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QUANTUM-MECHANICAL PERTURBATIONS GIVING RISE TO A STATISTICAL TRANSPORT EQUATION

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Synopsis

The quantum-mechanical theory of the transport equation is reconsidered for the case of transport processes produced by a small perturbation. On the basis of the most common applications of the equation to crystals (heat conduction, etc.) a characteristic property of the perturbation is recognized as being responsible for the appearance of dissipative effects in the time evolution of the system. With the help of this property a greatly improved derivation of the transport equation is obtained. It avoids the repeated use of a random phase assumption after each of a long succession of short time intervals, a common drawback of the conventional derivations. The validity of the transport equation is established without a priori statistical hypothesis for two special classes of initial states. It is also derived for arbitrary initial states with the help of a random phase assumption concerning the initial state alone.

1. *Introduction.* Considerable attention has been devoted to the quantum-mechanical derivation of the well known first order differential equations (transport equations)

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

describing under suitable conditions the irreversible approach to statistical equilibrium of a system with many degrees of freedom (or of an ensemble of such systems), and forming the mathematical basis for the derivation of the H-theorem. In these equations the P_α are the probabilities of finding the system in states or groups of states labelled by α, and the $W_{\alpha\beta}$ are transition probabilities per unit time.

In the customary justification of (1.1) for quantum systems, first given by P a u l i [1]), one imagines that the approach to equilibrium is produced by a perturbation term V in the hamiltonian of the system, small enough to ensure that the transition probabilities $W_{\alpha\beta}$ can be calculated by first order (time-dependent) perturbation calculus over times t_0 of such length that the unperturbed energy H be conserved in the transition. The α are then groups of stationary states of the unperturbed part H of the hamil-

tonian. The derivation rests upon a statistical assumption, namely that the phases of the quantum-mechanical amplitudes with respect to the eigenstates of H are randomly distributed, or equivalently, that the density matrix is diagonal in the unperturbed energy. This assumption of random phases is needed not only for the initial state of the system, but after each of a very long succession of time intervals of order of magnitude t_0. The necessity of making repeatedly use of the random phase assumption is of course most unsatisfactory, as is also in the classical kinetic theory of gases the necessity to use at all times the hypothesis of molecular chaos ("Stoszzahlansatz") for the derivation of the Boltzmann equation. This question is intimately connected with the main difficulty that any derivation of (1.1) has to face, namely the irreversibility in time of the equation to be derived as contrasted with the reversible character of the basic equations of motion. Attempts at justifying the random phase assumption for intermediate times by extraneous considerations, referring e.g. to measuring processes [2]), have not improved the situation.

Our object is to show that repeated use of the random phase assumption is superfluous in the derivation of (1.1) for quantum-mechanical systems whose approach to equilibrium is produced by a perturbation. At the foundation of our proof lies an analysis of the formal properties of the perturbation through which the presence of many degrees of freedom affect decisively the time evolution of the system and which are a prerequisite for an approach to equilibrium to occur at all. These properties, although easy to verify in the cases encountered in applications (e.g. interaction between phonons in crystals, between particles in slightly imperfect quantum gases, etc.), have been apparently overlooked in general discussions of the problem.

The most commonly mentioned consequence of the presence of many degrees of freedom is that the energy levels of the system are very densely distributed. The high density of levels is however, taken alone, not sufficient to ensure that a perturbation will give rise to a tendency toward equilibrium. As is indeed well known, for a system with an infinitely high density of levels, i.e. a system with a continuous energy spectrum, most perturbations give rise to scattering in a generalized sense of the word, meaning transitions that, for any wave packet, take entirely place within a finite time interval [3]). Such transitions are described by an S-matrix and are completely different from the persistent and dissipative effects to which equations of the type (1.1) are applicable. Our first task is therefore to find out which special property is needed for a perturbation to produce such dissipative effects. This property turns out to be fairly simple, and is given in the next section. With its help it becomes possible to analyze how the perturbation affects the time evolution of the system in greater detail than has been done before. In particular we will be able to derive

in a much more satisfactory way that for suitable initial states the time evolution can be described by a transport equation involving the occupation probabilities of the unperturbed stationary states.

The derivation here presented makes no use at all of the random phase assumption. It is carried out for two special classes of initial states. The first contains the states whose complex amplitudes with respect to the unperturbed stationary states vary slowly over energy intervals of order $\hbar/\tau_0$, where τ_0 is the relaxation time characterizing the approach to equilibrium. The derivation for this class is given in detail and occupies Sections 3 to 7. The second class contains the initial states for which the spread of the unperturbed energy is small compared to $\hbar/\tau_0$. For these the derivation is presented more briefly in Section 8. Although one knows from the familiar time reversal arguments that the transport equation cannot hold for arbitrary initial states, the two classes just mentioned do not exhaust the range of its applicability. We will not attempt to determine this range. It follows however immediately from our formal analysis that the transport equation is valid in a statistical sense for initial states whose amplitudes have randomly distributed phases. This remark will be found at the end of Section 8. To express it in other words, we can also derive the transport equation for arbitrary initial states, but use must then be made of the random phase assumption for the initial states. We do not want to decide in this paper which derivation must be preferred to the other. Whichever is chosen, the main contribution of our method is the elimination of any *repeated* use of the random phase hypothesis.

The three last sections of the paper discuss a few points concerning the significance of the transport equation and its relation to the reversibility of the Schrödinger equation.

The systems to which our derivation of (1.1) applies are no more general than was the case in the original paper of Pauli [1]). The transitions are supposed to take place between eigenstates of an unperturbed part of the hamiltonian, and are produced by the perturbation term assumed to be sufficiently small. Although this situation is by no means as special as one may think at first sight, — for a system of the generality of a liquid or a dense gas, one may divide the volume in many cells of small but macroscopic size and consider as perturbation the interactions across the cell walls —, the question still arises of the significance and validity to be attributed to equations such as (1.1) for general systems, independently of any separation of the hamiltonian in an unperturbed part and a small perturbation. The answer to be expected for this problem is described and thoroughly analyzed in a recent paper by Van Kampen [4]). Still, the very generality of the systems considered makes it of course impossible to arrive at a derivation, in the strict mathematical sense, of the irreversible equations (1.1). What Van Kampen does is rather to show where the

transport equation and its irreversible character find in all plausibility their justification. In doing so he makes use of a random phase argument for all intermediate times.

2. *Characteristic property of the perturbation.* The property of the perturbation energy V responsible for the approach to equilibrium, although to our knowledge never brought into evidence before, is easy to recognize in the well known applications of (1.1) to crystals, e.g. to cases where V is the interaction between phonons (theory of heat conduction in crystals [5])), or between spin waves or spin waves and phonons in ferromagnetics (ferromagnetic relaxation phenomena [6])). Using the occupation number representation for free excitation quanta (phonons or spin waves), in which the unperturbed energy is diagonal, one has for V the familiar type of expression involving absorption and emission operators for free quanta. Consider now any operator of the form VAV where A is diagonal in the occupation number representation. Its matrix element between two arbitrary basic states $|\alpha\rangle$, $|\alpha'\rangle$ of this representation is a sum over intermediate states $|\alpha''\rangle$

$$\langle\alpha'|VAV|\alpha\rangle = \Sigma_{\alpha''}\langle\alpha'|V|\alpha''\rangle A(\alpha'')\langle\alpha''|V|\alpha\rangle \tag{2.1}$$

where $A(\alpha'')$ is the eigenvalue of A in the state $|\alpha''\rangle$. Our basic remark is now that in all cases of interest the number of intermediate states contributing to (2.1) is larger by at least a factor cN ($c \neq 0$ and of the order of 1, N = number of atoms in the crystal) when $\alpha = \alpha'$ than when $\alpha \neq \alpha'$ *). In the limit of a large system, i.e. in the limit of a system with infinitely many degrees of freedom, this fact manifests itself through the appearance of a singularity of δ-function type in the matrix element (2.1) for $\alpha = \alpha'$, although no such singularity is present in $\langle\alpha'|V|\alpha\rangle$ itself †). We assert to have here the characteristic property of V which is responsible for the approach to equilibrium. Our object is to justify this assertion by studying the consequences of this property for the time evolution of the system and by establishing that this evolution can be described for suitable initial states by a transport equation.

