Dispersion Relations for Nonlinear Response*

WILLEM J. CASPERS
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

(Received 26 September 1963)

A class of dispersion relations for quadratic response is discussed. An experimental verification of these relations for magnetic systems is suggested. In a typical experiment there are two parallel high-frequency magnetic fields, perpendicular to a constant field. The response in the direction of the constant field has five components, corresponding with the sum and the difference of the frequencies of the perturbing fields, twice these frequencies, and frequency zero. The dispersion relations are integral relations for the corresponding susceptibilities. In a final section an integral relation connecting the second-order response with a component of the linear susceptibility tensor is formulated.

INTRODUCTION

RECENTLY, the theory of nonlinear response has been developed in some detail.[1–4] Whereas the interest of most authors has been in the field of nonlinear optics, we discuss some properties that may find experimental verification for magnetic systems. In a typical experiment there are two parallel high-frequency magnetic fields of different frequencies. Perpendicular to these fields there is a constant magnetic field in the direction of which the response at the sum and difference frequency is measured. These responses obey a dispersion relation, which is discussed below, together, with an integral relation that connects the responses with the linear susceptibility tensor.

If there is a set of perturbing "fields" or "forces" $h_p(t)=h_p\cos(\omega_p t+\varphi_p)$, $p=1, 2, \cdots$, acting on the variables μ_p of a quantum mechanical system, the nth-order reponse of variable k is given by

$$(\bar{\mu}_k)_n=(i\hbar)^{-n}\sum_{p,q\cdots,w}\int_0^\infty d\tau_1\int_0^\infty d\tau_2\ldots\int_0^\infty d\tau_n\,\mathrm{Tr}[\ldots[\rho_0,\mu_w(-\tau_1-\tau_2-\ldots-\tau_n)],\ldots,\mu_p(-\tau_1)]\mu_k$$
$$\times\cos[\omega_p(t-\tau_1)+\varphi_p]\ldots\cos[\omega_w(t-\tau_1-\tau_2-\ldots-\tau_n)+\varphi_w]h_p\ldots h_w,\quad \omega_p\geq 0.\quad (1)$$

The fields of forces are, for instance, components of electric or magnetic fields and the variables μ_p the components of the corresponding moments. This result follows directly from formula (16) of Butcher and McLean.[3] In Eq. (1), ρ_0 and $\mu_p(t)$ are the density matrix for the unperturbed state and the corresponding Heisenberg operators for the variables of the system. We should like to remark that the convergence of (1) for different n is a theoretically necessary condition for the existence of a nonzero steady-state response. For a finite system without heat contact with its surroundings, part of the response for $n=3, 4, \cdots$ will be infinitely large as a consequence of the heating up of the system. For instance, the response at ω_p, proportional to h_p^3, will diverge, whereas the third-order term of frequency $3\omega_p$ is convergent.

For finite isolated systems, not being perturbed in any way by other systems, one could insert proper convergence factors in the integrals (1), in order to make them finite. In our case, however, we suppose that there is always a heat contact between the proper system, subject to the perturbation of the oscillating fields, and its surroundings. The sign Tr includes in this case an averaging for the variables of these surroundings. The integrand in (1) will be a well-behaved function of the variables τ_1, τ_2, $\cdots$, and the corresponding integrals will converge.

NONLINEAR SUSCEPTIBILITIES

Now we specialize for the case of two perturbing fields $h_i(t)$ and $h_j(t)$ with frequencies ω_i, $\omega_j\geq 0$. Except when otherwise stated, all our frequencies are supposed to be positive quantities. The second-order response $(\bar{\mu}_k)_2$ now has five Fourier components. For $\omega_i\geq\omega_j$ the corresponding frequencies are $\omega_i+\omega_j$, $\omega_i-\omega_j$, $2\omega_i$, $2\omega_j$, and 0 and we have

$$\begin{aligned}(\bar{\mu}_k)_2=&\{\mathrm{Re}\chi^+{}_{k(ij)}(\omega_i,\omega_j)\exp i[(\omega_i+\omega_j)t+\varphi_i+\varphi_j]\\&+\mathrm{Re}\chi^-{}_{k(ij)}(\omega_i,\omega_j)\exp i[(\omega_i-\omega_j)t+\varphi_i-\varphi_j]\}h_ih_j\\&+\mathrm{Re}\chi^+{}_{k(ii)}(\omega_i)\exp[i2(\omega_it+\varphi_i)]h_i^2\\&+\mathrm{Re}\chi^+{}_{k(jj)}(\omega_j)\exp[i2(\omega_jt+\varphi_j)]h_j^2\\&+\chi^-{}_{k(ii)}(\omega_i)h_i^2+\chi^-{}_{k(jj)}(\omega_j)h_j^2.\end{aligned}\quad (2)$$

The susceptibilities $\chi^\pm{}_{k(ij)}$ may be expressed in terms of one function $\chi_{k(ij)}$ defined for positive as well as

* This research was supported jointly by the U. S. Office of Naval Research, the Signal Corps of the U. S. Army, and the U. S. Air Force.

