PHYSICAL REVIEW VOLUME 155, NUMBER 2 10 MARCH 1967

Green's-Function Theory of Nonlinear Transport Coefficients*

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(Received 25 August 1966)

The nonlinear transport coefficients are expressed in terms of many-time Green's functions. Except for the inhomogeneous term, the equation of motion for the many-time Green's functions is shown to be the same as that for the two-time Green's function. Some simple applications of the method are discussed.

I. INTRODUCTION

IN a celebrated paper, Kubo[1] derived the theory of linear transport coefficients for quantum-statistical systems and gave exact expressions for these coefficients in a closed form. Since then many attempts[2] have been made to actually calculate the transport coefficients starting from the so-called Kubo formula.

Since in the Kubo formulation the frequency-dependent linear transport coefficients are expressed in terms of Fourier transforms of appropriate correlation functions, the obvious connection with temperature-dependent two-time Green's functions has been noticed and extensively discussed in the literature.[3] The Green's-function method has the well-known advantage that it always deals with the directly measurable quantities and therefore avoids the need for first calculating the wave functions of the perturbed system.

Recently, with the advent of high-power microwave sources, high magnetic fields, and lasers, various nonlinear phenomena have been observed. Many microwave devices (e.g., power limiter, frequency doubler, and ferromagnetic amplifier) which utilize nonlinear effects have been developed[4] and a host of interesting nonlinear effects (e.g., harmonic generation, mixing, intensity-dependent index of refraction, quadratic polarization, parametric amplification, etc.) with exciting possibilities have been seen with the lasers.[5]

As is discussed in Kubo's original paper,[1] the formulation of the transport theory is not at all limited to the linear phenomena. The solution of the Liouville equation for the density matrix is given to an arbitrary order in the strength of disturbance, and hence the nonlinear transport coefficients can in principle be calculated by the Kubo formulation.

The main purpose of this paper is to show that it is indeed possible to find an explicit formula for the higher-order transport coefficients. In analogy with the connection between linear transport coefficients and the two-time Green's function referred to above, in Sec. II we show that the nonlinear transport coefficients can be expressed in terms of $(n+1)$-time $(n>1)$ Green's functions.[6] Except for the inhomogeneous term, the equation of motion for the $(n+1)$-time Green's function is found to be the same as for the two-time Green's function. In Sec. III we show some simple applications of the method in order to discuss the nonlinear susceptibilities of a Heisenberg ferromagnet and nonlinear polarizability of an anharmonic oscillator and a free-electron gas.

II. THEORY

A. Solution of the Liouville Equation

In order to make our discussion self-contained, the solution of the Liouville equation, correct up to arbitrary order in perturbation strength, is sketched below.

The equation of motion for the density matrix $\rho(t)$ of a system described by the Hamiltonian $\mathcal{H}$ and under the influence of an external disturbance $\mathcal{H}_1$ is

$$i\partial\rho/\partial t=[\mathcal{H}+\mathcal{H}_1,\rho],\quad \hbar=1. \tag{1}$$

The disturbance $\mathcal{H}_1$ is assumed to be harmonic and turned on adiabatically as

$$\mathcal{H}_1=-Ae^{-i(\omega+i\epsilon)t}, \tag{2}$$

where A is a dynamical variable of the system. The general case in which the external disturbance consists of a spectrum of frequencies instead of a single frequency is treated in the Appendix.

Correspondingly, the density matrix is also divided into two parts as

$$\rho(t)=\rho_0+\rho_1(t), \tag{3}$$

where ρ_0 is the equilibrium canonical distribution for the system with Hamiltonian $\mathcal{H}$,

$$\rho_0=e^{-\beta\mathcal{H}}/\mathrm{Trace}\,e^{-\beta\mathcal{H}},\quad [\rho_0,\mathcal{H}]=0, \tag{4}$$

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* Work supported by National Aeronautics and Space Administration Research Grant No. NsG 649.

