

# Note on the Quantum Theory of Irreversible Processes

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Perturbation treatments of irreversible processes are shown to rest on the assumption that the rate of dissipation of disturbances in a system exceeds their rate of input from an external source. This hypothesis is implicit in the concept of a dissipative system and is formulated mathematically in terms of the relaxation time of quantum-mechanical correlation functions or in terms of equivalent properties of the matrices that represent interaction operators in the energy scheme.

## 1. INTRODUCTION

EFFORTS have been directed recently by various authors towards establishing the theory of irreversible processes on a microscopic, quantum-mechanical basis. With this goal in mind, it is proposed here to develop the implications of perturbation procedures utilized by Callen and co-workers<sup>1</sup> and by Wangsness and Bloch.<sup>2</sup>

Callen and co-workers considered the reaction of a "large" system to an external disturbance represented by a term of the Hamiltonian having the form  $\sum_k V_k^0 Q_k \exp(i\omega t)$ , where the  $V_k^0$ 's are macroscopic constants and the  $Q_k$ 's are quantum-mechanical operators of the system. Specifically, they calculated the effect of the perturbation on the "mean velocities"  $\langle \dot{Q}_j \rangle$ . The coefficients  $Y_{jk}$  of  $\langle \dot{Q}_j \rangle = -\sum_k Y_{jk} V_k^0 \exp(i\omega t)$  represent a generalized "admittance" of the system. This calculation was performed by a first-order time-dependent perturbation method, but the validity of this approximation for an indefinite period after the onset of the perturbation was not discussed.

Wangsness and Bloch developed a microscopic theory of the relaxation of spin orientation in nuclear induction experiments. They treated the coupling of the nuclear spins with the surrounding medium by time-dependent perturbation method carried to the second-order approximation (the first order gives no significant contribution in their problem). This approximation procedure was adopted as reasonable for a sufficiently short time interval  $\tau$ . It was then applied to successive time intervals  $\tau$  with the understanding that the state of the surrounding medium may be regarded at all times as a state of thermal equilibrium, undisturbed by the interaction. This assumption was supported by qualitative arguments involving the macroscopic size of the medium and its thermal conductivity.

Indeed, the irreversibility of these phenomena does not hinge only on the *size* of the system considered but also on *transport properties* that are implied in the concept of a "dissipative system." In each of the examples considered, the perturbing action is understood to be

applied at one point of a large system—more properly, to a few among the numerous degrees of freedom of the large system. The disturbance thus applied during a short time interval is not likely to remain confined to its point of application, but is understood to propagate away quickly to other parts of the large system. Accordingly, the effects of the disturbance should not keep building up at the point of application in the course of time. A sort of steady state is presumably attained within a short time after the onset of the disturbance. This local steady state is all that matters with regard to the *localized reaction* to the disturbance, e.g., for the purpose of calculating the reaction of the medium to nuclear induction. Furthermore it is plausible to assume that the steady state differs but little from the unperturbed state because the disturbance gets dissipated through the large system rapidly as compared to the rate of the external action. (The very concept of an "external action" implies, for example, that the effects of nuclear induction are passed on from the nuclei to the adjacent particles no faster than they can be dissipated, i.e., passed on and on to other particles farther away. Otherwise the nuclei could not be regarded as "external" to the medium.)

Thus, the perturbation procedures of Callen and co-workers, and of Wangsness-Bloch appear to be justified by considerations of *comparative rates of transport* which were not introduced explicitly in the mathematical formalism. In fact, the role of rate-of-transport considerations becomes readily apparent when the analytical treatment is formulated in the manner of Feynman.<sup>3</sup> This will be shown through the analysis of a Callen-type problem; the analogous treatment of a Wangsness-Bloch problem will be outlined at the end of the paper.