[1] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[2] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).
[3] P. N. Butcher and T. P. McLean, Proc. Phys. Soc. (London) **81**, 219 (1963).
[4] P. J. Price, Phys. Rev. **130**, 1792 (1963).

negative frequencies:

$$\chi^{\pm}{}_{k(ij)}(\omega_i,\omega_j)=\chi_{k(ij)}(\omega_i,\pm\omega_j)\,,$$

$$\chi_{k(ij)}(\omega_i,\omega_j) = -\frac{1}{2\hbar^2}\int_0^\infty d\tau\int_0^\infty d\rho e^{-i(\omega_i+\omega_j)\tau} \times\{e^{-i\omega_j\rho}\,\mathrm{Tr}[[\rho_0,\mu_j(-\tau-\rho)],\mu_i(-\tau)]\mu_k + e^{-i\omega_i\rho}\,\mathrm{Tr}[[\rho_0,\mu_i(-\tau-\rho)],\mu_j(-\tau)]\mu_k\}\,. \tag{3}$$

It will be clear that for $\omega_j\geq\omega_i$ we have

$$\chi^{\pm}{}_{k(ji)}(\omega_j,\omega_i)=\chi_{k(ji)}(\omega_j,\pm\omega_i)=\chi_{k(ij)}(\pm\omega_i,\omega_j)\,.$$

The quadratic terms in (2) correspond with susceptibilities of the form

$$\chi^{+}{}_{k(ii)}=-\frac{1}{2\hbar^2}\int_0^\infty d\tau\int_0^\infty d\rho e^{-i2\omega_i\tau}e^{-i\omega_i\rho} \times\mathrm{Tr}[[\rho_0,\mu_i(-\tau-\rho)],\mu_i(-\tau)]\mu_k\,,$$
$$\chi^{-}{}_{k(ii)}=-\frac{1}{2\hbar^2}\int_0^\infty d\tau\int_0^\infty d\rho\,\cos\omega_i\rho \times\mathrm{Tr}[[\rho_0,\mu_i(-\tau-\rho)],\mu_i(-\tau)]\mu_k\,. \tag{4}$$

DISPERSION RELATIONS

As follows from (3) we may write $\chi_{k(ij)}(\omega_i,\omega_j)$ in the form

$$\int_0^\infty d\sigma e^{-\omega_i\sigma}F(\sigma,\omega_j)\,.$$

If $F(\sigma,\omega_j)$ obeys some very general conditions, it is clear that we can write down the usual Kramers–Kronig or dispersion relations for $\chi_{k(ij)}(\omega_i,\omega_j)$ as a function of ω_i[5]:

$$\chi_{k(ij)}(\omega_i,\omega_j)=\frac{i}{\pi}P\int_{-\infty}^{+\infty}d\bar\omega_i\frac{\chi_{k(ij)}(\bar\omega_i,\omega_j)}{\bar\omega_i-\omega_i}\,,\quad \chi_{i(ij)}(\infty,\omega_j)=0\,. \tag{5}$$

It is supposed without further proof that, in the case we are interested in, $\chi_{k(ij)}=0$ for the limit of one or both of the variables going to infinity.

Formula (5) has already been given by Price,[4] but he did not pay attention to its interpretation in terms of $\chi^{+}{}_{k(ij)}$, $\chi^{-}{}_{k(ij)}$, and $\chi^{-}{}_{k(ji)}$. This interpretation leads to a system of three integral equations, two of which are given by

$$\chi^{+}{}_{k(ij)}(\omega_i,\omega_j) =\frac{i}{\pi}\Big[P\int_0^\infty d\bar\omega_i\frac{\chi^{+}{}_{k(ij)}(\bar\omega_i,\omega_j)}{\bar\omega_i-\omega_i}-\int_0^{\omega_j}d\bar\omega_i\frac{\chi^{-}{}_{k(ji)}(\omega_j,\bar\omega_i)}{\bar\omega_i+\omega_i} -\int_{\omega_j}^\infty d\bar\omega_i\frac{\chi^{-*}{}_{k(ij)}(\bar\omega_i,\omega_j)}{\bar\omega_i+\omega_i}\Big]\,,$$