Modifying slightly our notation for the detailed discussion, we consider a system of hamiltonian $H + \lambda V$. The unperturbed energy H has a con-

*) An entirely analogous situation has been recognized long ago for another type of quantum systems, namely quantized fields. V is then the interaction between two free fields, e.g. between the electron field and the photon field. If one considers for example in the plane wave representation a second order matrix element of type (2.1) between two two-electron states, the sum $\Sigma_{\alpha''}$ extends over intermediate photons with all possible momenta for $\alpha = \alpha'$ (self energy effect), whereas it counts a finite number of terms when $\alpha \neq \alpha'$ (Møller interaction) [7]). The absence of dissipative effects for interacting fields is only due to the vanishing of $\langle\alpha'|V|\alpha\rangle$ for transitions conserving energy.

†) A δ-singularity in $\langle\alpha'|V|\alpha\rangle$ can be incorporated directly in the unperturbed part of the hamiltonian.

tinuous spectrum with eigenstates $|Ea\rangle$

$$H|Ea\rangle = E|Ea\rangle,\ \langle E'a'|Ea\rangle = \delta(E'-E)\,\delta(a'-a) \tag{2.2}$$

where E, a is a complete set of quantum numbers diagonalizing H, supposed to be all continuous. Although the presence of discrete quantum numbers among the a would only cause trivial modifications of the formalism, continuity of E is essential. We assume the a dimensionless. λ is a dimensionless parameter characterizing the size of the perturbation. The characteristic property of V will now be expressed in its simplest form: for any operator A diagonal in the $|Ea\rangle$-representation one has

$$\langle E'a'|VAV|Ea\rangle = \delta(E'-E)\,\delta(a'-a)\,W_A(Ea) + \langle E'a'|Y_A|Ea\rangle \tag{2.3}$$

where $\langle E'a'|Y_A|Ea\rangle$ denotes a function of E, a, E', a' without $\delta(E'-E)$-singularity. The matrix element $\langle E'a'|V|Ea\rangle$ itself has no $\delta(E'-E)$-singularity. The linearity of (2.3) in A implies, $A(E''a'')$ being the eigenvalues of A,

$$W_A(Ea) = \int \mathrm{d}E''\mathrm{d}a''\,A(E''a'')W(E''a'';Ea) \tag{2.4}$$

$W(E''a'';Ea)$ is of course non negative. We further assume that $W(Ea'';Ea)$ does not vanish identically *). Similarly

$$\langle E'a'|Y_A|Ea\rangle = \int \mathrm{d}E''\mathrm{d}a''A(E''a'')\,\langle E'a'|Y(E''a'')|Ea\rangle \tag{2.5}$$

Separations similar to the separation (2.3) and not implied by it may of course hold for matrix elements with more than two factors V, and this is actually the case in all practical applications †). They do not require special consideration on the level of approximation here adopted (limit of small λ).

The aim of our investigation is to study, in the limit of small λ, the time evolution of the system over time intervals t of order

$$t = \lambda^{-2}\tilde{t},\ (\tilde{t} \text{ independent of } \lambda). \tag{2.6}$$

We will show that equations of type (1.1) are satisfied by the occupation probabilities at time t of the unperturbed states $|Ea\rangle$, under suitable conditions for the state of the system at time 0. The relaxation time τ_0 for the approach to equilibrium will turn out to be of the order (2.6). The time evolution is described by the unitary operator

$$U(t) = \exp\,[-i(H+\lambda V)t].$$

We have put $\hbar = 1$. The discussion will be based on the well known ex-

*) This assumption does not hold for the interacting fields mentioned in a previous footnote, nor does any of the similar assumptions for matrix elements of higher order in V.

†) For example, in field theory, irreducible self energy effects of higher order.

pansion

$$U(t) = \exp[-iHt] - i\lambda \int_0^t \mathrm{d}t_1 \exp[-iH(t-t_1)]V \exp[-iHt_1] \ldots$$
$$+ (-i\lambda)^n \int_0^t \mathrm{d}t_n \int_0^{t_n} \mathrm{d}t_{n-1} \ldots \int_0^{t_2} \mathrm{d}t_1 \exp[-iH(t-t_n)]V \exp[-iH(t_n - t_{n-1})] \ldots$$
$$V \exp[-iHt_1] + \ldots \tag{2.7}$$

As often stressed, the physical meaning of this expansion is particularly intuitive. The integrand of the general term of order n in V represents processes where the perturbation produces n successive transitions, at times $t_1, t_2, \ldots t_n$, whereas the time evolution of the system in the intervals $(0, t_1), (t_1, t_2), \ldots (t_n, t)$ is determined by the unperturbed hamiltonian. This interpretation of (2.7) will be used hereafter to gain insight into the physical significance of the formal results.

Our discussion will be carried out for positive values of the time (2.6). The treatment of negative times is entirely similar.

3. *First order transitions.* Before considering the general term of (2.7) it is useful to exhibit on the low order terms the special effects produced by the δ-singularity in (2.3), i.e. the effects which make all the difference between the situation here studied and the usual quantum-mechanical theory of scattering processes.

Let us consider the term in $U(t)$ which describes first order transitions

$$U_1(t) = -i\lambda \int_0^t \mathrm{d}t_1 \exp[-iH(t-t_1)]V \exp[-iHt_1].$$

For initial states

$$\varphi = \int |E\alpha\rangle \, \mathrm{d}E\mathrm{d}\alpha \, c(E\alpha), \qquad \varphi' = \int |E\alpha\rangle \, \mathrm{d}E\mathrm{d}\alpha \, c'(E\alpha) \tag{3.1}$$

we consider the vectors

$$U_1(t)\varphi = \psi_1, \quad U_1(t)\varphi' = \psi_1'.$$

We calculate

$$\langle \psi_1 | \psi_1' \rangle = \lambda^2 \int_0^t \mathrm{d}t_1' \int_0^t \mathrm{d}t_1 \int c^*(E'\alpha') \mathrm{d}E'\mathrm{d}\alpha' \exp[iE't_1'] \langle E'\alpha' | V | E''\alpha'' \rangle .$$
$$. \exp[iE''(t_1 - t_1')] \mathrm{d}E''\mathrm{d}\alpha'' \langle E''\alpha'' | V | E\alpha \rangle \exp[-iEt_1] \mathrm{d}E\mathrm{d}\alpha \, c'(E\alpha)$$

and make use of the separation (2.3)

$$\langle \psi_1 | \psi_1' \rangle = \lambda^2 \int_0^t \mathrm{d}t_1' \int_0^t \mathrm{d}t_1 \int \mathrm{d}E''\mathrm{d}\alpha'' \exp[i(E'' - E)(t_1 - t_1')] W(E''\alpha''; E\alpha) \mathrm{d}E\mathrm{d}\alpha .$$
$$. c^*(E\alpha) c'(E\alpha) + \lambda^2 \int_0^t \mathrm{d}t_1' \int_0^t \mathrm{d}t_1 \int c^*(E'\alpha') \mathrm{d}E'\mathrm{d}\alpha' \exp[i(E' - E'')t_1'] .$$
$$. \langle E'\alpha' | Y(E''\alpha'') | E\alpha \rangle$$
$$\mathrm{d}E''\mathrm{d}\alpha'' \exp[i(E'' - E)t_1] \mathrm{d}E\mathrm{d}\alpha \, c'(E\alpha). \tag{3.2}$$

The second term in the right hand side depends on the relative phases of the amplitudes $c(E'\alpha')$, $c'(E\alpha)$ of φ and φ' for different unperturbed stationary states, whereas the first term does not. This distinction will

turn out to be a general feature and all terms depending on the above mentioned relative phases will be proved negligible for the special classes of initial states described in the introduction. We give now the detailed analysis for the first class, being the class of states φ, φ' whose amplitudes $c(Ea)$, $c'(Ea)$ vary little over energy intervals of order τ_0^{-1}, i.e. of order λ^2. This property can be taken into account very simply by taking initial states independent of λ and letting then λ become very small.

The well known asymptotic formula

$$\int_0^T \mathrm{d}t \int \mathrm{d}\varepsilon \exp[i\varepsilon t] F(\varepsilon) = \pi \frac{T}{|T|} F(0) + i \int \mathrm{d}\varepsilon F(\varepsilon) . \left(\frac{1}{\varepsilon}\right)_P , \tag{3.3}$$

where $(1/\varepsilon)_P$ indicates that the Cauchy principal part of the integral must be taken, will be used repeatedly in the following. It holds as soon as $|T|$ is long enough for the variation of $F(\varepsilon)$ over intervals of order $|T|^{-1}$ to be negligible. Let us denote by δE an energy such that the variation of $\langle E'a' | V | Ea\rangle$, $W(E''a''; Ea)$, $\langle E'a' | Y(E''a'')| Ea\rangle$, $c(Ea)$ and $c'(Ea)$ with E, E' and E'' is small over energy intervals small compared to δE. Equation (3.3) will then be applicable to (3.2) as soon as λ is small enough to have

$$t = \lambda^{-2} \tilde{t} \gg \delta E^{-1}. \tag{3.4}$$

The last term in (3.2) becomes accordingly for small λ

$$\lambda^2 \int \mathrm{d}E'' \mathrm{d}a'' \int c^*(E'a') \mathrm{d}E' \mathrm{d}a' \left[\pi \delta(E' - E'') + i \left(\frac{1}{E' - E''}\right)_P\right]$$

$$\langle E'a' | Y(E''a'')| Ea\rangle . \left[\pi \delta(E'' - E) + i \left(\frac{1}{E'' - E}\right)_P\right] \mathrm{d}E \mathrm{d}a \, c'(Ea).$$

It is seen to vanish for $\lambda \to 0$. This is the familiar situation in scattering theory. It actually holds for arbitrary times.

