities other than finite discontinuities across the real axis. The occurrence, for $J_E(\alpha_0) \neq 0$, of a pseudopole in the total expression $X_{E+l,E-l}$ $(\alpha\alpha_0)$ must then be attributed to the fact that the expansion becomes divergent when l vanishes. This lack of convergence can be verified by considering for the case under discussion the convergence properties of the expansion (4.19) in the limit of small λ. In this limit we may put everywhere, according to (4.17),

$$W_{ll'}(\alpha'\alpha) = W^{(0)}(\alpha'\alpha)$$

and we may approximate all functions D by

$$D_{l'}(\alpha) = \varepsilon(\alpha) - l' - \lambda^2 K_{\epsilon(\alpha)}(\alpha) \mp i\lambda^2 J_{\epsilon(\alpha)}(\alpha) \tag{6.12}$$

where the upper (lower) sign must be taken for positive (negative) value of $Im(l')$. The terms in λ^2 are important only when l' is near $\varepsilon(\alpha')$. Using the approximation (6.12) we find

$$D_{E+l}(\alpha) D_{E-l}(\alpha) = \{[\varepsilon(\alpha) - E - \lambda^2 K_{\epsilon(\alpha)}(\alpha)]^2 + [\lambda^2 J_{\epsilon(\alpha)}(\alpha) \mp il]^2\}^{-1}. \tag{6.13}$$

We are interested here in the case where $D_{l'}$ has no pole at $l' = E$. In the approximation (6.12) this condition is

$$J_{\epsilon(\alpha)}(\alpha) \neq 0. \tag{6.14}$$

When it is verified (6.13) remains bounded in the neighbourhood of $l = 0$ and in this point an integral of the form (6.5) becomes approximately

$$\int F(\alpha') D_{E+l}(\alpha')\, D_{E-l}(\alpha')\, \mathrm{d}\alpha' = \int F(\alpha')\, \{[\varepsilon(\alpha') - E - \lambda^2 K_{\epsilon(\alpha')}(\alpha')]^2 + \\ + \lambda^4 [J_{\epsilon(\alpha')}(\alpha')]^2\}^{-1}\, \mathrm{d}\alpha' = \pi\lambda^{-2} \int [J_{\epsilon(\alpha')}(\alpha')]^{-1}\, F(\alpha')\, \delta[\varepsilon(\alpha') - E]\, \mathrm{d}\alpha'. \tag{6.15}$$

It is consequently very large, of order λ^{-2}. Returning now to the expansion (4.19) for $X_{E+l,\, E-l}$, still in the case of small λ, we observe that when going from an arbitrary term of the expansion to the next, one gets an additional

factor λ^2 and an additional integration of the type (6.15). The coefficient λ^{-2} occurring in the latter integral for $l = 0$ compensates the factor λ^2, thus explaining why convergence of the expansion cannot be achieved by taking λ small enough. It should be noted that this compensation occurs only at the point $l = 0$. For all other values of l (even infinitely close to the real axis) the integral (6.15) remains finite when $\lambda \to 0$ and nothing prevents the increasing powers of λ in front of the successive terms of the expansion to ensure its convergence. No other singular points than $l = 0$ can therefore originate from lack of convergence of the series (4.19) for $X_{E+l,\,E-l}$.

We have encountered two different origins for the pseudopoles of the expression $X_{E+l,\,E-l}$, the first one being a pole of $D_{l'}(\alpha')$ at $l' = E$ for states $|\alpha'\rangle$ included in the domains of integration (or appearing as initial or final state), and the second one the divergence of the expansion of $X_{E+l,\,E-l}$ at $l = 0$. Just as we have seen that poles of $D_{l'}$ never can have a cumulative effect and produce higher order singularities by superposition of pseudopoles of degree one, no such cumulative effect can originate from the simultaneous occurrence of poles of D-functions and of a divergence in the expansion. To verify this point, we consider in the expansion of $X_{E+l,\,E-l}$ all terms (6.9) of order $n \geqslant m \geqslant 1$, leave out the integrations over the intermediate states $\alpha_1, \ldots \alpha_m$, but perform those over all other intermediate states. The result is

$$\lambda^{2m} X_{E+l,\,E-l}(\alpha\alpha_m)\, W_{E+l,\,E-l}(\alpha_m\alpha_{m-1}) D_{E+l}(\alpha_{m-1}) D_{E-l}(\alpha_{m-1}) \ldots$$
$$\ldots D_{E+l}(\alpha_1) D_{E-l}(\alpha_1)\, W_{E+l,\,E-l}(\alpha_1\alpha_0) D_{E+l}(\alpha_0) D_{E-l}(\alpha_0). \qquad (6.16)$$

Assume now that α_{m-1} would be such that $D_{l'}(\alpha_{m-1})$ has a pole at $l' = E$. It is then just as impossible for $X_{E+l,\,E-l}(\alpha\alpha_m)$ to have a pseudopole due to lack of convergence as to have one caused by poles in other D-functions. Indeed, from our assumption and from the property of the family y already used before, $D_l(\alpha')$ is regular at $l' = E$ for all states α' in the family $y_{\alpha_{m-1}}$, thus in particular for the state α_m. This implies

$$\lim_{l \to 0} [D_{E+l}(\alpha_m) - D_{E-l}(\alpha_m)] = 0.$$

Comparing with (6.11) we must indeed conclude that no pseudopole occurs in $X_{E+l,\,E-l}(\alpha\alpha_m)$.

