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Nonlinear response theory—I

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Abstract. A general nonlinear response theory for the case of linear coupling of physical systems to arbitrary external fields is formulated for applications in different branches of physics. This is done within the framework of non-relativistic density matrix approach of quantum mechanics. Some simple properties of response functions and other related functions, which are introduced here for convenience, are studied to obtain suitable representations of the nonlinear response functions, including important sum-rules. As an example, the sum rule for the second-order response function is applied to electronic dipole nonlinearity at optical frequencies which includes both the Raman nonlinearity arising from perturbation to the electronic motion from external ionic displacement field and the usual optical sum, difference and harmonic generations. This immediately allows us to visualize a rigorous connection between these two types of non-linearities.

Keywords. Nonlinear response theory; linear coupling; response function; sum-rules.

1. Introduction

Linear response theory is known to be a powerful method (Kubo 1957, 1959; Martin and Schwinger 1959; Forster 1975) to describe dynamical processes in many-particle physical systems which are usually investigated experimentally by means of weak external probes. In such non-equilibrium processes, the experiments only probe the dynamical behaviour of spontaneous fluctuations about the known equilibrium state, and these may be rigorously described in terms of time-dependent correlation functions of suitable pairs of dynamical variables of the system. The formal mathematical properties of these correlation functions or the corresponding linear response functions, in terms of their symmetries, sum rules, dispersion relations and fluctuation-dissipation theorems, have been extremely useful in analysing and understanding various physical systems. As opposed to the hydrodynamic approximation in which the induced changes must be slowly varying functions of space and time, the linear response theory is applicable to arbitrary space-time behaviour of the probe, except that its amplitude has to be weak enough for the linear approximation to be valid.

Of course, physical systems, in general, are nonlinear, even when the basic microscopic coupling to the external field may be linear. In many experiments, one indeed measures the second-order as well as higher-order responses systematically in, *e.g.* acoustics and optics, besides many other important branches of physics. In connection with the investigations related to optical nonlinearities, there have been several attempts in the past to study general properties of higher-order response functions (Price 1963; Kogan 1963; Butcher and McLean 1963; Bloembergen 1965; Ridener and Good 1974). However, most of these approaches have been too specific and restrictive to describe nonlinear response functions for the general case. The use of the electric-dipole approximation or the assumption of linear coupling to the external field is not always valid even in the case of nonlinear electromagnetic response at optical frequencies, in the framework of nonrelativistic dynamics (Jha 1965, 1966; Flytzanis 1975). Here, our aim is to formulate nonlinear response theory of nonrelativistic physical systems in such a way that it is useful and applicable not only to optical nonlinearities but also to other more general cases. However, to avoid the algebraic complication arising from the presence of the linear as well as bilinear basic coupling to external fields at the same time, which tends to obscure the general mathematical structure of the nonlinear response functions, in this first paper on the formulation we will examine the case of linear coupling only.

In §2 of this paper, we present the mathematical formulation for obtaining the linear as well as the nonlinear dynamical response of any physical system, in the framework of the familiar non-relativistic density matrix approach. In §3, we study some simple properties of these response functions, including the derivation of useful sum rules. As an example, in §4, the resulting sum rule for the second-order nonlinearity is applied to the case of optical dipole nonlinearity to explicitly relate it to the nonlinear force acting on the electrons in the system, including the force arising from the ionic motion. In this sense, our formulation includes Raman nonlinearity, when specialized to the optical case. The more general properties of higher-order nonlinearities and the case of basic bilinear coupling, including applications to specific non-optical problems will be taken up in a subsequent paper.