A completely different behaviour is found for the first term in the right hand side of (3.2). The time integrations are conveniently transformed to the new variables

$$\tau_1 = \tfrac{1}{2}(t_1 + t_1'), \quad \tau_1' = t_1 - t_1',$$

so that

$$\int_0^t \mathrm{d}t_1' \int_0^t \mathrm{d}t_1 = \int_0^t \mathrm{d}\tau_1 \int_{-f(\tau_1)}^{f(\tau_1)} \mathrm{d}\tau_1'$$

with

$$f(\tau_1) = \begin{cases} 2\tau_1 & \text{for } \tau_1 \leqslant t/2, \\ 2(t - \tau_1) & \text{for } \tau_1 \geqslant t/2. \end{cases}$$

Under the assumption (3.4) one has

$$f(\tau_1) \gg \delta E^{-1}$$

for the great majority of values of τ_1, so that we can write with the help of (3.3)

$$\lambda^2 \int_0^t \mathrm{d}\tau_1 \int_{-f(\tau_1)}^{f(\tau_1)} \mathrm{d}\tau_1' \int \mathrm{d}E'' \mathrm{d}a'' \exp\left[i(E''-E)\tau_1'\right] W(E''a''; Ea)\mathrm{d}E\mathrm{d}a\, c^*(Ea)c'(Ea) =$$

$$= 2\pi\lambda^2 \int_0^t \mathrm{d}\tau_1 \int \mathrm{d}E\mathrm{d}a''\, W(Ea''; Ea)\mathrm{d}a\, c^*(Ea)c'(Ea) =$$

$$= 2\pi\lambda^2 t \int \mathrm{d}E\mathrm{d}a''\, W(Ea''; Ea)\mathrm{d}a\, c^*(Ea)c'(Ea). \tag{3.5}$$

From (2.6) it is clear that this quantity remains finite and non vanishing in the limit of small λ, and we get in this limit

$$\langle \psi_1 \mid \psi_1' \rangle = 2\pi\lambda^2 t \int \mathrm{d}E\mathrm{d}a'' W(Ea''; Ea)\mathrm{d}a\, c^*(Ea)c'(Ea). \tag{3.6}$$

The most important feature of the foregoing equation is the absence of any interference term. The equation shows clearly that interference effects between different $|Ea\rangle$-components of the initial states are absent in the limiting case here considered. A less obvious but no less important lack of interference, manifesting itself through the linearity of $\langle \psi_1 | \psi_1' \rangle$ in t, is better understood by considering (3.5). From the validity condition of the asymptotic formula (3.3) it appears that the entire contribution of the τ_1'-integration in (3.5) originates from times τ_1' of order δE^{-1}, and thus very small compared to t. This means that interference between the partial wave resulting from a transition produced by V at time t_1 and the partial wave produced by a transition occurring at time t_1' is completely negligible unless

$$|t_1 - t_1'| \sim \delta E^{-1} \ll t.$$

In other words, talking for a moment in terms of a time scale with unit of order λ^{-2}, constructive interference takes place only between partial waves produced by almost simultaneous transitions. The total transition probability has thus indeed to be proportional to t.

The vanishing of interference effects for small λ, just derived for first order transitions, will turn out to be an entirely general feature valid for all orders. It is the fundamental reason why the time evolution of the system can be described, as in (1.1), in terms of probabilities, without making use of the complex amplitudes which enter the Schrödinger equation. A further example of vanishing interference effect is the absence of interference between the final waves produced by transitions of order 0 and 1. Writing

$$\psi_0 = \exp\left[-iHt\right]\varphi$$

we have

$$\langle \psi_0 | \psi_1' \rangle = -i\lambda \int_0^t \mathrm{d}t_1 \int c^*(E'a')\mathrm{d}E'\mathrm{d}a' \exp\left[i(E'-E)t_1\right]$$

$$\langle E'a' \mid V \mid Ea \rangle \, \mathrm{d}E\mathrm{d}a\, c'(Ea)$$

or asymptotically for small λ

$$\langle\psi_0|\psi_1'\rangle = -i\lambda\int c^*(E'a')\mathrm{d}E'\mathrm{d}a'\left[\pi\delta(E'-E)+i\left(\frac{1}{E'-E}\right)_P\right]$$

$$\langle E'a'\,|V|\,Ea\rangle\,\mathrm{d}E\mathrm{d}a\,c'(Ea).$$

This expression vanishes for $\lambda \to 0$.

4. *Second order transitions.* By means of (2.3) the second order term in the expansion (2.7) separates into a diagonal part $U_2^W(t)$, of matrix elements

$$\langle E'a'\,|U_2^W(t)|\,Ea\rangle = -\lambda^2\delta(E'-E)\delta(a'-a)\exp[-iEt]\,.$$
$$\int_0^t \mathrm{d}t_2\int_0^{t_2}\mathrm{d}t_1\int \mathrm{d}E''\mathrm{d}a''\exp[-i(E''-E)(t_2-t_1)]W(E''a'';Ea) \quad (4.1)$$

and a non diagonal part $U_2^V(t)$ which will not be written down explicitly. We introduce in (4.1) the time difference

$$\tau'' = t_2 - t_1$$

between the two successive transitions $Ea \to E''a''$ and $E''a'' \to Ea$ involved. The integral becomes

$$\int_0^t \mathrm{d}t_1\int_0^{t-t_1}\mathrm{d}\tau''\int \mathrm{d}E''\mathrm{d}a''\exp[-i(E''-E)\tau'']W(E''a'';Ea). \quad (4.2)$$

(3.4) implies that the inequality

$$t - t_1 \gg \delta E^{-1}$$

holds for the great majority of values of t_1, and (3.3) can thus be applied to the integral over τ'' and E'', giving a result independent of t_1. One finally gets

$$\langle E'a'\,|U_2^W(t)|\,Ea\rangle = -\delta(E'-E)\delta(a'-a)\exp[-iEt]\,.\lambda^2 t\,\{\Gamma(Ea)+i\Delta(Ea)\} \quad (4.3)$$

with the notation

$$\Gamma(Ea) = \pi\int \mathrm{d}a''W(Ea'';Ea), \quad (4.4)$$

$$\Delta(Ea) = \int \mathrm{d}E''\mathrm{d}a''\,W(E''a'';Ea)\left(\frac{1}{E-E''}\right)_P \quad (4.5)$$

(4.3) is seen to be finite and non vanishing in the limit of small λ.

The integral over the time difference τ'' in (4.2) gets all its contributions from values of τ'' of order δE^{-1}. In other words the only transition schemes contributing effectively to (4.3) are those for which the second transition $(E''a'' \to Ea)$ follows the first one $(Ea \to E''a'')$ within a time of order δE^{-1}, i.e. an interval very small compared to the time t altogether available.

Using again the notations of Section 3, we see from (4.3) that $U_2^W(t)\varphi'$ does interfere with ψ_0:

$$\langle\psi_0|U_2^W(t)\varphi'\rangle \neq 0$$

in the limit of small λ. One finds on the contrary by the methods already used, always in the same limit, that

$$\langle\psi_0|U_2^Y(t)\varphi'\rangle = \langle\psi_1|U_2^W(t)\varphi'\rangle = \langle\psi_1|U_2^Y(t)\varphi'\rangle = \langle U_2^W(t)\varphi|U_2^Y(t)\varphi'\rangle = 0.$$

Of course

$$\langle U_2^W(t)\varphi|U_2^W(t)\varphi'\rangle \neq 0, \quad \langle U_2^Y(t)\varphi|U_2^Y(t)\varphi'\rangle \neq 0.$$

The first expression can be determined immediately from (4.3). The calculation of the second one is a special case of the discussion of n-th order transitions in Section 6.

