THEORY OF MULTIPHOTON TRANSITION PROBABILITIES

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The formal quantal theory of first-, second-, and higher- order radiation processes inherent in electric and magnetic multipole transitions is developed. The calculated probabilities of two- or more-photon processes consist not only of indirect multipole transitions from initial to final states via one or more successive virtual states, but also of a direct multipole transition related to the second- or higher-order time-dependent interaction Hamiltonian. The general results are discussed in some special cases of electric or magnetic dipolar, quadrupolar, etc. transitions. Tensors of electric and magnetic multipole polarization are derived in the r-th — order approximation of quantal perturbation theory and expressed in terms of r-th — order multipole susceptibility tensors and electromagnetic field strengths in the r-th power. The multipole and nonlinear formalism is given in a compact tensorial notation and can be applied for computing various multiple-photon processes, the investigation of which is liable to provide information on the change undergone by atoms or molecules under the influence of intense electromagnetic fields, *e.g.* from lasers.

1. Introduction

The theory of radiation processes as initiated by Dirac [1] has been developed by many authors (see *e.g.* the monograph of Heitler [2] and the papers cited by him) basing on both semiclassical and quantum electrodynamics methods. A theory of two-photon electric dipole emission and absorption of light was first given by Goeppert-Mayer [3]. Nonlinear scattering processes in which three or more photons participate were considered by Blaton [4], Güttinger [5], Neugebauer [6], Kielich [7], Li [8] and Cyvin *et al* [9]. Recently, second-order nonlinear elastic scattering has been observed by Terhune *et al.* [10] in fused quartz and in a number of liquids (H_2O, CCl_4, CH_3CN) and by Maker[1] in methane pressurized to 100 atmospheres.

Two-photon electric dipole absorption in semiconductors has been considered by Braunstein [11] and in more detail by Loudon [12]. Other two-photon absorption estimations have been made for solids by Kleinman [13], Braunstein and Ockman [14] and other authors [15]. In molecular crystals, double-photon excitation has been discussed in various ways by Iannuzi and Polacco [16] (who suggested that double-photon absorption in anthra-

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[1] The author wishes to express his indebtedness to Dr P. D. Maker for making available his results on nonlinear light scattering in methane previous to their publication.

cene is due to the two-photon operator $A \cdot A$, Singh *et al* [17], Peticolas *et al* [18] and by Pao and Rentzepis [19] and, in alkali halides, by Hopfield and Worlock [20].

Experimental observations of various two-photon absorption processes induced by a ruby laser have been reported for a variety of materials including crystaline $CaF_2: Eu^{2+}$ [21], cesium [22] atomic vapour, CdS [14], crystalline KJ and CsJ [20, 23], molecular crystals [24, 25], as well as CS_2 and several other liquids [26] and gases[2]. The possibility of detecting other photon-photon processes in vacuum, plasma and matter has been discusses *e.g.* by Gardner [27], who also gave a review of the recent results relating to this subject. Three--photon absorption in naphtalene crystals by laser excitation has been reported by Singh and Bradley [28].

The above-mentioned theoretical papers on two-photon processes dealt with electric dipole transitions only. In the case of one-photon emission and absorption, electromagnetic multipole transitions have been studied by many authors (see *e.g.* Rubinowicz and Blaton and Humblet [29] and the monograph of Rose [30] with the papers cited there). Iannuzi and Polacco suggested that two photon absorption in anthracene is due to higher-order multipole interactions between the electronic system and a radiation field. Recently Guccione and Kranendonk [31] (see also Ref. [18]) have reported estimations of the electric quadrupole and magnetic dipole contributions to two-photon absorption processes and concluded that the higher multipole contributions are negligible with respect to the electric-dipole contribution. A general theory of nonlinear scattering processes to result from multipole interactions between molecules and an electromagnetic field has been developed recently by Kielich [32].

In this paper we shall present a formal extension of the radiation problem as stated above to multipole transition probabilities of second- and higher-order processes in which two-or more-photons are emitted or absorbed. We take into account not only the transition from initial to final quantum states through coupling with one or several intermediate states, but also direct transition by means of second- or higher-order interaction Hamiltonians. It is well-known that in the case of two-photon processes the first above mentioned transition results from second-order perturbation theory with the first-order Hamiltonian ($\sim \boldsymbol{p} \cdot \boldsymbol{A}$) [2, 3], whereas the direct transition results from first-order perturbation theory with second-order Hamiltonian ($\sim \boldsymbol{A} \cdot \boldsymbol{A}$) [2, 16, 18, 32]. The three-photon processes are composed of a direct transition by third-order interaction Hamiltonian, and indirect transitions through one and two successive virtual states. Obviously, at normal conditions, the probability transitions of second- or higher- order radiation processes to occur are very small and such processes have become accessible to detection since the coming of lasers, which are sources of coherent light beams of extremely high intensity. In the present paper more stress is laid on the construction of a general multipolar and nonlinear formalism, ratherthan on the physical aspect and details of mechanisms of the problem as already discussed for one- and two-photon radiative processes with insight in the monograph of Heitler [2] as well as in several papers (see *e.g.* references 3 and 11—20).

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[2] The author expresses his thanks to Prof. Papoular for sending him two typed copies of his and V. Chalmeton's papers on nonlinear absorption in gases previous to publication.

2. Multipole contributions to the electromagnetic equations

We consider an assembly of N identical micro-systems (atoms, molecules or their ions) in an electromagnetic field. Let the p-th micro-system consist of n_p point particles (nuclei and electrons) with electric charges e_{ps} $(s = 1, 2, \ldots, n_p)$ and positional vectors $\boldsymbol{r}_{ps} = \boldsymbol{R}_{ps} - \boldsymbol{r}_p$ relative to the center of mass of the micro-system whose position is $\boldsymbol{r}_p$. We write here the Lorentz microscopic electromagnetic field equations in the following form [33, 34]:

$$\nabla \times \boldsymbol{e} = -\frac{1}{c}\frac{\partial \boldsymbol{b}}{\partial t}, \quad \nabla \cdot \boldsymbol{b} = 0, \tag{2.1}$$

$$\nabla \cdot \boldsymbol{e} = \sum_{p=1}^{N} \sum_{s=1}^{np} e_{ps}\delta(\boldsymbol{r}_p + \boldsymbol{r}_{ps} - \boldsymbol{r}), \tag{2.2}$$

$$\nabla \times \boldsymbol{b} = \frac{1}{c}\frac{\partial \boldsymbol{e}}{\partial t} + \frac{2\pi}{c}\sum_{p=1}^{N} \sum_{s=1}^{np} \{(\dot{\boldsymbol{r}}_p + \dot{\boldsymbol{r}}_{ps})\delta(\boldsymbol{r}_p + \boldsymbol{r}_{ps} - \boldsymbol{r}) + \delta(\boldsymbol{r}_p + \boldsymbol{r}_{ps} - \boldsymbol{r})(\dot{\boldsymbol{r}}_p + \dot{\boldsymbol{r}}_{ps})\}, \tag{2.3}$$

where $\boldsymbol{e}$ and $\boldsymbol{b}$ are the microscopic electric and magnetic field strengths and $\delta(\boldsymbol{r}_p + \boldsymbol{r}_{ps} - \boldsymbol{r})$ is the three-dimensional Dirac δ-function.

On applying a suitable statistical averaging procedure (classical [33, 35] or quantal [34]) we can write the microscopic Equations (2.1)—(2.3) in the Maxwellian macroscopic form

$$\nabla \times \boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t}, \quad \nabla \cdot \boldsymbol{B} = 0, \tag{2.4}$$

$$\nabla \times \boldsymbol{H} = \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t} + \frac{4\pi}{c}\boldsymbol{J}, \quad \nabla \cdot \boldsymbol{D} = 4\pi\varrho_e, \tag{2.5}$$

where

$$\varrho_e(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \sum_{s=1}^{np} e_{ps}\delta(\boldsymbol{r}_p - \boldsymbol{r})\rangle, \tag{2.6}$$

$$\boldsymbol{J}(\boldsymbol{r}, t) = \frac{1}{2}\left\langle \sum_{p=1}^{N} \sum_{s=1}^{np} e_{ps}\{\dot{\boldsymbol{r}}_p\delta(\boldsymbol{r}_p - \boldsymbol{r}) + \delta(\boldsymbol{r}_p - \boldsymbol{r})\dot{\boldsymbol{r}}_p\} \right\rangle, \tag{2.7}$$

are the average true electric charge and current densities at the space-time point $(\boldsymbol{r}, t)$ and

$$\boldsymbol{D}(\boldsymbol{r}, t) = \boldsymbol{E}(\boldsymbol{r}, t) + 4\pi\boldsymbol{P}_e(\boldsymbol{r}, t), \tag{2.8}$$

$$\boldsymbol{H}(\boldsymbol{r}, t) = \boldsymbol{B}(\boldsymbol{r}, t) - 4\pi\boldsymbol{P}_m(\boldsymbol{r}, t), \tag{2.9}$$

are the macroscopic electric and magnetic displacement vectors for a medium at rest. The brackets $\langle \ \rangle$ symbolize appropriately defined statistical averages.

In the general case considered here, the electric and magnetic polarization vectors are of the form (for comparison see Refs 36, 37)

$$\boldsymbol{P}_e(\boldsymbol{r}, t) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t), \tag{2.10}$$

$$\boldsymbol{P}_m(\boldsymbol{r}, t) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t), \tag{2.11}$$

and contain the electric and magnetic multipole moment densities of arbitrary order given by

$$\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \boldsymbol{M}_{ep}^{(n)} \delta(\boldsymbol{r}_p - \boldsymbol{r})\rangle, \tag{2.12}$$

$$\boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t) = \frac{1}{2} \left\langle \sum_{p=1}^{N} \{\boldsymbol{M}_{mp}^{(n)} \delta(\boldsymbol{r}_p - \boldsymbol{r}) + \delta(\boldsymbol{r}_p - \boldsymbol{r}) \boldsymbol{M}_{mp}^{(n)}\} \right\rangle. \tag{2.13}$$

Here [32],

$$\boldsymbol{M}_{ep}^{(n)} = \sum_{s=1}^{np} e_{ps} r_{ps}^{n} \boldsymbol{Y}_{ps}^{(n)}, \tag{2.14}$$

$$\boldsymbol{M}_{mp}^{(n)} = \frac{n}{(n+1)c} \sum_{s=1}^{np} e_{ps} r_{ps}^{n} \boldsymbol{Y}_{ps}^{(n)} \times \dot{\boldsymbol{r}}_{ps} \tag{2.15}$$

define respectively the 2^n-pole electric and magnetic moment operators of a p-th micro--system in which $\boldsymbol{Y}_{ps}^{(n)}$ is an operator of order n having the properties of spherical harmonics. The symbol $[n-1]$ in Equations (2.10) and (2.11) denotes $(n-1)$-fold contraction of the tensors ∇^{n-1} and $\boldsymbol{P}^{(n)}$.