2. Mathematical formulation: Linear coupling to external fields

Let us consider a physical system described by an unperturbed Hamiltonian H in the presence of arbitrary external fields $a_i(\mathbf{r}, t)$, each of which couples linearly to dynamical variables $A_i(\mathbf{r})$ of the system. In Schrödinger representation, the density matrix ρ_s of the system satisfies the equation

$$i\hbar\frac{\partial \rho_s}{\partial t} = [H, \rho_s] + [h, \rho_s], \tag{1}$$

where the interaction with the external fields is given by

$$h = -\sum_i \int \mathrm{d}^3 r A_i(\mathbf{r}) a_i(\mathbf{r}, t), \tag{2}$$

the minus sign being introduced to follow the usual convention (Forster 1975). At time $t = -\infty$, the system is assumed to be in thermal equilibrium, with

$$\rho_s(t \to -\infty) = \rho_0;\ \rho_0 = \exp(-\beta H)/\mathrm{trace}\ [\exp(-\beta H)],\ \beta = 1/k_B T \tag{3}$$

and the external fields $a_i(\mathbf{r}, t \to -\infty) = 0$.

In terms of the Heisenberg operators for the unperturbed system, defined by

$$\begin{aligned} \rho(t) &\equiv \exp[(i/\hbar)Ht]\, \rho_s \exp[(-i/\hbar)Ht], \\ A_i(\mathbf{r}, t) &\equiv \exp[(i/\hbar)Ht]\, A_i(\mathbf{r}) \exp[(-i/\hbar)Ht], \\ h(t) &\equiv -\sum_i \int \mathrm{d}^3 r A_i(\mathbf{r}, t)\, a_i(\mathbf{r}, t), \end{aligned} \tag{4}$$

one has to solve the equation

$$i\hbar\frac{\partial\rho(t)}{\partial t}=[h(t),\rho(t)];\ \rho(-\infty)=\rho_0. \tag{5}$$

As a perturbative expansion in the powers of the external field amplitudes, (5) can be solved immediately in the form

$$\begin{aligned}\rho(t)=\rho_0&+\frac{1}{(i\hbar)}\int_{-\infty}^{t}dt_1\,[h(t_1),\rho_0]\\&+\frac{1}{(i\hbar)^2}\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\,[h(t_1),[h(t_2),\rho_0]]\\&+\frac{1}{(i\hbar)^3}\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\,[h(t_1),[h(t_2),[h(t_3),\rho_0]]]\\&+\ldots.\end{aligned} \tag{6}$$

In general, one may now calculate the induced non-equilibrium value of a physical variable $B_i(\mathbf{r})$ of the system as the deviation of its expectation value from the equilibrium:

$$\begin{aligned}\langle\delta B_i(\mathbf{r},t)\rangle_{\text{ind.}}&=\operatorname{trace}B_i(\mathbf{r})(\rho_s(t)-\rho_0)\\&=(\operatorname{trace}B_i(\mathbf{r},t)\rho(t))-\langle B_i(\mathbf{r})\rangle.\end{aligned} \tag{7}$$

Here, as a compact notation, the expectation value with respect to the equilibrium is written as

$$\langle A\rangle\equiv\operatorname{trace}A\rho_0. \tag{8}$$

In particular, one is often concerned with the induced changes in the variables A_i themselves to different orders in the external fields. For this case, one finds the result to be of the form

$$\langle\delta A_i(\mathbf{r},t)\rangle_{\text{ind.}}=\sum_{n=1}^{\infty}(A_i(\mathbf{r},t))_n \tag{9}$$

$$\begin{aligned}(A_i(\mathbf{r},t))_n=\sum_{j_1}\cdots\sum_{j_n}&\int d^3r_1\ldots\int d^3r_n\int_{-\infty}^{+\infty}dt_1\ldots\int_{-\infty}^{+\infty}dt_n\\&\times\chi^{(n)}_{ij_1\ldots j_n}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,t-t_1,\ldots,t-t_n)\\&\times a_{j_1}(\mathbf{r}_1,t_1)a_{j_2}(\mathbf{r}_2,t_2)\ldots a_{j_n}(\mathbf{r}_n,t_n),\end{aligned} \tag{10}$$

from which it is obvious that the response functions $\chi^{(n)}$ are symmetric with respect to simultaneous interchange of any two sets of variables: $j_p\rightleftarrows j_s$, $r_p\rightleftarrows r_s$, $t_p\rightleftarrows t_s$. In fact, the causal response functions can be written in a convenient form

