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Asymptotic behaviour and general properties of harmonic generation susceptibilities

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Abstract. We use the Kubo response function formalism to derive the asymptotic behaviour of the harmonic generation susceptibilities to all orders n. The results show a stringent correspondence with the ones previously obtained from the classical anharmonic oscillator model. They are characterized by a ω^{-2n-2} dependence and a coefficient proportional to the trace of the $(n+1)$th derivative of the potential energy on the equilibrium density matrix. Using the above results we derive new Kramers-Krönig relations and sum rules for all orders of harmonics susceptibilities.

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1 Introduction

The theoretical and experimental investigation of harmonic generation processes is one of the most important branches of nonlinear optics [1,2]. Since the pioneering work on second harmonic generation by Franken [3], a continuous development in this field has produced experimental and theoretical studies of harmonic generation in solids [4–7], molecules [8] and atoms [9,10], up to very high orders [11,12] in the last case.

In nonlinear optics the use of integral properties such as Kramers-Krönig (K.K.) relations and sum rules is not as common as in linear optics, where they are tools of fundamental importance for the interpretation of optical data [13,14]. One reason might have been the modest attention paid to the general theory of holomorphic and integral properties of nonlinear susceptibilities [15], relevant efforts in this direction having been made only in recent years [16–19].

The purpose of this paper is to determine the asymptotic behaviour of harmonic generation susceptibilities of every order and to establish Kramers-Krönig relations and sum rules, thus extending the results already obtained for the second [20] and third [21] harmonics. The general quantum theory of Kubo optical response function [22] is used.

The results obtained display a strict analogy with those previously derived [23] with the classical anharmonic oscillator model [1,24,25], thus demonstrating its relevance to the theory of nonlinear susceptibilities, as assumed by Peiponen [19].

In Section 2 we define the harmonic generation susceptibilities and obtain their explicit expressions. In Section 3 we analyse their asymptotic behaviours. In Section 4 we obtain K.K. relations and derive sum rules to all orders. In Section 5 we summarize our conclusions.

2 Quantum expression for the harmonic generation susceptibility $\chi^{(n)}_{ij_1j_2\ldots j_n}(n\omega;\omega,\ldots,\omega)$

We consider N electrons in a volume V interacting with an external static potential $V(\mathbf{r})$ and repelling each other with Coulomb interaction, and we study the effect of their coupling with the electromagnetic field of the incident radiation. Therefore the total Hamiltonian of the system is given by the sum of two terms: the first term H_0 represents the unperturbed Hamiltonian:

$$H_0=\sum_{\alpha=1}^{N}\frac{p_\alpha^2}{2m}+\sum_{\alpha=1}^{N}V(\mathbf{r}_\alpha)+\frac{1}{2}\sum_{\alpha\neq\beta=1}^{N}\frac{e^2}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}; \quad (1)$$

the second term H' is given by the interaction of the electrons with the electromagnetic field which we express in the velocity gauge [26]:

$$H'=\sum_{\alpha=1}^{N}\left(e\frac{p_j^\alpha A_j(t)}{mc}+\frac{A_j(t)A_j(t)}{2mc^2}\right), \quad (2)$$

where the dipolar approximation has been adopted.

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The polarization vector $\mathbf{P}(t)$ is defined as:

$$P_i(t) \equiv -\frac{e}{V}\mathrm{Tr}\left\{\sum_{\alpha=1}^{N} r_i^\alpha \rho(t)\right\} \tag{3}$$

where $\rho(t)$ is the density matrix evaluated at the time t which obeys the quantum Liouville equation [27]:

$$\mathrm{i}\hbar\frac{\partial\rho(t)}{\partial t} = [H,\rho(t)] = [H_0,\rho(t)] + [H',\rho(t)], \tag{4}$$

with the initial condition at $t = 0$ given by the Boltzmann equilibrium density matrix [27]:

$$\rho(0) = \frac{\sum_a \mathrm{e}^{-E_a/KT}|a\rangle\langle a|}{\sum_a \mathrm{e}^{-E_a/KT}}, \tag{5}$$

the sum being made on a complete set of eigenstates $|a\rangle$ of the unperturbed Hamiltonian H_0 in the Hilbert space of N identical fermionic particles.