In the well-known manner we obtain from Equations (2.4)—(2.9) the following electromagnetic wave equations:

$$\Box \boldsymbol{E}(\boldsymbol{r}, t) + 4\pi \boldsymbol{\Box} \cdot \boldsymbol{P}_e(\boldsymbol{r}\, t,) = 4\pi \left\{ \nabla \varrho_e(\boldsymbol{r}, t) + \frac{1}{c} \frac{\partial \boldsymbol{J}(\boldsymbol{r}, t)}{\partial t} + \frac{1}{c} \nabla \times \frac{\partial \boldsymbol{P}_m(\boldsymbol{r}, t)}{\partial t} \right\}, \tag{2.16}$$

$$\Box \boldsymbol{H}(\boldsymbol{r}, t) + 4\pi \boldsymbol{\Box} \cdot \boldsymbol{P}_m(\boldsymbol{r}, t) = -\frac{4\pi}{c} \nabla \times \left\{ \boldsymbol{J}(\boldsymbol{r}, t) + \frac{\partial \boldsymbol{P}_e(\boldsymbol{r}, t)}{\partial t} \right\}, \tag{2.17}$$

which, through the polarization vectors of (2.10) and (2.11), contain all multipole contributions. Above we have introduced the scalar Dalambertian operator $\Box = \nabla^2 - (1/c)^2 \frac{\partial^2}{\partial t^2}$ and an analogous tensorial operator $\boldsymbol{\Box} = \nabla\nabla - (1/c^2)\boldsymbol{U}\partial^2/\partial t^2$ with $\boldsymbol{U}$ denoting the second--rank unit tensor.

In the special case when $\varrho_e = 0$ and $\boldsymbol{J} = 0$, the electromagnetic wave Equations (2.16) and (2.17) can be simplified to symmetrical form

$$\Box \boldsymbol{E}(\boldsymbol{r}, t) + 4\pi \Box \cdot \boldsymbol{P}_e(\boldsymbol{r}, t) = \frac{4\pi}{c} \nabla \times \frac{\partial \boldsymbol{P}_m(\boldsymbol{r}, t)}{\partial t}, \tag{2.18}$$

$$\Box \boldsymbol{H}(\boldsymbol{r}, t) + 4\pi \Box \cdot \boldsymbol{P}_m(\boldsymbol{r}, t) = -\frac{4\pi}{c} \nabla \times \frac{\partial \boldsymbol{P}_e(\boldsymbol{r}, t)}{\partial t}, \tag{2.19}$$

or to the still simpler form

$$\Box \boldsymbol{E}(\boldsymbol{r}, t) = 0, \qquad \Box \boldsymbol{H}(\boldsymbol{r}, t) = 0, \tag{2.20}$$

if the medium is non-polarizing ($\boldsymbol{P}_e = 0$ and $\boldsymbol{P}_m = 0$).

3. Transition probability in quantal perturbation theory

Consider a micro-system for which the unperturbated Hamiltonian operator is H_0 and the time-dependent perturbation Hamiltonian is $V(t)$. Let us suppose that at the initial moment of time t_0 the micro-system is in the state $|l\rangle$, so that the probability for finding the micro-system at the final time t in the state $|k\rangle$ is

$$|\langle k|U(t, t_0)|l\rangle|^2,$$

where $U(t, t_0)$ is a unitary operator describing the time-evolution in the interval (t, t_0).

The transition probability per unit time, for the transition from state $|l\rangle$ to state $|k\rangle$ under the influence of a perturbation V(t) is thus

$$P_{kl} = \frac{1}{t - t_0} |\langle k|U(t, t_0)|l\rangle|^2, \tag{3.1}$$

where the time-evolution operator $U(t, t_0)$ may be expanded in powers of $V(t)$ as follows:

$$U(t, t_0) = \overset{(0)}{U}(t, t_0) + \sum_{r=1}^{\infty} \overset{(r)}{U}(t, t_0) \tag{3.2}$$

with the r-th order contribution

$$\overset{(r)}{U}(t, t_0) = \left(-\frac{i}{\hbar}\right)^r \int_{t_0}^{t} \hat{V}(t_1)dt_1 \int_{t_0}^{t_1} \hat{V}(t_2)dt_2 \ldots \int_{t_0}^{t_{r-1}} \hat{V}(t_r)dt_r \tag{3.3}$$

and the time-dependent perturbation operator in interaction representation

$$\hat{V}(t) = \exp\left(\frac{i}{\hbar} H_0 t\right) V(t) \exp\left(-\frac{i}{\hbar} H_0 t\right). \tag{3.4}$$

In the first step we assume that the perturbation acting on the micro-system is of the form

$$V(t) = \overset{(1)}{V}(t) = \sum_a \{\overset{(1)}{V_a^+} e^{i\omega_a t} + \overset{(1)}{V_a^-} e^{-i\omega_a t}\} \tag{3.5}$$

and obtain by (3.3), if the perturbation be switched on adiabatically at $t_0 = -\infty$

$$\langle k|\overset{(r)}{U}(t, -\infty)|l\rangle^{(1)} = \sum_{a_1\ldots a_r} \{\langle k|\overset{(r)}{U}(+\omega_{a_1}, \ldots, +\omega_{a_r})|l\rangle^{(1)} + \\ + \ldots + \langle k|\overset{(r)}{U}(-\omega_{a_1}, \ldots, -\omega_{a_r})|l\rangle^{(1)}\}, \tag{3.6}$$

where

$$\langle k|\overset{(r)}{U}(+\omega_{a_1}, \ldots, +\omega_{a_r})|l\rangle^{(1)}$$

$$= \frac{1}{r!}\left(-\frac{1}{\hbar}\right)^r \sum_{i_{r-1}} \cdots \sum_{i_1} S(a_1, \ldots, a_r) \frac{\langle k|\overset{(1)}{V}{}^+_{a_r}|i_{r-1}\rangle\, e^{it(\omega_{kl}+\omega_{a_1}+\ldots+\omega_{a_r})}}{(\omega_{kl}+\omega_{a_1}+\omega_{a_2}+\ldots+\omega_{a_{r-1}}+\omega_{a_r})} \times$$

$$\times \frac{\langle i_{r-1}|\overset{(1)}{V}{}^+_{a_{r-1}}|i_{r-2}\rangle}{(\omega_{i_{r-1}l}+\omega_{a_1}+\ldots+\omega_{a_{r-1}})} \cdots \frac{\langle i_2|\overset{(1)}{V}{}^+_{a_2}|i_1\rangle\langle i_1|\overset{(1)}{V}{}^+_{a_1}|l\rangle}{(\omega_{i_2l}+\omega_{a_1}+\omega_{a_2})(\omega_{i_1l}+\omega_{a_1})}; \tag{3.7}$$

$S(a_1, \ldots, a_r)$ is a symmetrizing operator consisting in summation over all permutations of $a_1, \ldots, a_r$, and $\omega_{kl} = (E_k^0 - E_l^0)/\hbar$ is the frequency of the transition $k \leftarrow l$ when the perturbation is absent and the various i_r run over all possible intermediate states of the micro--system.

In the case when the perturbation is switched on at time $t_0 = 0$ and is switched off at the end of an interval t, the expressions (3.3) and (3.5) becomes in the first-, second- and third-order approximation

$$\langle k|\overset{(1)}{U}(t, 0)|l\rangle^{(1)} = -\frac{1}{\hbar}\sum_a \{\langle k|\overset{(1)}{V}{}^+_a|l\rangle f(\omega_{kl}+\omega_a) + \langle k|\overset{(1)}{V}{}^-_a|l\rangle f(\omega_{kl}-\omega_a)\}, \tag{3.8}$$

$$\langle k|\overset{(2)}{U}(t, 0)|l\rangle^{(1)} = -\frac{1}{2\hbar^2}\sum_{ab}\sum_i S(a, b)\left\{\langle k|\overset{(1)}{V}{}^+_a|i\rangle \frac{\langle i|\overset{(1)}{V}{}^+_b|l\rangle}{(\omega_{il}+\omega_b)} f(\omega_{ki}+\omega_a) - \\ - \langle k|\overset{(1)}{V}{}^+_a|i\rangle \frac{\langle i|\overset{(1)}{V}{}^+_b|l\rangle}{(\omega_{il}+\omega_b)} f(\omega_{kl}+\omega_a+\omega_b) + c.c.\right\}, \tag{3.9}$$

$$\langle k|\overset{(3)}{U}(t, 0)|l\rangle^{(1)} = -\frac{1}{6\hbar^3}\sum_{abc}\sum_{ij} S(a, b, c)\left\{\left[\langle k|\overset{(1)}{V}{}^+_a|i\rangle \frac{\langle i|\overset{(1)}{V}{}^+_b|j\rangle\langle j|\overset{(1)}{V}{}^+_c|l\rangle}{(\omega_{ij}+\omega_b)(\omega_{jl}+\omega_c)} - \\ - \langle k|\overset{(1)}{V}{}^+_a|i\rangle \frac{\langle i|\overset{(1)}{V}{}^+_b|j\rangle\langle j|\overset{(1)}{V}{}^+_c|l\rangle}{(\omega_{il}+\omega_b+\omega_c)(\omega_{jl}+\omega_c)}\right] f(\omega_{ki}+\omega_a) + c.c. - \\ - \langle k|\overset{(1)}{V}{}^+_a|i\rangle \frac{\langle i|\overset{(1)}{V}{}^+_b|j\rangle\langle j|\overset{(1)}{V}{}^+_c|l\rangle}{(\omega_{ij}+\omega_b)(\omega_{jl}+\omega_c)} f(\omega_{kj}+\omega_a+\omega_b) + c.c. + \\ + \langle k|\overset{(1)}{V}{}^+_a|i\rangle \frac{\langle i|\overset{(1)}{V}{}^+_b|j\rangle\langle j|\overset{(1)}{V}{}^+_c|l\rangle}{(\omega_{il}+\omega_b+\omega_c)(\omega_{jl}+\omega_c)} f(\omega_{kl}+\omega_a+\omega_b+\omega_c) + c.c.\right\}, \tag{3.10}$$

where for brevity we have introduced the function

$$f(\omega_{kl}+\omega_a+\omega_b+\omega_c+\ldots)=\frac{\exp\{i(\omega_{kl}+\omega_a+\omega_b+\omega_c+\ldots)t\}-1}{(\omega_{kl}+\omega_a+\omega_b+\omega_c+\ldots)}. \tag{3.11}$$

In the first-order approximation given by (3.8) we have the direct transition $k \leftarrow l$, whereas in the second- and third-order approximations of (3.9) and (3.10) the microsystem proceeds from the state $|l\rangle$ to $|k\rangle$ by one or two virtual transitions, respectively, the summations being over all the virtual states, labeled i and j, for which the matrix elements of perturbation do not vanish.