This ends our determination of the singularities of $X_{E+l,\,E-l}(\alpha\alpha_0)$. Leaving out of consideration, when one of the states α, α_0 is non-dissipative, pseudopoles which disappear when an integration over these states is carried out, the only singularities we have found are finite discontinuities across the real axis and a pseudopole of degree one at $l = 0$. It is this last singularity which determines the asymptotic behaviour of $P_E(t \mid \alpha\alpha_0)$ for long times. Indeed it follows from Eq. (4.26) that

$$\lim_{t \to \pm\infty} P_E(t \mid \alpha\alpha_0) = \pi^{-1} \lim_{0 < \eta \to 0} \eta X_{E \mp i\eta,\,E \pm i\eta}(\alpha\alpha_0) \qquad (6.17)$$

where upper (lower) signs must be taken together. When the state α or

α_0 is non-dissipative this relation holds after averaging over the time or integrating over α or α_0. Otherwise it is strictly exact. From (6.17) the asymptotic value of the transition probability follows

$$\lim_{t\to\pm\infty} P(t \mid \alpha\alpha_0) = \pi^{-1} \int_{-\infty}^{\infty} dE \lim_{0<\eta\to 0} \eta X_{E\mp i\eta, E\pm i\eta}(\alpha\alpha_0). \qquad (6.18)$$

We note that the quantity (6.17) is non-negative; this follows from the definition (4.14), which implies more generally that X_{ll*} is never negative.

The last task is the determination of the limit in the righthand side of (6.17). On physical grounds the result is expected to depend very strongly on the nature of the system and on the dissipative or non-dissipative character of the states involved. For this reason a unified treatment applicable to all cases is not possible. An exhaustive analysis of the various possible situations seems at present very difficult. Here we shall restrict ourselves to the extension to general order of the case of dissipative behaviour which is usually discussed in lowest order on the basis of the master equation (3.16). However, before studying this case in the next section, we want to mention for the sake of completeness the value taken by (6.17) for the non-dissipative systems studied in I and II. The calculation of the limit (6.17) for such systems is very simple because the pseudopole of $X_{E+l, E-l}$ is here entirely determined by the poles of the D-functions. Assuming as in I and II that each function $D_l(\alpha)$ has only one pole $E(\alpha)$, one finds

$$\begin{aligned}
&\lim_{t\to+\infty} P_E(t \mid \alpha\alpha_0) = [N(\alpha)]^2\, \delta[E(\alpha) - E]\, \delta(\alpha - \alpha_0) \\
&+ \lambda^2 [N(\alpha)]^2\, \delta[E(\alpha) - E] \int W_{E-i0, E+i0}(\alpha\alpha_1)\, d\alpha_1 X_{E-i0, E+i0}(\alpha_1\alpha_0) \\
&+ \lambda^2 \int X_{E-i0, E+i0}(\alpha\alpha_1)\, d\alpha_1\, W_{E-i0, E+i0}(\alpha_1\alpha_0)[N(\alpha_0)]^2\, \delta[E(\alpha_0) - E] \\
&+ \lambda^4 \int X_{E-i0, E+i0}(\alpha\alpha_3)\, d\alpha_3\, W_{E-i0, E+i0}(\alpha_3\alpha_2)[N(\alpha_2)]^2 \\
&\quad \delta[E(\alpha_2) - E]\, d\alpha_2\, W_{E-i0, E+i0}(\alpha_2\alpha_1)\, d\alpha_1 X_{E-i0, E+i0}(\alpha_1\alpha_0).
\end{aligned}$$

The limit for $t \to -\infty$ is found by interchanging the indices $E \pm i0$. The symbol $N(\alpha)$ was defined in (6.7). This result is susceptible of a simple interpretation in terms of the perturbed stationary states of the system, know from II, but we shall not describe it in the present paper.

7. *The approach to statistical equilibrium.* It has often been shown how the lowest order master equation (3.16) implies that the system studied approaches microcanonical equilibrium under the influence of the perturbation [6]). The assumptions on which the derivation is most customarily based are the symmetry of the transition rate matrix, reading in our notation

$$W^{(0)}(\alpha'\alpha) = W^{(0)}(\alpha\alpha'), \qquad (7.1)$$

and the interconnection of all states of equal unperturbed energy, by which is meant that for any two states α, α' verifying

$$\varepsilon(\alpha) = \varepsilon(\alpha')$$

there exists a sequence of states connecting them

$$\alpha = \alpha_0, \alpha_1, \ldots \alpha_n, \alpha_{n+1} = \alpha' \tag{7.2}$$

with the properties

$$\varepsilon(\alpha_j) = \varepsilon(\alpha_{j+1}),\ W^{(0)}(\alpha_{j+1}\,\alpha_j) \neq 0,\ (j = 0, \ldots n). \tag{7.3}$$

Under these assumptions the long time limit of P is found to be in our notation

$$\lim_{t\to\pm\infty} P(t \mid \alpha\alpha_0) = \{\int \delta[\varepsilon(\alpha') - \varepsilon(\alpha)]\, d\alpha'\}^{-1} \cdot \delta[\varepsilon(\alpha) - \varepsilon(\alpha_0)]. \tag{7.4}$$

It corresponds to the microcanonical equilibrium distribution in absence of the perturbation, as is consistent with the lowest order nature of (3.16) *). It should be noted that the assumption of interconnection of states automatically implies that all states α are dissipative; indeed it implies that each state α is contained in its own family of states y_α, a situation incompatible with the occurrence of poles in $D_l(\alpha)$ (see I, section 4 or section 6 of the present paper).