5. *Diagonal transition schemes.* The second order transition schemes giving rise to the diagonal operator $U_2^W(t)$ given in (4.1) are a special case of the diagonal transition schemes obtained in the $2n$-th order term in $U(t)$:

$$(-i\lambda)^{2n}\int_0^t \mathrm{d}t_{2n}\int_0^{t_{2n}}\mathrm{d}t_{2n-1}\ldots\int_0^{t_2}\mathrm{d}t_1 \exp[-iH(t-t_{2n})]V\exp[-iH(t_{2n}- \\ -t_{2n-1})]V\ldots\exp[-iH(t_3-t_2)]V\exp[-iH(t_2-t_1)]V\exp[-iHt_1] \quad (5.1)$$

when the separation (2.3) is applied to the product of the 1st and 2d V operators, retaining only the W-term, then to the product of the 3d and 4th V operators, retaining again only the W-term, and so on for all V operators. The result obtained is a diagonal operator $U_{2n}^W(t)$ with matrix elements

$$\langle E'a'|U_{2n}^W(t)|Ea\rangle = (-\lambda^2)^n\delta(E'-E)\delta(a'-a)\exp[-iEt]\int_0^t \mathrm{d}t_{2n}\ldots\int_0^{t_2}\mathrm{d}t_1 \\ \int \mathrm{d}E_n''\,\mathrm{d}a_n''\exp[-i(E_n''-E)(t_{2n}-t_{2n-1})]W(E_n''a_n'';Ea)\int \mathrm{d}E_{n-1}''\,\mathrm{d}a_{n-1}''\ldots \\ \ldots\int \mathrm{d}E_1''\,\mathrm{d}a_1''\exp[-i(E_1''-E)(t_2-t_1)]W(E_1''a_1'';Ea). \quad (5.2)$$

It describes iterated transitions which we can represent by the following scheme

$$Ea\nearrow^{E_1''a_1''}\searrow Ea\nearrow^{E_2''a_2''}\searrow Ea\ldots Ea\nearrow^{E_n''a_n''}\searrow Ea. \quad (5.3)$$

They occur back and forth between the state $|Ea\rangle$ and arbitrary other states. The calculation of (5.2) for small λ is a straightforward extension of the derivation of (4.3) and leads to

$$\langle E'a'|U_{2n}^W(t)|Ea\rangle = \delta(E'-E)\delta(a'-a)\exp[-iEt] \\ \frac{(-\lambda^2 t)^n}{n!}\{\Gamma(Ea)+i\Delta(Ea)\}^n \quad (5.4)$$

Again, the only transition schemes contributing to this result are those in which, for each j from 1 to n, the time t_{2j} of the transition $E_j''a_j'' \to Ea$ follows the time t_{2j-1} of the preceding transition $Ea \to E_j''a_j''$ by an interval of order δE^{-1}. Each pair $Ea \to E_j''a_j'' \to Ea$ of inverse transitions occurs thus over a time interval very small compared to the intervals between such pairs.

The total effect of the diagonal transitions just considered can now be expressed in closed form by means of the operator

$$U^W(t) = \exp[-iHt] + \Sigma_{n=1}^{\infty} U_{2n}^W(t) \tag{5.5}$$

and (5.4) gives for the limiting case of small λ the very simple formula

$$\langle E'a'|U^W(t)|Ea\rangle = \delta(E'-E)\delta(a'-a)\exp[-i\{E+\lambda^2\Delta(Ea)\}t - \lambda^2\Gamma(Ea)t] \tag{5.6}$$

The physical significance of the energies $\Delta(Ea)$ and $\Gamma(Ea)$ is thereby clearly exhibited. They are respectively the energy shift and width of the state $|Ea\rangle$ made metastable by the perturbation. Such quantities are quite familiar for the case of a metastable discrete energy level, and their well known algebraic expressions have a great similarity with (4.4) and (4.5) [8]. Here however we deal with states belonging to a continuous energy spectrum and the occurrence of level shifts and widths is a consequence of the presence of the singular term in the matrix element (2.3).

The operator (5.5) contains a certain number of the terms diagonal in the $|Ea\rangle$-representation which are obtained when the separation (2.3) is applied in all possible manners in the series expansion (2.7) of $U(t)$. It does not contain all these diagonal terms, but the important point is that the remaining ones have all a vanishing limit for $\lambda \to 0$, i.e. that

$$\lim_{\lambda\to 0} U^D(t) = \lim_{\lambda\to 0} U^W(t) \tag{5.7}$$

where $U^D(t)$ denotes the complete diagonal part of $U(t)$. The general reason for this fact lies in the type of transition schemes, distinct of (5.3), which can produce a diagonal term. Such schemes always contain at least a section looking like

$$\begin{array}{ccccccc} & & & E'''a''' & & & \\ & & E''a'' \nearrow & & \searrow & & \\ Ea \nearrow & & & & & E''a'' & \searrow Ea \end{array} \tag{5.8}$$

or having more intermediate steps between the two occurrences of the state $|E''a''\rangle$. By $|Ea\rangle$ we denote as above the initial and final state of the whole scheme. As we have stressed before, the time interval between the transitions $Ea \to E''a''$ and $E''a'' \to Ea$ must be of order δE^{-1} to obtain a non vanishing contribution to the total matrix element. The intermediate diagonal transition scheme

$$\begin{array}{ccccc} & & E'''a''' & & \\ & E''a'' \nearrow & & \searrow & E''a'' \end{array}$$

of (5.8) must thus take place over such times, and will produce in the final result a factor λ^2 responsible for its vanishing in the limit $\lambda \to 0$.

Let us work out the details of the argument in a special case, namely the operator (5.1) with $n = 2$ and the transitions (5.8). We are thus concerned with the diagonal operator obtained by applying (2.3) to the two

middle V operators, retaining only the W-term, and doing then the same for the remaining two V operators. The resulting matrix element is

$$\lambda^4\delta(E'-E)\delta(\alpha'-\alpha)\exp[-iEt]\int_0^t \mathrm{d}t_4 \ldots \int_0^{t_2}\mathrm{d}t_1 \int \mathrm{d}E'''\mathrm{d}\alpha'''\mathrm{d}E''\mathrm{d}\alpha''$$
$$\exp[-i(E'''-E'')(t_3-t_2)]W(E'''\alpha''';E''\alpha'')\,.$$
$$.\ \exp[-i(E''-E)(t_4-t_1)]W(E''\alpha'';E\alpha).$$

One takes as new integration variables t_1, $\tau_2''=t_2-t_1$, $\tau_3''=t_3-t_2$ and $\tau_4''=t_4-t_3$. It is then easily seen that the integrations over τ_2'', τ_3'' and τ_4'' converge over intervals of order δE^{-1}, giving a limit independent of t_1, so that the final result is in $\lambda^4 t$ and decreases as λ^2 when $\lambda\to 0$.

The relation (5.7), just established for times t of order λ^{-2}, holds of course also for finite times or for times approaching infinity slower than with λ^{-2}. Both sides of the equation reduce then to $\exp[-iHt]$.

6. *General transition schemes.* We are now in the position of discussing the transitions produced by the general term in the series (2.7). The first step consists in separating out in all possible manners the diagonal parts of groups of successive V operators. This is easily done by means of the diagonal part $U^D(t)$ of $U(t)$ introduced above, with the result

$$U(t)=U^D(t)+\Sigma_{n=1}^{\infty}(-i\lambda)^n\int_0^t \mathrm{d}t_n\int_0^{t_n}\ldots\int_0^{t_2}\mathrm{d}t_1$$
$$\{U^D(t-t_n)VU^D(t_n-t_{n-1})V\ldots U^D(t_2-t_1)VU^D(t_1)\}_{nd} \qquad (6.1)$$

where the bracket $\{\ldots\}_{nd}$ indicates that all diagonal terms are avoided (*nd* stands for non diagonal). In other words, in the matrix elements

$$\langle E'\alpha'|\{U^D(t-t_n)V\ldots VU^D(t_1)\}_{nd}|E\alpha\rangle=\int \mathrm{d}E''_{n-1}\,\mathrm{d}\alpha''_{n-1}\ldots\mathrm{d}E''_1\,\mathrm{d}\alpha''_1$$
$$u^D(t-t_n;E'\alpha')\langle E'\alpha'|V|E''_{n-1}\alpha''_{n-1}\rangle u^D(t_n-t_{n-1};E''_{n-1}\alpha''_{n-1})\ldots$$
$$\ldots\langle E''_1\alpha''_1|V|E\alpha\rangle u^D(t_1;E\alpha)$$

where the notation $u^D(t;E\alpha)$ is defined by

$$\langle E'\alpha'|U^D(t)|E\alpha\rangle=u^D(t;E\alpha)\delta(E'-E)\delta(\alpha'-\alpha),$$

one has to restrict oneself to states $|E\alpha\rangle$, $|E''_1\alpha''_1\rangle$, $\ldots$ $|E''_{n-1}\alpha''_{n-1}\rangle$, $|E'\alpha'\rangle$ which are two by two different, the points $E\alpha$; $E''_1\alpha''_1$; $\ldots$ $E'\alpha'$ in the space of the parameters $E\alpha$ remaining two by two outside some infinitesimal neighborhood of each other.