$$\begin{aligned}&\chi^{(n)}_{ij_1\ldots j_n}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2\ldots\mathbf{r}_n,t_1,\ldots,t_n)\\&\quad=R^{(n)}_{ij_1\ldots j_n}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,t_1,\ldots,t_n)\theta(t_1)\theta(t_2)\ldots\theta(t_n)\end{aligned} \tag{11}$$

$$\begin{aligned}&R^{(n)}_{ij_1\ldots j_n}(\mathbf{r},\mathbf{r}_1,\ldots\mathbf{r}_n,t_1,\ldots,t_n)\\&\quad=\operatorname{sym}(j_1\mathbf{r}_1t_1,j_2\mathbf{r}_2t_2,\ldots,j_n\mathbf{r}_nt_n)\\&\qquad\times K^{(n)}_{ij_1\ldots j_n}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,t_1,t_2-t_1,\ldots,t_n-t_{n-1})\\&\qquad\times\theta(t_1)\theta(t_2-t_1)\ldots\theta(t_n-t_{n-1}),\end{aligned} \tag{12}$$

where the theta function is defined by the step function

$$\theta(x) = 1,\ x > 0,$$
$$\theta(x) = 0,\ x < 0, \tag{13}$$

and sym $(abc, def, \ldots)$ is the symmetrization operator:

$$\text{sym}\,(abc, def)\,F \equiv \tfrac{1}{2}\{F + F(a \rightleftarrows d,\ b \rightleftarrows e,\ c \rightleftarrows f)\}. \tag{14}$$

The substitution of the expression for $h(t)$ in (6) and some rearrangement of independent variables lead to the following explicit expression for $\mathbf{K}^{(n)}$:

$$K^{(n)}_{ij_1\ldots j_n}(\mathbf{r}, \mathbf{r}_1 \ldots \mathbf{r}_n, t_1, t_2, \ldots, t_n)$$
$$= \frac{1}{(-i\hbar)^n} \langle [\ldots [[A_i(\mathbf{r}), A_{j_1}(\mathbf{r}_1, -t_1)], A_{j_2}(\mathbf{r}_2, -t_2 - t_1)] \ldots],$$
$$A_{j_n}(\mathbf{r}_n, -t_n - t_{n-1} \ldots - t_1) \rangle. \tag{15}$$

While writing the above form for $\mathbf{K}^{(n)}$ in terms of the equilibrium expectation value of repeated commutators, we have used the identities

$$\text{trace}\,([A_1(t_1), [A_2(t_2) \ldots [A_n(t_n), \rho_0] \ldots]] A(t))$$
$$= \text{trace}\,(\rho_0 [[\ldots [[A(t), A_1(t_1)], A_2(t_2)] \ldots], A_n(t_n)]) \tag{16}$$

$$\langle A_1(t_1) A_2(t_2) \rangle = \langle A_1(0) A_2(t_2 - t_1) \rangle = \langle A_1(t_1 - t_2) A_2(0) \rangle \tag{17}$$

due to cyclic property of the trace operations.

Instead of the time-representation for the response functions $\chi^{(n)}$, we can use the more conventional frequency representation in the Fourier transform space to rewrite (10) as

$$(A_i(\mathbf{r}, t))_n = \int d^3 r_1 \ldots \int d^3 r_n \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \ldots \int_{-\infty}^{\infty} \frac{d\omega_n}{2\pi}$$
$$\times \exp[-i(\omega_1 + \omega_2 + \ldots + \omega_n)t]$$
$$\times \chi^{(n)}_{ij_1\ldots j_n}(\mathbf{r}, \mathbf{r}_1 \ldots \mathbf{r}_n, \omega_1, \omega_2 \ldots, \omega_n)$$
$$\times a_{j_1}(\mathbf{r}_1, \omega_1) a_{j_2}(\mathbf{r}_2, \omega_2) \ldots a_{j_n}(\mathbf{r}_n, \omega_n), \tag{18}$$