## 2. THE CALLEN PROBLEM

As a Callen-type problem, we shall describe the reaction of a system to a time-variable disturbance  $V$  by calculating the effect of the disturbance upon the mean value of an operator of the system,  $F$ . The Hamiltonian of the unperturbed system will be indicated by  $H_0$  and the complete Hamiltonian by  $H = H_0 + V$ . All energies are divided by  $\hbar$  in this paper, i.e., are expressed in radians/sec. For simplicity we shall assume a sinusoidal

<sup>1</sup> H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951); Callen, Barasch, and Jackson, Phys. Rev. **88**, 1382 (1952); M. L. Barasch and T. A. Kaplan, University of Pennsylvania, Report Nonr 69800, No. 7, 1954 (unpublished).

<sup>2</sup> R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

<sup>3</sup> R. P. Feynman, Phys. Rev. **84**, 108 (1951).

dependence of  $V$  on time, much as in reference 1, namely

$$V = Qe^{i\omega t}, \quad (1)$$

where  $Q$  is a time-independent operator. The unperturbed state of the system will be assumed to be constant in time, i.e., to be a state represented by a density matrix diagonal in the energy scheme, for which time-independent operators have constant mean values.

The calculation will be carried out in a Heisenberg representation, where the operators are variable in time, i.e., are automatically transformed back from the time  $t$  to the time  $t=0$ , which marks the onset of the disturbance and at which the state was still unperturbed. The operators indicated above by  $F, H_0, V, Q$  pertain to the ordinary (Schrodinger) representation. The operator of the Heisenberg representation which corresponds to  $F$  will be indicated by

$$\mathcal{F}(t) = e^{iH_0 t} F e^{-iH_0 t} = e^{i(H_0+V)t} F e^{-i(H_0+V)t}. \quad (2)$$

The specific purpose of the calculation is to express the mean value of  $\mathcal{F}(t)$  in terms of the mean values of  $F, V$ , and their combinations, all averages being taken over the unperturbed state. Utilizing the Feynman procedure<sup>3</sup> of disentangling operators by a sequence of infinitesimal unitary transformations, we write

$$\begin{aligned} \exp[i(H_0+V)t] \\ = \exp(iH_0 t) \exp\left[ie^{i\omega t} \int_0^t dt' V(t-t')\right], \end{aligned} \quad (3)$$

where

$$V(t-t') = e^{-i\omega(t-t')} e^{-iH_0(t-t')} Q e^{iH_0(t-t')}, \quad (4)$$

and a similar formula for  $\exp[-i(H_0+V)t]$ . Because  $H_0$  commutes with the density matrix of the constant unperturbed state, the factors  $\exp(\pm iH_0 t)$  do not contribute to the mean of  $\mathcal{F}$ , which can be written as

$$\begin{aligned} \langle \mathcal{F}(t) \rangle = & \left\langle \exp\left[ie^{i\omega t} \int_0^t dt' V(t-t')\right] F \right. \\ & \left. \times \exp\left[-ie^{i\omega t} \int_0^t dt' V(t-t')\right] \right\rangle. \end{aligned} \quad (5)$$

Expand now the exponentials in (5) into power series, which still involves no approximation. The terms of the same order in  $V$  operating part to the left and part to the right of  $F$  can be grouped into a single multiple integral, and the averaging can be performed before the integration, so that (5) becomes

$$\begin{aligned} \langle \mathcal{F}(t) \rangle = & \langle F \rangle + ie^{i\omega t} \int_0^t dt' \langle [V(t-t'), F] \rangle \\ & - e^{2i\omega t} \int_0^t dt' \int_0^{t'} dt'' \langle [V(t-t''), [V(t-t'), F]] \rangle - \dots, \end{aligned} \quad (6)$$

where the square bracket indicates, as usual, "commutator of."