The symmetry property (7.1), often referred to as principle of microscopic reversibility or principle of detailed balance, is usually claimed to be an immediate consequence of the hermiticity of the perturbation V, on the ground that $W^{(0)}(\alpha'\alpha)$ is essentially the absolute square of the matrix element $\langle\alpha' \mid V \mid \alpha\rangle$. Although of course partly valid, this argument is oversimplified. Taken in the framework of our analysis, it disregards the fact that the diagonal part must be taken in the definition (3.17) of $W^{(0)}$. Let us consider for example (see appendix) the system composed of one Bloch electron in interaction with the lattice vibrations of a crystal. We choose for α one electron states with the lattice in its unperturbed ground state and for α' states where, in addition to the electron, a phonon is present. The quantity $W^{(0)}(\alpha\alpha')$ then vanishes identically, whereas $W^{(0)}(\alpha'\alpha)$ has non-vanishing values, even on the energy shell $\varepsilon(\alpha) = \varepsilon(\alpha')$. Clearly (7.1) does not hold. Still the master equation (3.16) is fully applicable and describes in the limit of small phonon-electron interaction the dissipation of a state α with one electron and no phonon present into states where one, two, etc. phonons have been emitted by the electron. The vanishing of $W^{(0)}(\alpha\alpha')$ corresponds to the physically obvious fact that a state with one electron and one phonon will never dissipate, i.e. never go over for arbitrary phases, into a state without phonon; in other words phonon absorption by the electron is a phase dependent, transient process.

It is only for states with a very large number of elementary excitations present (of the order of the size of the system), in the foregoing example

*) The customary discussion of these matters treats the states α as discrete. In our presentation they are considered as continuous, but evidently we could also, by groupings of states, go over to a formulation in terms of discrete indices.

states with many phonons, that the symmetry property (7.1) can be expected to hold. For such states, – and most states are of this type for a large system not too close to its ground state –, one expects that if transitions in the neighbourhood of $\alpha_1 \to \alpha_2$ contribute to the value of $W^{(0)}(\alpha'\alpha)$ at $\alpha = \alpha_1$, $\alpha' = \alpha_2$ (see (3.17)), the transitions in the neighbourhood of $\alpha_2 \to \alpha_1$ will contribute the same amount to $W^{(0)}(\alpha_1\alpha_2)$, thus giving rise to the symmetry (7.1). Similarly, for such states, if a succession of transitions $\alpha_1 \to \alpha_2 \to \ldots \to \alpha_n$ and its neighbouring ones contribute to the value at $\alpha = \alpha_1$, $\alpha' = \alpha_n$ of the function $W_{ll'}(\alpha'\alpha)$ defined in (4.16), the transitions around $\alpha_n \to \ldots \ldots \alpha_2 \to \alpha_1$ are expected to contribute to $W_{ll'}(\alpha_1\alpha_n)$ and the hermiticity of V now gives the generalized symmetry relation

$$W_{ll'}(\alpha'\alpha) = W_{l'l}(\alpha\alpha'). \tag{7.5}$$

For a detailed verification of this conclusion in an actual case, e.g. for the electron-phonon system of the appendix (considering only states where the number of phonons is of order N or Ω), the labelling of the states α by the wave vectors of the elementary excitations, as described in Section 2, is not very convenient and it would be replaced with profit by a different one, namely a labelling by the numbers of excitations of each sort per small cell of wave vector space. The coordinates of the cells where these numbers are changed in the transitions caused by the perturbation would then play the role of the continuous variables present in our integrals.

For our discussion of the approach toward equilibrium to general order in the perturbation λV, we adopt the property (7.5) as the basic assumption generalizing (7.1). As for the assumption of interconnection of states, we keep it in the same form as above: for every pair α, α' of states of equal unperturbed energy there exists a sequence (7.2) verifying (7.3). We note again that it implies the dissipative property for all states α, and thus the boundedness of the function $D_{E\pm i0}(\alpha)$. Under these assumptions, we shall establish that for λ not too large one has

$$\lim_{t\to\pm\infty} P_E(t \mid \alpha\alpha_0) = [\int \Delta_E(\alpha')\, \mathrm{d}\alpha']^{-1} \cdot \Delta_E(\alpha)\Delta_E(\alpha_0), \tag{7.6}$$

with the abbreviation

$$\Delta_E(\alpha) = (2\pi i)^{-1}[D_{E+i0}(\alpha) - D_{E-i0}(\alpha)]. \tag{7.7}$$

If one remembers the relation (4.27) between P_E and P, and notices that (7.7) reduces to $\delta[\varepsilon(\alpha) - E]$ in the limit of small λ, one readily sees that in this limit (7.6) gives the lowest order value (7.4) for the long time expression of P. We now proceed to prove (7.6). We shall show afterwards that this result corresponds to establishment of the microcanonical equilibrium distribution in presence of the perturbation.