In order to obtain a more exact result we must also take into account small contributions to (3.4) arising from the second- and higher-order perturbation Hamiltonian namely

$$V(t)=\overset{(1)}{V}(t)+\overset{(2)}{V}(t)+\overset{(3)}{V}(t)+\ldots, \tag{3.12}$$

where the first-order perturbation is given by (3.5) and the second-order perturbation is of the form

$$\overset{(2)}{V}(t)=\sum_{ab}\{\overset{(2)}{V}{}^{++}_{ab}\mathrm{e}^{i(\omega_a+\omega_b)t}+\ldots+\overset{(2)}{V}{}^{--}_{ab}\mathrm{e}^{-i(\omega_a+\omega_b)t}\}. \tag{3.13}$$

By using the perturbation operator of (3.12) we obtain additional contributions to the expressions (3.8) and (3.9) resulting from the second-order perturbation Hamiltonian of (3.13),

$$\langle k|\overset{(1)}{U}(t,0)|l\rangle^{(2)}=-\frac{1}{\hbar}\sum_{ab}\{\langle k|\overset{(2)}{V}{}^{++}_{ab}|l\rangle f(\omega_{kl}+\omega_a+\omega_b)+c.c.\}, \tag{3.14}$$

$$\begin{aligned}\langle k|\overset{(2)}{U}(t,0)|l\rangle^{(2)}=&-\frac{1}{6\hbar^2}\sum_{abc}\sum_{i}S(a,b,c)\Bigg\{\langle k|\overset{(1)}{V}{}^{+}_{a}|i\rangle\frac{\langle i|\overset{(2)}{V}{}^{++}_{bc}|l\rangle}{(\omega_{il}+\omega_b+\omega_c)}f(\omega_{ki}+\omega_a)+\\&+c.c.+\langle k|\overset{(2)}{V}{}^{++}_{ab}|i\rangle\frac{\langle i|\overset{(1)}{V}{}^{+}_{c}|l\rangle}{(\omega_{il}+\omega_c)}f(\omega_{ki}+\omega_a+\omega_b)+c.c.-\Bigg[\langle k|\overset{(1)}{V}{}^{+}_{a}|i\rangle\frac{\langle i|\overset{(2)}{V}{}^{++}_{bc}|l\rangle}{(\omega_{il}+\omega_b+\omega_c)}+\\&+\langle k|\overset{(2)}{V}{}^{++}_{ab}|i\rangle\frac{\langle i|\overset{(1)}{V}{}^{+}_{c}|l\rangle}{(\omega_{il}+\omega_c)}\Bigg]f(\omega_{kl}+\omega_a+\omega_b+\omega_c)+c.c.\Bigg\}.\end{aligned} \tag{3.15}$$

4. *Multipole expansion of the perturbation hamiltonian*

The non-relativistic perturbation Hamiltonian of a micro-system in the presence of an electromagnetic field with vectors

$$\boldsymbol{E}=-\frac{1}{c}\frac{\partial\boldsymbol{A}}{\partial t}-\nabla\Phi,\quad \boldsymbol{B}=\nabla\times\boldsymbol{A}, \tag{4.1}$$

is of the form[2]

$$H'=\sum_s\left\{e_s\Phi_s-\frac{e_s}{2m_sc}(\boldsymbol{p}_s\cdot\boldsymbol{A}_s+\boldsymbol{A}_s\cdot\boldsymbol{p}_s)+\frac{e_s^2}{2m_sc^2}(\boldsymbol{A}_s\cdot\boldsymbol{A}_s)\right\}, \tag{4.2}$$

where Φ_s and $\boldsymbol{A}_s$ are the scalar and vector potentials at the point of the sth charged particle of the micro-system and $\boldsymbol{p}_s$ is the operator of its momentum.

The Hamiltonian (4.2) yields for the first- and second-order perturbations

$$\overset{(1)}{V}(t) = \sum_s \left\{ e_s\Phi_s - \frac{e_s}{2m_s c}(\boldsymbol{p}_s \cdot \boldsymbol{A}_s + \boldsymbol{A}_s \cdot \boldsymbol{p}_s) \right\}, \tag{4.3}$$

$$\overset{(2)}{V}(t) = \frac{1}{2} \sum_s \frac{e_s^2}{m_s c^2} (\boldsymbol{A}_s \cdot \boldsymbol{A}_s). \tag{4.4}$$

Assuming that the potentials Φ_s and $\boldsymbol{A}_s$ vary but slowly in the region of the microsystem we can expand it in a multipole series which permits the first-order perturbation (4.3) to be written in the following form:

$$\overset{(1)}{V}(t) = -\sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \{\boldsymbol{M}_e^{(n)}[n]\boldsymbol{E}^{(n)} + \boldsymbol{M}_m^{(n)}[n]\boldsymbol{B}^{(n)}\}, \tag{4.5}$$

if appropriate canonical gauge transformations are used [38] and if

$$\sum_s e_s = 0.$$

In expansion (4.5) we have introduced the electric and magnetic field strengths of degree n defined by (4.1) as

$$\boldsymbol{E}^{(n)} = \nabla^{n-1}\boldsymbol{E}(\boldsymbol{r}, t), \qquad \boldsymbol{B}^{(n)} = \nabla^{n-1}\boldsymbol{B}(\boldsymbol{r}, t). \tag{4.6}$$

Similarly the multipole expansion of the second-order perturbation of (4.4) is [32]

$$\overset{(2)}{V}(t) = -\frac{1}{2} \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} \frac{2^{n+n'} n!\, n'!}{(2n)!(2n')!} \boldsymbol{B}^{(n)}[n]^{(n)}\boldsymbol{A}_m^{(n')}[n']\boldsymbol{B}^{(n')}, \tag{4.7}$$

where we have the multipole (dia) magnetic polarizability operator

$$^{(n)}\boldsymbol{A}_m^{(n')} = \frac{nn'}{(n+1)(n'+1)c^2} \sum_s \frac{e_s^2}{m_s} r_s^{n+n'} \{\boldsymbol{Y}_s^{(n)}\boldsymbol{Y}_s^{(n')} - \boldsymbol{U}\boldsymbol{Y}_s^{(n)} \cdot \boldsymbol{Y}_s^{(n')}\}. \tag{4.8}$$

The vector potential of a classical field of electromagnetic waves may be expressed as

$$\boldsymbol{A}(\boldsymbol{r}, t) = \sum_a \{\boldsymbol{A}_a^+ e^{i\omega_a t} + \boldsymbol{A}_a^- e^{-i\omega_a t}\}, \qquad \boldsymbol{A}_a^{\pm} = \boldsymbol{A}_a^0 e^{\mp i\boldsymbol{k}_a \cdot \boldsymbol{r}} \tag{4.9}$$

whence, by (4.6),

$$\boldsymbol{E}^{(n)} = \sum_a \{(-i\boldsymbol{k}_a)^{n-1}\boldsymbol{E}_0^+ e^{i\omega_a t} + (i\boldsymbol{k}_a)^{n-1}\boldsymbol{E}_0^- e^{-i\omega_a t}\}, \tag{4.10}$$

$$\boldsymbol{B}^{(n)} = \sum_a \{(-i\boldsymbol{k}_a)^{n-1}\boldsymbol{B}_0^+ e^{i\omega_a t} + (i\boldsymbol{k}_a)^{n-1}\boldsymbol{B}_0^- e^{-i\omega_a t}\}, \tag{4.11}$$

In the quantized theory of the electromagnetic field, the vector potential (4.9) should be replaced by the photon operator (the Coulomb gauge is used)

$$\boldsymbol{A}(\boldsymbol{r}, t) = \sum_{\boldsymbol{k}\lambda} \left(\frac{2\pi c^2 \hbar}{V\omega_\lambda}\right)^{1/2} \boldsymbol{e}_\lambda\{a_\lambda^-(\boldsymbol{k}) e^{-i(\omega_\lambda t - \boldsymbol{k}_\lambda \cdot \boldsymbol{r})} + a_\lambda^+(\boldsymbol{k}) e^{i(\omega_\lambda t - \boldsymbol{k}_\lambda \cdot \boldsymbol{r})}\}, \tag{4.12}$$

where $\boldsymbol{e}_\lambda$ is a unit vector in the polarization direction of a photon with propagation vector $\boldsymbol{k}_\lambda$ and energy $\hbar\omega_\lambda = \hbar c|\boldsymbol{k}_\lambda|$.

The annihilation and creation operators $a_\lambda^-(\boldsymbol{k})$ and $a_\lambda^+(\boldsymbol{k})$, which anihilate or create one photon with wave vector $\boldsymbol{k}_\lambda$ and polarization λ satisfy the Bose-Einstein commutation relations

$$[a_\lambda^-(\boldsymbol{k}),\ a_\mu^+(\boldsymbol{k}')] = \delta_{\lambda\mu}\delta_{kk'},$$
$$[a_\lambda^-(\boldsymbol{k}),\ a_\mu^-(\boldsymbol{k}')] = [a_\lambda^+(\boldsymbol{k}),\ a_\mu^+(\boldsymbol{k}')] = 0, \tag{4.13}$$

and on quantizing the electromagnetic field its nonzero matrix elements can be written in terms of the number of photons N_λ as follows [2]:

$$\langle N_\lambda \pm 1|a_\lambda^\pm(\boldsymbol{k})|N_\lambda\rangle = \langle N_\lambda|a_\lambda^\mp(\boldsymbol{k})|N_\lambda \mp 1\rangle = \sqrt{N_\lambda + \binom{1}{0}}, \tag{4.14}$$

where in the brackets $\binom{1}{0}$ 1 stands for emission whereas 0 for absorption of a photon.