where

$$\chi^{(n)}(\mathbf{r}, \mathbf{r}_1 \ldots \mathbf{r}_n, \omega_1, \ldots, \omega_n)$$
$$= \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \ldots \int_{-\infty}^{\infty} dt_n \exp(i\omega_1 t_1) \exp(i\omega_2 t_2) \ldots \exp(i\omega_n t_n)$$
$$\times \chi^{(n)}(\mathbf{r}, \mathbf{r}_1 \ldots \mathbf{r}_n, t_1, t_2, \ldots t_n) \tag{19}$$

and where summations over repeated indices $j_1 \ldots j_n$ are implied. Explicitly, one obtains

$$\chi^{(1)}_{ij}(\mathbf{r}, \mathbf{r}_1, \omega_1) = \int_{-\infty}^{\infty} dt_1 \exp(i\omega_1 t_1) K^{(1)}_{ij}(\mathbf{r}, \mathbf{r}_1, t_1) \theta(t_1), \tag{20}$$

$$K^{(1)}_{ij}(\mathbf{r}, \mathbf{r}_1, t_1) = \frac{1}{(-i\hbar)} \langle [A_i(\mathbf{r}, 0), A_j(\mathbf{r}_1, -t_1)] \rangle, \tag{21}$$

$$\chi^{(2)}_{ijk}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\omega_1,\omega_2)$$
$$= \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \exp(i\omega_1 t_1)\exp(i\omega_2 t_2)\,\mathrm{sym}\,(j\mathbf{r}_1 t_1;\, k\mathbf{r}_2 t_2)$$
$$\theta(t_1)\theta(t_2-t_1)\, K^{(2)}_{ijk}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,t_1,t_2-t_1), \tag{22}$$

$$K^{(2)}_{ijk}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,t_1,t_2)$$
$$= \frac{1}{(-i\hbar)^2}\langle [[A_i(\mathbf{r},0), A_j(\mathbf{r}_1,-t_1)], A_k(\mathbf{r}_2,-t_2-t_1)]\rangle \tag{23}$$

$$\chi^{(3)}_{ijkl}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\omega_1,\omega_2,\omega_3)$$
$$= \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \exp(i\omega_1 t_1)\exp(i\omega_2 t_2)\exp(i\omega_3 t_3)$$
$$\times\,\mathrm{sym}\,(j\mathbf{r}_1 t_1, k\mathbf{r}_2 t_2, l\mathbf{r}_3 t_3)\theta(t_1)\theta(t_2-t_1)\theta(t_3-t_2)$$
$$\times\, K^{(3)}_{ijkl}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,t_1,t_2-t_1,t_3-t_2) \tag{24}$$

$$K^{(3)}_{ijkl}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,t_1,t_2,t_3) = \frac{1}{(-i\hbar)^3}\langle [[[A_i(\mathbf{r},0), A_j(\mathbf{r}_1,-t_1)],$$
$$A_k(\mathbf{r}_2,-t_2-t_1)], A_l(\mathbf{r}_3,-t_3-t_2-t_1)]\rangle, \tag{25}$$

etc. Note that each of the frequencies ω_i, $i = 1, 2 \ldots$, of the external fields can be assumed to contain a small imaginary part $i\delta$, $\delta > 0$, so that $\exp(-i\omega_i t)$ vanishes at $t = -\infty$, when there are no external fields.

For the case in which one wants to find the non-equilibrium expectation value of an arbitrary physical variable $B_i(\mathbf{r})$ which does not explicitly occur in the interaction h with the external fields, the more general expressions can be easily obtained from the expressions already derived for $A_i(\mathbf{r})$ in this section. One has to simply replace $A_i(\mathbf{r},0)$ by $B_i(\mathbf{r},0)$ in each of the results, *e.g.* in (15), (21), (23), (25), etc. However, in what follows we will not be interested in such a problem here. In the next section, we will study some of the general properties of the response functions $\chi^{(1)}$, $\chi^{(2)}$, etc., given by (20)–(25).