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[1] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[2] H. Nakano, Progr. Theoret. Phys. (Kyoto) **15**, 77 (1956); **17**, 145 (1957); S. F. Edwards, Phil. Mag. **3**, 350 (1962); S. Fujita, *ibid.* **3**, 359 (1962); **3**, 1246 (1962); B. Springer, Phys. Rev. **136**, A115 (1964).

[3] N. N. Bogolyubov and S. V. Tyablikov, Dokl. Akad. Nauk SSSR **1**, 53 (1959) [English transl.: Soviet Phys.—Doklady **4**, 589 (1959)]; D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)]; V. L. Bonch-Bruevich and S. V. Tyablikov, *The Green Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).

[4] K. J. Button and T. S. Hartwick, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. I.

[5] N. Bloembergen, *Non-Linear Optics* (W. A. Benjamin, Inc., New York, 1965).

[6] An earlier attempt to relate nonlinear response functions to lower-order driven correlation moments was included in a paper by W. Bernard and H. B. Callen, Rev. Mod. Phys. **31**, 1017 (1959).

and $\rho_1(t)$ is the deviation from the equilibrium distribution. Substituting Eq. (3) into Eq. (1), one obtains

$$\partial\rho_1/\partial t = -i\{\mathcal{H}^{\times}\rho_1 + \mathcal{H}_1^{\times}\rho_0 + \mathcal{H}_1^{\times}\rho_1\}. \tag{5}$$

The crossed operators are introduced as

$$a^{\times}b = [a,b]. \tag{6}$$

Equation (5) can be formally solved by the usual iteration procedure to yield the expression given by Kubo[1]

$$\rho_1(t) = \sum_{n=1}^{\infty} (i)^n \int_{-\infty}^{t} ds_1 \int_{-\infty}^{s_1} ds_2 \cdots \int_{-\infty}^{s_{n-1}} ds_n e^{-it\mathcal{H}^{\times}} A^{\times}(s_1) A^{\times}(s_2) \cdots A^{\times}(s_n) \rho_0 e^{-i(\omega+i\epsilon)(s_1+s_2+\cdots+s_n)}, \tag{7}$$

where

$$A(s_1) = e^{i\mathcal{H}s_1} A e^{-i\mathcal{H}s_1}, \quad \text{etc.} \tag{8}$$

Introducing the transformation of variables $\tau_n = s_{n-1} - s_n$ and using the identity $e^{a^{\times}}b = e^a b e^{-a}$, one can rewrite Eq. (7) as

$$\rho_1(t) = \sum_{n=1}^{\infty} i^n e^{-in(\omega+i\epsilon)t} \int_0^{\infty} d\tau_1 \cdots \int_0^{\infty} d\tau_n A^{\times}(-\tau_1) A^{\times}(-\tau_1-\tau_2) \cdots A^{\times}(-\tau_1 \cdots -\tau_n)\rho_0 \times \exp i(\omega+i\epsilon)[n\tau_1 + (n-1)\tau_2 + \cdots + 2\tau_{n-1} + \tau_n]. \tag{9}$$

The thermodynamic average of a dynamical variable B can now be calculated by

$$\begin{aligned} \bar{B} &= \operatorname{Trace} B(\rho_0+\rho_1) \\ &= \langle B\rangle + \sum_{n=1}^{\infty} i^n e^{-in(\omega+i\epsilon)t} \int_0^{\infty} d\tau_1 \cdots \int_0^{\infty} d\tau_n e^{i(\omega+i\epsilon)(n\tau_1+\cdots+\tau_n)} \\ &\qquad \times \langle [[\cdots[[B,A(-\tau_1)],A(-\tau_2)],\cdots],A(-\tau_1\cdots-\tau_n)]\rangle, \end{aligned} \tag{10}$$

where

$$\langle\cdots\rangle = \operatorname{Trace}(\cdots\rho_0).$$

B. The $(n+1)$-Time Green's Function

In analogy with the two-time Green's function the $(n+1)$-time Green's function and its Fourier transform are defined as