We can solve perturbatively equation (4) by expressing $\rho(t)$ as a sum [28] of terms of decreasing magnitude:

$$\rho(t) = \rho(0) + \rho^{(1)}(t) + \rho^{(2)}(t) + ... + \rho^{(n)}(t), \tag{6}$$

and using an iterative procedure. We thus derive the expression of $\rho^{(n)}(t)$ and use it to obtain the following explicit expression of the nth order nonlinear polarization at time t:

$$P_i^{(n)}(t) = -\frac{e}{V}\mathrm{Tr}\left\{\sum_{\alpha=1}^{N} r_i^\alpha \rho^{(n)}(t)\right\} = -\frac{e^{n+1}}{V(-\mathrm{i}\hbar mc)^n}$$
$$\times\ \mathrm{Tr}\left\{\int_{-\infty}^{+\infty}\mathrm{d}\tau_1\mathrm{d}\tau_2...\mathrm{d}\tau_n\theta(\tau_1)\theta(\tau_2-\tau_1)...\theta(\tau_n-\tau_{n-1})\right.$$
$$\times A_{j_1}(t-\tau_1)...A_{j_n}(t-\tau_n)\left[\sum_{\alpha=1}^{N} p_{j_n}^\alpha(-\tau_n)...,\left[\sum_{\alpha=1}^{N} p_{j_2}^\alpha(-\tau_2),\right.\right.$$
$$\left.\left.\left.\left[\sum_{\alpha=1}^{N} p_{j_1}^\alpha(-\tau_1),\sum_{\alpha=1}^{N} r_i^\alpha\right]\right]\right]\rho(0)\right\}, \tag{7}$$

where $\theta(\tau)$ is the usual step function. This is equivalent to the Kubo formulation [22], the difference being the choice of gauge.

We now focus on the typical experimental set-up where the incident radiation is given by a strictly monochromatic and linearly polarized field so that we can express $\mathbf{A}(t)$ as:

$$\mathbf{A}(t) = \sum_{j=1}^{3}\hat{\varepsilon}_j\frac{cE_j}{\mathrm{i}\omega}\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{c.c.} \tag{8}$$

where $\hat{\varepsilon}_j$ are the unit vectors $\hat{x}, \hat{y}, \hat{z}$.

Since we are interested in the study of the nth order harmonic generation processes we seek the $n\omega$ frequency component of the induced nonlinear polarization $P_i^{(n)}(t)$. This component is by definition proportional to $\mathrm{e}^{\mathrm{i}n\omega t}$ and is given by the contribution to the term $A_{j_1}(t-\tau_1)...A_{j_k}(t-\tau_n)$ in (7) obtained by the product of the only positive frequency components ($\propto \mathrm{e}^{-\mathrm{i}\omega t}$) of every factor $A_{j_i}(t-\tau_i)$. It can be written as:

$$P_i^{(n)}(t)_{n\omega} = \chi_{ij_1,...,j_n}^{(n)}\left(n\omega;\underbrace{\omega,...,\omega}_{n\,\text{times}}\right)E_{j_1}...E_{j_n}\mathrm{e}^{\mathrm{i}n\omega t}, \tag{9}$$

where the nth order harmonic generation susceptibility is:

$$\chi_{ij_1,...,j_n}^{(n)}\left(n\omega;\underbrace{\omega,...,\omega}_{n\,\text{times}}\right) \equiv -\frac{e^{n+1}}{V(\hbar m)^n\omega^n}$$
$$\times\int_{-\infty}^{+\infty}\mathrm{d}\tau_1...\mathrm{d}\tau_n\theta(\tau_1)\theta(\tau_2-\tau_1)...\theta(\tau_n-\tau_{n-1})$$
$$\times\mathrm{e}^{\mathrm{i}\omega\tau_1}\mathrm{e}^{\mathrm{i}\omega\tau_2}...\mathrm{e}^{\mathrm{i}\omega\tau_n}\mathrm{Tr}\left\{\left[\sum_{\alpha=1}^{N} p_{j_n}^\alpha(-\tau_n),...,\left[\sum_{\alpha=1}^{N} p_{j_2}^\alpha(-\tau_2),\right.\right.\right.$$
$$\left.\left.\left.\left[\sum_{\alpha=1}^{N} p_{j_1}^\alpha(-\tau_1),\sum_{\alpha=1}^{N} r_i^\alpha\right]\right]...\right]\rho(0)\right\}. \tag{10}$$

Also the linear susceptibility $\chi_{ij}^{(1)}(\omega)$ is included in the above expression when we set $n = 1$. For every n the function $\chi_{ij_1j_2\cdots j_n}^{(n)}(n\omega;\omega,...,\omega)$ is holomorphic in the upper complex ω-plane. In the linear case this can be deduced directly from Titmarsch's theorem [29,30], while in the nonlinear case the proof can be obtained applying Scandolo's theorem [17].

Another general property of the $\chi_{ij_1j_2\cdots j_n}^{(n)}(n\omega;\omega,...,\omega)$ is:

$$\chi_{ij_1j_2\cdots j_n}^{(n)}(n\omega;\omega,...,\omega) = \left(\chi_{ij_1j_2\cdots j_n}^{(n)}(-n\omega;-\omega,...,-\omega)\right)^* \quad \forall n, \tag{11}$$

which can be deduced from (9) taking into account that $\left(P_i^{(n)}(t)_{n\omega} + P_i^{(n)}(t)_{-n\omega}\right)$ has to be a real quantity, since it describes a real polarization.

