REVIEWS OF MODERN PHYSICS VOLUME 39, NUMBER 1 JANUARY 1967

Formal Theory of Nonlinear Response

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This paper presents the derivation of formal, exact expressions for "generalized response coefficients," quantities which characterize the response of a system to conservative forces of arbitrary strength and time dependence. The development avoids all expansions of the response in powers of the driving forces. The generalized response coefficients thus provide the basis for calculations of nonlinear effects in those situations for which expansions in powers of the forces are not suitable. It is shown how the linear and higher-order response functions obtained first by Kubo can be obtained in a relatively more compact way. The expressions corresponding to static forces are considered in some detail. Generalized response coefficients are also derived for systems in equilibrium; the lowest order of these is just the isothermal susceptibility as usually defined.

1. INTRODUCTION

The purpose of this article is twofold. First, we present new formulas characterizing the response of a system to conservative driving forces of arbitrary strength and time dependence. These results are obtained by techniques apparently not used previously in transport theory, and are obtained without the usual expansion in powers of the forces. The second purpose is pedagogical: We show how expressions for the linear and higher-order response functions obtained previously by Kubo[1] and others[2–4] can be derived in a more rigorous and more compact way. We also review briefly, below, some aspects of response theory in order to provide a background for the new work of this article. The article by Bernard and Callen[3] is an excellent review of the current theory of the response to conservative driving forces, often referred to as the "Kubo formalism."

By "response" is meant the generally time-dependent ensemble average of a dynamical operator, representing a quantity such as electric current density, magnetic moment, or electric polarization. A "response function" is the coefficient of an applied force in an expression for the response. This may be illustrated with a simple scalar example. Consider electric current density J as the response to an applied electric field $E(t)$. It is often possible to describe J by expanding it in powers of $E(t)$, retaining only the first few terms. One can obtain[1,3]

$$J(t)=\int_{t_0}^{t} dt_1 E(t_1)\phi_1(t-t_1)$$

$$+\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 E(t_1)\,E(t_2)\phi_2(t_1-t_2,\,t-t_2)+\cdots. \quad (1)$$

Here it is assumed that the field is turned on at t_0. The quantities $\phi_1(t-t_1)$ and $\phi_2(t_1-t_2, t-t_2)$ are the first- and second-order response functions. Kubo[1] was the first to show how to write formal, exact expressions for such functions, in a manner which completely bypasses the Boltzmann equation.[5] If $E(t)$ is a simple oscillating field, turned on adiabatically at $t_0=-\infty$, that is,

$$E(t)=Ee^{st}\cos\omega t, \quad (2)$$

where s is "small" and positive, the first-order term in Eq. (1) can be written

$$\Re\{E\exp[(i\omega+s)t]\int_0^\infty d\tau_1 \exp[-(i\omega+s)\tau_1]\phi_1(\tau_1)\}, \quad (3)$$

where $\Re\{\ \}$ means "real part of $\{\ \}$". The quantity

$$\int_0^\infty d\tau_1 \exp[-(i\omega+s)\tau_1]\phi_1(\tau_1) \quad (4)$$

is the linear complex conductivity (or susceptibility, or admittance). The second-order term in Eq. (1) can be written

$$\tfrac{1}{2}E^2\exp(2st)\int_0^\infty d\tau_1\int_0^\infty d\tau_2$$
$$\times\exp[-s(2\tau_1+\tau_2)]\phi_2(\tau_2,\tau_1+\tau_2)\cos\omega\tau_2$$
$$+\Re\{E^2\exp[2(i\omega+s)t]\tfrac{1}{2}\int_0^\infty d\tau_1\int_0^\infty d\tau_2$$
$$\times\exp[-(i\omega+s)(2\tau_1+\tau_2)]\phi_2(\tau_2,\tau_1+\tau_2)\}. \quad (5)$$

From Eq. (5) it is seen that the second-order contribution to the response contains a term oscillating at twice the driving frequency, and a "dc" term. These, and higher-order, terms are useful in calculating the efficiency of harmonic generation.[6] The development of lasers, the radiation from which can contain very large electric field amplitudes, has given added interest to these higher-order terms.

In the zero-frequency limit, that is, for static forces, the response in our example becomes

$$J=\sigma_1E+\sigma_2E^2+\cdots. \quad (6)$$

[1] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957). See also R. Kubo, in *Lectures in Theoretical Physics*, W. E. Brittin and L. G. Dunham, Eds. (Interscience Publishers, Inc., New York, 1959), Vol. I, p. 120.
[2] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).
[3] W. Bernard and H. B. Callen, Rev. Mod. Phys. **31**, 1017 (1959).
[4] P. J. Price, Phys. Rev. **130**, 1792 (1963).
[5] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 264ff.
[6] P. Franken and J. F. Ward, Rev. Mod. Phys. **35**, 23 (1963).

The response coefficients $\sigma_1, \sigma_2, \cdots$, although independent of frequency, are still not simply *material* constants, for the reason that E is the applied field (in the response theories referred to[1-4]) rather than the field inside the sample.[7] The response coefficients therefore generally depend upon the sample shape as well as upon the material properties.

As the applied forces are made stronger, and the nonlinear characteristics of the response become more important, an expansion in powers of the forces becomes less suitable, particularly for static forces. Not only does the expansion become less *practical* for describing the response, it does not readily bring out some of the physically interesting characteristics of the response. That is, in addition to the response itself, the rate of change of the response with respect to a change in the forces, at arbitrary values of the forces, is an important quantity. To a lesser extent, the second- and higher-order derivatives are also useful. The response coefficients mentioned above are, of course, just such derivatives, but evaluated at zero forces. They give the slope and curvatures of the response vs force curves at the "origin." It is clearly desirable to have formulas available for computing these same quantities at all values of the forces, particularly when the forces are strong. The primary purpose of this article is to supply such formulas.

We may state this from a slightly different point of view. Suppose that one wants to develop a formal theory of response in which all expansions in powers of the forces are avoided, since it is often true that response vs force curves have regions of strong curvature,[8,9] or possibly kinks.[10] One first must decide just what the physically important quantities in such a theory must be. The conclusion is inevitable: The physically interesting quantities are the response and its derivatives.

