

Reprinted from

*Proceedings of the
Physical Society*

The Institute of Physics and the Physical Society

Printed in Great Britain by J. W. Arrowsmith Ltd., Bristol 3

Non-linear processes to result from multipole interactions between molecules and electromagnetic fields

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MS. received 2nd March 1965, in revised form 29th April 1965

Abstract. A compact and at the same time general tensor formalism adapted to the theoretical prediction of a wide range of non-linear processes due in general to multipole interactions between atomic or molecular systems and electromagnetic fields is proposed. Recurring to a semi-classical method, the expectation values of the 2^n -pole induced electric moment $\mathbf{P}_e^{(n)}$ and 2^n -pole magnetic moment $\mathbf{P}_m^{(n)}$ for a transition $k \rightarrow l$ are computed explicitly to within the third order of quantum-mechanical perturbation theory approximation. The formalism is demonstrated with regard to its utility and simplicity on the example of electric and magnetic multipole light scattering with multiharmonic frequencies $\omega_{kl} + \omega_1 + \omega_2 + \dots + \omega_r$.

1. Introduction

The quantum-mechanical theory of electromagnetic radiation as initiated by Dirac (1927) allows one to compute the probability of various processes involving the emission, absorption or scattering of light quanta. In general, such processes can occur in two- or many-quantum acts. In the visible region, simultaneous absorption and emission of two quanta was dealt with by Goepfert-Mayer (1931). Blaton (1931), by second-order quantum-mechanical perturbation theory, showed that a system of atoms subjected to irradiation with frequency ν emits waves of double frequency 2ν . This light scattering with double frequency was subsequently investigated by Neugebauer (1959, 1963). The process considered by Blaton and Neugebauer (see also Kielich 1963, 1964 a) is a special case of the scattering process investigated by Güttinger (1932), wherein two light quanta of frequencies ν_1 and ν_2 vanish and a new quantum of frequency $\nu_1 + \nu_2$ results, the atomic system maintaining its energy state unchanged. In the general case, when an atomic or molecular system goes over from quantum state k to state l under the effect of incident photons of frequencies ν_1 and ν_2 , a new scattered photon arises with frequency $\nu_3 = \nu_1 + \nu_2 \pm \nu_{kl}$ (Güttinger 1932, Kielich 1963, 1964 b, c). On extending these considerations to the third-order approximation of quantum-mechanical perturbation calculus, it appears that additional non-linear scattering with frequencies $\nu_1 + 2\nu_2 \pm \nu_{kl}$ (see Kielich 1964 b, c) or, generally, $\nu_1 + \nu_2 + \nu_3 \pm \nu_{kl}$ is to be expected.

Of the various processes presenting great theoretical importance, those should be mentioned here which find a satisfactory explanation within the framework of the non-linear electrodynamics of Born and Infeld (1934 a, b, 1935). In non-linear theory of the Maxwell field, the principle of superposition is not fulfilled; the waves interact giving rise to characteristic non-linear effects as, for example, reflection of light on light or scattering of light on light (see e.g. Karplus and Neuman 1951, McKenna and Platzman 1963, and

the papers cited by them) and harmonics in the scattering of light on free electrons (see Vachaspati 1962, Mizushima 1963, Brown and Kibble 1964).

The probability of an n -photon process related with an electric transition of dipole type is proportional to $(E_1/E_a)^{2n}$, where E_1 is the electric field of the light wave and E_a the mean atomic electric field. Thus, the probability ratio of a two-photon and one-photon process or, quite generally, of an $(n+1)$ -photon and n -photon process is of the order of $(E_1/E_a)^2$. Consequently, at normal conditions, the probability for a two- or many-photon process to occur is 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. Owing to the use of lasers, a number of non-linear processes are at present the object of observations in laboratories, as for example generation of optical harmonics (see Franken and Ward 1963, and the list of papers given by them). The theory of generation of optical harmonics and that of related non-linear processes wherein two or more photons participate is discussed by Braunstein (1962), Armstrong *et al.* (1962), Loudon (1962), Kelley (1963), Price (1963), Butcher and McLean (1963, 1964), Ward and Franken (1964), Cheng and Miller (1964), Ducuing and Bloembergen (1964) and Caspers (1964). Higher order coherent Raman processes were considered by Bloembergen and Shen (1964) and Tang (1964).

In all the above-mentioned non-linear processes, the principal role is played by electric transitions of the dipole type; however, higher order transitions, of the quadrupole, octopole etc. types, are possible. Higher order transitions related with the multipole electric or magnetic radiation of atoms have been discussed from a theoretical viewpoint by Rubinowicz (1930, 1949) (see e.g. the reports by Rubinowicz and Blaton 1932 and by Bowen 1936). Contributions to the electric dipole moment from multipole moments are discussed by Armstrong *et al.* (1962) to within the second order of perturbation theory. Non-linear effects due to electric dipoles and quadrupoles and to magnetic dipoles have been dealt with phenomenologically by Pershan (1963) and quantum-mechanically by Adler (1964). Strictly, these non-linear processes have to be approached by the methods of quantum electrodynamics; nevertheless, in a number of cases, a semi-classical method is adequate for their quantitative description, and will be adhered to in the present paper. The basis of our theory is given by the multipole expansion of the Hamiltonian of interaction between a system of electrically charged particles and a classical electromagnetic field (see Power and Zienau 1959, Fiutak 1963†).