$$\chi^{-}{}_{k(ij)}(\omega_i,\omega_j) =\frac{i}{\pi}\Big[P\int_{\omega_j}^\infty d\bar\omega_i\frac{\chi^{-}{}_{k(ij)}(\bar\omega_i,\omega_j)}{\bar\omega_i-\omega_i}+\int_0^{\omega_j}d\bar\omega_i\frac{\chi^{-*}{}_{k(ji)}(\omega_j,\bar\omega_i)}{\bar\omega_i-\omega_i} -\int_0^\infty d\bar\omega_i\frac{\chi^{+*}{}_{k(ij)}(\bar\omega_i,\omega_j)}{\bar\omega_i+\omega_i}\Big]\,,\quad \omega_i\geq\omega_j\geq0\,. \tag{6}$$

These formulas express the real parts of χ^+ and χ^- in terms of the imaginary parts of these functions and vice versa. The real parts give the "in-phase" parts of the signals, going with $\cos[(\omega_i\pm\omega_j)t+\varphi_i\pm\varphi_j]$. The "out-of-phase" parts are given by $\mathrm{Im}\chi^{\pm}\sin[(\omega_i\pm\omega_j)t+\varphi_i\pm\varphi_j]$. A third equation can be found by interchanging i and j in the second of these formulas.

A simpler dispersion relation exists for $\chi^{+}{}_{k(ij)}(\omega_i,\omega_j)$, if the two frequencies ω_i and ω_j, have a fixed ratio

$$\omega=\omega_i+\omega_j,\ \omega_i=\alpha\omega,\ \omega_j=\beta\omega,\ \alpha+\beta=1,\quad \alpha,\ \beta\geq0,\ \alpha\text{ and }\beta\text{ constant.}$$

We now have a relation identical in form with the well-known dispersion relation for linear responses, which connects real and imaginary parts of the susceptibility in the following way

$$\chi^{+}{}_{k(ij)}(\omega)=\chi^{+\prime}{}_{k(ij)}(\omega)-i\chi^{+\prime\prime}{}_{k(ij)}(\omega)\,,$$
$$\chi^{+\prime}{}_{k(ij)}(\omega)=\frac{2}{\pi}\int_0^\infty d\bar\omega\frac{\bar\omega\chi^{+\prime\prime}{}_{k(ij)}(\bar\omega)}{\bar\omega^2-\omega^2}\,,$$
$$\chi^{+\prime\prime}{}_{k(ij)}(\omega)=-\frac{2}{\pi}\int_0^\infty d\bar\omega\frac{\omega\chi^{+\prime}{}_{k(ij)}(\bar\omega)}{\bar\omega^2-\omega^2}\,. \tag{7}$$

Quite analogous in form with (7) are dispersion relations for the double frequency responses at $2\omega_i$ and $2\omega_j$; it does not seem necessary to write them down explicitly in order to show this analogy. For the responses at $|\omega_i-\omega_j|$ and 0, no such relations exist. Price[4] gives still another dispersion relation for the variable $\omega_i+\omega_j$ when $\omega_i-\omega_j$ has a fixed value. A general set of dispersion relations can be found by introducing the variables

$$\omega_1=\gamma\omega_i+\delta\omega_j\,,\quad \omega_2=-\delta\omega_i+\gamma\omega_j\,.\qquad \gamma,\ \delta\geq0,\quad \gamma^2+\delta^2=1\,.$$

From (3) it follows that dispersion relations exist for $\chi(\omega_1,\omega_2)=\chi_{k(ij)}[\omega_i(\omega_1,\omega_2),\omega_j(\omega_1,\omega_2)]$ as a function of ω_1,

[5] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), p. 93.

for a fixed value of ω_2. All dispersion relations discussed so far are special cases of this general one.