In the limit of small λ, we apply (5.7) and obtain thus instead of (6.1)

$$U(t)=U^W(t)+\Sigma_{n=1}^{\infty}\tilde{U}_n(t), \qquad (6.2)$$
$$\tilde{U}_n(t)=(-i\lambda)^n\int_0^t \mathrm{d}t_n\ldots\int_0^{t_2}\mathrm{d}t_1\{U^W(t-t_n)VU^W(t_n-t_{n-1})\ldots VU^W(t_1)\}_{nd}. \qquad (6.3)$$

As in Section 3 we consider the initial states φ and φ', given by (3.1), and we define

$$\tilde{U}_n(t)\varphi=\Phi_n,\quad \tilde{U}_n(t)\varphi'=\Phi'_n. \qquad (6.4)$$

The scalar product $\langle \Phi_n | \Phi'_n \rangle$ can now be determined explicitly in the limit of small λ, and the calculation is a straightforward generalization of what was done to determine $\langle \psi_1 | \psi'_1 \rangle$ in Section 3. One writes out $\langle \Phi_n | \Phi'_n \rangle$ by means of (6.3), obtaining an expression that involves $2n$ factors V. One applies the separation (2.3) to the 2 middle V operators. The term involving Y converges to zero for $\lambda \to 0$. Only the term with W has thus to be retained. Among the $2n - 2$ remaining V operators one chooses again the two middle ones and makes use of (2.3). The term in Y is again negligible and the W-term is kept. This procedure is continued until all pairs of V operators have been considered. The final result contains n factors W. With the notation

$$\langle E'\alpha' | U^W(t) | E\alpha \rangle = u^W(t; E\alpha)\delta(E' - E)\delta(\alpha' - \alpha)$$

it is found to be

$$\langle \Phi_n | \Phi'_n \rangle = \lambda^{2n} \int_0^t \mathrm{d}t'_n \int_0^{t'_n} \ldots \mathrm{d}t'_1 \int_0^t \mathrm{d}t_n \int_0^{t_n} \ldots \mathrm{d}t_1 \int \mathrm{d}E''_n \, \mathrm{d}\alpha''_n \ldots \mathrm{d}E''_1 \, \mathrm{d}\alpha''_1 \, \mathrm{d}E \, \mathrm{d}\alpha$$
$$[u^W(t - t'_n, E''_n \alpha''_n)]^* u^W(t - t_n, E''_n \alpha''_n) W(E''_n \alpha''_n; E''_{n-1} \alpha''_{n-1})$$
$$[u^W(t'_n - t'_{n-1}; E''_{n-1} \alpha''_{n-1})]^* u^W(t_n - t_{n-1}; E''_{n-1} \alpha''_{n-1}) \ldots$$
$$\ldots W(E''_1 \alpha''_1; E\alpha) \, [u^W(t'_1; E\alpha)]^* u^W(t_1; E\alpha) c^*(E\alpha) c'(E\alpha).$$

As was the case for $\langle \psi_1 | \psi'_1 \rangle$ in Section 3, this result is independent of the relative phases of $c(E\alpha)$ and $c'(E\alpha)$ for different values of $E\alpha$. All terms which depend on these phases become negligible for small λ.

Introduce now the explicit value of u^W, known from (5.6),

$$u^W(t; E\alpha) = \exp[-iEt - i\lambda^2 t\Delta(E\alpha) - \lambda^2 t\Gamma(E\alpha)]$$

and go over to the time variables

$$\tau_j = \tfrac{1}{2}(t_j + t'_j), \quad \tau'_j = t_j - t'_j.$$

The integrand becomes

$$\exp[i\{E''_n - E''_{n-1} + \lambda^2\Delta(E''_n \alpha''_n) - \lambda^2\Delta(E''_{n-1} \alpha''_{n-1})\}\tau'_n] \ldots$$
$$\ldots \exp[i\{E''_1 - E + \lambda^2\Delta(E''_1 \alpha''_1) - \lambda^2\Delta(E\alpha)\}\tau'_1] . \exp[-2\lambda^2(t - \tau_n)\Gamma(E''_n \alpha''_n)]$$
$$W(E''_n \alpha''_n; E''_{n-1} \alpha''_{n-1}) \exp[-2\lambda^2(\tau_n - \tau_{n-1})\Gamma(E''_{n-1} \alpha''_{n-1})] \ldots$$
$$\ldots \exp[-2\lambda^2 \tau_1 \Gamma(E\alpha)] c^*(E\alpha) c'(E\alpha).$$

The integrations over the variables τ'_j are then carried out. This is easily achieved because for the great majority of values of $\tau_1, \ldots \tau_n$ the τ'_j vary freely over intervals extending far beyond $(-\delta E^{-1}, +\delta E^{-1})$. Use can thus be made of the formula (3.3), or, more conveniently for this case, of the formula

$$\lim_{T \to \infty} \int_{-T}^{T} \mathrm{d}\tau' \exp[i\varepsilon\tau'] = 2\pi\delta(\varepsilon).$$

One obtains a product of δ-functions

$$\delta[E''_n - E''_{n-1} + \lambda^2\Delta(E''_n \alpha''_n) - \lambda^2\Delta(E''_{n-1} \alpha''_{n-1})] \ldots \delta[E''_1 - E + \lambda^2\Delta(E''_1 \alpha''_1) - \lambda^2\Delta(E\alpha)]$$

in which the terms in λ^2 can be neglected for our purpose. The final result follows immediately:

$$\langle \Phi_n | \Phi'_n \rangle = (2\pi\lambda^2)^n \int_0^t \mathrm{d}\tau_n \int_0^{\tau_n} \mathrm{d}\tau_{n-1} \ldots \int_0^{\tau_2} \mathrm{d}\tau_1 \int \mathrm{d}E \int \mathrm{d}\alpha''_n \ldots \mathrm{d}\alpha''_1 \mathrm{d}\alpha$$
$$\exp[-2\lambda^2(t-\tau_n)\Gamma(E\alpha''_n)] W(E\alpha''_n; E\alpha''_{n-1}) \exp[-2\lambda^2(\tau_n-\tau_{n-1})\Gamma(E\alpha''_{n-1})] \ldots$$
$$\ldots W(E\alpha''_1; E\alpha) \exp[-2\lambda^2\tau_1\Gamma(E\alpha)] c^*(E\alpha)c'(E\alpha) \qquad (6.5)$$

Since t is of the form $\lambda^{-2}\tilde{t}$, $\tilde{t}$ independent of λ, this result is independent of λ. As in the special case $n = 1$ discussed in § 3, the algebraic form of (6.5) is characterized by the absence of interference terms. Transition schemes originating from different components $|E\alpha\rangle$ of the initial states, or passing through different successions of intermediate states $|E''_j\alpha''_j\rangle$ give rise to interference terms which vanish in the limit of small λ. The same holds true for transition schemes for which, although initial and intermediate states are the same, some of the differences $\tau'_j = t_j - t'_j$ between the transition times are large compared to δE^{-1}.