In this paper we propose a general tensor formalism allowing the determination of the multipole electric or magnetic moments induced by electromagnetic fields in atoms or molecules. By quantum-mechanical perturbation calculus, to the third-order approximation inclusively (without quantization of the electromagnetic field), we shall compute in explicit form the matrix element of the 2^n -pole electric moment for a transition $k \rightarrow l$. Accordingly, we introduce tensors of multipole polarizability of the first, second and third order accounting for the electric and magnetic properties of systems consisting of charged particles when these systems undergo the polarizing effect of electromagnetic fields. The expansions obtained by us for the dynamical quantity \mathbf{F} and the total induced multipole electric moment $\mathbf{P}_e^{(n)}$ and magnetic moment $\mathbf{P}_m^{(n)}$ can be of use in the quantitative treatment of various non-linear effects deriving from the presence of multipolar interactions between molecules and electromagnetic fields. In particular, the formalism developed here has been applied to compute the tensor of electric multipole light scattering with multiharmonic frequencies. The tensor is discussed for several

† The author wishes to thank Dr. J. Fiutak for drawing his attention to the paper by Power and Zienau (1959) and for discussions relating to the multipole expansion of the Hamiltonian.

special cases, successively in the first, second and third approximation of perturbation theory. The importance of investigating non-linear processes of this kind resides primarily in the possibility of obtaining information on the multipolar and non-linear properties of atoms and molecules in the presence of intense electromagnetic fields.

2. Fundamentals of the theory

Let us consider an atom or molecule subject to external periodically time-variable fields. Its total Hamiltonian is

$$H = H_0 + V(t) \tag{1}$$

where H_0 is the non-perturbed Hamiltonian, which is time-independent, and $V(t)$ is the time-dependent perturbation to H_0 .

We search for a wave function ψ fulfilling Schrödinger's equation

$$i\hbar \frac{\partial \psi}{\partial t} = \{H_0 + V(t)\}\psi. \tag{2}$$

Assume that, before the perturbation set in, the molecule was in quantum state k with energy E_k^0 . In the presence of the perturbation, the wave function of the state considered can be written as

$$\psi_k = \sum_j a_{jk}(t)\psi_j^0 \exp\left(-iE_j^0 \frac{t}{\hbar}\right) \tag{3}$$

where E_j^0 and ψ_j^0 are the eigenvalue and eigenfunction of H_0 .

By (1) and (2), the matrix element $a_{jk}(t)$ defining the transition of the molecule from the state k to j under the effect of the perturbation $V(t)$ is obtained in the form

$$a_{jk}(t) = \sum_{n=0}^{\infty} \langle j | U^{(n)} | k \rangle \tag{4}$$

where for $t \leq 0$ and $n = 0$ the initial condition is determined by

$$a_{jk}(0) = \langle j | U^{(0)} | k \rangle = \langle j | k \rangle = \delta_{jk}. \tag{5}$$

For $t \geq t_0$, the n th order of the evolution operator $U^{(n)}$ of the series (4) is defined by

$$U^{(n)}(t, t_0) = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t \hat{V}(t_1) dt_1 \int_{t_0}^{t_1} \hat{V}(t_2) dt_2 \dots \int_{t_0}^{t_{n-1}} \hat{V}(t_n) dt_n \tag{6}$$

wherein

$$\hat{V}(t) = \exp\left(\frac{i}{\hbar} H_0 t\right) V(t) \exp\left(-\frac{i}{\hbar} H_0 t\right) \tag{7}$$

is the perturbation operator in interaction representation.

With the Dyson time-ordering operator \mathbf{T} , equation (6) can be rewritten in symmetric form with respect to t_1, t_2, \dots, t_n ($t > t_1 > t_2 > \dots > t_n > t_0$)

$$U^{(n)}(t, t_0) = \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t \dots \int_{t_0}^t \mathbf{T}\{\hat{V}(t_1) \dots \hat{V}(t_n)\} dt_1 \dots dt_n. \tag{8}$$

Let us now assume, in general, the perturbation $V(t)$ in the Hamiltonian (1) to be the superposition of several perturbations $V_1, V_2 \dots V_a$ varying in time with angular frequencies $\omega_1, \omega_2 \dots \omega_a$, i.e.

$$V(t) = \overset{(1)}{V} + \overset{(2)}{V} + \overset{(3)}{V} + \dots = \sum_{n=1}^{\infty} \overset{(n)}{V} \quad (9)$$

in which the first-, second- and third-order perturbations are of the form

$$\begin{aligned} \overset{(1)}{V} &= \frac{1}{2} \sum_a \{ \overset{(1)}{V}_a^+ \exp(i\omega_a t) + \overset{(1)}{V}_a^- \exp(-i\omega_a t) \} \\ \overset{(2)}{V} &= \frac{1}{4} \sum_{ab} \{ [\overset{(2)}{V}_{ab}^{++} \exp\{i(\omega_a + \omega_b)t\} + \overset{(2)}{V}_{ab}^{+-} \exp\{i(\omega_a - \omega_b)t\} \\ &\quad + \overset{(2)}{V}_{ab}^{-+} \exp\{-i(\omega_a - \omega_b)t\} + \overset{(2)}{V}_{ab}^{--} \exp\{-i(\omega_a + \omega_b)t\}] \} \end{aligned} \quad (10)$$

$$\overset{(3)}{V} = \frac{1}{8} \sum_{abc} [\overset{(3)}{V}_{abc}^{+++} \exp\{i(\omega_a + \omega_b + \omega_c)t\} + \dots + \overset{(3)}{V}_{abc}^{---} \exp\{-i(\omega_a + \omega_b + \omega_c)t\}] ;$$

the brackets in V contain 2^3 components.