If k and l as previously relate to the quantization of the micro-system only, whereas α and β — to the quantization of electromagnetic field, we obtain from (4.3) and (4.4) by (4.12)—(4.14)

$$\langle k\alpha|\overset{(1)}{V}{}_\lambda^\pm|\, l\beta\rangle = -\sqrt{\frac{2\pi\hbar}{V\omega_\lambda}\left\{N_\lambda + \binom{1}{0}\right\}}\,\langle k|\boldsymbol{e}_\lambda \cdot \boldsymbol{P}(\mp \boldsymbol{k}_\lambda)|\, l\rangle, \tag{4.15}$$

$$\langle k\alpha|\overset{(2)}{V}{}_{\lambda\mu}^{\pm\mp}|\, l\beta\rangle = \frac{\pi\hbar}{V}\sqrt{\frac{1}{\omega_\lambda\omega_\mu}\left\{N_\lambda + \binom{1}{0}\right\}\left\{N_\mu + \binom{0}{1}\right\}}\ \times$$
$$\times (\boldsymbol{e}_\lambda \cdot \boldsymbol{e}_\mu)\langle k|A(\pm \boldsymbol{k}_\lambda,\ \pm \boldsymbol{k}_\mu)|\, l\rangle, \tag{4.16}$$

where the abbreviations have been introduced,

$$\boldsymbol{P}(\mp \boldsymbol{k}_\lambda) = \sum_s \frac{e_s}{m_s}\, \boldsymbol{p}_s e^{\mp i\boldsymbol{k}_\lambda \cdot \boldsymbol{r}_s}, \tag{4.17}$$

$$A(\mp \boldsymbol{k}_\lambda,\ \pm \boldsymbol{k}_\mu) = \sum_s \frac{e_s^2}{m_s}\, e^{\mp i(\boldsymbol{k}_\lambda - \boldsymbol{k}_\mu) \cdot \boldsymbol{r}_s}. \tag{4.18}$$

5. *One-photon multipole transition probability*

With respect to (3.1) and (3.8) we have for the first order transition probability per unit time

$$\overset{(1)}{P}_{kl} = \frac{1}{\hbar^2 t}\left|\sum_a \langle k|\overset{(1)}{V}{}_a^+|\, l\rangle f(\omega_{kl} + \omega_a) + c.c\right|^2, \tag{5.1}$$

which in the well-known manner can be expressed as follows:

$$\overset{(1)}{P}_{kl} = \sum_a \{\overset{(1)}{I}_{kl}(+a)\,\delta(\omega_{kl}+\omega_a) + \overset{(1)}{I}_{kl}(-a)\,\delta(\omega_{kl}-\omega_a)\} \tag{5.2}$$

with

$$\overset{(1)}{I}_{kl}(\pm a) = 2\pi |\langle k|\overset{(1)}{V}{}_a^{\pm}|l\rangle|^2. \tag{5.3}$$

On substituting here the first order perturbation (4.5) we obtain

$$\overset{(1)}{I}_{kl}(\pm a) = 2\pi \left| \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \langle k|\boldsymbol{M}_e^{(n)}[n]\,\overset{\pm}{\boldsymbol{E}}{}_a^{(n)} + \boldsymbol{M}_m^{(n)}[n]\overset{\pm}{\boldsymbol{B}}{}_a^{(n)}|\, l\rangle \right|^2 \tag{5.4}$$

with n-th order electric and magnetic field amplitudes (see 4.10 and 4.11)

$$\overset{\pm}{\boldsymbol{E}}{}_a^{(n)} = (\mp i\boldsymbol{k}_a)^{n-1}\boldsymbol{E}_a^{\pm}, \quad \overset{\pm}{\boldsymbol{B}}{}_a^{(n)} = (\mp i\boldsymbol{k}_a)^{n-1}\boldsymbol{B}_a^{\pm}. \tag{5.5}$$

The total intensity radiated per unit time in the direction of propagation $\boldsymbol{k}$ is given by integrating (5.4) over all angles,

$$S_{kl} = \int I_{kl}\,d\Omega, \tag{5.6}$$

and we obtain finally

$$\overset{(1)}{S}_{kl}(\pm a) = \sum_{n=1}^{\infty} \{{}_e\overset{(1)}{S}{}_{kl}^{(n)}(\pm a) + {}_m\overset{(1)}{S}{}_{kl}^{(n)}(\pm a)\}, \tag{5.7}$$

where

$${}_e\overset{(1)}{S}{}_{kl}^{(n)}(\pm a) = \frac{\pi^2 2^{2n+3}(n!)^2}{(2n)!\,(2n+1)!} \langle k|\boldsymbol{M}_e^{(n)}|\, l\rangle\,[n]\,\langle k|\boldsymbol{M}_e^{(n)}|\, l\rangle^*\, |\boldsymbol{E}_a^{\pm}|^2\, \boldsymbol{k}_a^{2n-2}, \tag{5.8}$$

$${}_m\overset{(1)}{S}{}_{kl}^{(n)}(\pm a) = \frac{\pi^2 2^{2n+3}(n!)^2}{(2n)!\,(2n+1)!} \langle k|\boldsymbol{M}_m^{(n)}|\, l\rangle\,[n]\langle k|\boldsymbol{M}_m^{(n)}|\, l\rangle^*\, |\boldsymbol{B}_a^{\pm}|^2\, \boldsymbol{k}_a^{2n-2}, \tag{5.9}$$

are the contributions to the total intensity resulting from the 2^n-pole electric and magnetic $k \leftarrow l$ transition processes.

If, in particular, the micro-system possesses the axial symmetry, the expressions (5.8) and (5.9) assume the simpler form

$${}_e\overset{(1)}{S}{}_{kl}^{(n)}(\pm a) = \frac{\pi^2 2^{n+3}}{(2n+1)!}\, |\langle k|M_e^{(n)}|l\rangle|^2\, |\boldsymbol{E}_a^{\pm}|^2 \boldsymbol{k}_a^{2n-2}, \tag{5.10}$$

$${}_m\overset{(1)}{S}{}_{kl}^{(n)}(\pm a) = \frac{\pi^2 2^{n+3}}{(2n+1)!}\, |\langle k|M_m^{(n)}|\, l\rangle|^2\, |\boldsymbol{B}_a^{\pm}|^2 \boldsymbol{k}_a^{2n-2}. \tag{5.11}$$

In the case when the electromagnetic field is quantized we should replace expression (5.2) by the following:

$$\overset{(1)}{P}_{kl} = \sum_\lambda \{\overset{(1)}{I}_{kl}(+\lambda)\,\delta(\omega_{kl}+\omega_\lambda) + \overset{(1)}{I}_{kl}(-\lambda)\,\delta(\omega_{kl}-\omega_\lambda)\}, \tag{5.12}$$

with

$$\overset{(1)}{I}_{kl}(\pm\lambda) = 2\pi |\langle k\alpha|\overset{(1)}{V}{}_\lambda^{\pm}|l\beta\rangle|^2. \tag{5.13}$$

The explicite form of (5.13) is

$$\overset{(1)}{I}_{kl}(\pm\lambda) = 2\pi \left| \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \{\langle k|\boldsymbol{M}_e^{(n)}|l\rangle [n] \langle\alpha|\overset{\pm}{\boldsymbol{E}}_\lambda^{(n)}|\beta\rangle + \langle k|\boldsymbol{M}_m^{(n)}|l\rangle [n] \langle\alpha|\overset{\pm}{\boldsymbol{B}}_\lambda^{(n)}|\beta\rangle\} \right|^2, \tag{5.14}$$

where by (4.11)—(4.13) and (5.5) we have

$$\langle\alpha|\overset{\pm}{\boldsymbol{E}}_\lambda^{(n)}|\beta\rangle = (\mp i\boldsymbol{k}_\lambda)^{n-1} \langle\alpha|\boldsymbol{E}_\lambda^{\pm}|\beta\rangle = (\mp i)^n \boldsymbol{e}_\lambda \boldsymbol{k}_\lambda^{n-1} \sqrt{\frac{2\pi\hbar\omega_\lambda}{V}} \left\{N_\lambda + \begin{pmatrix}1\\0\end{pmatrix}\right\},$$

$$\langle\alpha|\overset{\pm}{\boldsymbol{B}}_\lambda^{(n)}|\beta\rangle = (\mp i)^n (\boldsymbol{k}_\lambda \times \boldsymbol{e}_\lambda)\, \boldsymbol{k}_\lambda^{n-1} \sqrt{\frac{2\pi c^2\hbar}{V\omega_\lambda}} \left\{N_\lambda + \begin{pmatrix}1\\0\end{pmatrix}\right\}. \tag{5.15}$$

By (5.15) we may rewrite (5.14) as follows:

$$\overset{(1)}{I}_{kl}(\pm\lambda) = \frac{4\pi^2}{V} \hbar\omega_\lambda \left\{N_\lambda + \begin{pmatrix}1\\0\end{pmatrix}\right\} \left| \sum_{n=1}^{\infty} (-i)^{n-1} \frac{2^n n!}{(2n)!} \{\langle k|\boldsymbol{M}_e^{(n)}|l\rangle [n]\, \boldsymbol{e}_\lambda \boldsymbol{k}_\lambda^{n-1} + \right.$$

$$\left. + \langle k|\boldsymbol{M}_m^{(n)}|l\rangle [n]\, (\boldsymbol{e}_\lambda \times \boldsymbol{k}_\lambda^0)\, \boldsymbol{k}_\lambda^{n-1}\} \right|^2, \tag{5.16}$$

where $\boldsymbol{k}_\lambda^0$ is the unit propagation vector $\boldsymbol{k}_\lambda^0 |\boldsymbol{k}_\lambda| = \boldsymbol{k}_\lambda$.

By (5.6) and (5.16) we obtain for the electric 2^n-pole total radiation intensity

$$ {}_e\overset{(1)}{S}{}_{kl}^{(n)}(\pm\lambda) = \frac{\pi^3 2^{2n+4}(n!)^2}{V(2n)!\,(2n+1)!} \hbar\omega_\lambda \left\{N_\lambda + \begin{pmatrix}1\\0\end{pmatrix}\right\} \langle k|\boldsymbol{M}_e^{(n)}|l\rangle [n] \langle k|\boldsymbol{M}_e^{(n)}|l\rangle^* |\boldsymbol{e}_\lambda \boldsymbol{k}_\lambda^{n-1}|^2. \tag{5.17}$$

Analogical expressions can be written for the magnetic multipole part of the total radiation intensity.

When the quantum-mechanical Hamiltonian of (4.15) is used we obtain from (5.13) the result

$$\overset{(1)}{I}_{kl}(\pm\lambda) = \frac{4\pi^2\hbar}{V\omega_\lambda} \left\{N_\lambda + \begin{pmatrix}1\\0\end{pmatrix}\right\} |\langle k|\boldsymbol{e}_\lambda \cdot \boldsymbol{P}(\mp\boldsymbol{k}_\lambda)|l\rangle|^2, \tag{5.18}$$

which can be proved to be identical with (5.16).