The integrands in this equation are the mean values of products of operators "shifted in time" with respect to one another by intervals  $t-t', t'-t''$ , etc. They represent correlation functions analogous to those used in the analysis of fluctuations according to classical physics.<sup>4</sup> As pointed out earlier in this paper, a dissipative system is *intuitively* characterized by the fact that a disturbance applied at one point quickly travels away. Accordingly one would expect that the value of  $\mathcal{F}$  at the time  $t$  would be unaffected by a disturbance  $V$  applied at a time  $t'$  much earlier than  $t$ , and, therefore, that  $V(t-t')$  and  $F$  would be uncorrelated, if  $t-t'$  is too long. Lack of correlation means that  $\langle V(t-t')F \rangle = \langle V(t-t') \rangle \langle F \rangle$  and, hence, that  $\langle [V(t-t'), F] \rangle = 0$ . (It is implied here that  $F$  operates approximately at the same point as  $V$ ; otherwise the correlation would be highest for a value of  $t-t'$  which allows for the disturbance to propagate from one point to the other.) According to this argumentation, we suggest that a dissipative system is characterized *mathematically* by the property that the correlation functions of (6) vanish rapidly whenever the time intervals  $t-t'$  etc., exceed some suitably defined relaxation time  $\tau$ .<sup>5</sup>

Under this assumption, the entire contribution to the integrals arises from intervals of the order of  $\tau$ . Therefore, as we surmised in the initial qualitative discussion the effect of the disturbance does not keep building up in time. Moreover, each successive term of the expansion (6) differs dimensionally from the preceding one by an additional factor  $V$  (expressed in frequency units) and by an added integration extended over an interval of the order of  $\tau$ . Equation (6) is thus seen to be an expansion in powers of the rate of action of the disturbance—the commutator of  $V$ —integrated over the relaxation time  $\tau$ . A first order perturbation treatment, which disregards all terms on the right of (6) after the second, is thereby justified when the commutator of  $V\tau$  is much smaller than one. (As mentioned before, the opposite assumption would imply that the source of the disturbance  $V$  is so intimately coupled with the system under study as to be virtually a part of it.)

The vanishing of a correlation function for large values of the time interval may be regarded as the result of destructive interference between harmonic components of the function that oscillate with different frequencies. When the operator (4) is represented by a matrix in the energy scheme, with rows and columns labeled by values  $(\phi', \phi'')$  of the energy and by other

<sup>4</sup> See, e.g., N. Wiener, *Extrapolation, Interpolation, and Smoothing of Stationary Time Series* (John Wiley and Sons, Inc., New York, 1949). Quantum-mechanical averages are taken over the set of eigenvalues of the operator product concerned, whereas in classical physics each function is regarded as having a definite, albeit unknown, value at each instant and one resorts to dealing with averages over the values corresponding to extended intervals of time.

<sup>5</sup> This time interval  $\tau$  corresponds to the reciprocal of the "characteristic frequency"  $\omega^*$  of reference 2.

quantum numbers  $(\alpha', \alpha'')$ , if any, each matrix element is a sinusoidal function of the time interval,

$$\begin{aligned} \langle \alpha' \varphi' | V(t-t') | \alpha'' \varphi'' \rangle \\ = e^{-i(\omega + \varphi' - \varphi'')(t-t')} \langle \alpha' \varphi' | Q | \alpha'' \varphi'' \rangle. \end{aligned} \quad (7)$$

All matrix elements having the same value of  $\varphi' - \varphi'' = \varphi$  oscillate in phase. They constitute together the matrix of an operator that may be regarded as a harmonic component of  $V$ . Therefore we write

$$V(t-t') = \int_{-\infty}^{\infty} d\varphi Q_{\varphi} e^{-i(\omega + \varphi)(t-t')}, \quad (8)$$

where  $Q_{\varphi}$  is the operator with the matrix  $\langle \alpha' \varphi' | Q_{\varphi} | \alpha'' \varphi'' \rangle = \langle \alpha' \varphi' | Q | \alpha'' \varphi'' \rangle \delta(\varphi' - \varphi'' - \varphi)$ . Substituting (8) in the correlation functions of (6), we have

$$\langle [V(t-t'), F] \rangle = \int_{-\infty}^{\infty} d\varphi \langle [Q_{\varphi}, F] \rangle e^{-i(\omega + \varphi)(t-t')}, \quad (9)$$

$$\begin{aligned} \langle [V(t-t''), [V(t-t'), F]] \rangle \\ = \int_{-\infty}^{\infty} d\chi \int_{-\infty}^{\infty} d\varphi \langle [Q_{\chi}, [Q_{\varphi}, F]] \rangle \\ \times e^{-i[(\omega + \chi)(t-t'') + (\omega + \varphi)(t-t')]} \end{aligned}$$