$$G_{n+1}(B; A(-\tau_1);\cdots; A(-\tau_1\cdots-\tau_n)) \equiv (-i)^n \theta(\tau_1)\cdots\theta(\tau_n) \langle [[\cdots[B,A(-\tau_1)],\cdots],A(-\tau_1\cdots\tau_n)]\rangle, \tag{11}$$

$$G_{n+1}(B; A)_{\omega+i\epsilon} \equiv \frac{1}{(2\pi)^n} \int_{-\infty}^{\infty} d\tau_1 \cdots \int_{-\infty}^{\infty} d\tau_n G_{n+1}(B; A(-\tau_1);\cdots; A(-\tau_1\cdots-\tau_n)) \times \exp i(\omega+i\epsilon)[n\tau_1+(n-1)\tau_2+\cdots\tau_n], \tag{12}$$

where $\theta(\tau)$ is the step function.

Equation (10) for the thermodynamic average B can now be written as

$$\bar{B} = \langle B\rangle + \sum_{n=1}^{\infty} (-2\pi)^n e^{-in(\omega+i\epsilon)t} G_{n+1}(B; A)_{\omega+i\epsilon}. \tag{13}$$

Thus the higher harmonic components of a dynamical quantity B can be calculated if one knows the $(n+1)$-time Green's function for $n>1$. Its equation of motion can be set up by using the definition (12) and the following identity:

$$n(\omega+i\epsilon)G_{n+1}(B; A)_{\omega+i\epsilon} = \frac{1}{(2\pi)^n} \int_{-\infty}^{\infty} d\tau_1 \cdots \int_{-\infty}^{\infty} d\tau_n G_{n+1}(B; A(-\tau_1);\cdots; A(-\tau_1\cdots-\tau_n)) \times \frac{1}{i}\frac{\partial}{\partial\tau_1} \exp i(\omega+i\epsilon)(n\tau_1+\cdots+\tau_n). \tag{14}$$

Recognizing the time dependence of the Green's function and the fact that the Green's function is invariant under uniform translations of the time variable, one can transform the right-hand side of Eq. (14) by integrating by parts to obtain

$$n(\omega+i\epsilon)G_{n+1}(B; A)_{\omega+i\epsilon} = (1/2\pi)G_n([B,A]; A)_{\omega+i\epsilon} + G_{n+1}([B,\mathcal{H}]; A)_{\omega+i\epsilon}, \tag{15}$$

where

$$G_1([B,A]; A) = \langle [B,A]\rangle. \tag{16}$$

This is the equation of motion for the $(n+1)$-time Green's function. One immediately notices the similarity between Eq. (15) and the usual equation of motion for the two-time Green's function which can be obtained from

Eq. (15) by setting $n=1$.

$$(\omega+i\epsilon)\langle\langle B;A\rangle\rangle_{\omega+i\epsilon}=\frac{1}{2\pi}\langle[B,A]\rangle+\langle\langle[B,\mathcal{H}];A\rangle\rangle_{\omega+i\epsilon}, \tag{17}$$

where

$$\langle\langle B;A\rangle\rangle_{\omega+i\epsilon}=G_2(B;A)_{\omega+i\epsilon}.$$

III. APPLICATIONS

In this section we shall apply the formulation of Sec. II to discuss nonlinear properties of some simple systems.