The result (6.5) has still to be supplemented by the relation

$$\langle \Phi_n | \Phi'_{n'} \rangle = 0 \quad \text{for} \quad n \neq n', \qquad (6.6)$$

also valid in the limit $\lambda \to 0$. It can indeed be shown, once more by the same type of method, that $\langle \Phi_n | \Phi'_{n'} \rangle$ behaves for small λ as λ^m, with $m = |n - n'|$. Equation (6.6) establishes the absence of interference between states produced by transitions of different order. Together with (6.2) and (6.5) it leads to the formula

$$\langle U(t)\varphi | U(t)\varphi' \rangle = \int \mathrm{d}E \int \mathrm{d}\alpha'' P_t(E\alpha''; E\alpha) \mathrm{d}\alpha\, c^*(E\alpha)c'(E\alpha) \qquad (6.7)$$

where

$$P_t(E\alpha''; E\alpha) = \exp[-2\lambda^2 t\Gamma(E\alpha)]\delta(\alpha'' - \alpha) +$$
$$+ 2\pi\lambda^2 \int_0^t \mathrm{d}\tau_1 \exp[-2\lambda^2(t-\tau_1)\Gamma(E\alpha'')] W(E\alpha''; E\alpha) \exp[-2\lambda^2\tau_1\Gamma(E\alpha)] + \ldots$$
$$\ldots + (2\pi\lambda^2)^n \int_0^t \mathrm{d}\tau_n \int_0^{\tau_n} \mathrm{d}\tau_{n-1} \ldots \int_0^{\tau_2} \mathrm{d}\tau_1 \int \mathrm{d}\alpha''_{n-1} \ldots \mathrm{d}\alpha''_1 \cdot$$
$$\cdot \exp[-2\lambda^2(t-\tau_n)\Gamma(E\alpha'')] W(E\alpha''; E\alpha''_{n-1}) \cdot$$
$$\cdot \exp[-2\lambda^2(\tau_n - \tau_{n-1})\Gamma(E\alpha''_{n-1})] W(E\alpha''_{n-1}; E\alpha''_{n-2}) \ldots$$
$$\ldots W(E\alpha''_1; E\alpha) \cdot \exp[-2\lambda^2\tau_1\Gamma(E\alpha)] + \ldots \qquad (6.8)$$

A result slightly more general than (6.7) is obtained through an identical derivation, namely

$$\langle U(t)\varphi | A | U(t)\varphi' \rangle = \int \mathrm{d}E \int \mathrm{d}\alpha'' A(E\alpha'') P_t(E\alpha''; E\alpha) \mathrm{d}\alpha\, c^*(E\alpha)c'(E\alpha) \qquad (6.9)$$

where A is an operator independent of λ and diagonal in the $|E\alpha\rangle$-representation, with eigenvalues $A(E\alpha)$:

$$\langle E'\alpha' | A | E\alpha \rangle = A(E\alpha)\delta(E' - E)\delta(\alpha' - \alpha). \qquad (6.10)$$

(6.7) and (6.9) are of course only valid in the limiting case of small λ.

The physical significance of (6.7) and (6.9) is best seen for $\varphi' = \varphi$. As shown by (6.9) the probabilities of finding the system in the states $|Ea\rangle$ at time t are entirely determined by the corresponding probabilities at time 0, and the $P_t(Ea''; Ea)$ are thus the transition probabilities for the time interval t. Transitions are seen to occur between states with equal unperturbed energy E.

The transition probabilities are given by (6.8) in the form of a convergent series. As functions of t they satisfy a first order differential equation which follows immediately from (6.8)

$$\frac{\mathrm{d}}{\mathrm{d}t} P_t(Ea''; Ea) = 2\pi\lambda^2 \int W(Ea''; Ea')\mathrm{d}a' P_t(Ea'; Ea) - \\ - 2\lambda^2 \Gamma(Ea'') P_t(Ea''; Ea).$$

With (4.4) this takes the familiar form of a transport equation

$$\frac{\mathrm{d}}{\mathrm{d}t} P_t(Ea''; Ea) = 2\pi\lambda^2 \int W(Ea''; Ea')\mathrm{d}a' P_t(Ea'; Ea) - \\ - 2\pi\lambda^2 \{\int \mathrm{d}a' W(Ea'; Ea'')\} P_t(Ea''; Ea). \tag{6.11}$$

The solution $P_t(Ea''; Ea)$ is characterized by the initial condition

$$P_0(Ea''; Ea) = \delta(a'' - a).$$

Equation (6.11) is the exact analogue of (1.1) for the case of continuous parameters. The transition probabilities per unit time are given by

$$2\pi\lambda^2 W(Ea''; Ea).$$

Our aim to derive the transport equation without random phase assumption is thereby achieved for the first class of initial states mentioned in the introduction.

7. *Validity for finite systems.* For the sake of simplicity two mathematical idealizations have been introduced in the foregoing analysis: the unperturbed energy spectrum has been taken continuous, corresponding to the limit of an infinitely large system, and the time evolution has been studied over times of order λ^{-2} in the limiting case $\lambda \to 0$. It is useful to state under what conditions our results are applicable to a real system of large but finite size, with a small but non vanishing perturbation λV.

For a finite system the energy E as well as the other quantum numbers a are discrete. We call $\delta_l E$ an energy with the order of magnitude of the separation between the energy levels belonging to the same a's. Although very small for a large system, $\delta_l E$ is not to be confused with the still much smaller separation between all energy levels of the system, irrespective of the a-values to which they belong. This distinction is important and deserves a few further comments.

One could for example, barring accidental degeneracy, label all un-

perturbed eigenstates of the (finite but large) system by their energy alone, and one would then obtain a description without any additional quantum numbers α. This would however be entirely unsuitable for a proper treatment in the limit of a very large system, because the matrix elements of the perturbation, which would then be of the form $\langle E' | V | E \rangle$, would be completely irregular functions of E and E', fluctuating violently when E or E' varies from one level to the next. It is only with a proper choice of additional quantum numbers α that the matrix elements $\langle E'\alpha' | V | E\alpha \rangle$ can remain fairly regular functions of E and E', even when the size of the system grows indefinitely. In practical cases the number of α's will then often become very large or even infinite. In a crystal for example one would take for the α's some discrete quantum numbers giving how many phonons are excited and what their polarizations are, and further variables giving the direction of propagation of the phonons as well as the energies of all but one phonon. In this case $\delta_l E$ is essentially the separation between the energy values of one phonon and is thus inversely proportional to the number of atoms in the crystal.

For a large but finite system the δ-function in the right hand side of (2.3) is replaced by a finite Kronecker symbol with a large coefficient inversely proportional to δE_l and to the separations between successive values of the α's.

One has further to consider the energy δE already introduced before (Section 3), which is essentially independent of the size of the system whenever it is large enough. It characterizes the rapidity of the energy variation of the matrix elements $\langle E'\alpha' | V | E\alpha \rangle$ and of the functions W and Y. For a crystal δE would be given by the Debye temperature. In our discussion we have also assumed that the initial states φ and φ' there considered have amplitudes $c(E\alpha)$, $c'(E\alpha)$ which do not vary too rapidly over energy intervals of order δE. For given initial states not satisfying this condition one must of course choose for δE a smaller value. The λ values for which the above results hold with a given accuracy would then be correspondingly smaller.

The third energy to be considered is the energy corresponding through the uncertainty relation to the relaxation time of the transport processes produced by the perturbation, i.e. the "level width" $\lambda^2\Gamma$, where Γ characterizes the order of magnitude of (4.4). Introducing finally a number v, characteristic of the magnitude of the dimensionless matrix elements $\langle E'\alpha' | V | E\alpha \rangle$, we can state in the following form the conditions of applicability of our results:

$$\delta_l E \ll \lambda^2 \Gamma \ll \delta E, \tag{7.1}$$

$$\lambda v \ll 1. \tag{7.2}$$

The transport equation is then valid for the occupation probabilities at

time t if these probabilities are defined not for individual states but for groups of unperturbed states with an energy spread larger than $\lambda^2\Gamma$ and smaller than δE. The transition probabilities $P_t(E\alpha''; E\alpha)$ also refer to such groups of states and the conservation of the unperturbed energy holds only with an inaccuracy of order $\lambda^2\Gamma$.

8. *Further types of initial states.* In the preceding sections the validity of the transport equation has been established for the first class of initial states mentioned in the introduction. We discuss now the second class. Consider initial states $\varphi, \varphi', \ldots$ whose complex amplitudes $c(E\alpha), c'(E\alpha)\ldots$ as defined in (3.1) vanish outside an energy interval of width $\delta_0 E$ around some unperturbed energy value E_0:

$$c(E\alpha) = c'(E\alpha) = 0 \text{ for } |E - E_0| \geqslant \tfrac{1}{2}\delta_0 E.$$

We assert that equations (6.7), (6.8) and (6.9) are valid for such states under the condition

$$\delta_0 E \ll t^{-1} = \lambda^2 \tilde{t}^{-1}, \tag{8.1}$$

assuming of course as before that the inequalities (7.1) and (7.2) are satisfied (the initial states are now disregarded in the definition of δE). The time t, just as in previous sections, is of the order λ^{-2}, i.e. of the order of the relaxation time. We thus assume $\delta_0 E$ to be an order of magnitude smaller than the line width $\lambda^2\Gamma$. Another formulation of this condition would be to say that the states $\varphi, \varphi' \ldots$ would remain practically stationary in absence of the perturbation over time intervals of the order of the relaxation time. One should note that stationary states of the unperturbed hamiltonian are special examples of the initial states here considered.

To prove our assertion it is sufficient to show that all the expressions found to be negligible in Sections 3 to 6 for the first class of initial states are again vanishingly small for the present class. We shall give the detailed argument for the special case of first order transitions treated in Section 3. A straightforward extension takes care of the general case.