These Fourier integrals show that the correlation functions vanish for time intervals exceeding  $\tau$  when, and only when, the mean values  $\langle [Q_{\varphi}, F] \rangle$ ,  $\langle [Q_{\chi}, [Q_{\varphi}, F]] \rangle$  etc., are constant as functions of  $\varphi, \chi \dots$  over ranges of these variables of the order of  $\tau^{-1}$ . Therefore the mathematical characterization of a dissipative system in terms of the early vanishing of correlation functions is equivalent to a characterization in terms of properties of the operators  $Q$  and  $F$ . Thus a system has dissipative properties whenever the matrix elements of the pertinent operators  $Q$  and  $F$  have values independent of the row and column indices  $(\varphi', \varphi'')$  over a sufficient range of these variables.\* This requirement does not look unreasonable for operators acting on a few degrees of freedom of a large, tightly knit, system, because energy eigenfunctions of the system corresponding to rather different eigenvalues may well be effectively equal over the pertinent portion of the system.<sup>6</sup>

\* Footnote added in proof.—Dr. M. S. Green kindly points out that the criterion indicated here for the matrices of  $Z$  and  $F$  is unnecessarily restrictive and indeed unrealistic. The properties of  $Q$  and  $F$ , which characterize the system as dissipative and which should probably be the object of further study, are properties of the averages  $\langle [Q_{\varphi}, F] \rangle$ ,  $\langle [Q_{\chi}, [Q_{\varphi}, F]] \rangle \dots$  rather than of the matrices  $Q_{\varphi}$  and  $F$  per se.

<sup>6</sup> This discussion is admittedly sketchy and one ought to examine more closely the correspondence between the presumable mechanical properties of dissipative system and the mathematical properties of operators  $Q_{\varphi}$ . In this connection it might be relevant that matter has usually a rather homogeneous structure on a semi-macroscopic scale, i.e., it is invariant, in a limited fashion, with respect to translations in space. Because of this invariance, rows and columns of matrices might be labeled simultaneously with energy and momentum quantum numbers. The operators could then be resolved into components  $Q_{\varphi q}$  that change the energy of the system by  $\varphi$  and its momentum by  $q$ .

Substitution of (9) into (6) renders the integrations over time elementary. We have, for example,

$$\begin{aligned} \int_0^t dt' \langle [V(t-t'), F] \rangle \\ = \int_{-\infty}^{\infty} d\varphi \langle [Q_{\varphi}, F] \rangle (1 - e^{-i(\omega + \varphi)t}) / i(\omega + \varphi). \end{aligned} \quad (10)$$

The remaining integral over  $\varphi$  is familiar from perturbation theory. For large values of  $t$  the exponentials oscillate very rapidly as functions of the frequency and yield destructive interference, except within a narrow band of width  $\sim 1/t$  about the resonance  $\varphi = -\omega$ . The integral of the term with the exponential equals  $\pi \langle [Q_{-\omega}, F] \rangle$ , provided  $\langle [Q_{\varphi}, F] \rangle$  is constant over a range larger than  $1/t$  about  $\varphi = -\omega$ . This result, independent of  $t$ , confirms that the effects of the disturbance do not keep building up locally. The term in the integral that contains the factor  $1/i(\omega + \varphi)$ , without an exponential, represents the off-resonance effect of the disturbance, which may be negligible as compared to the resonance effect but has been included in the more recent papers by Callen *et al.* We shall not consider the off-resonance effects explicitly, but merely remind the reader of their possible effects by adding a prime to the symbols that represent the resonance effects. With this convention, all the successive terms of the expansion (6) take a very simple form and (6) becomes

$$\begin{aligned} \langle \mathcal{F}(t) \rangle = \langle F \rangle + e^{i\omega t} i\pi \langle [Q_{-\omega'}, F] \rangle \\ + e^{2i\omega t} (i\pi)^2 \langle [Q_{-\omega'}, [Q_{-\omega'}, F]] \rangle + \dots \end{aligned} \quad (11)$$