The expectation value of a dynamical operator $\mathbf{F}(t)$ for the transition $k \rightarrow l$

$$\mathbf{F}_{kl}(t) = \int \psi_k^* \mathbf{F}(t) \psi_l d\tau \quad (11)$$

can be expressed by (3)–(10) in the form

$$\mathbf{F}_{kl}(t) = \overset{(0)}{\mathbf{F}}_{kl} + \overset{(1)}{\mathbf{F}}_{kl} + \overset{(2)}{\mathbf{F}}_{kl} + \overset{(3)}{\mathbf{F}}_{kl} + \dots = \sum_{n=0}^{\infty} \overset{(n)}{\mathbf{F}}_{kl} \quad (12)$$

with $\overset{(0)}{\mathbf{F}}_{kl}$ denoting the zeroth-order approximation of \mathbf{F}_{kl} .

In the first-order perturbation theory the expectation value of \mathbf{F} is

$$\overset{(1)}{\mathbf{F}}_{kl}(t) = \frac{1}{2} \sum_a \{ \overset{(1)}{\mathbf{F}}_{kl}(+\omega_a) \exp(i\omega_a t) + \overset{(1)}{\mathbf{F}}_{kl}(-\omega_a) \exp(-i\omega_a t) \} \exp(i\omega_{kl} t) \quad (13)$$

with

$$\overset{(1)}{\mathbf{F}}_{kl}(+\omega_a) = -\frac{1}{\hbar} \sum_r \left(\frac{\langle k | \mathbf{F} | r \rangle \langle r | \overset{(1)}{V}_a^+ | l \rangle}{\omega_{rl} + \omega_a} + \frac{\langle k | \overset{(1)}{V}_a^+ | r \rangle \langle r | \mathbf{F} | l \rangle}{\omega_{rk} - \omega_a} \right). \quad (14)$$

Here, $\omega_{rk} = (E_r^0 - E_k^0)/\hbar$ is the frequency of the transition $r \rightarrow k$ when perturbation is absent.

The second-order expectation value of \mathbf{F} is given by

$$\begin{aligned} \overset{(2)}{\mathbf{F}}_{kl}(t) &= \frac{1}{4} \sum_{ab} [\overset{(2)}{\mathbf{F}}_{kl}(+\omega_a, +\omega_b) \exp\{i(\omega_a + \omega_b)t\} \\ &\quad + \overset{(2)}{\mathbf{F}}_{kl}(\omega_a, -\omega_b) \exp\{i(\omega_a - \omega_b)t\} + \overset{(2)}{\mathbf{F}}_{kl}(-\omega_a, +\omega_a) \exp\{-i(\omega_a - \omega_b)t\} \\ &\quad + \overset{(2)}{\mathbf{F}}_{kl}(-\omega_a, -\omega_b) \exp\{-i(\omega_a + \omega_b)t\}] \exp(i\omega_{kl} t) \end{aligned} \quad (15)$$

where

$$\mathbf{F}_{kl}^{(2)}(+\omega_a, +\omega_b) = \mathbf{F}_{kl}^{(1)}(+\omega_a, +\omega_b) + \mathbf{F}_{kl}^{(2)}(+\omega_a, +\omega_b). \quad (16)$$

The first part of (16) results from second-order perturbation theory when only the first-order perturbation Hamiltonian is used:

$$\begin{aligned} \mathbf{F}_{kl}^{(2)}(+\omega_a, +\omega_b) = \frac{1}{\hbar^2} \sum_{rs} \left\{ \frac{\langle k|\mathbf{F}|r\rangle\langle r|\mathbf{V}_a^+|s\rangle\langle s|\mathbf{V}_b^+|l\rangle}{(\omega_{rl} + \omega_a + \omega_b)(\omega_{sl} + \omega_b)} \right. \\ \left. + \frac{\langle k|\mathbf{V}_a^+|r\rangle\langle r|\mathbf{F}|s\rangle\langle s|\mathbf{V}_b^+|l\rangle}{(\omega_{rk} - \omega_a)(\omega_{sl} + \omega_b)} + \frac{\langle k|\mathbf{V}_a^+|r\rangle\langle r|\mathbf{V}_b^+|s\rangle\langle s|\mathbf{F}|l\rangle}{(\omega_{rk} - \omega_a)(\omega_{sk} - \omega_a - \omega_b)} \right\} \quad (17) \end{aligned}$$

whereas the second part of (16) results from first-order perturbation theory with the second-order perturbation Hamiltonian and is of the form

$$\mathbf{F}_{kl}^{(1)(2)}(+\omega_a, +\omega_b) = -\frac{1}{\hbar} \sum_r \left\{ \frac{\langle k|\mathbf{F}|r\rangle\langle r|\mathbf{V}_{ab}^{(2)}|l\rangle}{\omega_{rl} + \omega_a + \omega_b} + \frac{\langle k|\mathbf{V}_{ab}^{(2)}|r\rangle\langle r|\mathbf{F}|l\rangle}{\omega_{rk} - \omega_a - \omega_b} \right\}. \quad (18)$$

In the third-order approximation we have

$$\begin{aligned} \mathbf{F}_{kl}^{(3)}(t) = \frac{1}{8} \sum_{abc} \left[\mathbf{F}_{kl}^{(3)}(+\omega_a, +\omega_b, +\omega_c) \exp\{i(\omega_a + \omega_b + \omega_c)t\} + \dots \right. \\ \left. + \mathbf{F}_{kl}^{(3)}(-\omega_a, -\omega_b, -\omega_c) \exp\{-i(\omega_a + \omega_b + \omega_c)t\} \right] \exp(i\omega_{kl}t) \quad (19) \end{aligned}$$

with

$$\begin{aligned} \mathbf{F}_{kl}^{(3)}(+\omega_a, +\omega_b, +\omega_c) = \mathbf{F}_{kl}^{(1)(3)}(+\omega_a, +\omega_b, +\omega_c) + \mathbf{F}_{kl}^{(2)(2)}(+\omega_a, +\omega_b, +\omega_c) \\ + \mathbf{F}_{lk}^{(2)(2)}(-\omega_a, -\omega_b, -\omega_c) + \mathbf{F}_{kl}^{(1)(3)}(+\omega_a, +\omega_b, +\omega_c). \quad (20) \end{aligned}$$