Tani[11] has recently developed, without using the above-mentioned expansions, a formal expression for the response itself. Many investigators prefer to write Eq. (6), for example, in an Ohm's law form with a field-dependent conductivity:

$$J=\sigma(E)E. \tag{7}$$

Tani's result gives quantities such as $\sigma(E)$ directly. It is clear, however, that in the nonlinear region, J/E does not have the physical relevance that $\partial J/\partial E$ has, although Eq. (7) has a considerable amount of intuitive appeal because of our familiarity with the linear form.

In this article expressions are developed for the derivatives of the response, which we refer to as *generalized response coefficients*. A precise definition is given in Secs. 2 and 3, where forces of arbitrary strength and time dependence are considered. In Sec. 4 we examine further these expressions for the case of static forces. In Sec. 5 we derive generalized response coefficients for systems in thermal equilibrium, extending the work of Wilcox,[12] who has studied the static dielectric susceptibility of a dielectric medium in an arbitrarily large electric field. A review and discussion of the formalism developed in this paper is given in Sec. 6. In the Appendix, we give the derivation and result of Tani[11] for the response, and examine it in the static force case for comparison with the results in Sec. 4.

2. FIRST-ORDER GENERALIZED RESPONSE COEFFICIENTS FOR TIME-DEPENDENT FORCES

For times t earlier than t_0, the Hamiltonian $\mathcal{H}_0$ of the system of interest is assumed to be constant, characterizing the kinetic energies of the particles, their mutual interactions, and their interactions with other systems such as thermal reservoirs and impurities. $\mathcal{H}_0$ can also include the Hamiltonians of surrounding systems, to the extent that they are not time-dependent. At t_0, one or more conservative forces $F_j(t)$ are applied, so that the Hamiltonian takes the form

$$\mathcal{H}_t=\mathcal{H}_0-\sum_j A_jF_j(t), \qquad t\geq t_0. \tag{8}$$

The A_j are operators corresponding to position, magnetic moment, etc. The response corresponding to an operator B_i is the ensemble average of B_i:

$$\langle B_i\rangle_t=\operatorname{Tr}\{B_i\rho(t)\}. \tag{9}$$

Here "Tr" is the trace operation, and $\rho(t)$ is the density matrix, whose motion is described by the von Neumann equation[13]

$$i\hbar d\rho(t)/dt=[\mathcal{H}_t, \rho(t)]. \tag{10}$$

It is readily verified by differentiation that the formal solution to Eq. (10) can be written

$$\rho(t)=U(t, t_0)\rho(t_0)U^\dagger(t, t_0), \tag{11}$$

where the time-development operator $U(t, t_0)$ satisfies the equation of motion

$$i\hbar\partial U(t, t_0)/\partial t=\mathcal{H}_tU(t, t_0), \tag{12}$$

with initial condition $U(t_0, t_0)=1$. The solution to

[7] T. Izuyama, Progr. Theoret. Phys. (Kyoto) **25**, 964 (1961); J. R. Magan, dissertation, Lehigh University, 1965 (unpublished). These authors have shown how electrical conductivity (material constant) can be obtained from the linear Kubo formula.

[8] F. Llewellyn-Jones, *Ionization and Breakdown in Gases* (John Wiley & Sons, Inc., New York, 1957).

[9] J. B. Gunn, in *Progress in Semiconductor Physics*, A. F. Gibson, Ed. (John Wiley & Sons, Inc., New York, 1957), Vol. 2, p. 211.

[10] L. Esaki, Phys. Rev. Letters **8**, 4 (1962); L. Esaki and J. Heer, in *Proceedings of the International Conference on Semiconductor Physics*, Exeter, 1962, A. C. Stickland, Ed. (The Institute of Physics and The Physical Society, London, 1962), p. 603.

[11] K. Tani, Progr. Theoret. Phys. (Kyoto) **32**, 167 (1964).

[12] R. M. Wilcox (unpublished manuscript).

[13] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Chap. IX.

Eq. (12) can be written as[14]

$$U(t,t_0)=T\exp\left[(-i/\hbar)\int_{t_0}^{t}\mathcal{H}_{t'}\,dt'\right],\tag{13}$$

where T is the time-ordering operator, meaning that operators for later times operate after those for earlier times. The equation of motion for $U^\dagger(t,t_0)$, the Hermitian conjugate of $U(t,t_0)$, is just the Hermitian conjugate of Eq. (12), and its solution is obtained from Eq. (13) by replacing $-i$ by i, and reversing the time-ordering sequence. Equation (13) may also be written in the equivalent form

$$U(t,t_0)=\sum_{n=0}^{\infty}(-i/\hbar)^n\int_{t_0}^{t}dt_1\cdots\int_{t_0}^{t_{n-1}}dt_n\mathcal{H}_{t_1}\cdots\mathcal{H}_{t_n}.\tag{14}$$

Another expression for $U(t,t_0)$, which may be useful if the forces are small or if a diagram analysis is needed, is

$$U(t,t_0)=U_0(t,t_0)\sum_{n=0}^{\infty}(-i/\hbar)^n \times\int_{t_0}^{t}dt_1\cdots\int_{t_0}^{t_{n-1}}dt_n\mathcal{H}_1(t_1)\cdots\mathcal{H}_1(t_n),\tag{15}$$

where

$$\mathcal{H}_1(t)=-U_0^\dagger(t,t_0)\sum_j A_jF_j(t)U_0(t,t_0),\tag{16}$$

and

$$U_0(t,t_0)=\exp\left[-i\mathcal{H}_0(t-t_0)/\hbar\right].\tag{17}$$

Equation (15) follows from iteration of the identity

$$U(t,t_0)=U_0(t,t_0)\Big[1-(i/\hbar)\times\int_{t_0}^{t}dt'\mathcal{H}_1(t')U_0^\dagger(t',t_0)U(t',t_0)\Big].\tag{18}$$

Equation (18) clearly satisfies the equation of motion (12), and the initial condition $U(t_0,t_0)=1$. In the subsequent formal development, however, no use is made of Eq. (15), although we shall refer to it in later sections.