6. *Two-photon transition probability*

On substitution of (3.9) and (3.14) in the definition (3.1), the following expression is obtained for the two-photon transition probability per unit time

$$\overset{(2)}{P}_{kl} = \frac{1}{4\hbar^2 t} \left| \sum_{ab} S(a,b) \left\{ \langle k|\overset{(2)}{V}{}_{ab}^{++}|l\rangle + \frac{1}{\hbar} \sum_i \langle k|\overset{(1)}{V}{}_a^{+}|i\rangle \times \right.\right.$$

$$\left.\left. \times \frac{\langle i|\overset{(1)}{V}{}_b^{+}|l\rangle}{\omega_{il}+\omega_b} \right\} f(\omega_{kl}+\omega_a+\omega_b) + c.c. \right|^2, \tag{6.1}$$

which can be rewritten as

$$\overset{(2)}{P}_{kl} = \sum_{ab} \{ \overset{(2)}{I}_{kl}(+a, +b)\delta(\omega_{kl}+\omega_a+\omega_b) + \overset{(2)}{I}_{kl}(+a, -b)\delta(\omega_{kl}+\omega_a-\omega_b) +$$

$$+ \overset{(2)}{I}_{kl}(-a, +b)\delta(\omega_{kl}-\omega_a+\omega_b) + \overset{(2)}{I}_{kl}(-a, -b)\delta(\omega_{kl}-\omega_a-\omega_b)\}, \tag{6.2}$$

if only the terms having the properties of a δ-function are retained. In (6.2) we have[3]

$$\overset{(2)}{I}_{kl}(\pm a, \mp b) = \overset{(2)}{I}{}^{(1)}_{kl}(\pm a, \mp b) + \overset{(2)}{I}{}^{(2)}_{kl}(\pm a, \mp b), \tag{6.3}$$

where

$$\overset{(2)}{I}{}^{(1)}_{kl}(\pm a, \mp b) = \frac{\pi}{\hbar^2} \left| S(a, b) \sum_i \langle k|\overset{(1)}{V}{}^{\pm}_{a}| i\rangle \frac{\langle i|\overset{(1)}{V}{}^{\mp}_{b}| l\rangle}{\omega_{il} \mp \omega_b} \right|^2, \tag{6.4}$$

is the contribution to the two-photon process resulting from the transition $k \leftarrow l$ via intermediate states i which differ from the initial and final states, and

$$\overset{(2)}{I}{}^{(2)}_{kl}(\pm a, \mp b) = \pi|S(a, b)\langle k|\overset{(2)}{V}{}^{\pm\mp}_{ab}|l\rangle|^2 \tag{6.5}$$

— that by a direct transition.

In the case when the interaction Hamiltonian of (4.5) is used we can represent (6.4) in the form

$$\overset{(2)}{I}{}^{(1)}_{kl}(\pm a, \mp b) = \frac{\pi}{\hbar^2} \left| \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)!(2n_2)!} S(a, b) \sum_i \langle k|\boldsymbol{M}_e^{(n_1)}[n_1] \overset{\pm}{\boldsymbol{E}}{}_a^{(n_1)} + \right.$$

$$\left. + \boldsymbol{M}_m^{(n_1)}[n_1] \overset{\pm}{\boldsymbol{B}}{}_a^{(n_1)}| i\rangle (\omega_{il} \mp \omega_b)^{-1} \langle i|\boldsymbol{M}_e^{(n_2)}[n_2] \overset{\mp}{\boldsymbol{E}}{}_b^{(n_2)} + \boldsymbol{M}_m^{(n_2)}[n_2] \overset{\mp}{\boldsymbol{B}}{}_b^{(n_2)}| l\rangle \right|^2, \tag{6.6}$$

which contains all electric and magnetic multipole transitions.

Analogously we have by (4.7), (5.5) and (6.5) for the direct two-photon multipole transition

$$\overset{(2)}{I}{}^{(2)}_{kl}(\pm a, \mp b) = \frac{\pi}{4} \left| \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)!(2n_2)!} S(a, b) \times \right.$$

$$\left. \times \langle k|\overset{\pm}{\boldsymbol{B}}{}_a^{(n_1)}[n_1] \, {}^{(n_1)}\boldsymbol{A}_m^{(n_2)}[n_2] \overset{\mp}{\boldsymbol{B}}{}_b^{(n_2)}| l\rangle \right|^2. \tag{6.7}$$

If integration over all directions of $\boldsymbol{E}_a$, $\boldsymbol{B}_a$ and $\boldsymbol{E}_b$, $\boldsymbol{B}_b$ can be carried out independently, expression (6.6) becomes by (5.6)

$$\overset{(2)}{S}{}^{(1)}_{kl}(\pm a, \mp b) = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \{ {}_e\overset{(2)}{S}{}^{(n_1, n_2)}_{kl}(\pm a, \mp b) + {}_{em}\overset{(2)}{S}{}^{(n_1, n_2)}_{kl}(\pm a, \mp b) +$$

$$+ {}_{me}\overset{(2)}{S}{}^{(n_1, n_2)}_{kl}(\pm a, \mp b) + {}_m\overset{(2)}{S}{}^{(n_1, n_2)}_{kl}(\pm a, \mp b)\}, \tag{6.8}$$

---

[3] In general (6.3) contains the mixed term which we refrain from considering here.

where the pure electric $2^{n_1+n_2}$-pole contribution is of the form

$$\overset{(2)}{{}_eS}{}_{kl}^{(n_1,n_2)}(\pm a, \mp b) = \frac{16\pi^3 2^{2(n_1+n_2)}(n_1!n_2!)^2}{\hbar^2(2n_1)!\,(2n_1+1)!\,(2n_2)!\,(2n_2+1)!}\,|\overset{\pm}{\boldsymbol{E}}{}_a^{(n_1)}|^2\,|\overset{\mp}{\boldsymbol{E}}{}_b^{(n_2)}|^2\times$$

$$\times\left|S(an_1, bn_2)\sum_i \langle k|\boldsymbol{M}_e^{(n_1)}|\,i\rangle\frac{\langle i|\boldsymbol{M}_e^{(n_2)}|\,l\rangle}{\omega_{il}\pm\omega_b}\right|^2 \tag{6.9}$$

with notation $|\overset{\pm}{\boldsymbol{E}}{}_a^{(n_1)}|^2=(\overset{\pm}{\boldsymbol{E}}{}_a^{(n_1)}[n_1]\overset{\mp}{\boldsymbol{E}}{}_a^{(n_1)})$, *etc.*

The pure magnetic contribution to (6.8) is given by (6.9) if the electric multipole moments and fields are replaced by magnetic multipole moments and fields, respectively, whereas the "interference" electromagnetic contribution has also the form of (6.9) by replacing therein $\boldsymbol{M}_e^{(n_2)}$ by $\boldsymbol{M}_m^{(n_2)}$ and $\boldsymbol{E}_b^{(n_2)}$ by $\boldsymbol{B}_b^{(n_2)}$.

According to (5.5) the expression (6.9) may be rewritten as

$$\overset{(2)}{{}_eS}{}_{kl}^{(n_1,n_2)}(\pm a, \mp b) = \frac{16\pi^3 2^{2(n_1+n_2)}(n_1!n_2!)^2|\boldsymbol{k}_a^{n_1-1}|^2|\boldsymbol{k}_b^{n_2-1}|^2}{\hbar^2(2n_1)!(2n_1+1)!(2n_2)!(2n_2+1)!}\times$$

$$\times\left|S(an_1, bn_2)\sum_i \langle k|\boldsymbol{M}_e^{(n_1)}|i\rangle\frac{\langle i|\boldsymbol{M}_e^{(n_2)}|l\rangle}{\omega_{il}\mp\omega_b}\right|^2|\boldsymbol{E}_a^{\pm}|^2|\boldsymbol{E}_b^{\mp}|^2. \tag{6.10}$$

By the general expression of (6.10), we obtain for the consecutive electric dipole-electric dipole contribution

$$\overset{(2)}{{}_eS}{}_{kl}^{(1,1)}(\pm a, \mp b) = \frac{16\pi^3}{9\hbar^2}\left|S(a, b)\sum_i \langle k|\boldsymbol{M}_e|\,i\rangle\frac{\langle i|\boldsymbol{M}_e|\,l\rangle}{\omega_{il}\mp\omega_b}\right|^2|\boldsymbol{E}_a^{\pm}|^2|\boldsymbol{E}_b^{\mp}|^2, \tag{6.11}$$

electric dipole-electric quadrupole contribution

$$\overset{(2)}{{}_eS}{}_{kl}^{(1,2)}(\pm a, \mp b) = \frac{16\pi^3 k_b^2}{45\hbar^2}\left|S(a, b)\sum_i \langle k|\boldsymbol{M}_e|\,i\rangle\frac{\langle i|\boldsymbol{Q}_e|\,l\rangle}{\omega_{il}\mp\omega_b}\right|^2|\boldsymbol{E}_a^{\pm}|^2|\boldsymbol{E}_b^{\mp}|^2, \tag{6.12}$$

electric quadrupole-electric quadrupole contribution

$$\overset{(2)}{{}_eS}{}_{kl}^{(2,2)}(\pm a, \mp b) = \frac{16\pi^3 k_a^2 k_b^2}{225\hbar^2}\left|S(a, b)\sum_i \langle k|\boldsymbol{Q}_e|\,i\rangle\frac{\langle i|\boldsymbol{Q}_e|l\rangle}{\omega_{il}\mp\omega_b}\right|^2|\boldsymbol{E}_a^{\pm}|^2|\boldsymbol{E}_a^{\mp}|^2, \tag{6.13}$$

electric dipole-magnetic dipole contribution

$$\overset{(2)}{{}_{em}S}{}_{kl}^{(1,1)}(\pm a, \mp b) = \frac{16\pi^3}{9\hbar^2}\left|S(a, b)\sum_i \langle k|\boldsymbol{M}_e|\,i\rangle\frac{\langle i|\boldsymbol{M}_m|\,l\rangle}{\omega_{il}\mp\omega_b}\right|^2|\boldsymbol{E}_a^{\pm}|^2|\boldsymbol{B}_b^{\mp}|^2, \tag{6.14}$$

where with respect to the definitions of (2.14) and (2.15) we have for the electric dipole and quadrupole moment operators

$$\boldsymbol{M}_e\equiv\boldsymbol{M}_e^{(1)}=\sum_s e_s\boldsymbol{r}_s,\quad \boldsymbol{Q}_e\equiv\boldsymbol{M}_e^{(2)}=\frac{1}{2}\sum_s e_s(3\boldsymbol{r}_s\boldsymbol{r}_s-r_s^2\boldsymbol{U}), \tag{6.15}$$

and for the magnetic dipole operator

$$\boldsymbol{M}_m \equiv \boldsymbol{M}_m^{(1)} = \frac{1}{2c} \sum_s e_s \boldsymbol{r}_s \times \dot{\boldsymbol{r}}_s . \tag{6.16}$$

From (6.11)—(6.14) we can obtain the result estimated recently by Guccione and Kranendonk [31].