A. Nonlinear Susceptibilities of an Ideal Heisenberg Ferromagnet

To calculate the nonlinear susceptibility for an ideal Heisenberg ferromagnet, the system Hamiltonian is assumed to be given by

$$\mathcal{H}=-\sum_{f,g}J_{fg}\mathbf{S}_f\cdot\mathbf{S}_g-g\mu_BH_z\sum_f S_f{}^z, \tag{18}$$

where the first term is the usual Heisenberg exchange contribution and the second term is the Zeeman contribution due to the uniform static magnetic field H_z in the z direction. The disturbance

$$\mathcal{H}_1=-g\mu_BH_x\sum_f S_f{}^x e^{-i(\omega+i\epsilon)t} \tag{19}$$

is assumed to be applied in the x direction. Hence in this particular case the operators A and B are

$$A=g\mu_BH_xM_x \quad\text{and}\quad B=M_z,\,M_y,\,M_x, \tag{20}$$

where

$$M_{x,y,z}=\sum_f S_f{}^{x,y,z}. \tag{21}$$

It is important to note that in this system all three Cartesian components of the total magnetization commute with the exchange part of the Hamiltonian and thus the equations of motion for the $(n+1)$-time Green's function become extremely simple. The commutation relations lead to

$$\begin{aligned}
&[M_z,\mathcal{H}]=0, && [M_x,\mathcal{H}]=ig\mu_BH_zM_y,\\
&[M_y,\mathcal{H}]=-ig\mu_BH_zM_x, && [M_z,A]=ig\mu_BH_xM_y,\\
&[M_x,A]=0, && [M_y,A]=-ig\mu_BH_xM_z.
\end{aligned} \tag{22}$$

Introducing Eq. (20) into Eq. (15) and using the above commutation relations, we obtain

$$n(\omega+i\epsilon)G_{n+1}(M_z;A)_{\omega+i\epsilon}=(1/2\pi)G_n([M_z,A];A)_{\omega+i\epsilon}, \tag{23a}$$

$$\begin{aligned}n(\omega+i\epsilon)G_{n+1}(M_y;A)_{\omega+i\epsilon}&=(1/2\pi)G_n([M_y,A];A)_{\omega+i\epsilon}\\&\quad-ig\mu_BH_zG_{n+1}(M_x;A)_{\omega+i\epsilon},\end{aligned} \tag{23b}$$

and

$$n(\omega+i\epsilon)G_{n+1}(M_x;A)_{\omega+i\epsilon}=ig\mu_BH_zG_{n+1}(M_y;A)_{\omega+i\epsilon}. \tag{23c}$$

Solving Eqs. (23) for $G_{n+1}(M_x;A)_{\omega+i\epsilon}$, $G_{n+1}(M_y;A)_{\omega+i\epsilon}$, and $G_{n+1}(M_z;A)_{\omega+i\epsilon}$, we find

$$G_{n+1}(M_x;A)_{\omega+i\epsilon}=\frac{ig\mu_BH_zG_n([M_y,A];A)_{\omega+i\epsilon}}{2\pi[n^2(\omega+i\epsilon)^2-(g\mu_BH_z)^2]}, \tag{24a}$$

$$G_{n+1}(M_y;A)_{\omega+i\epsilon}=\frac{n(\omega+i\epsilon)G_n([M_y,A];A)_{\omega+i\epsilon}}{2\pi[n^2(\omega+i\epsilon)^2-(g\mu_BH_z)^2]}, \tag{24b}$$

$$G_{n+1}(M_z;A)_{\omega+i\epsilon}=\frac{G_n([M_z,A];A)_{\omega+i\epsilon}}{2\pi n(\omega+i\epsilon)}. \tag{24c}$$

Since the nth-order susceptibility tensor is related to the $(n+1)$-time Green's function, one can discuss nonlinear susceptibilities from the above equations. From Eq. (16) we have

$$G_1([M_y,A];A)_{\omega+i\epsilon}=\langle[M_y,A]\rangle=-ig\mu_BH_x\langle M_z\rangle \tag{25}$$

and

$$G_1([M_x,A];A)_{\omega+i\epsilon}=G_1([M_z,A];A)_{\omega+i\epsilon}=0.$$

The linear susceptibilities are obtained by combining Eqs. (24) for $n=1$ with Eq. (25):