Also, although the subsequent formal development does not require that the density matrix at t_0, $\rho(t_0)$, describe an equilibrium ensemble, there is no gain in generality here in assuming otherwise. Consistently with the assumption that the Hamiltonian is constant for all time prior to t_0, $\rho(t_0)$ is therefore taken to be a function of $\mathcal{H}_0$.

It is convenient to transfer the time dependence from $\rho(t)$ to B_i in Eq. (9). Defining the Heisenberg operator $B_i(t,t_0)$ by

$$B_i(t,t_0)\equiv U^\dagger(t,t_0)B_iU(t,t_0),\tag{19}$$

and using $\langle\ \rangle_{eq}$ to denote an ensemble average relative to $\rho(t_0)$, one can write Eq. (9) as

$$\langle B_i\rangle_t=\langle B_i(t,t_0)\rangle_{eq}.\tag{20}$$

[14] R. P. Feynman, Phys. Rev. **84**, 108 (1951).

The generalized response coefficients are defined as derivatives of the response with respect to the amplitudes of the forces. Writing

$$F_j(t)=F_ja_j(t),\tag{21}$$

where the $a_j(t)$ are dimensionless numbers, equal to zero for $t<t_0$, we define, for n forces,

$$\sigma_{ij}(F_1,\cdots,F_n;t)\equiv\partial\langle B_i\rangle_t/\partial F_j,$$
$$\sigma_{ijk}(F_1,\cdots,F_n;t)\equiv\partial\langle B_i\rangle_t/\partial F_k\partial F_j,\tag{22}$$

etc. One therefore must know how to take derivatives of the time-development operators.

Consider any parameter λ in $\mathcal{H}_t$. From Eq. (13), one obtains

$$\begin{aligned}\frac{\partial U(t,t_0)}{\partial\lambda}&=\frac{-i}{\hbar}T\int_{t_0}^{t}dt'\frac{\partial\mathcal{H}_{t'}}{\partial\lambda}\exp\left\{\frac{-i}{\hbar}\int_{t_0}^{t}\mathcal{H}_\tau d\tau\right\}\\&=\frac{-i}{\hbar}\int_{t_0}^{t}dt'U(t,t')\frac{\partial\mathcal{H}_{t'}}{\partial\lambda}U(t',t_0)\\&=\frac{-i}{\hbar}U(t,t_0)\int_{t_0}^{t}dt'U^\dagger(t',t_0)\frac{\partial\mathcal{H}_{t'}}{\partial\lambda}U(t',t_0).\end{aligned}\tag{23}$$

In the first and second of Eqs. (23), use has been made of the time-ordering operator in an evident way. In passing from the second to the third of Eqs. (23), use has been made of the group property of $U(t,t_0)$, which follows immediately from Eq. (13):

$$U(t,t_0)=U(t,t')U(t',t_0),\qquad t>t'>t_0;\tag{24}$$

and the unitary property of $U(t,t_0)$:

$$U(t,t_0)U^\dagger(t,t_0)=U^\dagger(t,t_0)U(t,t_0)=1,\tag{25}$$

which follows from Eq. (13) and the discussion following it.

One may easily verify Eq. (23) by noting that each side of the equation satisfies the same differential equation in t with the same initial condition. That is, using $\Gamma(t,t_0)$ to represent either side, and using Eqs. (12) and (25), one obtains

$$\frac{\partial\Gamma(t,t_0)}{\partial t}=-\frac{i}{\hbar}\frac{\partial\mathcal{H}_t}{\partial\lambda}U(t,t_0)-\frac{i}{\hbar}\mathcal{H}_t\Gamma(t,t_0),$$

with $\Gamma(t_0,t_0)=0$.

Equation (23) together with its Hermitian conjugate then gives a commutator form to the derivative of any Heisenberg operator $C(t,t_0)$, and real λ:

$$\frac{\partial C(t,t_0)}{\partial\lambda}=\frac{i}{\hbar}\int_{t_0}^{t}dt'\left[\frac{\delta\mathcal{H}_{t'}(t',t_0)}{\delta\lambda},C(t,t_0)\right]+\frac{\delta C(t,t_0)}{\delta\lambda},\tag{26}$$

where

$$[\delta A(t,t_0)]/\delta\lambda\equiv U^\dagger(t,t_0)(\partial A/\partial\lambda)U(t,t_0)$$

for any operator A. We investigate the higher derivatives in the following section.

The first-order generalized response coefficient σ_{ij} now follows immediately. Taking B_i and $\rho(t_0)$ to be independent of the F_j, one finds from Eqs. (8), (20), (21), and (26), that

$$\sigma_{ij}(F_1,\cdots,F_n;t)$$
$$=-(i/\hbar)\int_{t_0}^{t}dt'a_j(t')\,\langle[A_j(t',t_0),B_i(t,t_0)]\rangle_{eq}. \quad (27)$$

Equation (27) is the principal result of this paper.

By analogy with Eq. (1), a first-order generalized response *function* may be defined by

$$\phi_{ij}(F_1,\cdots,F_n;t,t',t_0)$$
$$=-(i/\hbar)\,\langle[A_j(t',t_0),B_i(t,t_0)]\rangle_{eq}. \quad (28)$$

In appearance, Eq. (28) is identical to the first-order response function of Kubo.[1] The difference is that the Heisenberg operators in Eq. (28) are defined relative to the total Hamiltonian $\mathcal{H}_t$, rather than $\mathcal{H}_0$ as in the response function formula. The response function may therefore be obtained by evaluating Eq. (28) at zero forces.

The first-order generalized response function as defined here does not have the simple physical meaning that the usual first-order response function has; that is, it is not the response at time t to a delta-function force applied at t', inasmuch as it is a functional of the applied forces. This fact means that the generalized response function does not possess the interesting symmetry properties[3] under time-reversal that the response function has, unless the prescribed time-dependence of the applied forces is such that $\sum_j A_jF_j(t)$ is invariant to the transformation $t-t_0\to t_0-t$. In this special case one finds that

$$\phi_{ij}(-\mathbf{H};-t,-t',-t_0)=-\phi_{ij}(\mathbf{H};t,t',t_0).$$

The symbol $\mathbf{H}$ is used here to signify not only a dc magnetic field which may be present in $\mathcal{H}_0$, but also any magnetic fields which are found among the forces F_j. In establishing this relation, the reality of ϕ_{ij}, which follows from Eq. (28), is used, together with the fact that axial vectors, such as $\mathbf{H}$, reverse direction upon time-reversal. The first-order response function at zero forces is also antisymmetric under time-reversal,[3] for $A_i=B_i$. This property is not shared by the generalized response function since the time-development operators do not commute with $\rho(t_0)$.