A difficulty in the experimental verification of (6) arises from the fact that, in general, one does not know the phases of the signals at sum and difference frequency. The "in-phase" and "out-of-phase" parts of the signals, going with $\cos[(\omega_i \pm \omega_j)t + \varphi_i \pm \varphi_i]$ and $\sin[(\omega_i \pm \omega_j)t + \varphi_i \pm \varphi_j]$, respectively, are not related with two different physical phenomena like dispersion and absorption, as is the case for first-order responses. The $\chi^{\pm}{}_{k(ij)}$ may be determined by measuring induced currents in a coil, which currents are compensated by signals of the same frequencies and given phase. In the experiment suggested in the first paragraph, the phases of the induced currents are known theoretically for an infinitely large constant field: $\chi^{\pm}{}_{i(ij)}$ are real for this case.

We denote the direction of the high-frequency fields by x and that of the constant field $\mathbf{H}$ by z. The susceptibilities now are represented by $\chi^{\pm}{}_{z(xx)}(\omega_i,\omega_j)$. If the magnetic system is composed of spins 1/2, the limiting values of $\chi^{\pm}{}_{z(xx)}$ for $H \to \infty$ and $T \to \infty$ (the usual high-temperature approximation) are given by

$$\chi^{\pm}{}_{z(xx)}(\omega_i,\omega_j) \approx \frac{(g\beta_0)^3}{8kT\hbar\omega_H}N, \quad \omega_H = -\frac{g\beta_0 H}{\hbar}, \tag{8}$$

except for the $\omega_i \pm \omega_j \leq \tau_{\mathrm{sl}}^{-1}$, τ_{sl} being the spin-lattice relaxation time. In (8), β_0 is the Bohr magneton and N the number of spins. The special value $S=1/2$ is only an example. For other values of S we find similar results, that is, $\chi^{\pm}$ real and positive for $H \to \infty$. It is possible, in principle, to make compensating signals with the phase of the response for $H \to \infty$, for a given set of frequencies ω_i and ω_j. These signals may be used to determine phases and amplitudes of the responses at $\omega_i \pm \omega_j$ for other values of H.

INTEGRAL PROPERTY

We finally give a relation between the susceptibilities $\chi^{\pm}{}_{z(xx)}$ and the cross term $\chi_{y(x)}$ of the first-order susceptibility tensor. This relation is based on the integral property

$$\int_0^\infty d\omega \int_0^\infty d\tau \cos\omega\tau F(\tau) = \frac{\pi}{2}F(0), \tag{9}$$

which is a special case of the inversion of a Fourier cosine transformation. From (3) and (9) we derive

$$\begin{aligned}\int_{-\infty}^{+\infty} d\omega_i \chi_{z(xx)}(\omega_i,\omega_j) &= -\frac{\pi}{2\hbar^2}\int_0^\infty d\rho e^{-i\omega_j\rho}\,\mathrm{Tr}[\rho_0,\mu_x(-\rho)][\mu_x,\mu_z] \\ &= -\frac{\pi g\beta_0}{2i\hbar^2}\int_0^\infty d\rho e^{-i\omega_j\rho}\,\mathrm{Tr}[\rho_0,\,\mu_x(-\rho)]\mu_y \\ &= -\frac{\pi g\beta_0}{2\hbar}\chi_{y(x)}(\omega_j),\end{aligned}$$

which relation may be put into the form

$$\int_0^\infty d\omega_i \chi^{+}{}_{z(xx)}(\omega_i,\omega_j) + \int_0^{\omega_j} d\omega_i \chi^{-}{}_{z(xx)}(\omega_j,\omega_i) + \int_{\omega_j}^\infty d\omega_i \chi^{-*}{}_{z(xx)}(\omega_i,\omega_j) = -\frac{\pi g\beta_0}{2\hbar}\chi_{y(x)}(\omega_j).$$

This is an example of a general type of relations that exist between responses of nth and $(n-1)$th orders, if we have a magnetic moment that obeys the commutation relation

$$[\mu_x,\mu_z] = -ig\beta_0\mu_y,$$

which is correct within a given manifold, characterized by an isotropic g tensor. This g tensor may connect the magnetic moment of the individual ions with the corresponding total angular momentum, if we have a (degenerate) eigenstate for this angular momentum. Another case is given by a low-lying group of energy levels of a paramagnetic ion corresponding with a given value of the real or ficititious spin. In this case the g tensor connects the magnetic moment with this spin.

ACKNOWLEDGMENTS

The author is much indebted to Professor Bloembergen and Professor Pershan for helpful discussions. He also acknowledges the criticism of Professor Ehrenreich as well as his suggestions for possible applications. The experiment with the two high-frequency fields was discussed with Dr. J. C. Verstelle of the Kamerlingh Onnes Laboratorium in Leiden and with C. Y. Huang.