Introducing the notation

$$\lim_{t\to\pm\infty} P_E(t \mid \alpha\alpha_0) = q_E^{\pm}(\alpha\alpha_0), \tag{7.8}$$

we recall the main result of Section 6, equation (6.17),

$$q_E^{\pm}(\alpha\alpha_0) = \pi^{-1} \lim \eta X_{E\mp i\eta,\, E\pm i\eta}(\alpha\alpha_0) \tag{7.9}$$

where η is a positive number tending to zero. We note incidentally that in view of the relation (4.19) between X and W, the symmetry relation (7.5) implies a similar property for X:

$$X_{ll'}(\alpha'\alpha) = X_{l'l}(\alpha\alpha') \tag{7.10}$$

and consequently, from (7.9),

$$q_E^{+}(\alpha\alpha_0) = q_E^{-}(\alpha_0\alpha). \tag{7.11}$$

We have mentioned earlier that the assumption of interconnection of states requires the function $D_{E\pm i0}(\alpha)$ to be bounded. As we have seen in detail in Section 6, the limit (7.9) originates then entirely from divergence of the series (4.19) when l and l' approach from opposite sides the point E of the real axis. From the boundedness of $D_{E\pm i0}(\alpha)$, the first term in the righthand side of (4.19) gives a vanishing contribution to the limit (7.9). The latter consequently verifies the two following equations:

$$q_E^{\pm}(\alpha\alpha_0) = \lambda^2 D_{E+i0}(\alpha) D_{E-i0}(\alpha) \int W_{E\mp i0,\, E\pm i0}(\alpha\alpha')\, \mathrm{d}\alpha'\, q_E^{\pm}(\alpha'\alpha_0), \tag{7.12}$$

$$q_E^{\pm}(\alpha\alpha_0) = \lambda^2 \int q_E^{\pm}(\alpha\alpha')\, \mathrm{d}\alpha'\, W_{E\mp i0,\, E\pm i0}(\alpha'\alpha_0)\, D_{E+i0}(\alpha_0) D_{E-i0}(\alpha_0). \tag{7.13}$$

Our determination of q_E will be based on the first; one could however use the second one as well *). Equation (7.12) shows that q_E is eigenfunction of an eigenvalue problem. It belongs to the eigenvalue 1.

Consider this eigenvalue problem in the limit of small λ. Since we are dealing with the dissipative case, equation (6.14) holds and we may use equation (6.15), which states that one has approximately

$$\lambda^2 D_{E+i0}(\alpha) D_{E-i0}(\alpha) = \pi [J_{\epsilon(\alpha)}(\alpha)]^{-1}\, \delta[\varepsilon(\alpha) - E].$$

The quantity J must be taken in the limit $\lambda \to 0$; its value is then

$$J_{\epsilon(\alpha)}(\alpha) = \pi \int \mathrm{d}\alpha'\, \delta[\varepsilon(\alpha') - \varepsilon(\alpha)]\, W^{(0)}(\alpha'\alpha). \tag{7.14}$$

The limiting form of the eigenvalue equation is

$$q_E^{\pm}(\alpha\alpha_0) = \pi [J_{\epsilon(\alpha)}(\alpha)]^{-1}\, \delta[\varepsilon(\alpha) - E] \int W^{(0)}(\alpha\alpha')\, \mathrm{d}\alpha' q_E^{\pm}(\alpha'\alpha_0). \tag{7.15}$$

The solution is necessarily of the form

$$q_E^{\pm}(\alpha\alpha_0) = \delta[\varepsilon(\alpha) - E] f(\alpha)$$

with

$$f(\alpha) = \pi [J_{\epsilon(\alpha)}(\alpha)]^{-1} \int W^{(0)}(\alpha\alpha')\, \delta[\varepsilon(\alpha) - \varepsilon(\alpha')]\, \mathrm{d}\alpha' f(\alpha').$$

The latter equation is to be taken on the energy shell $\varepsilon(\alpha) = E$ only. The

*) An equation closely connected to (7.12) would be obtained by inserting (7.8) in the master equation (4.31). The form (7.12) is however more practical for the following considerations.

function $f(\alpha) =$ constant is a solution, as results immediately from (7.14) and the symmetry relation (7.5) in its lowest order form (7.1). Using the non-negative nature of $W^{(0)}(\alpha\alpha')$ and the assumed interconnection of all states on the energy shell $\varepsilon(\alpha) = E$, one furthermore concludes by a well known argument [6]) that the solution mentioned is the only one. Finally the transposed eigenvalue equation of (7.15), which is

$$q'(\alpha') = \pi \int \mathrm{d}\alpha\, q'(\alpha)[J_{\epsilon(\alpha)}(\alpha)]^{-1}\, \delta[\varepsilon(\alpha) - E]\, W^{(0)}(\alpha\alpha')$$

is easily seen from (7.14) to have the solution

$$q'(\alpha) = \pi \int \mathrm{d}\alpha'\, \delta[\varepsilon(\alpha') - E]\, W^{(0)}(\alpha'\alpha).$$

This solution is not orthogonal to the unique solution we have found for (7.15). As a consequence of known theorems [7]) we can therefore conclude that the eigenvalue 1 is a simple root of the characteristic equation of the eigenvalue problem.