3 Asymptotic behaviour of the harmonic generation susceptibility $\chi_{ij_1j_2\cdots j_n}^{(n)}(n\omega;\omega,...,\omega)$

The main goal of our study is to determine the asymptotic behaviour of the factor $\chi_{ij_1j_2\cdots j_n}^{(n)}(n\omega;\omega,...,\omega)$. We shall see that it is substantially determined by the short time behaviour of the factor $\mathrm{Tr}\{[...]\rho(0)\}$ in expression (10), as expected from the fact that the frequency dependent susceptibility is its Fourier transform. Our approach is similar to that used in previous works for the study of integral properties of $\chi_{ij_1j_2}^{(2)}(2\omega;\omega,\omega)$ [20] and $\chi_{ij_1j_2j_3}^{(3)}(3\omega;\omega,\omega)$ [21], but allows a natural extension to all orders n.

We begin our analysis by applying in (10) the following variables change:

$$\tau_j = \sum_{i=1}^{j} t_i \qquad 1 \le j \le n \tag{12}$$

$$\chi^{(n)}_{ij_1j_2\ldots j_n}\left(n\omega;\underbrace{\omega,\ldots,\omega}_{n\,\text{times}}\right)=-\frac{e^{n+1}}{V(\hbar m)^n\omega^n}\int_{-\infty}^{+\infty}\mathrm{d}t_1\ldots\mathrm{d}t_n\theta(t_1)\theta(t_2)\ldots\theta(t_n)\mathrm{e}^{\mathrm{i}\omega\sum_{j=1}^{n}(n+1-j)t_j}\mathrm{Tr}\left\{\left[\sum_{m_n=0}^{\infty}\sum_{\alpha=1}^{N}b^{\alpha}_{m_n,j_n},\ldots,\left[\sum_{m_2=0}^{\infty}\sum_{\alpha=1}^{N}b^{\alpha}_{m_2,j_2},\left[\sum_{m_1=0}^{\infty}\sum_{\alpha=1}^{N}b^{\alpha}_{m_1,j_1},\sum_{\alpha=1}^{N}r^{\alpha}_i\right]\right]\ldots\right]\rho(0)\right\}\frac{(t_1+\ldots+t_n)^{m_n}}{m_n!}\ldots\frac{(t_1+t_2)^{m_2}}{m_2!}\frac{t_1^{m_1}}{m_1!}=-\frac{e^{n+1}}{V(\hbar m)^n\omega^n}$$
$$\times\int_{-\infty}^{+\infty}\mathrm{d}t_1\ldots\mathrm{d}t_n\theta(t_1)\theta(t_2)\ldots\theta(t_n)\mathrm{e}^{\mathrm{i}\omega\sum_{j=1}^{n}(n+1-j)t_j}\sum_{m_n=0}^{\infty}\ldots\sum_{m_2=0}^{\infty}\sum_{m_1=0}^{\infty}B^{m_1,m_2,\ldots,m_n}_{i,j_1,j_2,\ldots,j_n}\frac{(t_1+\ldots+t_n)^{m_n}}{m_n!}\ldots\frac{(t_1+t_2)^{m_2}}{m_2!}\frac{t_1^{m_1}}{m_1!}\quad(16)$$

and obtain for the harmonic generation susceptibilities:

$$\chi^{(n)}_{ij_1j_2\ldots j_n}\left(n\omega;\underbrace{\omega,\ldots,\omega}_{n\,\text{times}}\right)=-\frac{e^{n+1}}{V(\hbar m)^n\omega^n}\times\int_{-\infty}^{+\infty}\mathrm{d}t_1\ldots\mathrm{d}t_n\theta(t_1)\theta(t_2)\ldots\theta(t_n)\mathrm{e}^{\mathrm{i}\omega\sum_{j=1}^{n}(n+1-j)t_j}\times\mathrm{Tr}\left\{\left[\sum_{\alpha=1}^{N}p^{\alpha}_{j_n}(-t_n-\ldots-t_1),\ldots,\left[\sum_{\alpha=1}^{N}p^{\alpha}_{j_2}(-t_2-t_1),\left[\sum_{\alpha=1}^{N}p^{\alpha}_{j_1}(-t_1),\sum_{\alpha=1}^{N}r^{\alpha}_i\right]\right]\ldots\right]\rho(0)\right\}.\quad(13)$$

Now we perform a Taylor expansion of the time-dependent momentum operators about the value zero of their argument:

$$\sum_{\alpha=1}^{N}p^{\alpha}_{j_i}(-t)=\sum_{\alpha=1}^{n}p^{\alpha}_{j}+\sum_{m=1}^{\infty}\sum_{\alpha=1}^{N}\left(\frac{1}{\mathrm{i}\hbar}\right)^m\times\underbrace{[[\ldots[[p^{\alpha}_j,H_0],\ldots,]H_0]}_{m\,\text{times}}\frac{(-t)^m}{m!}=\sum_{\alpha=1}^{n}p^{\alpha}_{j}+\sum_{m=1}^{\infty}\sum_{\alpha=1}^{N}\left(\frac{1}{\mathrm{i}\hbar}\right)^m\times\underbrace{[H_0,\ldots,[H_0,[H_0,p^{\alpha}_j]]\ldots]}_{m\,\text{times}}\frac{t^m}{m!}=\sum_{m=0}^{\infty}\sum_{\alpha=1}^{N}b^{\alpha}_{m,j}\frac{t^m}{m!}\quad(14)$$