$$\begin{aligned}
G_2(M_z;A)_{\omega+i\epsilon}&=0,\\
G_2(M_x;A)_{\omega+i\epsilon}&=\frac{(g\mu_B)^2H_zH_x}{2\pi[(\omega+i\epsilon)^2-(g\mu_BH_z)^2]}\langle M_z\rangle,\\
G_2(M_y;A)_{\omega+i\epsilon}&=\frac{-ig\mu_BH_x(\omega+i\epsilon)}{2\pi[(\omega+i\epsilon)^2-(g\mu_BH_z)^2]}\langle M_z\rangle,
\end{aligned} \tag{26}$$

and the lowest-order nonlinear susceptibilities, obtained by putting $n=2$ in Eqs. (24), are

$$G_3(M_z;A)_{\omega+i\epsilon}=\frac{(g\mu_BH_x)^2}{4\pi[(\omega+i\epsilon)^2-(g\mu_BH_z)^2]}\langle M_z\rangle \tag{27a}$$

and

$$G_3(M_x;A)_{\omega+i\epsilon}=G_3(M_y;A)_{\omega+i\epsilon}=0. \tag{27b}$$

Equation (27a) reflects the known result[7] that the lowest-order nonlinear susceptibility is proportional to the saturation magnetization and square of the strength of the disturbing field.

The above calculation is independent of the sign of the exchange integral; hence the results are equally applicable to the Heisenberg antiferromagnet. However, for an antiferromagnet, $\langle M_z\rangle$ should be replaced by

$$\langle M_z\rangle=\chi_{\parallel}H_z, \tag{28}$$

where $\chi_{\parallel}$ is the static parallel susceptibility.

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[7] R. W. Roberts, W. P. Ayres, and P. H. Vartanian, in *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1960).

It should be pointed out that the treatment presented here is based on an oversimplified model, so that the results obtained are useful only for qualitative interpretation of the phenomenon. In a more realistic treatment, effects such as the demagnetization field, anisotropy energy, spin-lattice interaction, etc., should be incorporated in the theory. However, the tensor character of the susceptibility and the order of magnitude of various harmonic contributions is given correctly.

B. Nonlinear Ionic Polarization

As a second example, we consider the contribution of ionic motion to the nonlinear electric polarization P^{nl}. Such contributions arise from forced vibrations of charged ions in an anharmonic potential. Following Armstrong *et al.*,[8] we simplify the Hamiltonian of the system in the absence of radiation by decoupling the spatial coordinates:

$$\mathcal{H}=\tfrac{1}{2}\sum_{i=x,y,z}\left(\frac{p_i^2}{m_i}+m_i\omega_{0i}^2r_i^2\right)-\tfrac{1}{3}\sum_{i=x,y,z}\lambda_ir_i^3-\tfrac{1}{4}\sum_{i=x,y,z}\eta_ir_i^4, \qquad (29)$$

where the last two terms represent the anharmonic part of the potential in which the ions oscillate. The interaction of the system with radiation is represented by

$$\mathcal{H}_1=-\sum_{i=x,y,z}e_ir_iE_ie^{-i(\omega+i\epsilon)t} \qquad (30)$$

in the electric-dipole approximation. We will discuss the particular case of second-harmonic generation [$\eta=0$ in Eq. (29)] and calculate the contribution of ionic motion to the x component of second-order polarizability due to E_x^2. In this case the operators A and B are both equal to E_x and the Green's function of interest is $G_3(x;x)_\omega$.