Here

$$\begin{aligned} \mathbf{F}_{kl}^{(1)(3)}(+\omega_a, +\omega_b, +\omega_c) = -\frac{1}{\hbar^3} \sum_{rst} \left\{ \frac{\langle k|\mathbf{F}|r\rangle\langle r|\mathbf{V}_a^+|s\rangle\langle s|\mathbf{V}_b^+|t\rangle\langle t|\mathbf{V}_c^+|l\rangle}{(\omega_{rl} + \omega_a + \omega_b + \omega_c)(\omega_{sl} + \omega_b + \omega_c)(\omega_{tl} + \omega_c)} \right. \\ + \frac{\langle k|\mathbf{V}_a^+|r\rangle\langle r|\mathbf{F}|s\rangle\langle s|\mathbf{V}_b^+|t\rangle\langle t|\mathbf{V}_c^+|l\rangle}{(\omega_{rk} - \omega_a)(\omega_{sl} + \omega_b + \omega_c)(\omega_{tl} + \omega_c)} \\ + \frac{\langle k|\mathbf{V}_a^+|r\rangle\langle r|\mathbf{V}_b^+|s\rangle\langle s|\mathbf{F}|t\rangle\langle t|\mathbf{V}_c^+|l\rangle}{(\omega_{rk} - \omega_a)(\omega_{sk} - \omega_a - \omega_b)(\omega_{tl} + \omega_c)} \\ \left. + \frac{\langle k|\mathbf{V}_a^+|r\rangle\langle r|\mathbf{V}_b^+|s\rangle\langle s|\mathbf{V}_c^+|t\rangle\langle t|\mathbf{F}|l\rangle}{(\omega_{rk} - \omega_a)(\omega_{sk} - \omega_a - \omega_b)(\omega_{tk} - \omega_a - \omega_b - \omega_c)} \right\} \quad (21) \end{aligned}$$

is the first and, in general, most important contribution to (20) obtained by third-order perturbation theory in the approximation of the first-order perturbation Hamiltonian of (9).

The second and third terms in (20) correspond to the expectation values of \mathbf{F} which can be obtained in second-order perturbation theory if the second-order perturbation Hamiltonian of (9) is used. In this case we have the result

$$\begin{aligned} \mathbf{F}_{kl}^{(2)}(+\omega_a, +\omega_b, +\omega_c) = & \frac{1}{\hbar^2} \sum_{rs} \left\{ \frac{\langle k|\mathbf{F}|r\rangle \langle r|\overset{(1)}{V}_a^{++}|s\rangle \langle s|\overset{(2)}{V}_{bc}^{+++}|l\rangle}{(\omega_{rl} + \omega_a + \omega_b + \omega_c)(\omega_{sl} + \omega_b + \omega_c)} \right. \\ & + \frac{\langle k|\overset{(1)}{V}_a^{++}|r\rangle \langle r|\mathbf{F}|s\rangle \langle s|\overset{(2)}{V}_{bc}^{+++}|l\rangle}{(\omega_{rk} - \omega_a)(\omega_{sl} + \omega_b + \omega_c)} \\ & \left. + \frac{\langle k|\overset{(1)}{V}_a^{++}|r\rangle \langle r|\overset{(2)}{V}_{bc}^{+++}|s\rangle \langle s|\mathbf{F}|l\rangle}{(\omega_{rk} - \omega_a)(\omega_{sk} - \omega_a - \omega_b - \omega_c)} \right\}. \end{aligned} \quad (22)$$

In order to obtain the exact result we must also take into account a small contribution to (20) arising from first-order perturbation theory with the third-order perturbation Hamiltonian and given as

$$\mathbf{F}_{kl}^{(1)\text{(3)}}(+\omega_a, +\omega_b, +\omega_c) = -\frac{1}{\hbar} \sum_r \left(\frac{\langle k|\mathbf{F}|r\rangle \langle r|\overset{(3)}{V}_{abc}^{++++}|l\rangle}{\omega_{rl} + \omega_a + \omega_b + \omega_c} + \frac{\langle k|\overset{(3)}{V}_{abc}^{++++}|r\rangle \langle r|\mathbf{F}|l\rangle}{\omega_{rk} - \omega_a - \omega_b - \omega_c} \right). \quad (23)$$

3. Electric and magnetic multipole moments induced in a molecule

Our further considerations require that the explicit form of the perturbing Hamiltonian $V(t)$ shall be well-defined. Accordingly, let us consider an atom or a molecule consisting of particles of electric charge e_i and mass m_i , with $\sum_i e_i = 0$. Let \mathbf{r}_i denote the position vector of the i th particle and \mathbf{p}_i the operator of its generalized momentum. Thus, if the molecule is acted on by an electromagnetic field with vectors

$$\mathbf{E} = -\frac{1}{c} \dot{\mathbf{A}} - \nabla\phi, \quad \mathbf{H} = \nabla \times \mathbf{A} \quad (24)$$

its total Hamiltonian in the non-relativistic approximation is given by

$$H = \sum_i \left\{ \frac{1}{2m_i} \left(\mathbf{p}_i - \frac{e_i}{c} \mathbf{A}_i \right)^2 + e_i \phi_i \right\} \quad (25)$$

where ϕ_i and \mathbf{A}_i are the scalar and vector potentials at the point of the i th particle of the molecule and ∇ is the derivation operator. In (25) we neglected for simplicity the interaction between electron spin and the field and assume Coulomb interaction between the particles in the molecule to be contained in the term $e_i \phi_i$.