where we have used the commutators' antisymmetry and have defined the coefficients $b^{\alpha}_{m,j}$ as:

$$b^{\alpha}_{m,j}\equiv\left(\frac{1}{\mathrm{i}\hbar}\right)^m\underbrace{[H_0,\ldots,[H_0,p^{\alpha}_j]]\ldots]}_{m\,\text{times}}.\quad(15)$$

Inserting the above expression in (13) we obtain:

see equation (16) above

where we have introduced the following tensorial constants for every term corresponding to the set of upper indexes $\{m1,\ldots,m_n\}$:

$$B^{m_1,m_2,\ldots,m_n}_{i,j_1,j_2,\ldots,j_n}\equiv\mathrm{Tr}\left\{\left[\sum_{\alpha=1}^{N}b^{\alpha}_{m_n,j_n},\ldots,\left[\sum_{\alpha=1}^{N}b^{\alpha}_{m_2,j_2},\left[\sum_{\alpha=1}^{N}b^{\alpha}_{m_1,j_1},\sum_{\alpha=1}^{N}r^{\alpha}_i\right]\right]\ldots\right]\rho(0)\right\}.\quad(17)$$

We now concentrate on the term of the summation inside the integral (16) having $B^{m_1,m_2,\ldots,m_n}_{i,j_1,j_2,\ldots,j_n}$ as common factor, with the purpose of considering only those terms which give the lowest asymptotic decrease in ω and are then responsible for the asymptotic behaviour of the susceptibility. We expand the polynomials of the temporal variables t_i and obtain the sum of many contributions which, apart from numerical factors and the $B^{m_1,m_2,\ldots,m_n}_{i,j_1,j_2,\ldots,j_n}$ coefficient, are:

$$\theta(t_1)\theta(t_2)\ldots\theta(t_n)t_i^{p_1}t_2^{p_2}\ldots t_n^{p_n}\mathrm{e}^{\mathrm{i}\omega l_j t_j}\quad\text{where}\quad l_j=n+1-j,\quad(18)$$

with sets $\{p_1,\ldots,p_n\}$ such as $m_1+\ldots+m_n=p_1+\ldots+p_n$ thanks to the homogeneity in the total power of the temporal variables. Using the well known result of distributions theory [31]:

$$\int_{-\infty}^{+\infty}\theta(t_1)t_i^{p}\mathrm{e}^{\mathrm{i}l\omega t}=\left(\frac{-\mathrm{i}}{l}\right)^p\frac{\mathrm{d}^p}{\mathrm{d}\omega^p}\left(\mathrm{i}P\left(\frac{1}{l\omega}\right)+\pi\delta(l\omega)\right),\quad(19)$$

we notice that the asymptotic behaviour in ω of the integral in (19) is $\propto\omega^{-p-1}$. This result can be used to integrate expression (18) variable by variable and to obtain:

$$\int_{-\infty}^{+\infty}\mathrm{d}t_1\mathrm{d}t_2\ldots\mathrm{d}t_n\theta(t_1)\theta(t_2)\ldots\theta(t_n)t_i^{p_1}t_2^{p_2}\ldots t_n^{p_n}\mathrm{e}^{\mathrm{i}\omega\sum_{j=1}^{n}l_jt_j}\propto\left(\frac{1}{\omega}\right)^{p_1+p_2+\ldots+p_n+n}=\left(\frac{1}{\omega}\right)^{m_1+m_2+\ldots+m_n+n}.\quad(20)$$

We notice that the power dependence of the Fourier transform of expression (18) is given by n plus the sum on the exponents of the temporal variables, which is fixed to be $m_1+\ldots+m_n$ for every term having $B^{m_1,m_2,\ldots,m_n}_{i,j_1,j_2,\ldots,j_n}$ as common factor. Therefore each of these terms, carrying out the integration in (16), results to be proportional to $B^{m_1,m_2,\ldots,m_n}_{i,j_1,j_2,\ldots,j_n}\omega^{-2n-(\sum_{j=1}^{n}m_j)}$. From this we derive that