From Eq. (15) it immediately follows that ($\epsilon\rightarrow 0$)

$$2\omega G_3(x;x)_\omega=(i/m_x)G_3(p_x;x)_\omega, \qquad (31)$$

$$2\omega G_3(p_x;x)_\omega=-im_x\omega_{0x}^2G_3(x;x)_\omega+i\lambda_xG_3(x^2;x)_\omega, \qquad (32)$$

and[9]

$$G_3(x^2;x)_\omega=\frac{1}{2}\frac{1}{(2\pi m_x)^2(\omega^2-\omega_{0x}^2)^2}. \qquad (33)$$

Combining Eqs. (32) and (33) and substituting the result into Eq. (31), we obtain

$$G_3(x;x)_\omega=\frac{1}{2}\frac{1}{(2\pi)^2}\frac{1}{m_x^3}\lambda_x\frac{1}{(\omega^2-\omega_{0x}^2)^2(\omega_{0x}^2-4\omega^2)}, \qquad (34)$$

and the contribution to P^{nl} due to E_x^2 is

$$\begin{aligned}P_x^{nl}&(2\omega,\text{ ionic})\\&=G_3(e_xx;e_xx)_\omega E_x^2e^{-2i\omega t}\\&=\frac{1}{2(2\pi)^2}\left(\frac{e_x}{m_x}\right)^3\lambda_x\frac{E_x^2e^{-2i\omega t}}{(\omega^2-\omega_{0x}^2)^2(\omega_{0x}^2-4\omega^2)},\end{aligned} \qquad (35)$$

which is the same expression[10] as obtained by Armstrong *et al.*[8] One can similarly discuss third-harmonic generation; the last term containing η in Eq. (29) must now be retained and the appropriate Green's function is $G_4(x;x)_\omega$.

C. Nonlinear Susceptibility of an Electron Gas

Recently, Bloembergen and Shen[11] have given an expression for the lowest-order nonlinear susceptibility of an electron gas under the influence of a transverse electromagnetic wave. The dominant terms in the perturbation Hamiltonian, which includes the self-consistent Coulomb screening potential ϕ_s,[12] are[11]

$$\mathcal{H}_1=(e^2/2mc^2)\mathbf{A}^2+e\phi_s. \qquad (36)$$

Taking $A=\mathbf{A}_0e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$, we can write $\mathcal{H}_1$, in second-quantized formulation, as

$$\mathcal{H}_1=\{e\mathbf{A}_0^2/2mc^2+\phi_S(2\mathbf{q})\}\rho_{-2\mathbf{q}}e^{-2i\omega t}, \qquad (37)$$

where $\rho_\mathbf{q}=e\sum_\mathbf{k}a_\mathbf{k}^\dagger a_{\mathbf{k}+\mathbf{q}}$ is the charge-density fluctuation operator. It can readily be shown that the effect of screening potential on the external perturbation is to modify it by a factor $\epsilon^l(2\mathbf{q},2\omega)$, which is the longitudinal linear dielectric constant. Hence,

$$\mathcal{H}_1=[e\mathbf{A}_0^2/2mc^2\epsilon^l(2\mathbf{q},2\omega)]\rho_{-2\mathbf{q}}e^{-2i\omega t}, \qquad (38)$$

where

$$\epsilon^l(\mathbf{q},\omega)=1-\frac{4\pi e^2}{q^2}\sum_\mathbf{k}\frac{f_0(\epsilon_k)-f_0(\epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon_\mathbf{k}-\epsilon_{\mathbf{k}+\mathbf{q}}+\omega+i\epsilon}.$$

Also, the unperturbed Hamiltonian $\mathcal{H}$ of the system is given by

$$\mathcal{H}=\sum_\mathbf{k}\epsilon_\mathbf{k}a_\mathbf{k}^\dagger a_\mathbf{k}, \qquad (39)$$

and the dynamic variable of interest is the current operator

$$\mathbf{j}_q=\frac{e}{2m}\sum_\mathbf{k}(\mathbf{k}+2\mathbf{q})a_\mathbf{k}^\dagger a_{\mathbf{k}+\mathbf{q}}. \qquad (40)$$

The nonlinear second-harmonic current density is given

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[8] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[9] Since $G_3(x^2;x)_\omega$ appears in Eq. (32) in the term proportional to λ_x, $G_3(x^2;x)_\omega$ is evaluated up to the zeroth-order term with respect to the anharmonic term in $\mathcal{H}$.