The expression for the usual first-order complex frequency-dependent admittance [conductivity, susceptibility, etc.; see Eqs. (3) and (4)] is obtained from Eq. (27) by assuming that the forces are turned on adiabatically at $t_0=-\infty$, such that

$$a_j(t')=\exp[(i\omega+s)t'],\qquad s\to 0+,$$

then dividing $\exp[(i\omega+s)t]$ from the resulting expression, and evaluating it at zero forces. This readily gives the now-familiar form[1]

$$\sigma_{ij}(\omega)=-(i/\hbar)$$
$$\times\int_0^\infty d\tau\exp[-(i\omega+s)\tau]\langle[A_j,B_i^{(0)}(\tau)]\rangle_{eq}, \quad (29)$$

where $B_i^{(0)}(\tau)$ is the Heisenberg operator at zero forces, given by

$$B_i^{(0)}(\tau)=\exp(i\mathcal{H}_0\tau/\hbar)B_i\exp(-i\mathcal{H}_0\tau/\hbar). \quad (30)$$

An alternative form of Eq. (27) is interesting and is referred to in Sec. 4. Using Eqs. (11), (24), and (25), and permuting operators within the trace, one can write

$$\sigma_{ij}(F_1,\cdots,F_n;t)=-(i/\hbar)\int_{t_0}^{t}dt'a_j(t')$$
$$\times\mathrm{Tr}\,\{\rho(t)[U(t,t')A_jU^\dagger(t,t'),B_i]\}. \quad (31)$$

The interesting features in this form are that the time dependence has been removed from B_i, and the ensemble average is taken with respect to the density matrix *at the time of the measurement.* This can be a very useful simplification for calculational purposes, for although one should strictly evaluate $\rho(t)$ according to Eq. (11), the physics of the system and the nature of the forces may be such that by the time of the measurement the system will have settled into an equilibrium condition, or a steady-state condition, enabling one to use for $\rho(t)$ an appropriate ensemble. We discuss this further when considering static forces in Sec. 4.

Equations (27)–(29), and the expressions for the higher-order generalized response coefficients which follow, can be written in another form which is sometimes convenient, if $\rho(t_0)$ is assumed to be canonical:

$$\rho(t_0)=\exp(-\beta\mathcal{H}_0)/\,\mathrm{Tr}\,\{\exp(-\beta\mathcal{H}_0)\}, \quad (32)$$

where $\beta=(kT)^{-1}$, $k=$Boltzmann's constant, and $T=$ absolute temperature. Then, for any operators A and B,

$$\langle[A,B]\rangle_{eq}=-\int_0^\beta d\beta'\partial$$
$$\times\langle\exp(\beta'\mathcal{H}_0)A\exp(-\beta'\mathcal{H}_0)B\rangle_{eq}/\partial\beta'$$
$$=i\hbar\int_0^\beta d\beta'\langle\dot{A}^{(0)}(-i\hbar\beta')B\rangle_{eq}. \quad (33)$$

The first equation in (33) is an obvious identity. In the last term, the notation of Eq. (30) is used, and the dot refers to differentiation with respect to the argument. Equation (33) was first used by Kubo,[1] and is convenient when $\dot{A}$ is proportional to B, as in the electrical conductivity problem.[1] The use of Eq. (33) is not essential to the present development, and we introduce it only when considering static electric fields in Sec. 4 and in the Appendix.

3. HIGHER-ORDER GENERALIZED RESPONSE COEFFICIENTS FOR TIME-DEPENDENT FORCES

We now return to the development of the expressions for the higher-order generalized response coefficients.

Equation (26), with $\lambda = F_j$ and $C(t, t_0) = B_i(t, t_0)$, can be written

$$\partial B_i(t, t_0)/\partial F_j = \int_{t_0}^{t} dt_1 [A_{j1}, B_i(t, t_0)], \tag{34}$$

where

$$A_{j1} \equiv (-i/\hbar) a_j(t_1) A_j(t_1, t_0). \tag{35}$$

It is straightforward to find the second derivative of B_i from Eq. (34). We will present here an alternate method which allows a more compact notation. We define the "super-operator" $\mathcal{A}_{j1}$ by

$$\mathcal{A}_{j1} C = [A_{j1}, C] \tag{36}$$

for any operator C. This super-operator is similar to the Liouville operator as used by Kubo[1] and many others.[15] With the understanding that $\mathcal{A}_{k2}\mathcal{A}_{j1}C$ means $\mathcal{A}_{k2}(\mathcal{A}_{j1}C)$, one can readily verify that

$$[\mathcal{A}_{k2}, \mathcal{A}_{j1}]C = [[A_{k2}, A_{j1}], C]. \tag{37}$$

With the definition of the derivative of $\mathcal{A}_{j1}$,

$$(\partial \mathcal{A}_{j1}/\partial F_k) C \equiv [\partial A_{j1}/\partial F_k, C],$$

one can write, with the use of Eqs. (34), (36), and (37),

$$\partial \mathcal{A}_{j1}/\partial F_k = \int_{t_0}^{t_1} dt_2 [\mathcal{A}_{k2}, \mathcal{A}_{j1}]. \tag{38}$$

With Eqs. (34) and (38), the second derivative of $B_i(t, t_0)$ can be written immediately:

$$\begin{aligned} [\partial^2 B_i(t, t_0)/\partial F_k \partial F_j] &= \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 [\mathcal{A}_{k2}, \mathcal{A}_{j1}] B_i(t, t_0) + \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \mathcal{A}_{j1}\mathcal{A}_{k2} B_i(t, t_0) \\ &= \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 (\mathcal{A}_{k2}\mathcal{A}_{j1} + \mathcal{A}_{j2}\mathcal{A}_{k1}) B_i(t, t_0). \end{aligned} \tag{39}$$

The total operator acting upon $B_i(t, t_0)$ is symmetric in k and j, as it must be, and has the earlier time (t_2) always standing to the left of the later time (t_1). The third derivative is obtained similarly with the aid of Eq. (38); the total operator acting upon $B_i(t, t_0)$ is then the sum of six triple products of $\mathcal{A}$'s, representing the six possible permutations of the three derivative indices, again with the earlier times standing to the left of the later times. This clearly indicates the form of the rth derivative. Proof by induction is straightforward.