3. General properties of response functions

In the last section, we have defined the nth-order response function $\chi^{(n)}_{ij_1\ldots j_n}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,t_1\ldots t_n)$ which is symmetric under the simultaneous interchanges of $j_p \rightleftarrows j_s$, $r_p \rightleftarrows r_s$, $t_p \rightleftarrows t_s$, and which is zero for any time argument $t_p < 0$. For all time arguments positive, its value is given by the function $\mathbf{R}^{(n)}$ of (11). Since the expectation value of a hermitian operator, like any of the physical operators A_p, is real, of a commutator of two such hermitian operators is imaginary, of a double commutator of three hermitian operators is real, etc., it is easy to see from the definitions of $\mathbf{K}^{(n)}$ and $\mathbf{R}^{(n)}$ of (11), (12) and (15) that each of the functions $\mathbf{K}^{(n)}$, $\mathbf{R}^{(n)}$ and $\chi^{(n)}$ in time space is real. The reality condition in time space also implies the following obvious conditions in the complex frequency space:

$$\chi^{(n)}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,\omega_1,\omega_2,\ldots,\omega_n) = \chi^{(n)*}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,-\omega_1^*,-\omega_2^*,\ldots,-\omega_n^*)$$
$$\mathbf{K}^{(n)}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,\omega_1,\omega_2,\ldots,\omega_n) = \mathbf{K}^{(n)*}(\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_n,-\omega_1^*,-\omega_2^*,\ldots,-\omega_n^*). \tag{26}$$

It means that the real part of $\chi^{(n)}$ of arbitrary order in the *real* frequency space is symmetric whereas the imaginary part is antisymmetric, with respect to simultaneous changes in sign of all the real frequency arguments.

Explicitly, for the linear response function, one has

$$\chi_{ij}^{(1)}(\mathbf{r},\mathbf{r}_1,\omega_1) = \int_{-\infty}^{\infty} \mathrm{d}t_1 \exp(i\omega_1 t_1) K_{ij}^{(1)}(\mathbf{r},\mathbf{r}_1,t_1)\theta(t_1)$$
$$= \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_1'}{2\pi i} \frac{K_{ij}^{(1)}(\mathbf{r},\mathbf{r}_1,\omega_1')}{(\omega_1'-\omega_1-i0^+)} \tag{27}$$

where

$$K_{ij}^{(1)}(\mathbf{r},\mathbf{r}_1,t_1) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_1}{2\pi} \exp(-i\omega_1 t_1) K_{ij}^{(1)}(\mathbf{r},\mathbf{r}_1,\omega_1)$$
$$= \frac{1}{(-i\hbar)} \langle [A_i(\mathbf{r},t_1), A_j(\mathbf{r}_1,0)] \rangle. \tag{28}$$

The sum-rules for the frequency moments of $\mathbf{K}^{(1)}(\omega_1)$ may be obtained by taking repeated time derivatives of the above equations, and then putting $t_1 = 0$. With the use of the relation

$$i\frac{\partial A(t)}{\partial t} = \frac{1}{(-\hbar)}[H, A(t)], \tag{29}$$

one then finds

$$-\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_1}{2\pi i} \omega_1^m K_{ij}^{(1)}(\omega_1) = \frac{1}{(-\hbar)^{m+1}}$$
$$\langle [[H,[H,\ldots[H,A_i(\mathbf{r})]\ldots]], A_j(\mathbf{r}_1)] \rangle. \tag{30}$$

As done above, when it is not likely to cause any confusion, we will sometimes omit writing spatial variables explicitly. From (30), the high-frequency expansion of $\chi^{(1)}(\omega_1)$ can then be calculated by using the series

$$\chi_{ij}^{(1)}(\mathbf{r},\mathbf{r}_1,\omega_1) = -\sum_{m=0}^{\infty} \frac{1}{\omega_1^{m+1}} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_1'}{2\pi i} (\omega_1')^m K_{ij}^{(1)}(\mathbf{r},\mathbf{r}_1,\omega_1'). \tag{31}$$