The parameter of the expansion of  $\langle \mathcal{F}(t) \rangle$ , which we had identified loosely as the commutator of  $V\tau$ , becomes now defined somewhat more precisely as the commutator of  $\pi Q_{-\omega'}$ . Notice from (8) that, since  $V$  has the dimension of a frequency,  $Q_{\varphi}$  has the dimensions of a pure number. Notice further from (9) that, for a given value of the rate of disturbance

$$\langle [V(0), F] \rangle = \int_{-\infty}^{\infty} d\varphi \langle [Q_{\varphi}, F] \rangle,$$

the larger is the range over which  $\langle [Q_{\varphi}, F] \rangle$  is constant, the smaller must be the values of  $\langle [Q_{\varphi}, F] \rangle$  in this range.<sup>7</sup> Thus the commutator of  $Q_{-\omega'}$  appears to constitute a suitable comparative index of the rate of transport of mechanical action from the outside to a point of the system vs the rate of transport from this point away to the rest of the system. When this index is much smaller than one, the expansion (11) may be broken off after its term of first order in  $Q$  and the Callen perturbation treatment is justified.

Some additional points may be noted. The evaluation of (10) assumes that  $\langle [Q_{\varphi}, F] \rangle$  is constant over a fre-

<sup>7</sup> Similarly, for a given value of  $\text{Tr}(Q^2)$ , the larger is the area of the matrix  $\langle \varphi' | Q | \varphi'' \rangle$  over which the elements are constant, the smaller must be the matrix elements themselves.

quency band width  $\sim 1/t$ . This condition implies, in turn, that  $t$  is much longer than the relaxation time  $\tau$ , which is the reciprocal of the band width over which  $\langle [Q_\varphi, F] \rangle$  is constant; for  $t \lesssim \tau$  no steady state is attained. The band of constant  $\langle [Q_\varphi, F] \rangle$  extends presumably, barring unusual circumstances, from  $\varphi=0$  upwards. Accordingly, it should be understood in the derivation of (11) that the driving frequency  $\omega$  lies within this band, that is, that the disturbance varies but little within the relaxation time of the system. This requirement appears plausible for reasonably slow irreversible processes and has been explicitly postulated by Wangness and Bloch<sup>2,5</sup> though not by Callen *et al.*

To verify that the main result of Callen, Barasch, and Jackson is contained in (11), one should set  $Q = \sum_k V_k Q_k$  and  $F = Q_j$ . The first-order term takes the form  $\exp(i\omega t) \sum_k V_k i\pi \langle [Q_{k-\omega}, Q_j] \rangle$ , and the expression of  $i\pi \langle [Q_{k-\omega}, Q_j] \rangle$  for an unperturbed state of thermal equilibrium actually coincides with the admittance matrix  $Y_{jk}(\omega)$  of reference 1.

### 3. THE WANGNESS-BLOCH PROBLEM

The problem of nuclear spin relaxation is closely similar in essence to the Callen problem but sufficiently different in formal structure to deserve a brief treatment. Further details and a discussion from a different point of view will be given in another paper.

The spin relaxation process involves two systems: system No. 1, with unperturbed Hamiltonian  $H_1$ , consists of the nuclear spins, and system No. 2, with unperturbed Hamiltonian  $H_2$ , consists of the surrounding medium and is regarded as large and dissipative. The coupling of the two systems is indicated in the Schrodinger representation by a time-independent operator  $V$ , which operates on both systems. The complete Hamiltonian is  $H = H_1 + H_2 + V$ .