The rth-order generalized response coefficient is therefore

$$\sigma_{ij_1 \ldots j_r}(F_1, \cdots, F_n; t) = \sum(p) \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{r-1}} dt_r \langle \mathcal{A}_{j_r r} \cdots \mathcal{A}_{j_1 1} B_i(t, t_0) \rangle_{eq}, \tag{40}$$

where the summation $\sum(p)$ is over all permutations of the indices $j_1 \cdots j_r$. By factoring $a_{j_k}(t_k)$ from $\mathcal{A}_{j_k k}$, noting the definition of $\mathcal{A}_{j_k k}$ by Eqs. (35) and (36), we can define an rth-order generalized response function by

$$\phi_{ij_1 \ldots j_r}(F_1, \cdots, F_n; t) = (-i/\hbar)^r \langle [A_{jr}(t_r, t_0), \cdots, [A_{j1}(t_1, t_0), B_i(t, t_0)], \cdots] \rangle_{eq}. \tag{41}$$

It is related to $\sigma_{ij}(F_1, \cdots, F_n; t)$ by

$$\sigma_{ij}(F_1, \cdots, F_n; t) = \sum(p) \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{r-1}} dt_r a_{j_1}(t_1) \cdots a_{j_r}(t_r) \phi_{ij_1 \ldots j_r}(F_1, \cdots, F_n; t). \tag{42}$$

By evaluating Eqs. (40) and (41) at zero forces, one recovers the usual rth-order response coefficients and functions.

4. GENERALIZED RESPONSE COEFFICIENTS FOR STATIC FORCES

We now consider the expressions for the first-order generalized response coefficients $\sigma_{ij}(F_1, \cdots, F_n; t)$ for forces applied as step functions or applied adiabatically, but which otherwise are constant. The higher-order coefficients can be discussed in a similar manner.

For purposes of exposition, we assume first that the forces are turned on stepwise at t_0. The turning-on functions $a_j(t)$ are then unity for $t > t_0$, and the time-development operator $U(t, t_0)$ becomes, from Eq. (13),

$$U(t, t_0) = \exp[-i\mathcal{H}(t - t_0)/\hbar],$$

where $\mathcal{H}$ is the total Hamiltonian, including the forces;

[15] Liouville operators are discussed and used extensively by U. Fano, Rev. Mod. Phys. **29**, 74 (1957); and R. W. Zwanzig, in *Lectures in Theoretical Physics*, W. E. Brittin, B. W. Downs, and J. Downs, Eds. (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106.

that is,

$$\mathcal{H}=\mathcal{H}_0-\sum_j A_jF_j. \tag{43}$$

Using the form (31), one can write the first-order generalized response coefficient as

$$\sigma_{ij}(F_1,\cdots,F_n;t)=-(i/\hbar)\int_0^{t-t_0}d\tau\,\mathrm{Tr}\,\{\rho(t)[A_j(-\tau),B_i]\}, \tag{44}$$

where

$$\rho(t)=\exp[-i\mathcal{H}(t-t_0)/\hbar]\rho(t_0)\exp[i\mathcal{H}(t-t_0)/\hbar], \tag{45}$$

and

$$A_j(-\tau)=\exp(-i\mathcal{H}\tau/\hbar)A_j\exp(i\mathcal{H}\tau/\hbar). \tag{46}$$

Since $\mathcal{H}$ does not generally commute with $\rho(t_0)$, which is a function of $\mathcal{H}_0$, the time dependence of A_j in Eq. (44) cannot be transferred to B_i, giving $B_i(+\tau)$, as it can be in the linear (that is, zero-force) formula. However, if the system is such that $\rho(t)$ becomes stationary for sufficiently large $t-t_0$, and hence commutes with $\mathcal{H}$ according to Eq. (10), then Eq. (44) becomes identical to the response coefficient formula of Kubo.[1] Examples for which this is true are magnetic systems in the presence of a static magnetic field, and electrically polarizable systems in the presence of a static electric field.

For electric current induced by a static electric field, however, the situation is usually quite different. The current in an isolated block of conducting material will soon come to a stop due to the collection of charges on the surfaces. Kohn and Luttinger[16] have shown, however, that the use of periodic boundary conditions on the charge-carrier wave functions in an isolated cube allows a steady current. They show that this device is equivalent to assuming that the system is in the shape of a torus. They also point out that there need be no physical contact between the source of the electric field and the system. That is, if a magnetic field whose strength is changed adiabatically is applied along the axis of a toroidal conductor, a tangential electric field will be set up in the torus, which will induce a steady current. Bernard and Callen have also discussed this.[3] It is thus possible to apply consistently the formalism developed here and in the earlier theories[1,3,16] to steady currents in isolated systems.

However, these techniques still do not shed much light upon the question of how to construct a nonequilibrium steady-state density matrix for conservative forces. Kohn and Luttinger[16] did derive implicit expressions for steady-state density-matrix elements to first order in the (adiabatically turned on) electric field. These results could be used in principle in Eq. (31), although certainly not very directly, and then only for small fields. Further, for large fields, there will be Joule heating, and if the system is not in contact with a heat bath, its temperature will rise and one would not expect a steady state. On the other hand, $\mathcal{H}_0$ can certainly include interaction with a heat bath, allowing for physical situations in which the temperature of the system can be kept constant in spite of Joule heating. McLennan[17,18] considers the case in which the interaction, which allows for current flow between the system and the apparatus which sets up the field, is not conservative (that is, non-Hamiltonian). Purely Hamiltonian dynamics *may* not, therefore, allow a nonequilibrium steady state, except for those devices mentioned above in which particle exchange between source and system is not required. (Even then, a heat bath must be provided to dissipate the Joule heat.) To sum up: There is no conventionally recognized form for a nonequilibrium steady-state ensemble for systems exposed to conservative forces.