The Hamiltonian (25) can, in the well-known manner, be resolved into a non-perturbed part H_0 and perturbed part $V(t)$ given by expansion of (9) with the following first- and second-order contributions:

$$\overset{(1)}{V}(t) = - \sum_i \left\{ \frac{e_i}{2m_i c} (\mathbf{p}_i \cdot \mathbf{A}_i + \mathbf{A}_i \cdot \mathbf{p}_i) - e_i \phi_i \right\} \quad (26)$$

$$\overset{(2)}{V}(t) = \frac{1}{2} \sum_i \frac{e_i^2}{m_i c^2} (\mathbf{A}_i \cdot \mathbf{A}_i). \quad (27)$$

As to the explicit form of the third-order perturbation Hamiltonian inherent in equations (9), (10) and (23), it can be derived formally from the Hamiltonian of classical relativistic mechanics which for the term proportional to \mathbf{A}^3 yields

$$V^{(3)}(t) = \frac{1}{4} \sum_i \frac{e_i^3}{m_i^3 c^5} (\mathbf{p}_i \cdot \mathbf{A}_i + \mathbf{A}_i \cdot \mathbf{p}_i) (\mathbf{A}_i \cdot \mathbf{A}_i) \left\{ 1 + O\left(\frac{v_i^2}{c^2}\right) \right\}. \quad (28)$$

This perturbation indeed represents one of the relativistic corrections to H which should be dealt with by a consistent quantal and relativistic procedure including *inter alia* electron spin terms. The treatment of this type of higher-order effects is in general no mathematically unequivocal affair and we shall not take them into consideration here, restricting ourselves to the non-linear formalism in a non-relativistic approximation, i.e. with perturbation Hamiltonian given by the sum of the perturbations (26) and (27).

The total vector potential of several electromagnetic waves is

$$\mathbf{A} = \frac{1}{2} \sum_a \{ \mathbf{A}_a^+ \exp(i\omega_a t) + \mathbf{A}_a^- \exp(-i\omega_a t) \}; \quad \mathbf{A}_a^\pm = \mathbf{A}_a^0 \exp(\mp i \mathbf{k}_a \cdot \mathbf{r}) \quad (29)$$

whence, by (24),

$$\begin{aligned} \mathbf{E} &= \frac{1}{2} \sum_a \{ \mathbf{E}_a^+ \exp(i\omega_a t) + \mathbf{E}_a^- \exp(-i\omega_a t) \}, \quad \mathbf{E}_a^\pm = \mp i \frac{\omega_a}{c} \mathbf{A}_a^\pm \\ \mathbf{H} &= \frac{1}{2} \sum_a \{ \mathbf{H}_a^+ \exp(i\omega_a t) + \mathbf{H}_a^- \exp(-i\omega_a t) \}, \quad \mathbf{H}_a^\pm = \mp i \mathbf{k}_a \times \mathbf{A}_a^\pm \end{aligned} \quad (30)$$

\mathbf{k}_a being the wave vector of the a th electromagnetic wave of wavelength ω_a/c .

By the expressions (10), (29) and (30) and suitable gauge transformations, the first-order perturbation Hamiltonian (26) can be represented in the form of the following multipole expansion (this form can be also derived from Fiutak's (1963) multipole expansion)

$$V^{(1)} = - \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \{ \mathbf{M}_e^{(n)}[n] \mathbf{E}^{(n)} + \mathbf{M}_m^{(n)}[n] \mathbf{H}^{(n)} \} \quad (31)$$

wherein

$$\mathbf{M}_e^{(n)} = \sum_i e_i r_i^n \mathbf{Y}_i^{(n)} \quad (32)$$

is the operator of the 2^n -pole electric moment of the molecular system, and

$$\mathbf{M}_m^{(n)} = \frac{n}{(n+1)c} \sum_i e_i r_i^n \mathbf{Y}_i^{(n)} \times \dot{\mathbf{r}}_i \quad (33)$$

is the operator of its 2^n -pole magnetic moment, whereas $\mathbf{Y}_i^{(n)}$ is an operator having the properties of spherical harmonics and determined as follows:

$$\begin{aligned} \mathbf{Y}_i^{(n)} &= \frac{1}{n! r_i^n} \{ (2n-1)!! \mathbf{r}_{i1} \mathbf{r}_{i2} \dots \mathbf{r}_{in} - (2n-3)!! r_i^2 \sum \mathbf{U}_{12} \mathbf{r}_{i3} \dots \mathbf{r}_{in} + \dots \\ &\quad + (-1)^k (2n-2k-1)!! r_i^{2k} \sum \mathbf{U}_{12} \dots \mathbf{U}_{2k-1, 2k} \mathbf{r}_{i2k+1} \dots \mathbf{r}_{in} + \dots \} \end{aligned} \quad (34)$$

with \mathbf{U}_{12} denoting the unit vector of rank two, $\sum \mathbf{U}_{12} \mathbf{r}_{i3} \dots \mathbf{r}_{in}$ etc. being sums of terms derived from the one written out by interchanging the indices 1, 2, ... n . The symbol $[n]$ in equation (31) according to Jansen's notation (1958) denotes n fold contraction of two tensors of rank n , thus for example $\mathbf{M}_e^{(n)}$ and $\mathbf{E}^{(n)}$.