The latter property, just established in the limit of small λ, implies by continuity that for $|\lambda|$ smaller than a positive quantity λ_c the characteristic equation of the exact eigenvalue problem (7.12) has one and only one root in the neighbourhood of 1, and that this root is simple. The corresponding eigenfunction is consequently unique (except for an arbitrary multiplicative constant). We show now that the root in question is 1 and that the corresponding eigenfunction is $\Delta_E(\alpha)$, as defined by (7.7). For this purpose we insert $\Delta_E(\alpha')$ instead of q_E in the righthand side of (7.12). Applying the symmetry relation (7.5), we obtain for the integral

$$(2\pi i)^{-1} \int [D_{E+i0}(\alpha') - D_{E-i0}(\alpha')]\, \mathrm{d}\alpha' W_{E\pm i0\, E\mp i0}(\alpha'\alpha).$$

In view of the identity (4.21) this expression is simply, for both values of the double signs,

$$(2\pi i)^{-1}\, [G_{E+i0}(\alpha) - G_{E-i0}(\alpha)].$$

The righthand side of (7.12) is thus equal to

$$(2\pi i)^{-1}\, \lambda^2\, [G_{E+i0}(\alpha) - G_{E-i0}(\alpha)] D_{E+i0}(\alpha) D_{E-i0}(\alpha). \tag{7.16}$$

We make use of the identity (4.23) for $l = E + i0$, $l' = E - i0$. In view of the boundedness of $D_{E\pm i0}$, the term in $l - l'$ gives no contribution and (7.16) reduces to

$$(2\pi i)^{-1}\, [D_{E+i0}(\alpha) - D_{E-i0}(\alpha)] = \Delta_E(\alpha).$$

Our statement is thereby established.

On the basis of the foregoing, the determination of $q_E^{\pm}$ is easily completed. From the unicity of the eigenfuction $\Delta_E(\alpha)$, it is clear that q_E must have the form

$$q_E^{\pm}(\alpha\alpha_0) = \Delta_E(\alpha)\, f_E^{\pm}(\alpha_0). \tag{7.17}$$

Remembering the identity

$$D_{E+l}(\alpha_0) - D_{E-l}(\alpha_0) = 2l \int d\alpha \, X_{E+l,E-l}(\alpha\alpha_0)$$

already mentioned in (6.11) we find from (7.9) and (7.7)

$$\int d\alpha \, q_E^{\pm}(\alpha\alpha_0) = \Delta_E(\alpha_0).$$

Insertion of (7.17) gives

$$f_E^{\pm}(\alpha_0) = [\int \Delta_E(\alpha') \, d\alpha']^{-1} \Delta_E(\alpha_0)$$

independently of the double sign. We have thereby established, for $|\lambda| < \lambda_c$, the announced expression (7.6) for the long time limit of P_E.

From (7.6), the long time limit of P is

$$\lim_{t \to \pm\infty} P(t \mid \alpha\alpha_0) = \int_{-\infty}^{\infty} dE \, [\int \Delta_E(\alpha') \, d\alpha']^{-1} \Delta_E(\alpha) \, \Delta_E(\alpha_0). \tag{7.18}$$

We shall denote by T a time such that this limit is practically attained for $|t| \gtrsim T$. This is the time T already considered in Section 3. Let our system be at time $t = 0$ in the quantum state

$$\varphi_0 = \int |\alpha\rangle \, d\alpha \, c(\alpha) \tag{7.19}$$

and let us assume this initial state to have phases sufficiently incoherent for the interference term (3.13) to remain negligible over the time interval $|t| \lesssim T$. The expectation value at time t of a diagonal operator A is then given for $|t| \lesssim T$ by the formula

$$\langle A \rangle_t = \int A(\alpha) \, d\alpha \, P(t \mid \alpha\alpha_0) \, d\alpha_0 \mid c(\alpha_0)|^2.$$

In view of (7.18) it approaches for $t \to \pm T$ the limit

$$\lim \langle A \rangle_t = \int_{-\infty}^{\infty} dE \, \langle A \rangle_E p_E, \tag{7.20}$$

where we have put

$$\langle A \rangle_E = [\int \Delta_E(\alpha') \, d\alpha']^{-1} \int A(\alpha) \, \Delta_E(\alpha) \, d\alpha, \tag{7.21}$$

$$p_E = \int |c(\alpha)|^2 \, \Delta_E(\alpha) \, d\alpha. \tag{7.22}$$

As will now be established, this limit agrees with the value which would be calculated for A from the microcanonical distribution taken for the complete hamiltonian $H + \lambda V$. We introduce to this end the projection operator Q_E on the energy shell $H + \lambda V = E$, given by

$$Q_E = (2\pi i)^{-1} \lim_{\eta \to 0} (R_{E+i\eta} - R_{E-i\eta}), \quad \eta > 0,$$

and already used in II, Section 2. Note that the diagonal part $\{Q_E\}_d$ of this operator is simply the diagonal operator Δ_E, the eigenvalues of which are given by (7.7). The microcanonical average of a diagonal operator A on the energy shell $H + \lambda V = E$ can be written as (Sp denotes the trace)

$$Sp(AQ_E)/Sp(Q_E).$$

Calculating the trace in the $|\alpha\rangle$-representation, one can replace Q_E by its diagonal part Δ_E, and, in the limit of an infinite system, one finds the expression (7.21). Consequently the quantity $\langle A\rangle_E$ is the microcanonical average of A on the shell of total energy E. On the other hand, when the system is in its initial state (7.19) the probability for the total energy $H + \lambda V$ to have a value between E and $E + \mathrm{d}E$ is

$$\langle \varphi_0 | Q_E | \varphi_0 \rangle \, \mathrm{d}E. \tag{7.23}$$

In view of the phase incoherence of the amplitudes $c(\alpha)$, the only contribution to (7.23) comes from the diagonal part of Q_E. The expectation value $\langle \varphi_0 | Q_E | \varphi_0 \rangle$ thus reduces to (7.22) and we conclude that p_E gives the probability distribution of the total energy in the initial state. The announced result is thereby reached: the righthand side of (7.20) is the microcanonical average of A corresponding to the statistical distribution of total energy in the initial state φ_0.