Similarly, using (22) and (23), the second-order response function has the explicit form

$$\chi_{ijk}^{(2)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\omega_1,\omega_2) = \mathrm{sym}(j\mathbf{r}_1\omega_1, k\mathbf{r}_2\omega_2) \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_1'}{2\pi i} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_2'}{2\pi i}$$
$$\times \frac{K_{ijk}^{(2)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\omega_1',\omega_2')}{(\omega_1'-\omega_1-\omega_2-i0^+)(\omega_2'-\omega_2-i0^+)}, \tag{32}$$

where

$$K_{ijk}^{(2)}(t_1,t_2) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega_2}{2\pi}$$
$$\exp(-i\omega_1 t_1)\exp(-i\omega_2 t_2) K_{ijk}^{(2)}(\omega_1,\omega_2)$$
$$= \frac{1}{(-i\hbar)^2} \langle [[A_i(\mathbf{r}), A_j(\mathbf{r}_1,-t_1)], A_k(r_2,-t_2-t_1)] \rangle. \tag{33}$$

Again, the moment sum rules may be obtained by repeated differentiation with respect to t_1 and t_2, to find

$$\int \frac{d\omega_1}{2\pi i} \int \frac{d\omega_2}{2\pi i} K^{(2)}_{ijk}(\omega_1, \omega_2)\, \omega_1^n \omega_2^m$$
$$= \frac{1}{(-\hbar)^n (\hbar)^{m+2}} \langle [[H, [H, .. [H, A_i(\mathbf{r})] ..], A_j(\mathbf{r}_1)],$$
$$[H, [H, .. [H, A_k(r_2)] ..]]] \rangle, \tag{34}$$

where the first term involves n derivatives and the last term m derivatives. The high frequency expansion of $\chi^{(2)}$ is then given by

$$\chi^{(2)}_{ijk}(\omega_1, \omega_2) = \mathrm{sym}\,(j\mathbf{r}_1\omega_1, k\mathbf{r}_2\omega_2) \int \frac{d\omega_1'}{2\pi i} \int \frac{d\omega_2'}{2\pi i} K^{(2)}_{ijk}(\omega_1', \omega_2')$$
$$\times \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(\omega_1')^n (\omega_2')^m}{(\omega_1 + \omega_2)^{n+1} \omega_2^{m+1}}. \tag{35}$$

It is straightforward to obtain similar results for the third-order response function $\chi^{(3)}$ by using (24) and (25). For this, the explicit representation is given by

$$\chi^{(3)}_{ijkl}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \omega_1, \omega_2, \omega_3)$$
$$= \mathrm{sym}\,(j\mathbf{r}_1\omega_1, k\mathbf{r}_2\omega_2, l\mathbf{r}_3\omega_3) \int_{-\infty}^{\infty} \frac{d\omega_1'}{2\pi i} \int_{-\infty}^{\infty} \frac{d\omega_2'}{2\pi i} \int_{-\infty}^{\infty} \frac{d\omega_3'}{2\pi i}$$
$$\times \frac{K^{(3)}_{ijkl}\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \omega_1', \omega_2', \omega_3')}{(\omega_1' - \omega_1 - \omega_2 - \omega_3 - i0^+)(\omega_2' - \omega_2 - \omega_3 - i0^+)(\omega_3' - \omega_3 - i0^+)}. \tag{36}$$

The frequency moment sum rules and the high-frequency expansion for $\chi^{(3)}$ can be derived by the method already described for $\chi^{(1)}$ and $\chi^{(2)}$.