The first term of equation (31) describes interaction between an electric molecular 2^n -pole and an electric field

$$\mathbf{E}^{(n)} = (\nabla^{n-1} \mathbf{E})_{r=0}$$

of degree n , whereas the second term accounts for interaction between a magnetic molecular 2^n -pole and a magnetic field

$$\mathbf{H}^{(n)} = (\nabla^{n-1}\mathbf{H})_{r=0}$$

of degree n , with

$$\begin{aligned}\overset{\pm}{\mathbf{E}}_a^{(n)} &= \{\nabla^{n-1}\overset{0}{\mathbf{E}}_a \exp(\mp i\mathbf{k}_a \cdot \mathbf{r})\}_{r=0} = (\mp i\mathbf{k}_a)^{n-1}\overset{0}{\mathbf{E}}_a \\ \overset{\pm}{\mathbf{H}}_a^{(n)} &= \{\nabla^{n-1}\overset{0}{\mathbf{H}}_a \exp(\mp i\mathbf{k}_a \cdot \mathbf{r})\}_{r=0} = (\mp i\mathbf{k}_a)^{n-1}\overset{0}{\mathbf{H}}_a.\end{aligned}\quad (35)$$

3.1. The pure electric contributions

We shall first derive an expression for the 2^n -pole electric moment $\mathbf{P}_e^{(n)}(t)$ induced in a molecule by an oscillating electric field whose matrix element for the transition $k \rightarrow l$ is given by

$$\mathbf{P}_{ekl}^{(n)}(t) = \int \psi_k^* \mathbf{M}_e^{(n)} \psi_l d\tau - \int \psi_k^{0*} \mathbf{M}_e^{(n)} \psi_l^0 d\tau. \quad (36)$$

Expressions (3) and (36) yield to within the third order of quantal perturbation theory

$$\mathbf{P}_{ekl}^{(n)}(t) = \sum_a \overset{(1)}{\mathbf{P}}_{ekl}^{(n)}(t)_a + \frac{1}{2} \sum_{ab} \overset{(2)}{\mathbf{P}}_{ekl}^{(n)}(t)_{ab} + \frac{1}{6} \sum_{abc} \overset{(3)}{\mathbf{P}}_{ekl}^{(n)}(t)_{abc} + \dots \quad (37)$$

The terms of the above expansion are given in general by the expressions of (13)–(23) on replacing \mathbf{F}_{kl} by $\mathbf{P}_{ekl}^{(n)}$ and $\langle k|\mathbf{F}|r\rangle$ by $\langle k|\mathbf{M}_e^{(n)}|r\rangle$.

In the first approximation, the perturbation is given by (31) (in this sub-section we omit the magnetic part of the perturbation Hamiltonian) and the first-order electric multipole moment appearing in the expansion (37) is given, with regard to (13) and (14), by

$$\overset{(1)}{\mathbf{P}}_{ekl}^{(n)}(t)_a = \frac{1}{2} \{ \overset{(1)}{\mathbf{P}}_{ekl}^{(n)}(+\omega_a) + \overset{(1)}{\mathbf{P}}_{ekl}^{(n)}(-\omega_a) \} \exp(it\omega_{kl}) \quad (38)$$

wherein the tensor

$$\overset{(1)}{\mathbf{P}}_{ekl}^{(n)}(\pm\omega_a) = \sum_{n_a=1}^{\infty} \frac{2^{n_a} n_a!}{(2n_a)!} \overset{(n)}{\mathbf{A}}_{ekl}^{(n_a)}(\pm\omega_a) [n_a] \overset{\pm}{\mathbf{E}}_a^{(n_a)} \exp(\pm it\omega_a) \quad (39)$$

of rank $n + n_a$ determines the linear, i.e. first-order, polarization of the electric molecular 2^n -pole induced by an electric field of degree n_a . With regard to (14), its matrix element for the transition $k \rightarrow l$ is given by

$$\overset{(n)}{\mathbf{A}}_{ekl}^{(n_a)}(+\omega_a) = \frac{1}{\hbar} \sum_r \left(\frac{\langle k|\mathbf{M}_e^{(n)}|r\rangle \langle r|\mathbf{M}_e^{(n_a)}|l\rangle}{\omega_{rl} + \omega_a} + \frac{\langle k|\mathbf{M}_e^{(n_a)}|r\rangle \langle r|\mathbf{M}_e^{(n)}|l\rangle}{\omega_{rk} - \omega_a} \right). \quad (40)$$

In the dipolar approximation ($n = 1, n_a = 1$), the expressions (38)–(40) are identical with the well-known results of Kramers and Heisenberg (1925).

If the electric field is not homogeneous within the region occupied by a molecule, the following expansion is obtained from (39):

$$\begin{aligned}\overset{(1)}{\mathbf{P}}_{ekl}^{(n)}(+\omega_a) &= \{ \overset{(n)}{\mathbf{A}}_{ekl}^{(1)}(+\omega_a) \cdot \overset{+}{\mathbf{E}}_a^{(1)} + \frac{1}{3} \overset{(n)}{\mathbf{A}}_{ekl}^{(2)}(+\omega_a) \cdot \overset{+}{\mathbf{E}}_a^{(2)} \\ &+ \frac{1}{15} \overset{(n)}{\mathbf{A}}_{ekl}^{(3)}(+\omega_a) \cdot \overset{+}{\mathbf{E}}_a^{(3)} + \dots \} \exp(it\omega_a)\end{aligned}\quad (41)$$

which, by (35), can be put in the form

$$\begin{aligned} \mathbf{P}_{ekl}^{(1)}(+\omega_a) = \{ & {}^{(n)}\mathbf{A}_{ekl}{}^{(1)}(+\omega_a) \cdot \overset{0}{\mathbf{E}}_a - \frac{1}{3}i^{(n)}\mathbf{A}_{ekl}{}^{(2)}(+\omega_a) : \mathbf{k}_a \overset{0}{\mathbf{E}}_a \\ & - \frac{1}{15}{}^{(n)}\mathbf{A}_{ekl}{}^{(3)}(+\omega_a) : \mathbf{k}_a \mathbf{k}_a \overset{0}{\mathbf{E}}_a + \dots \} \exp(it\omega_a). \end{aligned} \quad (42)$$