$$B^{2,0,\dots,0}_{i,j_1,j_2,\dots,j_n} \equiv \mathrm{Tr}\left\{\left[\sum_{\alpha=1}^N p^\alpha_{j_n},\dots,\left[\sum_{\alpha=1}^N p^\alpha_{j_2},\left[\sum_{\alpha=1}^N b_{m_1=2,j_i},\sum_{\alpha=1}^N r^\alpha_i\right]\right]\dots\right]\rho(0)\right\}$$
$$= \mathrm{Tr}\left\{\left[\sum_{\alpha=1}^N p^\alpha_{j_n},\dots,\left[\sum_{\alpha=1}^N p^\alpha_{j_2},\mathrm{i}\hbar\sum_{\alpha=1}^N \frac{\partial^2 V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_i}\partial r^\alpha_i}\right]\dots\right]\rho(0)\right\}$$
$$= (\mathrm{i}\hbar)^n(-1)^{n-1}\mathrm{Tr}\left\{\sum_{\alpha=1}^N \frac{\partial^{n+1}V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_n}\dots\partial r^\alpha_{j_2}\partial r^\alpha_{j_i}\partial r^\alpha_i}\rho(0)\right\} = (\mathrm{i}\hbar)^n(-1)^{n-1}N\,\mathrm{Tr}\left\{\frac{\partial^{n+1}V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_n}\dots\partial r^\alpha_{j_2}\partial r^\alpha_{j_i}\partial r^\alpha_i}\rho(0)\right\}, \tag{26}$$

the problem of finding the asymptotic behaviour of the $\chi^{(n)}_{i,j_1,j_2,\dots,j_n}(n\omega;\omega,\dots,\omega)$ is equivalent for every order n to seeking the nonvanishing terms $B^{m_1,m_2,\dots,m_n}_{i,j_1,j_2,\dots,j_n}$ which have the minimum value of the sum of the upper indexes.

To exemplify the procedure we first carry out the calculations for the linear case ($n = 1$). The susceptibility is:

$$\chi^{(1)}_{ij}(\omega) = -\frac{e^2}{V\hbar m\omega}\int_{-\infty}^{+\infty} \mathrm{d}t_1\theta(t_1)\mathrm{e}^{\mathrm{i}\omega t} \times \mathrm{Tr}\left\{\left[\sum_{\alpha=1}^N p^\alpha_j(-t_1),\sum_{\alpha=1}^N r^\alpha_i\right]\rho(0)\right\}. \tag{21}$$

The nonvanishing B^m_{ij} with the minimum value of m is B^0_{ij}:

$$B^0_{ij} = \mathrm{Tr}\left\{\left[\sum_{\alpha=1}^N p^\alpha_j,\sum_{\alpha=1}^N r^\alpha_i\right]\rho(0)\right\} = \mathrm{Tr}\left\{-\mathrm{i}\hbar N\delta_{ij}\rho(0)\right\} = -\mathrm{i}\hbar N\delta_{ij}. \tag{22}$$

and we obtain the well known result of linear optics:

$$\chi^{(1)}_{ij}(\omega) = \frac{e^2}{V\hbar m\omega}\int_{-\infty}^{+\infty} \mathrm{d}t_1(\theta(t_1)\mathrm{e}^{\mathrm{i}\omega t}(-\mathrm{i}\hbar N\delta_{ij}) + O(t_1^0))$$
$$= -\frac{e^2N}{mV}\frac{1}{\omega^2}\delta_{ij} + o(\omega^{-2}) = -\frac{\omega_p^2}{4\pi}\frac{1}{\omega^2}\delta_{ij} + o(\omega^{-2}), \tag{23}$$

where $O(t_1^0))$ represents all the powers of t_1 having degree higher than zero, and $o(\omega^{-2})$ represents all the terms having a power decrease at infinity faster than ω^{-2}.

In the nonlinear case ($n > 1$) the factor $B^{m_1,m_2,\dots,m_n}_{i,j_1,j_2,\dots,j_n}$ (17) having nonvanishing value and minimum sum $m_1+m_2+\dots+m_n$ is unique for every n considered. We prove that $B^{2,0,\dots,0}_{i,j_1,j_2,\dots,j_n}$ is such a term. The proof relies on the fact that terms with $m_1 < 2$ vanish and the others have higher sum of the upper indexes. If $m_1 = 0$ the inmost commutator in the expression of $B^{0,m_2,\dots,m_n}_{i,j_1,j_2,\dots,j_n}$:

$$B^{0,m_2,\dots,m_n}_{i,j_1,j_2,\dots,j_n} \equiv \mathrm{Tr}\left\{\left[\sum_{\alpha=1}^N b^\alpha_{m_k,j_k},\dots,\left[\sum_{\alpha=1}^N b^\alpha_{m_2,j_2}, \left[\sum_{\alpha=1}^N p^\alpha_{j_i},\sum_{\alpha=1}^N r^\alpha_i\right]\right]\dots\right]\rho(0)\right\} \tag{24}$$

has a constant value and so the expression vanishes. In the case m_1, the inmost commutator of $B^{1,m_2,\dots,m_n}_{i,j_1,j_2,\dots,j_n}$ is:

$$\left[\sum_{\alpha=1}^N b^\alpha_{m_1,j_1},\sum_{\alpha=1}^N r^\alpha_i\right] = \left[\sum_{\alpha=1}^N\left(\frac{1}{\mathrm{i}\hbar}\right)\left[H_0,p^\alpha_{j_i}\right],\sum_{\alpha=1}^N r^\alpha_i\right]$$
$$= \left[\sum_{\alpha=1}^N \frac{\partial V(r^\alpha_{j_i})}{\partial r^\alpha_{j_i}} + \frac{1}{2}\sum_{\alpha\neq\beta=1}^N \frac{\partial}{\partial r^\alpha_{j_i}}\left(\frac{e^2}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}\right)\right.$$
$$\left.+\frac{\partial}{\partial r^\beta_{j_i}}\left(\frac{e^2}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}\right),\sum_{\alpha=1}^N r^\alpha_i\right] = \left[\sum_{\alpha=1}^N\frac{\partial V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_i}},\sum_{\alpha=1}^N r^\alpha_i\right] = 0, \tag{25}$$

since both commutator arguments are operators depending only on spatial variables. Therefore $B^{1,m_2,\dots,m_n}_{i,j_1,j_2,\dots,j_n} = 0$. We notice that the relevance of the Coulombian $e-e$ repulsive potential is always null since it is invariant for translations of the whole set of particles and so commutes with the sum of all the momenta of the particles. In the case of $m_1 = 2$ we directly prove that have that the term $B^{m_1=2,m_2=0,\dots,m_n=0}_{i,j_1,j_2,\dots,j_n}$ is not identically vanishing:

see equation (26) above

where we have used the fact that the electrons are indistinguishable. This term $B^{m_1=2,m_2=0,\dots,m_n=0}_{i,j_1,j_2,\dots,j_n}$ determines the asymptotic behaviour $\chi^{(n)}_{ij_1,\dots,j_n}(n\omega;\omega,\dots,\omega)$ because it doesn't vanish and has the minimum sum of the upper indexes.

Using this result in equation (17) we obtain the final result:

see equation (27) next page

where $O(\{t\}^2)$ denotes all the monomials having a total power degree in the temporal variables higher that two and $o(\omega^{-2n-2})$ denotes the terms with an asymptotic behaviour faster than ω^{-2n-2}.

We observe that the fundamental quantum constant $\hbar$ doesn't appear in the formula (27) which gives the asymptotic behaviour of the nth order harmonic generation susceptibility, since it cancels out between denominator and numerator. The quantum aspect of the expression we have obtained appears only in the definition of expectation value of the derivatives of the potential energy on the equilibrium density matrix of the system.

The results we have obtained through a fully quantum mechanical treatment show a clear correspondence

$$\chi^{(n)}_{ij_1,\ldots,j_n}\Bigg(n\omega;\underbrace{\omega,\ldots,\omega}_{n\,\text{times}}\Bigg) = -\frac{e^{n+1}}{V(\hbar m)^n\omega^n}\int_{-\infty}^{+\infty}\mathrm{d}t_1\ldots\mathrm{d}t_n\Bigg(\theta(t_1)\theta(t_2)\ldots\theta(t_n)\mathrm{e}^{\mathrm{i}\omega\sum_{j=1}^{n}(n+1-j)t_j}B^{2,0,\ldots,0}_{i,j_1,j_2,\ldots,j_n}$$
$$\times\frac{(t_1+\ldots+t_n)^{m_n}}{m_n!}\ldots\frac{(t_1+t_2)^{m_2}}{m_2!}\frac{t_1^{m_1}}{m_1!}\Bigg|_{m_1=2,m_2=0,\ldots,m_n=0}+O\left(\{t\}^2\right)\Bigg) = \frac{e^{n+1}}{V(\hbar m)^n\omega^n}B^{2,0,\ldots,0}_{i,j_1,j_2,\ldots,j_n}\int_{-\infty}^{+\infty}\mathrm{d}t_1\ldots\mathrm{d}t_n$$
$$\Big(\theta(t_1)\theta(t_2)\ldots\theta(t_n)\mathrm{e}^{\mathrm{i}\omega\sum_{j=1}^{n}(n+1-j)t_j}+O(\{t\}^2)\Big) = \frac{e^{n+1}}{V(\hbar m)^n\omega^n}(-1)^{n-1}\frac{(\mathrm{i}\hbar)^n}{m}\mathrm{Tr}\left\{\sum_{\alpha=1}^{N}\frac{\partial^{n+1}V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_n}\ldots\partial r^\alpha_{j_2}\partial r^\alpha_{j_i}\partial r^\alpha_i}\rho(0)\right\}\left(\frac{\mathrm{i}}{n\omega}\right)^3$$
$$\times\prod_{j=2}^{N}\left(\frac{\mathrm{i}}{(n+1-j)\omega}\right)+o(\omega^{-2n-2}) = \frac{(-1)^n}{m^2 n!}\frac{e^{n+1}}{m^{n+1}}\frac{1}{V}\mathrm{Tr}\left\{\sum_{\alpha=1}^{N}\frac{\partial^{n+1}V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_n}\ldots\partial r^\alpha_{j_2}\partial r^\alpha_{j_i}\partial r^\alpha_i}\rho(0)\right\}\frac{1}{\omega^{n+2}}+o(\omega^{-2n-2})$$
$$= \frac{(-1)^n}{m^2 n!}\frac{e^{n+1}}{m^{n+1}}\frac{N}{V}\mathrm{Tr}\left\{\frac{\partial^{n+1}V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_n}\ldots\partial r^\alpha_{j_2}\partial r^\alpha_{j_i}\partial r^\alpha_i}\rho(0)\right\}\frac{1}{\omega^{2n+2}}+o(\omega^{-2n-2}) \quad (27)$$