We end with a few comments on the results of this section. It is only for diagonal operators A and for initial states φ_0 with rapidly varying phases that we have established the approach to microcanonical equilibrium values. The first restriction has already been discussed in Section 3. One would expect the approach to equilibrium values to hold true for a wider class of operators, to know the operators which have simple matrix elements in the $|\alpha\rangle$-representation, even in the limit of a large system. Such an extension of our results would however require a proper generalization of our mathematical treatment. As for the second restriction, its only purpose is to make the contribution of the interference term (3.13) negligible for a time interval as long as T *). The more rapidly the phases of the initial amplitudes vary, the longer will be the time interval over which no interference effects occur. More cannot be said in general, however, because one can imagine initial states such that $\langle A\rangle_t$, having reached the equilibrium value (7.20) at a time $t \sim T$, retains it for a time much longer than T whereupon a new deviation from the equilibrium value sets in because of a sudden appearance of contributions from the interference term.

It should be clear that the assumption of rapidly varying phases for the initial state φ_0 has little in common and is even in contradiction with the conventional assumption of incoherent phases at all times. The former assumption singles out the initial state and implies for all $t \neq 0$ coherent phase relations between the amplitudes $c_t(\alpha)$ of

$$\varphi_t = \exp\left[-i(H + \lambda V)\, t\right]\varphi_0 = \int |\alpha\rangle \, \mathrm{d}\alpha \, c_t(\alpha).$$

These phase relations are all-important when the effects of the perturbation are taken into account to general order. It is only to lowest order that their

*) We note that for $\Delta\alpha$ small enough initial states of the type considered in (3.19), (3.20) satisfy this property. They form another class of states for which (7.20) holds.

influence is weakened: it may then for example be neglected in the derivation of the master equation but remains essential when time inversion is applied to the system [1]). To general order in the perturbation, the initial time $t = 0$ is completely singled out by its incoherence of phases. Starting from it, the system behaves dissipatively both toward the future and toward the past. This is why the general master equation (4.31) imparts a special role to the instant $t = 0$. This special role is no longer explicitly visible in the lowest order master equation (3.16), but it is still implied by it, because, as is well known, a non-stationary solution of (3.16) cannot be continued indefinitely toward the past without taking negative values. In connection with the coherence of phases of the amplitudes $c_t(\alpha)$ for all non-vanishing times, we may also mention the close relation of this property with the non-markovian nature of the general master equation (4.31). This non-markovian nature can be understood as resulting from interference effects between the various waves produced by the perturbation. Such interference effects are a manifestation of definite phase relationships. As was discussed in detail in A, they become negligible for small perturbations, and this circumstance is responsible for the markovian character of the lowest order equation (3.16).

Our discussion of the approach to statistical equilibrium has been carried out under the assumptions of symmetry (7.5) and of interconnection of states. It is for systems with a large number of excitations present (of the order of the number of particles in the system) that we may expect these assumptions to hold. For such systems, the master equation (4.31) can be used to follow in detail the time evolution of the system toward equilibrium. There are however also other situations to which the master equation is directly applicable, namely all situations where initially a very few excitations are present in the system, so that the dissipative process consists in their decay into an ever increasing number of other modes of motion. An example of this sort, the system composed of one Bloch electron in interaction with a lattice initially in its ground state, has already been quoted and can in principle be studied completely starting from the equations in the appendix. In such cases of shower-like processes it is no longer strictly possible to describe the long time behaviour of the system as an approach to equilibrium, because the total excitation energy is too low. One must rather think in terms of a shower phenomenon which, governed by the master equation, continues as long as dissipative states are involved and can only be interrupted if and when low-lying non-dissipative states are reached.

Appendix. We illustrate in this appendix a few aspects of the general formalism used throughout the paper by considering a special example. We assume a perfect non-conducting crystal, add a few electrons in the lowest unoccupied Bloch band and consider their interaction with longitudinal

lattice vibrations (to be called phonons). The hamiltonian of this system is composed of a part H for the non-interacting electrons and phonons, and a part λV describing the interaction. In the simplest approximation one has

$$H = \sum_{\mathbf{k}} \varepsilon(\mathbf{k})\, \alpha_{\mathbf{k}}^* \alpha_{\mathbf{k}} + \sum_{\mathbf{q}} \omega(\mathbf{q}) a_{\mathbf{q}}^* a_{\mathbf{q}}, \tag{A.1}$$

$$\lambda V = i\lambda\, (8\pi^3/\Omega)^{\frac{1}{2}}\, \gamma \sum_{\mathbf{k},\mathbf{q}} [\omega(\mathbf{q})]^{\frac{1}{2}} (a_{\mathbf{q}}^* \alpha_{\mathbf{k}-\mathbf{q}}^* \alpha_{\mathbf{k}} - \alpha_{\mathbf{k}}^* \alpha_{\mathbf{k}-\mathbf{q}} a_{\mathbf{q}}). \tag{A.2}$$