The problem is to establish the smallness of the last term in (3.2) under the present assumptions. The integrations in E and E' extend over intervals of length $\delta_0 E$ around E_0. According to (8.1) the only factors under the integral sign which can vary appreciably over such intervals are $c^*(E'\alpha')$ and $c'(E\alpha)$, so that the term can be written

$$\lambda^2 \int_0^t \mathrm{d}t_1' \int_0^t \mathrm{d}t_1 \int \gamma^*(\alpha')\mathrm{d}\alpha' \exp[i(E_0 - E'')t_1']$$
$$\langle E_0\alpha' | Y(E''\alpha'')| E\alpha\rangle \, \mathrm{d}E''\mathrm{d}\alpha'' \exp[i(E'' - E_0)t_1]\mathrm{d}\alpha\gamma'(\alpha)$$

with the notation

$$\gamma(\alpha) = \int \mathrm{d}E c(E\alpha), \ \gamma'(\alpha) = \int \mathrm{d}E c'(E\alpha). \tag{8.2}$$

The time integrations are now of the same type as was the case for the

first term in the right hand side of (3.2). Carrying them out one gets for small λ

$$2\pi\lambda^2 t \int \gamma^*(\alpha')\mathrm{d}\alpha' \langle E_0\alpha' | Y(E_0\alpha'')| E_0\alpha\rangle \, \mathrm{d}\alpha''\mathrm{d}\alpha\gamma'(\alpha). \tag{8.3}$$

A simple application of the Schwarz inequality shows that the quantities (8.2) are of the order $(\delta_0 E)^{1/2}$. One has for example for $\gamma(\alpha)$

$$|\gamma(\alpha)|^2 \leqslant \int \mathrm{d}E \, |c(E\alpha)|^2 . \int_{E_0-\frac{1}{2}\delta_0 E}^{E_0+\frac{1}{2}\delta_0 E} \mathrm{d}E = \delta_0 E . \int \mathrm{d}E \, |c(E\alpha)|^2.$$

The occupation probabilities $\int \mathrm{d}E \, |c(E\alpha)|^2$ and $\int \mathrm{d}E \, |c'(E\alpha)|^2$ are of the order 1, and the quantity $\langle E_0\alpha' | Y(E_0\alpha'')| E_0\alpha\rangle$ is of order v^2. One finds for the order of magnitude of (8.3) at most

$$\lambda^2 t v^2 \delta_0 E.$$

On account of (8.1) this is small compared to $\lambda^2 v^2$ and a fortiori small compared to 1, as was to be established.

The essential point in the foregoing argument is clearly the occurrence in the expression studied of the amplitudes $c^*(E'\alpha')$, $c'(E\alpha)$ for E distinct from E' and integrated independently over E and E', or in other words its dependence on the relative phases of the amplitudes with respect to different unperturbed eigenstates. This is a common feature of all terms that must be negligible to ensure the validity of the transport equation. It is therefore not surprising that the smallness of all these terms can be established on the basis of (8.1) by a straightforward extension of the above method. Despite the fact that the initial states here considered have an energy spread $\delta_0 E$ small compared to $\lambda^2\Gamma$, this spread increases as time goes on and eventually becomes of order $\lambda^2\Gamma$.

The terms just discussed, of course, cannot be negligible for arbitrary initial states. For example, if one chooses as initial state an eigenstate of the total hamiltonian $H + \lambda V$ or some state prepared by time reversal over an interval of the order of the relaxation time, the transport equation does not hold for all t of order λ^{-2}, and this can only result from the contributions of the terms containing $c^*(E'\alpha')c'(E\alpha)$. Consider now however the occupation probabilities at time t for an arbitrary initial state

$$\varphi = \int |E\alpha\rangle \, \mathrm{d}E\mathrm{d}\alpha c(E\alpha).$$

From (6.9) they are given by

$$|\langle E\alpha| \, U(t)\varphi\rangle|^2 = \int P_t(E\alpha; E\alpha')\mathrm{d}\alpha' \, |c(E\alpha')|^2 + \ldots$$

in the limit of small λ, the unwritten terms being all integrals of the form

$$\int c^*(E'\alpha')\mathrm{d}E'\mathrm{d}\alpha' \ldots \mathrm{d}E\mathrm{d}\alpha c(E\alpha).$$

Although these terms may be quite large, they average to zero when the phases of $c(E\alpha)$ are considered random. Under the random phase assumption

for the initial state we can therefore conclude to the validity of the transport equation for the mean values of the occupation probabilities.

Whether this statistical validity of the transport equation for general initial states with randomly distributed phases is to be preferred for the discussion of actual physical situations to the exact validity of the equation for well defined initial states of restricted type is a question which can only be answered by studying what kind of initial states are expected to occur in the practical applications of the equation. We shall not try to clarify this problem in the present paper. We might still mention however that the derivation of the transport equation for uniquely defined initial states, even of restricted type, is of real interest in itself because it is equivalent with the proof of an ergodic theorem without any recourse to a priori probability considerations. Such a proof differs on the latter point from the well known quantum-mechanical derivation of ergodicity [9]).

9. *Expectation values of operators.* In the light of the discussion of Sections 3 to 8, we consider the following problem. Let B be an operator, independent of λ, with matrix elements

$$\langle E'a' \,|B|\, Ea\rangle = B_1(Ea)\delta(E' - E)\delta(a' - a) + \langle E'a' \,|B_2|\, Ea\rangle$$

where the second term in the right hand side has no singularity as strong as the first one. The expectation value of B for the state $U(t)\varphi$ originating from an initial state

$$\varphi = \int |Ea\rangle \, \mathrm{d}E\mathrm{d}a \, c(Ea)$$

of one of the two classes discussed above is then easily obtained in the limit of small λ. The term in B_2 gives a vanishing contribution in this limit because the expression

$$\langle U(t)\varphi \,|B_2|\, U(t)\varphi\rangle \tag{9.1}$$

expanded with help of (6.2), will contain no products of the type VAV, with A diagonal in the $|Ea\rangle$-representation. The term in B_1, on the contrary, gives a contribution immediately obtained from (6.9) and (6.10), with the result

$$\langle U(t)\varphi \,|B|\, U(t)\varphi\rangle = \int \mathrm{d}E\mathrm{d}a B_1(Ea)p_t(Ea) \tag{9.2}$$

where

$$p_t(Ea) = \int P_t(Ea; Ea')\mathrm{d}a' \,|c(Ea')|^2$$

is the occupation probability of the state $|Ea\rangle$ at time t. The probability function $p_t(Ea)$ can be obtained by integration of the transport equation with the initial condition

$$p_0(Ea) = |c(Ea)|^2.$$

The expectation value of B after times of order λ^{-2} can thus be found from the occupation probabilities without use of the complex amplitudes.

The important point is of course the vanishing of (9.1) for small λ. It must be understood as a consequence of the complete lack of coherence between the various amplitudes

$$\langle Ea \,|U(t)\varphi\rangle = c_t(Ea)$$

of the final state in the $|Ea\rangle$-representation. The expectation value of B must thus be equal to the mean value of the integral

$$\int c_t^*(E'a')\mathrm{d}E'\mathrm{d}a' \langle E'a' \,|B|\, Ea\rangle \,\mathrm{d}E\mathrm{d}a c_t(Ea)$$

when the phases of $c_t(Ea)$ are varied at random. This average is (9.2).

We do not claim to have discussed hereby the most general operators whose expectation value for $U(t)\varphi$ can be obtained by means of the solution of the transport equation. One should rather consider B as representing the simplest type of such operators. A systematic search for other types would probably have to begin with the operators of practical interest in the systems studied in applications.

10. *Interference and reversible effects.* The necessity to impose restrictions on the initial state φ for the derivation of the tranport equation makes it clear that no conflict exists between the irreversibility embodied in this equation and the basic reversibility of the Schrödinger equation. If one considered in particular the evolution for long negative times (of order λ^{-2}) of a state that reduces at time 0 to a state of one of our two classes, one would again find that its occupation probabilities would satisfy a transport equation, namely the equation obtained from (6.11) by time inversion.