with the ones we derived from the anharmonic oscillator model [23], provided we consider the expectation value of the derivatives of the potential energy as the quantum analogue of the same derivatives of the classical potential energy evaluated at the equilibrium position. Therefore the asymptotic behaviours of the harmonic generation susceptibilities and consequently their integral properties do not essentially depend on the microscopic treatment of the interaction between light and matter, but are connected to the validity of the causality principle in physical systems.

4 K.K. relations and sum rules for the $\chi^{(n)}_{ij_1j_2\ldots j_n}(n\omega;\omega,\ldots,\omega)$

In the case of non-metallic matter the knowledge of the asymptotic behaviour of the $\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega;\omega,\ldots,\omega)$ and its properties of holomorphicity in the upper complex ω plane due to the application of Scandolo's theorem [17] allow us to write the following set of $2n+2$ K.K. type equations for the nonlinear harmonic susceptibilities:

$$\omega^{2\alpha}\Re\left(\chi^{(k)}_{ij_1,j_2,\ldots,j_n}(n\omega;\omega,\ldots,\omega)\right) = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega'\frac{\omega'^{2\alpha+1}\Im\left(\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega';\omega',\ldots,\omega')\right)}{\omega'^2-\omega^2} \quad (28a)$$

$$\omega^{2\alpha-1}\Im\left(\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega;\omega,\ldots,\omega)\right) = -\frac{2}{\pi}\int_0^\infty \mathrm{d}\omega'\frac{\omega'^{2\alpha}\Re\left(\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega';\omega',\ldots,\omega')\right)}{\omega'^2-\omega^2} \quad (28b)$$

$$\text{with}\qquad 0\le\alpha\le n,$$

where α is such that the αth moment of the harmonic susceptibility considered decrease at infinity at least as fast as ω^{-2}. In the linear case, due to the ω^{-2} asymptotic decrease of the susceptibility, only the case $\alpha=0$ can be considered.

We observe that the number of independent K.K. relations grows with the order of the process of harmonic generation considered. The relations (28a, 28b) generalize to all orders the results previously obtained for the second [20] and third [21] harmonic susceptibilities.
For what concerns the experimental use of such K.K. type relations we recall that Kishida *et al.* [32] have experimentally verified their validity for the third harmonic process in the case $\alpha=0$. This K.K. relation has been used in theoretical studies of second and third harmonic generation susceptibilities by Moss *et al.* [33] to obtain the real parts from the theoretical evaluation of the imaginary parts.

Comparing the asymptotic behaviours as obtained from expression (27) with those obtained by applying the superconvergence theorem [34] to the K.K. relations (28) we immediately obtain the following set of sum rules:

$$\int_0^\infty \mathrm{d}\omega'\omega'^{2\alpha}\Re\left(\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega';\omega',\ldots,\omega')\right)=0 \qquad \text{with}\ \ 0\le\alpha\le n \quad (29a)$$

$$\int_0^\infty \mathrm{d}\omega'\omega'^{2\alpha+1}\Im\left(\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega';\omega',\ldots,\omega')\right)=0 \qquad \text{with}\ \ 0\le\alpha\le n \quad (29b)$$

$$\int_0^\infty \mathrm{d}\omega'\omega'^{2n+1}\Im\left(\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega';\omega',\ldots,\omega')\right) = \frac{\pi}{2}\frac{(-1)^n}{m^2 n!}\frac{e^{n+1}}{m^{n+1}}\frac{1}{V}\mathrm{Tr}\left\{\sum_{\alpha=1}^{N}\frac{\partial^{n+1}V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_n}\ldots\partial r^\alpha_{j_2}\partial r^\alpha_{j_i}\partial r^\alpha_i}\rho(0)\right\} = \frac{\pi}{2}\frac{(-1)^n}{m^2 n!}\frac{e^{n+1}}{m^{n+1}}\frac{N}{V}\mathrm{Tr}\left\{\frac{\partial^{n+1}V(\mathbf{r}_\alpha)}{\partial r^\alpha_{j_n}\ldots\partial r^\alpha_{j_2}\partial r^\alpha_{j_i}\partial r^\alpha_i}\rho(0)\right\}. \quad (29c)$$

All the moments of the susceptibility vanish except the one of order $2n+1$ of the imaginary part of $\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega;\omega,\ldots,\omega)$. Its value relates the nonlinearity of the potential energy of the system to the measurements of the imaginary part of the $\chi^{(n)}_{ij_1,j_2,\ldots,j_n}(n\omega;\omega,\ldots,\omega)$.