We have put $\hbar = 1$. The wave vector and energy of an electron are represented by $\mathbf{k}$, $\varepsilon(\mathbf{k})$, the corresponding quantities for a phonon by $\mathbf{q}$, $\omega(\mathbf{q})$. One often adopts for the energies the simple expressions

$$\varepsilon(\mathbf{k}) = |\mathbf{k}|^2/2m, \; \omega(\mathbf{q}) = s|\mathbf{q}|. \tag{A.3}$$

A very important feature is that the electron velocity $|\mathbf{k}|/m$ is usually much larger than the phonon velocity s. This fact is essential for the dissipative nature of the electron states. The operators a, α and a^*, α^* are the annihilation and creation operators for phonons and electrons. We have

$$a_{\mathbf{q}} a_{\mathbf{q}}^* - a_{\mathbf{q}}^* a_{\mathbf{q}} = 1, \quad \alpha_{\mathbf{k}} \alpha_{\mathbf{k}}^* + \alpha_{\mathbf{k}}^* \alpha_{\mathbf{k}} = 1. \tag{A.4}$$

All other commutators of a, a^* and all other anticommutators of α, α^* vanish. Every a or a^* further commutes with every α or α^*. The volume of the crystal is Ω. We assume it to have a cubic shape and quantize the wave vectors $\mathbf{q}$, $\mathbf{k}$ so as to verify periodic boundary conditions. The constant γ can be written

$$\gamma = (d/m)^{\frac{1}{2}} \tag{A.5}$$

where d is the lattice constant. The dimensionless constant λ is then not far from having the order of magnitude one in realistic cases. We remark that electron-electron and phonon-phonon interactions as well as the electron spin are completely neglected in the hamiltonian (A.1), (A.2).

The unperturbed representation $|\alpha\rangle$, as introduced in Section 2, is composed of the following states

$$|\mathbf{k}_1, \ldots \mathbf{k}_n, \mathbf{q}_1, \ldots \mathbf{q}_r\rangle = (\Omega/8\pi^3)^{(n+r)/2}\, \alpha_{\mathbf{k}_1}^* \ldots \alpha_{\mathbf{k}_n}^*\, a_{\mathbf{q}_1}^* \ldots a_{\mathbf{q}_r}^* |0\rangle. \tag{A.6}$$

$|0\rangle$ denotes the no-electron, no-phonon state. It corresponds to the case where the Bloch band is empty and the lattice in its ground state. We assume for simplicity all $\mathbf{k}$-vectors to be different, and we assume them to be written in succession according to a prescribed order. The same assumption is made for the $\mathbf{q}$-vectors. We avoid in this way formal complications which are known from the practice of quantum field theory to play no role in actual calculations. Under our assumptions we have, in the limit $\Omega \to \infty$,

$$\langle \mathbf{k}_1, \ldots \mathbf{k}_n, \mathbf{q}_1, \ldots \mathbf{q}_r \,|\, \mathbf{k}_1', \ldots \mathbf{k}_{n'}', \mathbf{q}_1, \ldots \mathbf{q}_{r'}' \rangle =$$
$$\delta_{nn'} \delta_{rr'}\, \delta(\mathbf{k}_1 - \mathbf{k}_1') \ldots \delta(\mathbf{k}_n - \mathbf{k}_n')\, \delta(\mathbf{q}_1 - \mathbf{q}_1') \ldots \delta(\mathbf{q}_r - \mathbf{q}_r') \tag{A.7}$$

where the δ-functions originate from Kronecker symbols through

$$\lim_{\Omega\to\infty} (\Omega/8\pi^3)\, \delta_{kk'} = \delta(\mathbf{k} - \mathbf{k}') \tag{A.8}$$

and similarly for $\mathbf{q}$-vectors. (A.7) corresponds to eq. (2.2) of the text. In the representation (A.6) the perturbation V has matrix elements with a simple limiting expression for $\Omega \to \infty$. One finds for example by application of (A.8)

$$\langle \mathbf{k}, \mathbf{q} \,|V|\, \mathbf{k}' \rangle = i\gamma\, [\omega(\mathbf{q})]^{\frac{1}{2}}\, \delta(\mathbf{k} + \mathbf{q} - \mathbf{k}'), \tag{A.9}$$

$$\langle \mathbf{k}, \mathbf{q}_1, \mathbf{q}_2 \,|V|\, \mathbf{k}', \mathbf{q}' \rangle = i\gamma[\omega(\mathbf{q}_1)]^{\frac{1}{2}}\delta(\mathbf{k} + \mathbf{q}_1 - \mathbf{k}') \times$$
$$\times\, \delta(\mathbf{q}_2 - \mathbf{q}') + i\gamma\, [\omega(\mathbf{q}_2)]^{\frac{1}{2}}\, \delta(\mathbf{k} + \mathbf{q}_2 - \mathbf{k}')\, \delta(\mathbf{q}_1 - \mathbf{q}'). \tag{A.10}$$