We are interested here in the effect of the coupling upon the dynamics of the nuclear spins. This effect is described by the influence of  $V$  upon operators  $F$  that operate on the nuclear spins (system No. 1), the effect being *averaged over* the unperturbed state of system No. 2, the surrounding medium. This unperturbed state is assumed to have been constant in time prior to the onset of the disturbance, as in the Callen problem. Therefore the quantity to be calculated is

$$\langle \mathcal{F}(t) \rangle_2 = \langle e^{i(H_1+H_2+V)t} F e^{-i(H_1+H_2+V)t} \rangle_2. \quad (12)$$

The operators in the exponents are conveniently disentangled here by

$$e^{i(H_1+H_2+V)t} = \exp \left\{ i \int_0^t V(t') dt' \right\} e^{i(H_1+H_2)t}, \quad (13)$$

and an analogous formula, where

$$V(t) = e^{i(H_1+H_2)t} V e^{-i(H_1+H_2)t}. \quad (14)$$

The operator  $\exp(iH_2t)$  commutes with  $H_1$  and  $F$  and therefore cancels with  $\exp(-iH_2t)$  in (12), after disentanglement, so that (12) reduces to

$$\langle \mathcal{F}(t) \rangle_2 = \left\langle \exp \left[ i \int_0^t V(t') dt' \right] e^{iH_1 t} F e^{-iH_1 t} \right. \\ \left. \times \exp \left[ -i \int_0^t V(t') dt' \right] \right\rangle_2. \quad (15)$$

The factor  $\exp(iH_1t)F\exp(-iH_1t)$  does not operate on the system No. 2 and can be removed from the averaging procedure provided one keeps track of the ordering of operators. To this end we introduce a dummy symbol  $I$  which serves as an ordering parameter such that operators formally on the left of  $I$  act on the left of  $F$  and operators on the right of  $I$  act on the right of  $F$ . Accordingly (15) can be written in the form

$$\langle \mathcal{F}(t) \rangle_2 = F e^{i[H_1, I]t} \left\langle \exp \left\{ i \int_0^t [V(t'), I] dt' \right\} \right\rangle_2. \quad (16)$$

The mean value of an operator of the form  $\exp A$ , such as we have on the right of (16), can be expressed in terms of the "cumulants,"  $C_n$ , of  $A$  according to the theorem of probability,<sup>8</sup>

$$\langle \exp A \rangle = \exp \left[ \sum_n C_n / n! \right]. \quad (17)$$

The first cumulant,  $C_1$ , is simply the mean value  $\langle A \rangle$ ; the cumulants  $C_2$  and  $C_3$  are the mean square and cube deviations of  $A$  from its mean; the higher cumulants  $C_n$  are simple functions of mean deviations  $\langle (A - \langle A \rangle)^r \rangle$  with  $r \leq n$ . The theorem can be proved by expanding  $\exp A$  into powers of  $A$ , taking the mean of each power, and manipulating the series thus obtained. The first cumulant of the exponent of (16) is

$$C_1 = i \int_0^t dt' \langle [V(t'), I] \rangle_2 \\ = i \int_0^t dt' [e^{iH_1 t'} \langle V \rangle_2 e^{-iH_1 t'}, I]. \quad (18)$$

In the expression on the right,  $V(t')$  has been replaced with its expression (14), the factors with  $H_1$  have been removed from the averaging and the factors with  $H_2$  have cancelled because they commute with the unperturbed density matrix of system No. 2. Because  $\langle V \rangle_2$  is constant in time, it represents a constant interaction energy due to the average electric and magnetic forces exerted by the medium on the nuclear spins.