In the foregoing expansions, the tensor ${}^{(n)}\mathbf{A}_e{}^{(1)}$ defined the polarizability of an electric multipole due to a field of the first degree $\mathbf{E}_a{}^{(1)} \equiv \overset{0}{\mathbf{E}}_a$ homogeneous throughout the region of the molecule. The further tensors ${}^{(n)}\mathbf{A}_e{}^{(2)}$, ${}^{(n)}\mathbf{A}_e{}^{(3)}$, ..., on the other hand, defined additional polarizabilities of the electric multipole as being due to fields of the second, third, etc. degrees, i.e. to inhomogeneities of the electric field within the molecular region. In particular, expansions (41) and (42) determine for $n = 1$ a dipole moment of the first order, for $n = 2$ a quadrupole moment of the first order, for $n = 3$ an octopole moment of the first order, and so forth. The matrix elements of the respective polarizability tensors, i.e. of that of dipole-dipole polarizability ${}^{(1)}\mathbf{A}_e{}^{(1)}$, dipole-quadrupole polarizability ${}^{(1)}\mathbf{A}_e{}^{(2)}$, dipole-octopole polarizability ${}^{(1)}\mathbf{A}_e{}^{(3)}$, ... and of quadrupole-dipole polarizability ${}^{(2)}\mathbf{A}_e{}^{(1)}$, quadrupole-quadrupole polarizability ${}^{(2)}\mathbf{A}_e{}^{(2)}$, ... etc. result immediately from equation (40) for the appropriate values of n and n_a .

By (15) and (17), the second-order electric multipole moment of the expansion (37) is of the form

$$\begin{aligned} (\mathbf{P}_{ekl}^{(2)})_{ab} = \frac{1}{4} \{ & \mathbf{P}_{ekl}^{(2)}(+\omega_a, +\omega_b) + \mathbf{P}_{ekl}^{(2)}(+\omega_a, -\omega_b) \\ & + \mathbf{P}_{ekl}^{(2)}(-\omega_a, +\omega_b) + \mathbf{P}_{ekl}^{(2)}(-\omega_a, -\omega_b) \} \exp(it\omega_{kl}) \end{aligned} \quad (43)$$

where

$$\begin{aligned} \mathbf{P}_{ekl}^{(2)}(+\omega_a, +\omega_b) = \sum_{n_a=1}^{\infty} \sum_{n_b=1}^{\infty} \frac{2^{n_a+n_b} n_a! n_b!}{(2n_a)!(2n_b)!} \\ \times {}^{(n)}\mathbf{B}_{ekl}{}^{(n_a+n_b)}(+\omega_a, +\omega_b) [n_a + n_b] \overset{\dagger}{\mathbf{E}}_a{}^{(n_a)} \overset{\dagger}{\mathbf{E}}_b{}^{(n_b)} \exp\{it(\omega_a + \omega_b)\}. \end{aligned} \quad (44)$$

The matrix element of the tensor of rank $n+n_a+n_b$ appearing above is given in accordance with (17) by

$$\begin{aligned} {}^{(n)}\mathbf{B}_{ekl}{}^{(n_a+n_b)}(+\omega_a, +\omega_b) = \frac{1}{\hbar^2} S(n_a, n_b) \sum_{rs} \left\{ \frac{\langle k | \mathbf{M}_e^{(n)} | r \rangle \langle r | \mathbf{M}_e^{(n_a)} | s \rangle \langle s | \mathbf{M}_e^{(n_b)} | l \rangle}{(\omega_{rl} + \omega_a + \omega_b)(\omega_{sl} + \omega_b)} \right. \\ \left. + \frac{\langle k | \mathbf{M}_e^{(n_a)} | r \rangle \langle r | \mathbf{M}_e^{(n)} | s \rangle \langle s | \mathbf{M}_e^{(n_b)} | l \rangle}{(\omega_{rk} - \omega_a)(\omega_{sl} + \omega_b)} + \frac{\langle k | \mathbf{M}_e^{(n_a)} | r \rangle \langle r | \mathbf{M}_e^{(n_b)} | s \rangle \langle s | \mathbf{M}_e^{(n)} | l \rangle}{(\omega_{rk} - \omega_a)(\omega_{sk} - \omega_a - \omega_b)} \right\} \end{aligned} \quad (45)$$

where $S(n_a, n_b, \dots)$ is a symmetrizing operator consisting in summation over all permutations of $\omega_a n_a, \omega_b n_b, \dots$.

The tensor of (45) describes the non-linear or, rather, second-order polarization of the electric multipole induced in a molecule by the electric fields $\mathbf{E}_a{}^{(n_a)}$ and $\mathbf{E}_b{}^{(n_b)}$.