[10] See Ref. 8, Eq. (2.25).

[11] N. Bloembergen and Y. R. Shen, Phys. Rev. **141**, 298 (1966).

[12] In the preceding part of the paper the perturbation Hamiltonian $\mathcal{H}_1$ has always represented the interaction of an external disturbance with the system. But in this part we include the screening Coulomb potential in $\mathcal{H}_1$ since its only influence is to modify external perturbation and it gives rise to a self-consistent field in which the free electrons [Eq. (39)] move.

by the expression

$$\langle \mathbf{j}_{2\mathbf{q}}\rangle_{2\omega+i\epsilon}=2\pi\langle\langle \mathbf{j}_{2\mathbf{q}};\rho_{-2\mathbf{q}}\rangle\rangle\frac{e\mathbf{A}_0{}^2}{2mc^2}\frac{1}{\epsilon^l(2\mathbf{q},2\omega)}$$

$$=2\pi\frac{e^2}{m}\frac{e\mathbf{A}_0{}^2}{2mc^2}\frac{1}{\epsilon^l(2\mathbf{q},2\omega)}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}(\mathbf{k}+\mathbf{q})$$

$$\times\langle\langle a_{\mathbf{k}}{}^\dagger a_{\mathbf{k}+2\mathbf{q}};a_{\mathbf{k}'+2\mathbf{q}}{}^\dagger a_{\mathbf{k}'}\rangle\rangle_{2\omega+i\epsilon}. \quad (41)$$

We notice that in the particular case of the free electron gas, the calculation of the nonlinear coefficient involves the two-time Green's function only. This is because one is essentially calculating the linear response to the nonlinear perturbation $\mathbf{A}^2$, which arises from the dominance of the nonlinear contribution from $\mathbf{A}^2$ over that from the linear term $-(e/2mc)(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p})$. The equation of motion for $\langle\langle a_{\mathbf{k}}{}^\dagger a_{\mathbf{k}+2\mathbf{q}};a_{\mathbf{k}'+2\mathbf{q}}{}^\dagger a_{\mathbf{k}'}\rangle\rangle_{2\omega+i\epsilon}$ is easily solved to yield

$$\langle\langle a_{\mathbf{k}}{}^\dagger a_{\mathbf{k}+2\mathbf{q}};a_{\mathbf{k}'+2\mathbf{q}}{}^\dagger a_{\mathbf{k}'}\rangle\rangle_{2\omega+i\epsilon}$$

$$=\frac{\delta_{\mathbf{k}\mathbf{k}'}}{2\pi}\frac{\langle a_{\mathbf{k}}{}^\dagger a_{\mathbf{k}'}\rangle-\langle a_{\mathbf{k}+2\mathbf{q}}{}^\dagger a_{\mathbf{k}'+2\mathbf{q}}\rangle}{\epsilon_k-\epsilon_{k+2q}+2\omega+i\epsilon}. \quad (42)$$

Introducing Eq. (42) into Eq. (41) we obtain

$$\langle \mathbf{j}_{2\mathbf{q}}\rangle_{2\omega+i\epsilon}$$

$$=\frac{e^3\mathbf{A}_0{}^2}{2m^2c^2\epsilon^l(2\mathbf{q},2\omega)}\sum_{\mathbf{k}}(\mathbf{k}+\mathbf{q})\frac{f_0(\epsilon_{\mathbf{k}})-f_0(\epsilon_{\mathbf{k}+2\mathbf{q}})}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+2\mathbf{q}}+2\omega+i\epsilon}, \quad (43)$$

which is the same expression[13] as obtained by Bloembergen and Shen.[11]

IV. CONCLUSION

In this paper we have extended Kubo's formula for the linear transport coefficients, and its connection with the two-time Green's function, to the discussion of nonlinear transport coefficients by introducing $(n+1)$-time Green's functions. A method of calculating nonlinear transport coefficients by solving the equation of motion for the $(n+1)$-time Green's function is proposed. It is found that the equation of motion for the $(n+1)$-time Green's function is the same as that for the two-time Green's function except for the inhomogeneous term. Thus the proposed method has the same advantages as the two-time Green's function in the calculation of linear transport coefficients. To demonstrate the applicability of the present formulation we have treated nonlinear susceptibilities of a Heisenberg ferromagnet as well as some other known results in the literature.