In a similar manner expression (6.7) becomes for the direct magnetic transition

$$\overset{(2)}{{}_mS}{}^{(2)}_{kl}(\pm a, \mp b) = 16\pi^3 \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{2(n_1+n_2)}(n_1!n_2!)^2}{(2n_1)!(2n_1+1)!(2n_2)!(2n_2+1)!} \times$$
$$\times |\langle k|^{(n_1)}\boldsymbol{A}_m^{(n_2)}|\, l\rangle|^2 \, |\overset{\pm}{\boldsymbol{B}}{}_a^{(n_1)}|^2 \, |\overset{\mp}{\boldsymbol{B}}{}_b^{(n_2)}|^2, \tag{6.17}$$

which yields in the first approximation

$$\overset{(2)}{{}_mS}{}^{(2)}_{kl}(\pm a, \mp b) = \frac{16\pi^3}{9} |\langle k|\boldsymbol{A}_m|l\rangle|^2 \, |\boldsymbol{B}_a^{\pm}|^2 |\boldsymbol{B}_b^{\mp}|^2, \tag{6.18}$$

where by (4.8) we have for the dipole (dia-) magnetic polarizability operator

$$\boldsymbol{A}_m \equiv {}^{(1)}\boldsymbol{A}_m^{(1)} = -\frac{1}{4c^2} \sum_s \frac{e_s^2}{m_s} (r_s^2 \boldsymbol{U} - \boldsymbol{r}_s \boldsymbol{r}_s). \tag{6.19}$$

In the case when the radiation field is quantized we obtain from (6.4) and (6.5) by (4.15) and (4.16):

$$\overset{(2)}{I}{}^{(1)}_{kl}(\pm\lambda, \mp\mu) = \frac{4\pi^3}{V^2 \omega_\lambda \omega_\mu} \left\{ N_\lambda + \begin{pmatrix}1\\0\end{pmatrix} \right\} \left\{ N_\mu + \begin{pmatrix}0\\1\end{pmatrix} \right\} \times$$
$$\times \left| \sum_i S(\lambda, \mu) \langle k|\, \boldsymbol{e}_\lambda \cdot \boldsymbol{P}(\mp \boldsymbol{k}_\lambda)|\, i\rangle \frac{\langle i|\boldsymbol{e}_\mu \cdot \boldsymbol{P}(\pm \boldsymbol{k}_\mu)|l\rangle}{\omega_{il} \mp \omega_\mu} \right|^2, \tag{6.20}$$

$$\overset{(2)}{I}{}^{(2)}_{kl}(\pm\lambda, \mp\mu) = \frac{\pi^3 \hbar^2}{V^2 \omega_\lambda \omega_\mu} \left\{ N_\lambda + \begin{pmatrix}1\\0\end{pmatrix} \right\} \left\{ N_\mu + \begin{pmatrix}0\\1\end{pmatrix} \right\} \times$$
$$\times \; |\boldsymbol{e}_\lambda \cdot \boldsymbol{e}_\mu|^2 \langle k|A(\mp \boldsymbol{k}_\lambda, \pm \boldsymbol{k}_\mu)|\, l\rangle|^2. \tag{6.21}$$

The expressions (6.20) and (6.21) yield in the electric dipole approximation the result derived previously by Goeppert-Mayer [3]

$$\overset{(2)}{I}_{kl}(\pm\lambda, \mp\mu) = \frac{4\pi^3}{V^2} \omega_\lambda \omega_\mu \left\{ N_\lambda + \begin{pmatrix}1\\0\end{pmatrix} \right\} \left\{ N_\mu + \begin{pmatrix}0\\1\end{pmatrix} \right\} \times$$
$$\times \left| \sum_i S(\lambda, \mu) \langle k|\, \boldsymbol{e}_\lambda \cdot \boldsymbol{M}_e|\, i\rangle \frac{\langle i|\boldsymbol{e}_\mu \cdot \boldsymbol{M}_e|\, l\rangle}{\omega_{il} \mp \omega_\mu} \right|^2, \tag{6.22}$$

which has been discussed in detail for appropriate materials by several other authors [11—20].

In a good approximation, (6.21) may be expanded as

$$\overset{(2)}{I}{}^{(2)}_{kl}(\pm\lambda,\ \pm\mu) = \frac{\pi^3\hbar^2}{V^2\omega_\lambda\omega_\mu}\left\{N_\lambda + \begin{pmatrix}1\\0\end{pmatrix}\right\}\left\{N_\mu + \begin{pmatrix}1\\0\end{pmatrix}\right\}|\boldsymbol{e}_\lambda\cdot\boldsymbol{e}_\mu|^2 \times$$

$$\times\left|\left\langle k\left|\sum_s \frac{e_s^2}{m_s}\left\{1\mp i(\boldsymbol{k}_\lambda+\boldsymbol{k}_\mu)\cdot\boldsymbol{r}_s - \frac{1}{2}[(\boldsymbol{k}_\lambda+\boldsymbol{k}_\mu)\cdot\boldsymbol{r}_s]^2+\ldots\right\}\right|l\right\rangle\right|^2. \tag{6.23}$$

Here the term linear in the wave vector has recently been discussed by Iannuzi and Polacco [16] (see also Refs 15, 18) for the explanation of two-photon absorption in anthracene.

7. Three- and more-photon transition probabilities

In the third-order approximation the three-photon transition probability per unit time is, according to (3.1), (3.10), (3.14) and (3.15), given by

$$\overset{(3)}{P}_{kl} = \frac{1}{36\hbar^2 t}\left|\sum_{abc} S(a,b,c)\left\{\langle k|\overset{(3)}{V}{}^{+++}_{abc}|l\rangle + \right.\right.$$

$$+\frac{1}{\hbar}\sum_i\left[\langle k|\overset{(1)}{V}{}^{+}_{a}|i\rangle\frac{\langle i|\overset{(2)}{V}{}^{++}_{bc}|l\rangle}{\omega_{il}+\omega_b+\omega_c} + \langle k|\overset{(2)}{V}{}^{++}_{ab}|i\rangle\frac{\langle i|\overset{(1)}{V}{}^{+}_{c}|l\rangle}{\omega_{il}+\omega_c}\right] +$$

$$\left.\left.+\frac{1}{\hbar^2}\sum_{ij}\langle k|\overset{(1)}{V}{}^{+}_{a}|i\rangle\frac{\langle i|\overset{(1)}{V}{}^{+}_{b}|j\rangle\langle j|\overset{(1)}{V}{}^{+}_{c}|l\rangle}{(\omega_{il}+\omega_b+\omega_c)\ (\omega_{jl}+\omega_c)}\right\}f(\omega_{kl}+\omega_a+\omega_b+\omega_c)+c.c.\right|^2, \tag{7.1}$$

and may be further rewritten as

$$\overset{(3)}{P}_{kl} = \sum_{abc}\{\overset{(3)}{I}_{kl}(+a,\ +b,\ +c)\delta(\omega_{kl}+\omega_a+\omega_b+\omega_c)+\ldots\}, \tag{7.2}$$

where in the special case when only the first-order Hamiltonian is considered we have

$$\overset{(3)}{I}{}^{(1)}_{kl}(\pm a,\ \pm b,\ \mp c) = \frac{\pi}{6\hbar^4}\left|S(a,b,c)\sum_{ij}\langle k|\overset{(1)}{V}{}^{\pm}_{a}|i\rangle\frac{\langle i|\overset{(1)}{V}{}^{\pm}_{b}|j\rangle\langle j|\overset{(1)}{V}{}^{\mp}_{c}|l\rangle}{(\omega_{il}\pm\omega_b\mp\omega_c)\ (\omega_{jl}\mp\omega_c)}\right|^2. \tag{7.3}$$

This expression describes the three-photon transition $k\leftarrow l$ through two intermediate states i and j.

For the electric-dipole transition we obtain from (7.3) in the semi-classical case

$$_e\overset{(3)}{I}{}^{(1)}_{kl}(\pm a,\ \pm b,\ \mp c) = \frac{\pi}{6\hbar^4}\left|S(a,b,c)\sum_{ij}\langle k|\boldsymbol{M}_e\cdot\boldsymbol{E}^{\pm}_{a}|i\rangle\times\right.$$

$$\left.\times\frac{\langle i|\boldsymbol{M}_e\cdot\boldsymbol{E}^{\pm}_{b}|j\rangle\langle j|\boldsymbol{M}_e\cdot\boldsymbol{E}^{\mp}_{c}|l\rangle}{(\omega_{il}\pm\omega_b\mp\omega_c)(\omega_{jl}\mp\omega_c)}\right|^2. \tag{7.4}$$

If solely the first-order interaction Hamiltonian is taken into account, we obtain for the r-th order transition probability per unit time

$$\overset{(r)}{P}{}^{(1)}_{kl} = \frac{1}{(r!\hbar^r)^2}\Bigg|\sum_{a_1\ldots a_r}\sum_{i_{r-1}}\cdots\sum_{i_1} S(a_1, a_2, \ldots a_r)\langle k|\overset{(1)}{V}{}^{+}_{a_r}|i_{r-1}\rangle\times$$

$$\times\frac{\langle i_{r-1}|\overset{(1)}{V}{}^{+}_{a_{r-1}}|i_{r-2}\rangle}{(\omega_{i_{r-1}l}+\omega_{a_1}+\ldots+\omega_{a_{r-1}})}\cdots\frac{\langle i_1|\overset{(1)}{V}{}^{+}_{a_1}|l\rangle}{(\omega_{i_1l}+\omega_{a_1})}f(\omega_{kl}+\omega_{a_1}+\omega_{a_2}+\ldots\omega_{a_r})+c.c.\Bigg|^2, \tag{7.5}$$

wherein

$$f(\omega_{kl}+\omega_{a_1}+\omega_{a_2}+\ldots+\omega_{a_r}) = \frac{\exp\{i(\omega_{kl}+\omega_{a_1}+\omega_{a_2}+\ldots+\omega_{a_r})t\}-1}{\omega_{kl}+\omega_{a_1}+\omega_{a_2}+\ldots+\omega_{a_r}}. \tag{7.6}$$

We see that in the general case of r-photon processes the transition $k \leftarrow l$ can occur through $r-1$ virtual states $i_1, i_2, \ldots i_{r-1}$.

If the micro-system is subjected to a single electromagnetic wave the expression (7.6) reduces to the result derived by Gold and Bebb [39] for multiphoton photoionization of "transparanet" gases.