In these nonequilibrium cases resulting from step-function applied forces, one would therefore ordinarily write in place of Eq. (44) a form (identically equivalent) derived from Eq. (27):

$$\sigma_{ij}(F_1,\cdots,F_n;t)=-(i/\hbar)\int_0^{t-t_0}d\tau\,\langle[A_j(t),B_i(t-t_0)]\rangle_{eq}, \tag{47}$$

where the notation of Eq. (46) is used, and $\langle\ \rangle_{eq}$ refers to the ensemble average with respect to $\rho(t_0)=f(\mathcal{H}_0)$. If a future development of nonequilibrium steady-state statistical mechanics shows how to write a steady-state density matrix, then one would of course use the form (44). The latter would undoubtedly be the simpler to evaluate. Still, a careful evaluation of either form is no trivial matter, as is evident from some of the efforts to evaluate the (zero-force) first-order conductivity expressions.[7,19,20] The complications arise from the existence of interparticle interactions in $\mathcal{H}_0$. The inclusion of the interactions with external forces would not be expected to increase the difficulty of evaluation substantially, since these are single-particle interactions.

As an example in electrical conductivity, consider the formal expression for the "generalized conductivity" $\sigma_{xx}(E;t)$, corresponding to electric current in the x direction resulting from a field $\mathbf{E}$ applied stepwise at t_0 in the x direction. Then

$$A_x=ex,\qquad A_y=A_z=0;\qquad F_x=E,\qquad F_y=F_z=0;\qquad B_x=J_x. \tag{48}$$

[16] W. Kohn and J. M. Luttinger, Phys. Rev. **108,** 590 (1957).

[17] J. A. McLennan, Jr., Phys. Rev. **115,** 1405 (1959); *Advances in Chemical Physics,* edited by I. Prigogine (Interscience Publishers, Inc., New York, 1963), Vol. V, p. 261. In these articles, steady-state Gibbsian ensembles are derived for systems acted upon by nonconservative forces, such as temperature and concentration gradients.

[18] J. A. McLennan, Jr. (private communication).

[19] J. S. Langer, Phys. Rev. **120,** 714 (1960); **124,** 1003 (1961); **127,** 5 (1962); **128,** 110 (1962).

[20] J. A. McLennan, Jr., and R. J. Swenson, J. Math. Phys. **4,** 1527 (1963).

If $\rho(t_0)$ is assumed to be canonical, we can use the first part of the identity (33) to obtain from Eq. (47)

$$\sigma_{xx}(E;t)=(ie/\hbar)\int_0^{t-t_0}d\tau\int_0^\beta d\beta'$$
$$\times\langle(d/d\beta')\exp(\beta'\mathcal{H}_0)x(\tau)\exp(-\beta'\mathcal{H}_0)J_x(t-t_0)\rangle_{eq}. \tag{49}$$

Now

$$J_x(t)=e\,dx(t)/dt.$$

The "zeroth approximation" to the current operator for argument $-i\hbar\beta'$ is

$$J_x^{(0)}(-i\hbar\beta')=e[dx^{(0)}(-i\hbar\beta')/d(-i\hbar\beta')]$$
$$=(ie/\hbar)(d/d\beta')\exp(\beta'\mathcal{H}_0)x\exp(-\beta'\mathcal{H}_0). \tag{50}$$

At zero electric field, the τ dependence of x in Eq. (49) can be transferred onto the $J_x^{(0)}(t-t_0)$ by cyclically permuting time-development operators within the trace. Equation (50) can then be used, giving an autocorrelation function of the zero-order current operators. When $E\neq0$, the simple correlation picture is destroyed. Equation (49) can still be manipulated into several equivalent forms, none of which has the formal simplicity of the zero-force expression. One could define an extended current operator by

$$J_x(-i\hbar\beta'\mid\tau)$$
$$\equiv(ie/\hbar)(d/d\beta')\exp(\beta'\mathcal{H}_0)x(\tau)\exp(-\beta'\mathcal{H}_0), \tag{51}$$

and write Eq. (49) as

$$\sigma_{xx}(E,t)=\int_0^{t-t_0}d\tau\int_0^\beta d\beta'\langle J_x(-i\hbar\beta'\mid\tau)J_x(t-t_0)\rangle_{eq}. \tag{52}$$

However, the form of Eq. (47) with the substitution of Eq. (48) is probably the most convenient to use when $E\neq0$. Finally, we note the appearance of $t-t_0$ in the expressions such as (47), (49), and (52). This is expected since these expressions are exact. However, for "large" systems and values of $t-t_0$ larger than the relaxation times which characterize the system, it is an experimental fact that the current becomes steady when the Joule heat can be dissipated. A calculation based upon the above equations should reflect this if $\mathcal{H}_0$ allows for contact with a heat bath. However, one cannot simply set $t-t_0$ equal to infinity in the *integrands* of these equations, because the time-development operators are then undefined.

Instead of assuming the forces to be turned on stepwise at t_0, one may take them as turned on adiabatically at $t_0=-\infty$; that is, $a_j(t)=\exp(st)$ with $s\to0+$. The comments made above regarding the possible forms the density matrix might take apply here as well. But instead of using expressions such as (44)–(46), one would have to go back to Eqs. (27) or (31), that is, the expressions involving the time-ordered operators. This is not necessarily a complication, however, since for many physical systems, some kind of expansion technique would have to be used in either case, for the calculation of physical properties. There is a definite calculational advantage, in fact, in having the factor $\exp(st)$ present in the evaluation of the first-order ordinary conductivities[19–21] [see Eq. (29)]. Available reduction techniques are those of Izuyama,[7] Goldstone,[22] and Hubbard,[23] involving diagram expansion and resummation, starting with Eq. (15) with $t_0=-\infty$. Equation (15), of course might also be used for step fields, with similar techniques.[24]

5. GENERALIZED RESPONSE COEFFICIENTS AT EQUILIBRIUM: ISOTHERMAL SUSCEPTIBILITIES

In the preceding sections, the formal theory of the response to time-dependent forces has been developed. In this section we consider forces of such a nature that the system is in equilibrium at the time of the measurement, and described by the canonical distribution of Eq. (32). This implies that the forces are static and that the system has been placed in contact with a heat bath at some time in its history. The restriction to static forces can be weakened however, to permit slowly varying forces if contact with a heat bath is sufficiently good. The treatment here is an extension, to arbitrary systems and derivatives of arbitrarily high order, of a technique used by Wilcox[12] in a discussion of static dielectric susceptibility.