APPENDIX

The problem in which the external disturbance involves more than one frequency is of interest in nonlinear phenomena such as mixing. Here we treat the case in which the disturbance has a spectrum of frequencies. The perturbation Hamiltonian is modified as

$$\mathcal{H}_1=-Af(t), \quad (A1)$$

where

$$f(t)=\int_{-\infty}^{\infty}f(\omega)e^{-i\omega t}d\omega. \quad (A2)$$

Correspondingly the expressions for $\rho_1(t)$ [Eq. (7)] and $\bar{B}$ [Eq. (10)] are replaced by

$$\rho_1(t)=\sum_{n=1}^{\infty}i^n\int_{-\infty}^{t}ds_1\int_{-\infty}^{s_1}ds_2\cdots\int_{-\infty}^{s_{n-1}}ds_n e^{-it\mathcal{H}^\times}A^\times(s_1)$$

$$\times A^\times(s_2)\cdots A^\times(s_n)\rho_0 f(s_1)f(s_2)\cdots f(s_n), \quad (A3)$$

and

$$\bar{B}=\langle B\rangle+\sum_{n=1}^{\infty}i^n\int_{-\infty}^{\infty}ds_1\cdots\int_{-\infty}^{\infty}ds_n$$

$$\times G_{n+1}[B(t);A(s_1);\cdots,A(s_n)]$$

$$\times f(s_1)f(s_2)\cdots f(s_n), \quad (A4)$$

where the $(n+1)$-time Green's function has been introduced through

$$G_{n+1}(B(t);A(s_1);\cdots A(s_n))$$

$$=(-i)^n\theta(t-s_1)\theta(s_1-s_2)\cdots\theta(s_{n-1}-s_n)$$

$$\times\langle\{\cdots[(B(t);A(s_1),A(s_2)),\cdots]A(s_n)\}\rangle. \quad (A5)$$

Substituting Eq. (A2) into Eq. (A4) and introducing the transformation of variables $\tau_n=s_{n-1}-s_n$, we obtain

$$\bar{B}=\langle B\rangle+\sum_{n=1}^{\infty}(2\pi i)^n\int_{-\infty}^{\infty}d\omega_1\cdots\int_{-\infty}^{\infty}d\omega_n$$

$$\times e^{-i(\omega_1+\omega_2+\cdots+\omega_n)t}G_{n+1}(B;A)_{\omega_1,\omega_2,\cdots\omega_n}$$

$$\times f(\omega_1)f(\omega_2)\cdots f(\omega_n), \quad (A6)$$

where

$$G_{n+1}(B;A)_{\omega_1,\omega_2,\cdots\omega_n}=\frac{1}{(2\pi)^n}\int_{-\infty}^{\infty}d\tau_1\cdots\int_{-\infty}^{\infty}d\tau_n$$

$$\times e^{i(\omega_1+\cdots+\omega_n)\tau_1}e^{i(\omega_2+\cdots+\omega_n)\tau_2}\cdots e^{i\omega_n\tau_n}G_{n+1}$$

$$\times[B;A(-\tau_1);\cdots;A(-\tau_1\cdots-\tau_n)]. \quad (A7)$$

Equation (A6) now replaces Eq. (13).

For example, when the perturbation Hamiltonian involves two frequencies ω' and ω'', the appropriate Green's function for the discussion of sum frequency $(\omega'+\omega'')$ is $G_3(B;A)_{\omega',\omega''}$.

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[13] Equation (43) follows if in Ref. 11 one substitutes Eq. (5) into Eq. (7).