Before we conclude this section, it is instructive to examine the representations of $\chi^{(1)}(\omega_1)$, $\chi^{(2)}(\omega_1, \omega_2)$ and $\chi^{(3)}(\omega_1, \omega_2, \omega_3)$ given by (27), (32) and (36), respectively. Calculations of $\mathbf{K}^{(n)}$ defined by (15) in time space, in the representation where the system Hamiltonian is diagonal, show that these well-behaved real functions vary in time with periodic exponential factors like $\exp\{\pm(i/\hbar)|\Delta E|t\}$ where ΔE's are the differences in any two energy eigenvalues of the system Hamiltonian H. Therefore, the multiple Fourier transform of $\mathbf{K}^{(n)}$ in the frequency space has strength only when its frequencies ω_m' coincide with any of the quantities $\pm|\Delta E|/\hbar$. This implies that $\chi^{(1)}(\omega_1)$ has a resonant structure when $\hbar\omega_1 = \pm|\Delta E|$. Similarly, $\chi^{(2)}(\omega_1, \omega_2)$ has resonances whenever ω_1 or ω_2 or $(\omega_1 + \omega_2)$ coincides with any $\pm|\Delta E|/\hbar$ and $\chi^{(3)}(\omega_1, \omega_2, \omega_3)$ has resonances when ω_1 or ω_2 or ω_3 or $(\omega_1 + \omega_2)$ or $(\omega_2 + \omega_3)$ or $(\omega_3 + \omega_1)$ or $(\omega_1 + \omega_2 + \omega_3)$ coincides with any $\pm|\Delta E|/\hbar$ of the system.

4. Application of sum-rules

As a simple example, let us apply our general sum rule for the second-order response function $\chi^{(2)}$ in the case of optical dipole nonlinearity. In this case, it is enough to consider the induced electronic polarizabilities of the system. The unperturbed Hamiltonian for the electronic system may be taken to be a *sum* of single-particle Hamiltonians of the type

$$H = \frac{p^2}{2m} + V(\mathbf{x}, \mathbf{Q} = 0), \tag{37}$$

where the complete single-particle potential $V(\mathbf{x}, \mathbf{Q})$ depends on the c-number normal coordinates $\mathbf{Q}$ of the ionic motion from the equilibrium ionic positions. The external interaction for the ionic system may be assumed to arise from both the ionic motion field and also from external optical field $\mathbf{E}$. In the electric dipole approximation, to the lowest order in the ionic motion, one, therefore, has

$$h = e\mathbf{x}\cdot E(t) + (\partial V/\partial \mathbf{Q})\cdot \mathbf{Q}(t). \tag{38}$$

Identification of h in terms of the physical variables A_i and external fields $a_i(\mathbf{r}, t)$ introduced in §2, leads to

$$A_i = -ex_i;\; A_{3+i} = -\frac{\partial V}{\partial Q_i},$$
$$a_i(\mathbf{r}_i, t_i) = E_i(t_i);\; a_{3+i} = Q_i; \quad i = 1, 2, 3. \tag{39}$$

The *electronic* response is now related to the evaluation of the expectation value of A_i, $i = 1, 2, 3$ only.

Using the commutation relations of the type

$$[x_i, p_j] = i\hbar\delta_{ij},$$
$$[H, x_i] = \frac{-i\hbar}{m} p_i,$$
$$[H, [H, x_i]] = (-i\hbar/m)(i\hbar)\frac{\partial V}{\partial x_i},$$
$$[p_i, f_j(\mathbf{x})] = -i\hbar\frac{\partial}{\partial x_i} f_j, \tag{40}$$

and other higher order relations, one can evaluate the leading terms in (35) and (34). If the susceptibility for N electrons is split into the pure electronic part and the Raman part in the form ($n_e = N$/volume):

$$n_e\langle -ex_i(\omega_1+\omega_2)\rangle_{2eEE} = \chi^{(2)eEE}_{ijk}(\omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2)$$
$$+ (\omega_1 \rightleftarrows \omega_2) \text{ term (if } \omega_1 \neq \omega_2)$$
$$n_e\langle -ex_i(\omega_1+\omega_2)\rangle_{2eQE} = \chi^{(2)eQE}_{ijk}(\omega_1, \omega_2)Q_j(\omega_1)E_k(\omega_2) \tag{41}$$
$$n_e\langle -ex_i(\omega_1+\omega_2)\rangle_{2eEQ} = \chi^{(2)eQE}_{ikj}(\omega_2, \omega_1)Q_k(\omega_2)E_j(\omega_1), \text{ etc.,}$$