The second cumulant and the higher ones are functions of the deviation of  $V$  from its mean  $\langle V \rangle_2$ . Therefore

<sup>8</sup> See, e.g., H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, 1946), p. 186. The mean of an operator behaves in this respect like the mean of an ordinary random variable because it can be calculated in the scheme where the operator is diagonal and reduces to its set of eigenvalues.

it simplifies the formulas to introduce the operator  $\bar{V} = V - \langle V \rangle_2$  whose mean vanishes and whose second and third cumulants are simply  $\langle \bar{V}^2 \rangle$  and  $\langle \bar{V}^3 \rangle$ . The second and third cumulants of the exponent of (16) are given by

$$C_2/2! = - \int_0^t dt' \int_0^{t'} dt'' \langle [\bar{V}(t''), [\bar{V}(t'), I]] \rangle_2, \quad (19)$$

$$C_3/3! = -i \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' \langle [\bar{V}(t'''), [\bar{V}(t''), [\bar{V}(t'), I]]] \rangle_2.$$

Multiple correlations in the successive cumulants represent the effects of fluctuating electric and magnetic fields on the spins. Owing to their presence, the series of cumulants of the exponent of (16) must converge rapidly if system No. 2 exhibits the properties of a dissipative medium indicated in Sec. 2. Accordingly we shall break off the series after the term  $C_2/2!$ , an approximation equivalent to that of Wangsness-Bloch, and write

$$\langle \mathfrak{F}(t) \rangle_2 = F e^{i[H_1, I]t} e^{C_1 + \frac{1}{2}C_2}. \quad (20)$$

The integration over  $t''$  in (19) can be handled as the integration over  $t'$  in (10), but  $\bar{V}(t'')$  must be first changed into  $\bar{V}(t'' - t')$  by a regrouping of the exponentials in (14) which brings the correlation function to the form

$$e^{iH_1 t'} \langle [\bar{V}(t'' - t'), [V, I]] \rangle_2 e^{-iH_1 t'}. \quad (21)$$

The integration then yields

$$\frac{1}{2}C_2 = - \int_0^t dt' e^{iH_1 t'} \pi \langle [\bar{V}_0', [\bar{V}, I]] \rangle_2 e^{-iH_1 t'}, \quad (22)$$

where, as in Sec. 2, the subscript characterizes a harmonic component of the operator  $\bar{V}$ , which in this

case oscillates with zero frequency, i.e., conserves energy, and the prime reminds one of the possible additional contribution of off-resonance transitions.

The integrands of  $C_1$  and  $C_2$  contain now explicitly the transformation  $\exp(iH_1 t)$ . Therefore,  $C_1$  and  $C_2$  can be conveniently brought back in the same exponential as  $H_1$  by a transformation inverse to that of (14), which yields

$$\langle \mathfrak{F}(t) \rangle = F \exp\{i([H_1, I] + [\langle \bar{V} \rangle_2, I] + i\pi \langle [\bar{V}_0', [\bar{V}, I]] \rangle_2)t\}. \quad (23)$$

Equation (23) shows that the mean interaction  $\langle V \rangle_2$  may simply be added to the unperturbed Hamiltonian  $H_1$ . The next cumulant, however, takes the form of an imaginary contribution to  $H_1$ , which is in line with the dissipative character of the effect it represents.

Wangsness and Bloch have represented their result in the form of a Boltzmann equation which is, in essence, the differential counterpart of (23) and may be regarded as a generalization of the Schroedinger equation for the operator  $F$ , extended to include the effect of the dissipative interaction with system No. 2. Differentiation of (23) with respect to  $t$  yields

$$d\langle \mathfrak{F}_2(t) \rangle / dt = i([H_1 + \langle V \rangle_2, F] + i\pi \langle [\bar{V}_0', [\bar{V}, F]] \rangle_2) \exp\{\dots\}, \quad (24)$$

where the exponent is the same as in (23). As emphasized in reference 2, the integration performed over  $t''$  when deriving (23) assumes that the duration of the disturbance from  $t=0$  to  $t$  greatly exceeds the relaxation time  $\tau$  of system No. 2. Therefore the differential law (24), and also (23), cannot be extrapolated back to  $t=0$ , in principle, but holds only for the steady state, which becomes established after the interaction has been in effect for a time longer than  $\tau$ .

In practice, however, extrapolation back to  $t=0$  involves a negligible error because the effect of interaction during  $\tau$  is assumed to be small.