On substituting the quantized Hamiltonian of (4.15) in the general expression (7.5), we obtain

$$\overset{(r)}{P}_{kl} = \sum_{\lambda_1\ldots\lambda_r}\{\overset{(r)}{I}{}^{(1)}_{kl}(+\lambda_1, \ldots, +\lambda_r)\delta(\omega_{kl}+\omega_{\lambda_1}+\ldots+\omega_{\lambda_r})+\ldots\}, \tag{7.7}$$

wherein the brackets $\{\ \}$ contain 2^r terms of the form:

$$\overset{(r)}{I}{}^{(1)}_{kl}(\pm\lambda_1, \ldots, \mp\lambda_r) = \frac{r(2\pi)^{r+1}\left\{N_{\lambda_1}+\begin{pmatrix}1\\0\end{pmatrix}\right\}\left\{N_{\lambda_2}+\begin{pmatrix}1\\0\end{pmatrix}\right\}\cdots\left\{N_{\lambda_r}+\begin{pmatrix}0\\1\end{pmatrix}\right\}}{(r!)^2\hbar^{r-2}V^r\omega_{\lambda_1}\omega_{\lambda_2}\ldots\omega_{\lambda_r}}\times$$

$$\times\Bigg|\sum_{i_{r-1}}\cdots\sum_{i_1} S(\lambda_1, \lambda_2, \ldots\lambda_r)\langle k|\boldsymbol{e}_{\lambda_r}\cdot\boldsymbol{P}(\mp\boldsymbol{k}_{\lambda_r})|i_{r-1}\rangle\times$$

$$\frac{\langle i_{r-1}|\boldsymbol{e}_{\lambda_{r-1}}\cdot\boldsymbol{P}(\mp\boldsymbol{k}_{\lambda_{r-1}})|i_{r-2}\rangle}{(\omega_{i_{r-1}l}\pm\omega_{\lambda_1}\pm\ldots\pm\omega_{\lambda_{r-1}})}\cdots\frac{\langle i_1|\boldsymbol{e}_{\lambda_1}\cdot\boldsymbol{P}(\pm\boldsymbol{k}_{\lambda_1})|l\rangle}{(\omega_{i_1l}\mp\omega_{\lambda_1})}\Bigg|^2. \tag{7.8}$$

In particular for the three-photon processes Expression (7.8) becomes

$$\overset{(3)}{I}{}^{(1)}_{kl}(\pm\lambda, \pm\mu, \mp\nu) = \frac{4\pi^4\left\{N_\lambda+\begin{pmatrix}1\\0\end{pmatrix}\right\}\left\{N_\mu+\begin{pmatrix}1\\0\end{pmatrix}\right\}\left\{N_\nu+\begin{pmatrix}0\\1\end{pmatrix}\right\}}{3\hbar V^3\omega_\lambda\omega_\mu\omega_\nu}\times$$

$$\times\Bigg|\sum_{ij} S(\lambda, \mu, \nu)\langle k|\boldsymbol{e}_\lambda\cdot\boldsymbol{P}(\mp\boldsymbol{k}_\lambda)|i\rangle\frac{\langle i|\boldsymbol{e}_\mu\cdot\boldsymbol{P}(\mp\boldsymbol{k}_\mu)|j\rangle\langle j|\boldsymbol{e}_\nu\cdot\boldsymbol{P}(\pm\boldsymbol{k}_\nu)|l\rangle}{(\omega_{il}\pm\omega_\mu\mp\omega_\nu)(\omega_{jl}\mp\omega_\nu)}\Bigg|^2. \tag{7.9}$$

It is thus seen that, whereas in first-order transition processes by Eq. (5.2) we deal with the emission or absorption of one photon, in second-order transition processes we have by Eq. (6.2) four possibilities: simultaneous emission or absorption of two photons and the disappearance and appearance of one photon, or *vice versa*. From Eq. (7.2), third--order transitions are seen to comprise in general eight possible processes, two of which consist in the simultaneous emission or absorption of three photons, the remaining ones being processes wherein one photon vanishes and two photons appear or, *vice versa*, two photons vanish and one photon appears. Similarly, by considering in accordance with Eq. (7.7) transitions of the r-th order, we obtain in general 2^r theoretically possible radiation processes involving r photons simultaneously.

8. *Nonlinear electric and magnetic multipole polarization tensors*

In the case when the incident light beam is coherent, multi-photon absorption processes are related to the imaginary part of the nonlinear susceptibility of the medium.

The tensor of the dynamical electric permittivity tensor is given by the equation

$$(\boldsymbol{\epsilon}-\boldsymbol{U})\cdot\boldsymbol{E}(\boldsymbol{r},t)=4\pi\boldsymbol{P}_e(\boldsymbol{r},t), \tag{8.1}$$

in which the electric polarization vector $\boldsymbol{P}_e$ having in general the form of (2.10) containing the electric 2^n-pole moment density is now defined as

$$\boldsymbol{P}_e^{(n)}(\boldsymbol{r},t)=\langle \varrho U^*(t,t_0)\boldsymbol{M}_e^{(n)}U(t,t_0)\rangle, \tag{8.2}$$

where ϱ is the density number operator.

If the expression of (3.2) is used, the expression of (8.2) can be expanded as follows:

$$\boldsymbol{P}_e^{(n)}(\boldsymbol{r},t)=\sum_{r=0}^{\infty}\overset{(r)}{\boldsymbol{P}}{}_e^{(n)}=\overset{(0)}{\boldsymbol{P}}{}_e^{(n)}+\overset{(1)}{\boldsymbol{P}}{}_e^{(n)}+\overset{(2)}{\boldsymbol{P}}{}_e^{(n)}+\overset{(3)}{\boldsymbol{P}}{}_e^{(n)}+\ldots, \tag{8.3}$$

where the r-th-order electric multipole density is given by

$$\overset{(r)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r},t)=\sum_{s=0}^{r}\langle \varrho \overset{(s)}{U^*}(t,t_0)\boldsymbol{M}_e^{(n)}\overset{(r-s)}{U}(t,t_0)\rangle. \tag{8.4}$$

By the expressions (3.6) and (3.7) and a symmetrizing operation we obtain from (8.4) in explicite form

$$\overset{(r)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r},t)=\sum_{a_1\ldots a_r}\{\overset{(r)}{\boldsymbol{P}}{}^{(n)}(+\omega_{a_1},\ldots,\omega_{a_r})e^{i(\omega_{a_1}+\ldots+\omega_{a_r})t}+\ldots\}, \tag{8.5}$$

where

$$\overset{(r)}{\boldsymbol{P}}{}_e^{(n)}(\pm\omega_{a_1},\ldots\pm\omega_{a_r})=\frac{1}{r!}\sum_{n_{a_1}=1}^{\infty}\cdots\sum_{n_{a_r}=1}^{\infty}\frac{2^{n_{a_1}+\ldots+n_{a_r}}n_{a_1}!\ldots n_{a_r}!}{(2n_{a_1})!\ldots(2n_{a_r})!}\times$$

$$\times\,{}^{(n)}\boldsymbol{\chi}_a^{(n_{a_1}+\ldots+n_{a_r})}(\pm\omega_{a_1},\ldots\pm\omega_{a_r})\,[n_{a_1}+\ldots+n_{a_r}]\,\overset{\pm}{\boldsymbol{E}}{}_{a_1}^{(n_{a_1})}\ldots\overset{\pm}{\boldsymbol{E}}{}_{a_r}^{(n_{a_r})} \tag{8.6}$$

if in (3.7) only the purely electric part of the first-order interaction Hamiltonian of (4.5) is used.

The qunatum-mechanical form of the r-th-order electric multipole susceptibility tensor is (see Refs 32, 40, 41)

$$ {}^{(n)}\chi_e^{(na_1+na_2+\ldots+na_r)}(\pm\omega_{a_1}, \pm\omega_{a_2}, \ldots, \pm\omega_{a_r}) = \varrho\hbar^{-r}\sum_{t=0}^{r}\sum_{ki_1\ldots i_rl}\bar{\varrho}_{kl}S(a_1, a_2, \ldots a_r)\times $$
$$ \frac{\langle k|M_e^{(na_1)}|i_1\rangle\langle i_1|M_e^{(na_2)}|i_2\rangle\ldots\langle i_{t-1}|M_e^{(na_t)}|i_t\rangle\langle i_t|M_e^{(n)}|i_{t+1}\rangle\langle i_{t+1}|M_e^{(na_{t+1})}|i_{t+2}\rangle\ldots\langle i_r|M_e^{(na_r)}|l\rangle}{\prod_{u=1}^{t}(\omega_{i_uk}\mp\omega_{a_1}\mp\omega_{a_2}\mp\ldots\mp\omega_{a_u}+i\Gamma_{i_uk})\prod_{u=t+1}^{r}(\omega_{i_ul}\pm\omega_{a_u}\pm\omega_{a_{u+1}}\pm\ldots\pm\omega_{a_r}+i\Gamma_{i_ul})} \tag{8.7} $$

where ϱ_{kl} is the statistical matrix for the transition $k\leftarrow l$ with relaxation time Γ_{kl}^{-1}.

From (8.7) we obtain *e.g.* for the second-order electric multipole susceptibility tensor

$$ {}^{(n)}\chi_e^{(na+nb)}(\pm\omega_a, \pm\omega_b) = \varrho\hbar^{-2}S(n_a, n_b)\sum_{kijl}\varrho_{kl}\left\{\frac{\langle k|M_e^{(n)}|i\rangle\langle i|M_e^{(na)}|j\rangle\langle j|M_e^{(nb)}|l\rangle}{(\omega_{il}\pm\omega_a\pm\omega_b+i\Gamma_{il})(\omega_{jl}\pm\omega_b+i\Gamma_{jl})}+\right. $$
$$ \left.+\frac{\langle k|M_e^{(na)}|i\rangle\langle i|M_e^{(n)}|j\rangle\langle j|M_e^{(nb)}|l\rangle}{(\omega_{ik}\mp\omega_a+i\Gamma_{ik})(\omega_{jl}\pm\omega_b+i\Gamma_{jl})}+\frac{\langle k|M_e^{(na)}|i\rangle\langle i|M_e^{(nb)}|j\rangle\langle j|M_e^{(n)}|l\rangle}{(\omega_{ik}\mp\omega_a+i\Gamma_{ik})(\omega_{jk}\mp\omega_a\mp\omega_b+i\Gamma_{jk})}\right\}. \tag{8.8} $$

In the special case when the spatial variation of the electric field can be ignored, expressions (8.5) and (8.6) reduce to the following simpler form:

$$ \overset{(r)}{P}{}_e^{(n)}(r, t) = \frac{1}{r!}\sum_{a_1\ldots a_r}\{{}^{(n)}\chi_e^{(r)}(+\omega_{a_1}, \ldots, +\omega_{a_r})[r]E_{a_1}^+\ldots E_{a_r}^+e^{i(\omega_{a_1}+\ldots+\omega_{a_r})t}+c.c.\} \tag{8.9} $$

which corresponds to generation of the r-th mixed waves.