It is nonetheless interesting to stress how closely the absence of interference which we know to be the fundamental reason for the validity of the transport equation (Sections 3 and 6) is connected with the flowing of the time in one and the same direction (this direction being indifferently toward the future or the past). To illustrate this point let us consider the well known group property

$$U(t'')U(t') = U(t'' + t') \tag{10.1}$$

of the unitary operator of the motion, and let us assume that t' and t'' are both of order λ^{-2}

$$t' = \lambda^{-2}\,\tilde{t},\ t'' = \lambda^{-2}\,\tilde{t}'',\ \tilde{t}' \text{ and } \tilde{t}'' \text{ independent of } \lambda. \tag{10.2}$$

As long as t' and t'' have the same sign, the property (10.1) finds it analogue in the well-known semi-group property of the transport equation (6.11), expressed by

$$\int P_{t''}(Ea''; Ea')\mathrm{d}a' P_{t'}(Ea'; Ea) = P_{t''+t'}\,(Ea''; Ea). \tag{10.3}$$

This holds for positive t' and t''. The corresponding property holds for negative t' and t''.

It is clear however that no property of the type (10.3) can hold when t' and t'' have opposite signs, because the time evolution between t' and $t' + t''$ must exactly reverse some or all of the dissipative effects that occurred between the times 0 and t'.

The interference mechanism which produces these reversible effects will now be briefly described in the limiting case of small λ. As we have remarked after the derivation of (6.5), in order for two transition schemes of order n to give rise to interfering contributions in the expansion of the scalar product $\langle \Phi_n | \Phi'_n \rangle$ there calculated, the times t_j, t'_j of the j-th transitions must differ by an interval of the order δE^{-1} at most, for all values of j from 1 to n. In the case studied in Section 6, i.e. in the case of $U(t)$, for given times $t_1, \ldots t_n$ the relevant values of $t'_1, \ldots t'_n$ are each limited to an interval of order δE^{-1} around the t_j of same index.

If one studies on the contrary the contributions of n-th order transition schemes to the product in the left hand side of (10.1), assuming of course (10.2), another situation develops when t' and t'' are of opposite sign. Suppose for example $t' > 0$, $t'' < 0$. Since the time intervals $(0, t')$ and $(t', t' + t'')$ are then oriented the first toward the future and the second toward the past, the successive transitions of a transition scheme occur at times $t_1, \ldots t_n$ which first increase and then decrease

$$0 \leqslant t_1 \leqslant t_2 \ldots \leqslant t_j \leqslant t', \; t' \geqslant t_{j+1} \geqslant \ldots \geqslant t_n \geqslant t' + t''. \qquad (10.4)$$

The j first transitions contribute to the factor $U(t')$ of the product $U(t'')U(t')$, the remaining ones to the other factor. Among all n-th order transition schemes there are two groups of schemes whose contributions in the scalar product $\langle U(t'')U(t')\varphi \,|\, U(t'')U(t')\varphi' \rangle$ interfere with the contribution of one given scheme. The schemes of both groups have the same initial and intermediate states as the given scheme, and their transition times $t'_1, \ldots t'_n$ are related to the transition times $t_1, \ldots t_n$ of the latter by

$$|t'_k - t_k| \lesssim \delta E^{-1}, \; (k = 1, \ldots n).$$

If j is defined by (10.4) for the given scheme and if similarly

$$0 \leqslant t'_1 \leqslant \ldots \leqslant t'_{j'} \leqslant t'; \; t' \geqslant t'_{j'+1} \geqslant \ldots \geqslant t'_n \geqslant t' + t'',$$

the first group of schemes is characterized by $j' = j$, whereas the second group corresponds to $j' = j - 1$ if $t_j > t_{j+1}$ and to $j' = j + 1$ for $t_j < t_{j+1}$ (the exceptional case $t_j = t_{j+1}$ can be left out of consideration since one must eventually integrate over the t_k). The two groups are illustrated for $t_j > t_{j+1}$ in the adjoining figure where the dots mark the values of the t_k and the thick intervals show the possible values of the t'_k. The given scheme clearly belongs to the first group. There is thus interference between any scheme of one group and the schemes of the other group as well as between schemes within any one of the two groups.

The important point is now the following. The contribution to

$$\langle U(t'')U(t')\varphi \,|\, U(t'')U(t')\varphi' \rangle$$

of the schemes of one group, the contribution of the schemes of the other group, and the cross-terms between schemes of one group and schemes of the other give altogether a vanishing result by exact compensation. The only transition schemes whose contributions are not suppressed by such interference effects are those for which the two groups cannot exist simul-

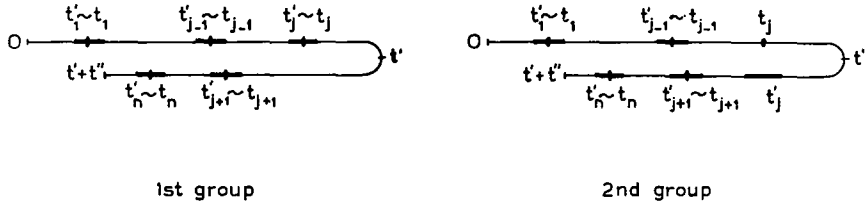

Fig. 1. Graphical representation of transition times in interfering transition schemes for the evolution of the system over two successive time intervals, the first one $(0, t')$ being positive and the second one $(t'; t' + t'')$ negative.

taneously. As seen immediately on the figure, they have transition times verifying

$$0 \leqslant t_1 \leqslant \ldots \leqslant t_n \leqslant t' + t'' \text{ if } t' + t'' > 0, \ (j = n),$$

or

$$0 \geqslant t_1 \geqslant \ldots \geqslant t_n \geqslant t' + t'' \text{ if } t' + t'' < 0, \ (j = 0).$$

They are exactly the schemes contributing to $\langle U(t'+t'')\varphi \,|\, U(t'+t'')\varphi' \rangle$. We shall not give here the proof of the above assertion. Its main lines can easily be found by considering the case $n = 1$.

11. *Concluding remarks.* The main conclusion of our analysis can be formulated by saying that repeated use of a random phase assumption becomes entirely superfluous in the derivation of the quantum-mechanical transport equation when proper account is taken of the special property of the perturbation which is responsible for the occurrence of transport effects. This property is expressed in formula (2.3). The whole discussion shows clearly that non vanishing of the quantity $W(Ea; Ea')$ is the necessary condition for occurrence of dissipation. If this condition were not satisfied the effect of the perturbation would become entirely different. Apart from possible self-energy effects it would be similar to the situation in scattering processes, and would be vanishingly small in the limit of a vanishing perturbation, even over very long time intervals. One must therefore realize that the presence of the singular term in (2.3) is a feature of highly non trivial character and of far-reaching physical significance. The oc-

currence of a δ-singularity in the matrix (2.3) of second order in V is remarkable also from the mathematical standpoint because the matrix elements of V itself have no similar singularity. Actually, if $\langle E'\alpha' | V | E\alpha \rangle$ had a $\delta(E' - E)$-singularity one would have to incorporate first this diagonal part of the perturbation into the unperturbed part of the hamiltonian. In all practical cases the occurrence of the W-term in (2.3) turns out to be intimately connected with the large size of the system and the presence of many degrees of freedom, features which manifest themselves also through the large number of auxiliary quantum numbers α. A mathematical study of the exact conditions under which an operator V can give rise to second order matrix elements (2.3) with $W \neq 0$ would probably be of considerable interest.

Despite its remarkable character the property (2.3) is far from exceptional whenever one deals with physical systems possessing a large number of degrees of freedom and considers the limiting case where this number becomes infinite. A few examples were already mentioned in Section 2. For the case of a liquid or a gas divided in a very large number of macroscopic cells, the interaction between particles in different cells is a perturbation satisfying (2.3) after subtraction of its part diagonal in the total energy of the individual cells. Another example is the interaction of an electron with the ions of a conducting crystal (theory of electrical conduction).

Other important cases of energies V satisfying (2.3) are provided by the interaction between a particle and the systems most commonly used as detecting or measuring devices, like counters, photographic emulsions, cloud chambers, etc. In such cases the term in W in equation (2.3) gets a δ-singularity in the limit of a large size for the detecting device, and it becomes thus quite clear how the statistical nature of the result of the measuring process is conditioned by the macroscopic size of the measuring instrument. A detailed discussion of the bearing of our above analysis on the quantum-mechanical theory of measurement will be left for another publication. We should mention however that the relation between the irreversible nature of a measurement and the macroscopic size of the measuring device has often been stressed before. A detailed discussion of this question will be found in a recent publication of L u d w i g [10]).

As a final remark one should notice that our analysis of the time evolution of the system under the effect of the perturbation has been carried out only in the simplest case, namely in the limit of a small perturbation. Nothing is known at present on the effects of a finite perturbation satisfying (2.3) with non vanishing W. This fact should be contrasted with the case of scattering processes, for which the theory has been thoroughly studied to all orders in the perturbation. To develop the corresponding

theory for perturbations of the type discussed here is a problem of obvious importance. We can only mention it at present.

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