so that i, j, k are allowed values 1, 2, 3 only, one finds that the leading terms in the expansion (35) arise from $n = 4$, $m = 0$ and $n = 3$, $m = 1$ for $\chi^{(2)eEE}(\omega_1, \omega_2)$, and from $n = 1, m = 1$ for $\chi^{(2)eQE}(\omega_1, \omega_2)$. For optical frequencies, we assume Q to be zero.

Explicitly, to the leading orders, we find

$$\chi^{(2)eEE}_{ijk}(\omega_1,\omega_2)$$

$$= \mathrm{sym}\,(j\omega_1, k\omega_2)\frac{-e^3}{m^3}\langle \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\frac{\partial}{\partial x_k} V\rangle$$

$$\times \left\{\frac{2}{(\omega_1+\omega_2)^5\,\omega_2}+\frac{1}{(\omega_1+\omega_2)^4\,\omega_2^2}\right\} n_e$$

$$= \frac{-e^3}{m^3}\frac{n_e}{(\omega_1+\omega_2)^2\,\omega_1^2\omega_2^2}\left\langle\left\{\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\frac{\partial}{\partial x_k} V\right\}\right\rangle, \tag{42}$$

and

$$\chi^{(2)eQE}_{ijk}(\omega_1,\omega_2) = \frac{-e^2}{m^2}\left\langle\left\{\frac{\partial}{\partial x_i}\frac{\partial}{\partial Q_j}\frac{\partial}{\partial x_k} V\right\}\right\rangle \frac{n_e}{(\omega_1+\omega_2)^2\,\omega_2^2}. \tag{43}$$

In the last equation, ω_2 and $\omega_1+\omega_2$ are both in the optical frequency range, the ionic frequency ω_1 being small compared to these frequencies.

Examination of (42) and (43) immediately shows that the second-order electronic nonlinearities at high frequencies, either of the optical mixing type or the Raman type, are related to the third derivative of the electronic potential $V(\mathbf{x},\mathbf{Q})$. The second derivative with respect to the electronic coordinate $\mathbf{x}$, of course, gives the linear harmonic force. The additional third derivative with respect to $\mathbf{x}$ leads to nonlinearity describing mixing, difference frequency generation and harmonic generations of two optical waves, whereas the additional derivative with respect to $\mathbf{Q}$ leads to the Raman process. Similarly, the existence of nonvanishing higher-order derivatives of V implies that the higher-order nonlinear response functions are non-zero for such systems. The explicit proof given here for the second-order nonlinearity justifies the use of such a nonlinear force term (Agarwal and Jha 1983) to model the dynamics of electronic system in a simplified way. The external ionic displacement field $\mathbf{Q}(\pm\omega_1)$ can, of course, be generated, *e.g.*, by mixing two optical fields $\mathbf{E}(\omega_2)$ and $\mathbf{E}(\pm\omega_1-\omega_2)$. When this is put in the second equation of (41), we immediately see how the Raman dipole polarization at $\omega_2\pm\omega_1$ gets related to a pure third-order nonlinear optical susceptibility, since it is then proportional to $\mathbf{E}(\omega_2)\,\mathbf{E}(\omega_2)\,\mathbf{E}(\pm\omega_1-\omega_2)$, on elimination of $\mathbf{Q}(\pm\omega_1)$ (Agarwal and Jha 1983).

Without further discussion, we conclude this paper by reminding ourselves that we have still not considered the consequences of the dispersion relations arising from the causality (Goldberger 1960) of linear as well as non-linear responses. The importance of these relations as well as other interesting applications of the nonlinear response theory will be considered in another paper.

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