The calculation of matrix elements $\langle \alpha |\, VA_1\, V \ldots A_n V \,|\alpha' \rangle$ with diagonal $A_1, \ldots A_n$ can be performed either by application of equations of the type (A.9), (A.10), or by direct use of (A.2) for finite Ω, the limit $\Omega \to \infty$ being taken at the end of the calculation. We illustrate on the case $n = 1$ the occurrence of diagonal parts. In the evaluation of $\langle \mathbf{k}, \mathbf{q} \,|VAV|\, \mathbf{k}', \mathbf{q}' \rangle$ the possible transitions are

$$\mathbf{k}, \mathbf{q} \leftarrow \mathbf{k}'' \leftarrow \mathbf{k}', \mathbf{q}',$$
$$\mathbf{k}, \mathbf{q} \leftarrow \mathbf{k}'', \mathbf{q}, \mathbf{q}' \leftarrow \mathbf{k}', \mathbf{q}',$$
$$\mathbf{k}, \mathbf{q} \leftarrow \mathbf{k}'', \mathbf{q}', \mathbf{q}'' \neq \mathbf{q} \leftarrow \mathbf{k}', \mathbf{q}'.$$

In the last transition scheme the same phonon $\mathbf{q}''$ is emitted and reabsorbed, whereas in the last but one $\mathbf{q}$ is emitted and $\mathbf{q}'$ absorbed. The calculation gives

$$\langle \mathbf{k}, \mathbf{q} \,|VAV|\, \mathbf{k}', \mathbf{q}' \rangle = \gamma^2\, \delta(\mathbf{k} - \mathbf{k}')\, \delta(\mathbf{q} - \mathbf{q}') \int A(\mathbf{k} - \mathbf{q}'', \mathbf{q}, \mathbf{q}'')\, \omega(\mathbf{q}'')\, d\mathbf{q}''$$
$$+\gamma^2\, \delta(\mathbf{k} + \mathbf{q} - \mathbf{k}' - \mathbf{q}')\, [A(\mathbf{k} + \mathbf{q}) + A(\mathbf{k}' - \mathbf{q}, \mathbf{q}, \mathbf{q}')]\, [\omega(\mathbf{q})\, \omega(\mathbf{q}')]^{\frac{1}{2}}. \tag{A.11}$$

The first term in the righthand side, which originates from the third transition scheme, is the diagonal part of the matrix element. The second term stems from the two first transition schemes.

We take next the case $n = 3$ to illustrate the concept of irreducible diagonal part. The transition schemes contributing to the diagonal part of $\langle \mathbf{k}, \mathbf{q} \,|VA_1VA_2VA_3V|\, \mathbf{k}', \mathbf{q}' \rangle$ are easily seen to be

$$\mathbf{k}, \mathbf{q} \leftarrow \mathbf{k}_3, \mathbf{q}, \mathbf{q}_2 \leftarrow \mathbf{k}_2, \mathbf{q}, \mathbf{q}_1, \mathbf{q}_2 \leftarrow \mathbf{k}_1, \mathbf{q}, \mathbf{q}_1 \leftarrow \mathbf{k}, \mathbf{q}$$
$$\mathbf{k}, \mathbf{q} \leftarrow \mathbf{k}_1, \mathbf{q}, \mathbf{q}_1 \leftarrow \mathbf{k}_2, \mathbf{q}, \mathbf{q}_1, \mathbf{q}_2 \leftarrow \mathbf{k}_1, \mathbf{q}, \mathbf{q}_1 \leftarrow \mathbf{k}, \mathbf{q}$$
$$\mathbf{k}, \mathbf{q} \leftarrow \mathbf{k}_2, \mathbf{q}, \mathbf{q}_2 \leftarrow \mathbf{k}, \mathbf{q} \leftarrow \mathbf{k}_1, \mathbf{q}, \mathbf{q}_1 \leftarrow \mathbf{k}, \mathbf{q}$$

Only the first scheme contributes to the irreducible diagonal part. The second one involves the diagonal part of the subproduct VA_2V, while the third scheme involves the diagonal parts of VA_1V and VA_3V. Similar examples can be worked out for states involving more than one electron. The formal analogy of such calculations with the quantum theory of fields

is of course striking. One can in particular introduce a graphical representation of the transition schemes by means of Feynman diagrams, a method which has already been applied to a Fermi gas with interactions by Goldstone [8]) and Hugenholtz [4]).

Before closing we still calculate to lowest order in λ the functions $G_l(\alpha)$ and $W_{ll'}(\alpha'\alpha)$. One finds directly from (A.11)

$$G_l(\mathbf{k}, \mathbf{q}) = \gamma^2 \int [\varepsilon(\mathbf{k} - \mathbf{q}') + \omega(\mathbf{q}) + \omega(\mathbf{q}') - l]^{-1} \omega(\mathbf{q}')\, d\mathbf{q}',$$

$$W_{ll'}(\mathbf{k}', \mathbf{q}_1', \mathbf{q}_2'; \mathbf{k}, \mathbf{q}) = \gamma^2 \omega(\mathbf{q}_1')\, \delta[\mathbf{q}_2' - \mathbf{q}]\, \delta[\mathbf{k}' + \mathbf{q}_1' - \mathbf{k}].$$

The phonon $\mathbf{q}$ is seen to play no role in these functions, except for a shift in l, l'. One can easily calculate such functions to higher order and determine in this way the quantities f_E and w_E which enter the master equation (4.31) for the case at hand.

Received 16-3-57.

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4) Hugenholtz, N. M., Physica **23** (1957), 481 (this issue).
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