Consider, for instance, the case when a DC uniform electric field is applied to the medium; we obtain, instead of (8.9)

$$ \overset{(r)}{P}{}_e^{(n)}(r, t) = \frac{1}{(r-1)!}\sum_{a_1\ldots a_{r-1}}\{{}^{(n)}\chi_e^{(r)}(+\omega_{a_1}, \ldots, +\omega_{a_{r-1}})\times $$
$$ [r]E_{a_1}^+\ldots E_{a_{r-1}}^+E_{\mathrm{DC}}e^{i(\omega_{a_1}+\ldots+\omega_{a_{r-1}})t}+c.c.\} \tag{8.10} $$

for the linear DC electric field induced generation of the $(r-1)$th mixed waves.

If the frequencies of all interacting waves are the same, Expressions (8.9) and (8.10) describe, respectively, r-th-harmonic generation and DC electric field induced $(r-1)$th-harmonic generation.

In the case of small spatial dispersion, the general Expressions (8.5) and (8.6) yield in a good approximation for the second-order electric multipole polarization

$$ \overset{(2)}{P}{}_e^{(n)}(r, t) = \frac{1}{2}\sum_{ab}\left\{{}^{(n)}\chi_e^{(1+1)}(+\omega_a, +\omega_b) - \frac{i}{3}[{}^{(n)}\chi_e^{(2+1)}(+\omega_a, +\omega_b)\cdot k_a+\right. $$
$$ \left.+{}^{(n)}\chi_e^{(1+2)}(+\omega_a, +\omega_b)\cdot k_b] - \frac{1}{9}{}^{(n)}\chi_e^{(2+2)}(+\omega_a, +\omega_b):k_ak_b+\ldots\right\}:E_a^+E_b^+e^{i(\omega_a+\omega_b)t}. \tag{8.11} $$

In the dipole approximation ($n = 1$) the first term in the foregoing expansion determines sum-frequency generation in crystals lacking inversion symmetry [42, 43], whereas the two terms linear in $\boldsymbol{k}$ (electric dipole-quadrupole effect) — that in material media having a centre of symmetry [42—44]. Similarly in the quadrupole approximation ($n = 2$) the first term of (8.11) is responsible for sum-frequency radiation from material systems, irrespective of their symmetry.

On replacing in the Expressions of (8.6) and (8.7) the electric fields $\boldsymbol{E}_{a_1}^{(n_{a_1})}, \ldots$ by magnetic fields $\boldsymbol{H}_{a_1}^{(n_{a_1})}, \ldots$, and the electric multipole moments operators $\boldsymbol{M}_e^{(n)}, \ldots$ by the magnetic multipole moments $\boldsymbol{M}_m^{(n)}, \ldots$, we obtain automatically expressions for the rth-order magnetic multipole polarization $\overset{(r)}{\boldsymbol{P}}{}_m^{(n)}$ and susceptibility tensor ${}^{(n)}\chi_m^{(n_{a_1}+\ldots+n_{a_r})}$. Since the electric and magnetic vectors are associated with the radiation field simultaneously, one has to take into consideration in Equation (4.5) both the electric and magnetic multipole parts of the Hamiltonian. In this general case, as a result, in addition to pure electric and magnetic multipole polarizations $\boldsymbol{P}_e^{(n)}$ and $\boldsymbol{P}_m^{(m)}$, one obtains in the second and higher order approximations of perturbation theory the additional mixed multipole polarizations $\boldsymbol{P}_{em}^{(n)}$ and $\boldsymbol{P}_{me}^{(n)}$ dependent on the electric and magnetic field strengths simultaneously. In the absence of spatial dispersion the second- and third-order electric multipole polarizations are given by

$$\overset{(2)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r}, t) = \frac{1}{2} \sum_{ab} \{ {}^{(n)}_{e}\chi_{ee}^{(1+1)}(\omega_a, \omega_b) : \boldsymbol{E}_a^+ \boldsymbol{E}_b^+ + {}^{(n)}_{e}\chi_{em}^{(1+1)}(\omega_a, \omega_b) : \boldsymbol{E}_a^+ \boldsymbol{H}_b^+ +$$

$$+ {}^{(n)}_{e}\chi_{me}^{(1+1)}(\omega_a, \omega_b) : \boldsymbol{H}_a^+ \boldsymbol{E}_b^+ + {}^{(n)}_{e}\chi_{mm}^{(1+1)}(\omega_a, \omega_b) : \boldsymbol{H}_a^+ \boldsymbol{H}_b^+ \} \, e^{i(\omega_a+\omega_b)t}, \tag{8.12}$$

$$\overset{(3)}{\boldsymbol{P}}{}_e^{(n)}(\boldsymbol{r}, t) = \frac{1}{6} \sum_{abc} \{ {}^{(n)}_{e}\chi_{eee}^{(1+1+1)}(\omega_a, \omega_b, \omega_c) \vdots \boldsymbol{E}_a^+ \boldsymbol{E}_b^+ \boldsymbol{E}_c^+ +$$

$$+ {}^{(n)}_{e}\chi_{eem}^{(1+1+1)}(\omega_a, \omega_b, \omega_c) \vdots \boldsymbol{E}_a^+ \boldsymbol{E}_b^+ \boldsymbol{H}_c^+ + {}^{(n)}_{e}\chi_{emm}^{(1+1+1)}(\omega_a, \omega_b, \omega_c) \vdots \boldsymbol{E}_a^+ \boldsymbol{H}_b^+ \boldsymbol{H}_c^+ +$$

$$+ \ldots + {}^{(n)}_{e}\chi_{mmm}^{(1+1+1)}(\omega_a, \omega_b, \omega_c) \vdots \boldsymbol{H}_a^+ \boldsymbol{H}_b^+ \boldsymbol{H}_c^+ \} \, e^{i(\omega_a+\omega_b+\omega_c)t}. \tag{8.13}$$

When ω_a, ω_b, and ω_c are nonzero, the expansion (8.13) is responsible for triple sum-frequency generation [42—45], whereas if $\omega_c = 0$ — for the DC electric or magnetic field induced double sum-frequency radiation. In the case when $\omega_a \neq 0$ and all $\omega_b = \omega_c = 0$ the first term in the expansion of (8.13) describes the well-known Kerr effect whereas the third accounts for the Cotton-Mouton effect in an isotropic medium [46].

The Maxwell Equations (2.4) and (2.5) with the electric and magnetic field strength vectors (2.8) and (2.9), as well as the wave equations (2.16) and (2.17) with the multipole expansions of the electric and magnetic polarization vectors (2.10) and (2.11), together with the quantal-perturbation expansions (8.6) and (8.7) jointly, determine the general fundamentals of nonlinear optics with time- and spatially variable electromagnetic fields, as *e.g.* conveyed by a light wave from a laser.

9. *Conclusions and final remarks*

As we have just seen, a theory of multi-photon processes can be derived by a formal procedure, and taking into account not only electric dipolar but, quite generally, electric and magnetic multipolar transitions. In general, the probabilities of electric 2^{n+1}-polar transitions are of the same order as for magnetic 2^n-polar transitions. Whereas in first-order processes (one-photon transition) no interference occurs between the electric 2^{n+1}-polar and the magnetic 2^n-polar transition probability, such interference does exist in processes of the second- and higher-orders. Notwithstanding the fact that in these processes the probabilities for multipole transitions are insignificant in comparison with the electric dipolar transition probability, they (in particular the electric quadrupolar transition probability) nevertheless can play an essential role in all cases when transitions of the dipolar type are forbidden.

We have also been able to show that the transition probability of an r-photon process consists generally of r terms, the first determining exclusively the direct transition from the initial to the final state as defined by the non-zero Hamiltonian $V^{(r)}$ of order r (obviously, orders higher than the second will yield relativistic corrections [37]), while the further $r-1$ terms determine indirect transitions involving virtual states — the first of these occurs by way of one virtual state connecting the product of matrix elements of the Hamiltonian $V^{(r-1)}$ of order $r-1$ and $V^{(1)}$ of order 1, whereas the last of these terms occurs by way of $r-1$ virtual states connecting products of matrix elements of the Hamiltonian $V^{(1)}$ of order 1. Just which of these transitions, direct or indirect, of order higher than 2 will have priority depends on the specifically existing conditions (*e.g.* the type of substance and multipolar transition). Generally, the probability for a direct transition contributes but insignificantly to the value of that for indirect transitions, although the inverse is not to be ruled out. Various substances can reveal various ratios of the probabilities for the respective transitions. The roles of the various mechanisms underlying the higher-order (multi-photon) processes can be assessed with clarity in each case only after detailed numerical evaluations of matrix elements for transitions of various types have been made. Regrettably, in most cases such evaluations involve serious computational difficulties, even if far-reaching simplifications are introduced. Some insight into these rather intricate problems of higher-order transitions is to be hoped for from research on generation of optical harmonics and on other related nonlinear processes (see Refs 19, 27, 32, 37, 40—46).

The formalism developed in Sections 2—4 and 8 can be successfully applied for the quantitative description of various nonlinear electro- and magneto-optical processes [46], for calculating variations of the electric nad magnetic permittivity [41] due to intense electromagnetic fields, as well as of nonlinear induced optical activity, Faraday's effect, *etc.* Clearly, it would be most indicated to complete the present formalism by including the statistical and coherence properties of electromagnetic fields [47, 48].

There is still something to be said concerning the direct and indirect transitions related with interaction Hamiltonians of order higher than the second which, as a matter of fact, are already relativistic corrections. This is at once obvious on expanding formally the classical relativistic Hamiltonian $H = e\Phi + \{m^2c^4 + (c\boldsymbol{p} - e\boldsymbol{A})^2\}^{1/2}$ in a series in powers of the vector potential $\boldsymbol{A}$. Thus, strictly speaking, the theory of morethan two-photon processes should be a not only quantal but moreover relativistic theory basing on the wave- equation $i\hbar\dot{\psi} = H_D\psi$ with the Dirac Hamiltonian $H_D = \beta mc^2 + \alpha \cdot (c\boldsymbol{p} - e\boldsymbol{A}) + e\Phi$. By applying consecutively the canonical transformations of Foldy-Wouthuysen [49] and Eriksen [50] we can then obtain interaction Hamiltonians of order higher than the second containing only even operators. One can thus derive a consistent theory of multi-photon transitions for relativistic particles.

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