The equilibrium response to the forces F_j is just

$$\langle B_i\rangle=\mathrm{Tr}[B_i\exp(-\beta\mathcal{H})/\mathrm{Tr}[\exp(-\beta\mathcal{H})], \tag{53}$$

where $\mathcal{H}$ includes the forces and is defined in Eq. (43). The quantities of physical interest here are

$$\chi_{ij}(F_1,\cdots,F_n)\equiv\partial\langle B_i\rangle/\partial F_j, \tag{54}$$

and higher derivatives. For example, if B_i is a magnetic moment per unit volume, and F_j is an applied magnetic field, then χ_{ij} is the isothermal magnetic susceptibility.[25] To carry out the differentiation in Eq. (54), one needs to have an expression for $\partial[\exp(-\beta\mathcal{H})]/\partial F_j$. This is readily obtained from Eq. (23) by substituting $\exp(-\beta\mathcal{H})$ for $U(t,t_0)$ and $-i\hbar\beta$ for t, setting the lower limit on the integral equal to zero to give the proper "initial condition" $\exp(-\beta\mathcal{H})\mid_{\beta=0}=1$. This

[21] M. Lax, Phys. Rev. **109**, 1921 (1958).
[22] J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957).
[23] J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957).
[24] For adiabatically turned-on forces, one must not, of course, take the limit $s\to0+$ until after the formal operations, as in Eq. (27), have been performed. Taking this limit earlier is equivalent to using a step-function for the forces.
[25] H. B. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960), Chap. 14. In Callen's language, χ_{ij} as we have defined it is called the "susceptance," the term "susceptibility" being reserved for the derivative relative to the local field. However, there seems to be no universal agreement on such usage.

procedure is justified because the equation of motion (12) for $U(t, t_0)$ is identical to that for $\exp(-\beta\mathcal{H})$, with the substitution for $t=-i\hbar\beta$. Using Eq. (43) also, one finds

$$\partial[\exp(-\beta\mathcal{H})]/\partial F_j = \exp(-\beta\mathcal{H})\int_0^\beta d\beta' A_j(-i\hbar\beta'), \tag{55}$$

where the notation of Eq. (46) is used.

Combining Eqs. (53)–(55), one obtains

$$\chi_{ij}(F_1, \cdots, F_n) = \int_0^\beta d\beta' \{\langle A_j(-i\hbar\beta')B_i\rangle - \langle A_j\rangle\langle B_i\rangle\}$$
$$= \int_0^\beta d\beta' \langle \Delta A_j(-i\hbar\beta')\Delta B_i\rangle, \tag{56}$$

where

$$\Delta A_j(-i\hbar\beta) = A_j(-i\hbar\beta) - \langle A_j\rangle. \tag{57}$$

Equation (56) is identical in appearance to the zero-force isothermal susceptibility.[26] The latter is obtained by evaluating Eq. (56) at zero forces.

The usual physical application of Eq. (56) would be to those systems for which both A_i and B_i are dipole moment operators M_i, electric or magnetic. In this case the isothermal susceptibility tensor is symmetric. Per unit volume, it is

$$\chi_{ij}(F_1, \cdots, F_n) = V^{-1}\int_0^\beta d\beta' \langle \Delta M_j(-i\hbar\beta')\Delta M_i\rangle$$
$$= V^{-1}\int_0^\beta d\beta' \langle \Delta M_i(-i\hbar\beta')\Delta M_j\rangle$$
$$= \chi_{ji}(F_1, \cdots, F_n). \tag{58}$$

The second equation follows by rearranging terms within the trace, and changing β' to $\beta-\beta'$.

The second derivative, $\chi_{ijk}(F_1, \cdots, F_n)$, is similarly obtained. The following are useful intermediate results:

$$\partial A_{j1}/\partial F_k = \int_0^{\beta_1} d\beta_2 [A_{j1}, A_{k2}], \tag{59}$$

$$\langle \partial(\Delta A_{j1}\Delta B_i)/\partial F_k\rangle = \int_0^{\beta_1} d\beta_2 \langle [\Delta A_{j1}, \Delta A_{k2}]\Delta B_i\rangle, \tag{60}$$

where the abbreviation

$$A_{j1} \equiv A_j(-i\hbar\beta_1) \tag{61}$$

is used. Equation (59) is the analog of Eq. (26), and Eq. (60) follows straightforwardly. Combining Eqs. (56) and (60), one obtains

$$\chi_{ijk}(F_1, \cdots, F_n) = \int_0^\beta d\beta_1 \int_0^{\beta_1} d\beta_2$$
$$\times \langle \Delta A_{k1}\Delta A_{j2}\Delta B_i + \Delta A_{j1}\Delta A_{k2}\Delta B_i\rangle. \tag{62}$$

[26] See the second paper of Ref. 1, p. 146.

A greater similarity to Eq. (40) is obtained by letting $\beta=\beta_0$, rearranging terms within the trace in Eq. (62), and introducing ΔB_{i0} in the notation of Eq. (61). One can then write

$$\chi_{ijk}(F_1, \cdots, F_n) = \int_0^{\beta_0} d\beta_1 \int_0^{\beta_1} d\beta_2$$
$$\times \langle \Delta B_{i0}\Delta A_{k1}\Delta A_{j2} + \Delta B_{i0}\Delta A_{j1}\Delta A_{k2}\rangle, \tag{63}$$

in which all operators corresponding to larger values of β stand to the left of those for smaller values of β.