Up to now we do not have knowledge of experimental results related to the sum rules of harmonic generation processes, while pump and probe sum rules [35,36], have been used in the interpretation of an E.I.T. experiment [37] and in other cases mentioned in the review paper by Sheik-Bahae [38].

Metallic solids are characterized by the presence of a nonvanishing static conductance, which changes the integral properties of their nth order harmonic generation susceptibilities as in linear optics [8,39–42]. Remembering that at every order the susceptibility can always be expressed in terms of the conductivity:

$$\chi^{(n)}_{ij_1,j_2,...,j_n}(n\omega;\omega,...,\omega) = \mathrm{i}\frac{\sigma^{(n)}_{ij_1,j_2,...,j_n}(n\omega;\omega,...,\omega)}{n\omega}, \tag{30}$$

for frequencies close to zero in the case of metals we have:

$$\chi^{(n)}_{ij_1,j_2,...,j_n}(n\omega;\omega,...,\omega)|_{\omega\approx 0} \approx \mathrm{i}\frac{\sigma^{(n)}_{ij_1,j_2,...,j_n}(0)}{n\omega}, \tag{31}$$

where $\sigma^{(n)}_{ij_1,j_2,...,j_n}(0)$ is the nonvanishing real tensor of nonlinear static conductance of order n.

The presence of this pole at the origin of the ω-axe changes the second one of the K.K. relations (28b) in the case $\alpha = 0$:

$$P\int_0^\infty \mathrm{d}\omega' \frac{\Re\left(\chi^{(n)}_{ij_1,j_2,...,j_n}(n\omega';\omega',...,\omega')\right)}{\omega'^2-\omega^2} = -\frac{\pi}{2\omega}\Im\left(\chi^{(n)}_{ij_1,j_2,...,j_n}(n\omega;\omega,...,\omega)\right) + \frac{\pi}{2}\frac{\sigma^{(n)}_{ij_1,j_2,...,j_n}(0)}{n\omega^2}, \tag{32}$$

and the related sum rule (29a):

$$P\int_0^\infty \mathrm{d}\omega' \Re\left(\chi^{(n)}_{ij_1,j_2,...,j_n}(n\omega';\omega',...,\omega')\right) = -\frac{\pi}{2n}\sigma^{(n)}_{ij_1,j_2,...,j_n}(0). \tag{33}$$

They extend to the nonlinear case the well known results of linear optics, which have been experimentally verified [39–42].

The K.K. relations and related sum rules we obtain in the nonlinear case setting $1 \leq \alpha \leq n$ remain unchanged for metallic matter because the moments of the susceptibilities $\omega^{2\alpha}\chi^{(n)}_{ij_1,j_2,...,j_n}(n\omega;\omega,...,\omega)$ don't have poles at the origin.

In all the applications to solid material we have considered the Maxwell average electromagnetic field as external perturbation. If strongly localized states have to be taken into account we should consider for those transitions the local field corrections, and our expression for the nth order harmonic generation susceptibility should be multiplied by the nth power of:

$$\frac{E_{\mathrm{loc}}(\omega)}{E(\omega)} = \frac{n^2_{\mathrm{lin}}(\omega)+2}{3}\,. \tag{34}$$

This factor doesn't change the analytical properties and the asymptotic behaviour of the harmonic generation susceptibilities since the linear refractive index $n_{\mathrm{lin}}(\omega)$ is analytical in the upper complex ω plane and the asymptotic limit of expression (34) for $\omega \to \infty$ is 1. Therefore the K.K. relations and the sum rules are not affected by the inclusion of the local field corrections. Modifications to the susceptibilities considered occur in the individual transitions.

5 Conclusions

We can summarize the main results obtained above as follows.

With a rigorous quantum mechanical perturbative treatment we have derived general integral properties of the $\chi^{(n)}_{ij_1j_2...j_n}(n\omega,\omega,...,\omega)$, in particular $2n+2$ new K.K. type relations and sum rules. They impose many constraints which must be verified by all experimental data and must be obeyed by any detailed theory regarding harmonic generation susceptibilities.

The above results display a stringent correspondence with the ones previously obtained from the anharmonic oscillator model [23], the reason being that the temporal causality is the only basic ingredient determining the integral properties of the susceptibility.

We have also included in our treatment the particular case of metallic solids, presenting the modifications appearing order by order in one K.K. relation and in its related sum rule because of the nonvanishing of the static nonlinear conductivity.

We conclude that the general results here presented are of interest for the interpretation of experimental data in all materials, and for the elaboration of approximate models, as done in the case of second [43] and third [21] harmonics. The basic factor which distinguishes different systems is the trace of the directional derivatives of the potential energy on the equilibrium density matrix.

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