The third and higher derivatives are similarly obtained. The rth derivative, $\chi_{ij1\ldots j_r}(F_1, \cdots, F_n)$, consists of a sum of $r!$ terms, representing the $r!$ ways of arranging $\Delta A_{j1}(-i\hbar\beta_1)\cdots\Delta A_{jr}(-i\hbar\beta_r)$ with the larger values of β_i always appearing to the left of the smaller values. When $A_i=B_i$, the $\chi_{ij1\ldots j_r}(F_1, \cdots, F_n)$ are symmetric with respect to interchange of any pair of indices, as in Eq. (58).

6. DISCUSSION

Our purpose in this article has been to present a formal theory of nonlinear response which avoids all expansions in powers of the driving forces. Our motivation has been to but the "Kubo formalism" on a more rigorous and compact basis by bypassing these expansions. We have also wanted to develop formulas—the generalized response coefficients—that have more physical relevance in the nonlinear region than do the usual response coefficients and response functions. The generalized response coefficients are the derivatives of the response relative to the amplitudes of the applied forces. They are analogous to the quantities of interest in equilibrium thermodynamics. We have shown how to write formal expressions for these derivatives in both the equilibrium and nonequilibrium cases.

The nth-order derivatives evaluated at certain values of the forces are just the nth-order coefficients in a Taylor's series expansion of the response about those values of the forces. The generalized response coefficients may therefore be thought of as the usual response coefficients generalized to arbitrary values of the force amplitudes.

The development makes use of some properties of, and manipulations upon, time-ordered time-development operators. These operators are still not very familiar to many working in statistical mechanics and related subjects, and may appear to give a formidable aspect to the evaluation of the generalized response coefficients. It is true that, for example, one cannot generally take matrix elements directly of these time-ordered operators. However there are often cases in which the time-ordered operators can be reexpressed in closed form. For constant forces $U(t, t_0)$ is just

$\exp[-i\mathcal{H}(t-t_0)/\hbar]$. Louisell[27] shows how to write $U(t, t_0)$ in closed form for a linear harmonic oscillator driven in an arbitrary fashion. A particle with angular momentum in the presence of a static magnetic field and a perpendicular rotating magnetic field is another example; the method for writing $U(t,t_0)$ in closed form has been discussed by Slichter.[28] This method can be extended trivially to include an arbitrary number of spin particles connected by isotropic exchange interaction. But whether the forces are static or variable, in most cases of physical interest the *evaluation* of the generalized response coefficients will require some form of perturbation expansion and resummation technique, similarly to that for the zero-force response coefficients.

ACKNOWLEDGMENTS

I wish to thank Dr. R. M. Wilcox for several useful discussions. His work on the theory of static dielectric susceptibility provided the impetus for the work presented here. I also wish to thank Professor J. A. McLennan, Jr., for helpful correspondence.

APPENDIX

We here derive a formal expression for the response, following the method of Tani.[11] and examine it for the case of static forces, and for the electric current resulting from a step-function applied electric field.

As before, the forces are assumed to be turned on at t_0, thereafter having arbitrary time dependence. The density matrix is now separated as

$$\rho(t)=\rho(t_0)+\rho'(t). \tag{A1}$$

Assuming that $\rho(t_0)=f(\mathcal{H}_0)$, one obtains the equation of motion for $\rho'(t)$ from Eqs. (8) and (10):

$$i\hbar d\rho'(t)/dt=[\mathcal{H}_t, \rho'(t)]-[\sum_j A_jF_j(t), \rho(t_0)]. \tag{A2}$$

This has the formal solution

$$\rho'(t)=(i/\hbar)\int_{t_0}^{t} dt' U(t, t') \times[\sum_j A_jF_j(t'), \rho(t_0)]U^\dagger(t, t'), \tag{A3}$$

where $U(t, t')$ is defined by Eq. (13). The response $\langle B_i\rangle_t$ is then

$$\langle B_i\rangle_t=\langle B_i\rangle_{eq}-(i/\hbar)\sum_j\int_{t_0}^{t} dt' \times\langle[A_j, B_i(t, t')]\rangle_{eq}F_j(t'). \tag{A4}$$

This is equivalent to Tani's formal expression for the response. Its advantage over the expression (20) is that the "equilibrium response," which is often zero, or if not zero, not of direct interest, is separated out. For developing the generalized response coefficients, however, it is much more convenient to begin with Eq. (20).

For static forces turned on suddenly at t_0, Eq. (A4) becomes

$$\langle B_i\rangle_t=\langle B_i\rangle_{eq}-(i/\hbar)\sum_j F_j\int_0^{t-t_0} d\tau\,\langle[A_j, B_i(\tau)]\rangle_{eq}, \tag{A5}$$

where $B_i(\tau)$ is defined by Eq. (46).

As an illustration of Eq. (A5), we consider the same example that was considered in Sec. 4, namely the current $\langle J_x\rangle_t$ due to an applied field $\mathbf{E}$ in the x-direction. Using Eq. (48), one has

$$\langle J_x\rangle_t=-(i/\hbar)E\int_0^{t-t_0} d\tau\,\langle[ex, J_x(\tau)]\rangle_{eq}, \tag{A6}$$

since $\langle J_x\rangle_{eq}=0$. Using Eqs. (32), (33), and (50), one obtains

$$\langle J_x\rangle_t=E\int_0^{t-t_0} d\tau\int_0^{\beta} d\beta'\,\langle J_x^{(0)}(-i\hbar\beta')\,J_x(\tau)\,\rangle_{eq}. \tag{A7}$$

Equation (A7), which is exact, may be compared to Eqs. (51) and (52), and to the slightly different formula used by Miyake and Kubo,[29] in their attempt to account for the "kink effect" found by Esaki.[10] As $t-t_0\to\infty$, and provided the time integral converges, as one expects for sufficiently large systems, the coefficient of E in Eq. (A7) becomes the "field-dependent conductivity" as discussed in the Introduction. It is not a generalized response coefficient as defined in the preceding sections.

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[27] W. H. Louisell, *Radiation and Noise in Quantum Electronics* (McGraw-Hill Book Co., Inc., New York, 1964), pp. 119–124.

[28] C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, Inc., New York, 1963), pp. 26, 27.

[29] S. J. Miyake and R. Kubo, Phys. Rev. Letters **9**, 62 (1962). Although the adiabatic nature of the applied field E is not explicitly indicated in this paper, it was used in the calculation (private communication from S. J. Miyake).