Taking the electric field to an accuracy of degree two, we obtain from (44), with regard to (35),

$$\begin{aligned} \mathbf{P}_{ekl}^{(2)}(+\omega_a, +\omega_b) = \{ & {}^{(n)}\mathbf{B}_{ekl}{}^{(1+1)}(+\omega_a, +\omega_b) : \overset{0}{\mathbf{E}}_a \overset{0}{\mathbf{E}}_b \\ & - \frac{1}{3}i^{(n)}\mathbf{B}_{ekl}{}^{(1+2)}(+\omega_a, +\omega_b) : \overset{0}{\mathbf{E}}_a \mathbf{k}_b \overset{0}{\mathbf{E}}_b - \frac{1}{3}i^{(n)}\mathbf{B}_{ekl}{}^{(2+1)}(+\omega_a, +\omega_b) : \mathbf{k}_a \overset{0}{\mathbf{E}}_a \overset{0}{\mathbf{E}}_b \\ & - \frac{1}{9}{}^{(n)}\mathbf{B}_{ekl}{}^{(2+2)}(+\omega_a, +\omega_b) : \mathbf{k}_a \overset{0}{\mathbf{E}}_a \mathbf{k}_b \overset{0}{\mathbf{E}}_b + \dots \} \exp\{it(\omega_a + \omega_b)\}. \end{aligned} \quad (46)$$

In the above expansion, the first term defines the second-order polarization of the electric multipole as a product of the square of the electric field, whereas the subsequent terms define additional contributions related with spatial variations of the electric fields. In particular, for $n = 1, 2, 3, \dots$ equation (44) or (46) yields expansions for the second-order dipole, quadrupole, octopole, etc., electric moments.

Similarly, expressions (19) and (21) lead to the third-order multipole electric moment in the form

$$(\mathbf{P}_{ekl}^{(3)})_{abc} = \frac{1}{8} \{ \mathbf{P}_{ekl}^{(3)}(+\omega_a, +\omega_b, +\omega_c) + \dots + \mathbf{P}_{ekl}^{(3)}(-\omega_a, -\omega_b, -\omega_c) \} \exp(it\omega_{kl}) \quad (47)$$

wherein the braces contain eight terms which can be derived from the expression

$$\begin{aligned} \mathbf{P}_{ekl}^{(3)}(+\omega_a, +\omega_b, +\omega_c) &= \sum_{n_a=1}^{\infty} \sum_{n_b=1}^{\infty} \sum_{n_c=1}^{\infty} \frac{2^{n_a+n_b+n_c} n_a! n_b! n_c!}{(2n_a)!(2n_b)!(2n_c)!} \\ &\times {}^{(n)}\mathbf{C}_{ekl}^{(n_a+n_b+n_c)}(+\omega_a, +\omega_b, +\omega_c) [n_a+n_b+n_c] \mathbf{E}_a^{(n_a)} \mathbf{E}_b^{(n_b)} \mathbf{E}_c^{(n_c)} \exp\{it(\omega_a + \omega_b + \omega_c)\}. \end{aligned} \quad (48)$$

By (21), the tensor of third-order multipole polarizability is defined as

$$\begin{aligned} &{}^{(n)}\mathbf{C}_{ekl}^{(n_a+n_b+n_c)}(+\omega_a, +\omega_b, +\omega_c) \\ &= \frac{1}{\hbar^3} S(n_a, n_b, n_c) \sum_{rst} \left\{ \frac{\langle k | \mathbf{M}_e^{(n)} | r \rangle \langle r | \mathbf{M}_e^{(n_a)} | s \rangle \langle s | \mathbf{M}_e^{(n_b)} | t \rangle \langle t | \mathbf{M}_e^{(n_c)} | l \rangle}{(\omega_{rl} + \omega_a + \omega_b + \omega_c)(\omega_{st} + \omega_b + \omega_c)(\omega_{tl} + \omega_c)} \right. \\ &\quad + \frac{\langle k | \mathbf{M}_e^{(n_a)} | r \rangle \langle r | \mathbf{M}_e^{(n)} | s \rangle \langle s | \mathbf{M}_e^{(n_b)} | t \rangle \langle t | \mathbf{M}_e^{(n_c)} | l \rangle}{(\omega_{rk} - \omega_a)(\omega_{st} + \omega_b + \omega_c)(\omega_{tl} + \omega_c)} \\ &\quad + \frac{\langle k | \mathbf{M}_e^{(n_a)} | r \rangle \langle r | \mathbf{M}_e^{(n_b)} | s \rangle \langle s | \mathbf{M}_e^{(n)} | t \rangle \langle t | \mathbf{M}_e^{(n_c)} | l \rangle}{(\omega_{rk} - \omega_a)(\omega_{sk} - \omega_a - \omega_b)(\omega_{tl} + \omega_c)} \\ &\quad \left. + \frac{\langle k | \mathbf{M}_e^{(n_a)} | r \rangle \langle r | \mathbf{M}_e^{(n_b)} | s \rangle \langle s | \mathbf{M}_e^{(n_c)} | t \rangle \langle t | \mathbf{M}_e^{(n)} | l \rangle}{(\omega_{rk} - \omega_a)(\omega_{sk} - \omega_a - \omega_b)(\omega_{tk} - \omega_a - \omega_b - \omega_c)} \right\}. \end{aligned} \quad (49)$$

Neglecting higher order terms, we have from (48)

$$\begin{aligned} \mathbf{P}_{ekl}^{(3)}(+\omega_a, +\omega_b, +\omega_c) &= \{ {}^{(n)}\mathbf{C}_{ekl}^{(1+1+1)}(+\omega_a, +\omega_b, +\omega_c) : \mathbf{E}_a^0 \mathbf{E}_b^0 \mathbf{E}_c^0 \\ &\quad - \frac{1}{8} i^{(n)} \mathbf{C}_{ekl}^{(1+1+2)}(+\omega_a, +\omega_b, +\omega_c) : \mathbf{E}_a^0 \mathbf{E}_b^0 \mathbf{k}_c \mathbf{E}_c^0 + \dots \} \exp\{it(\omega_a + \omega_b + \omega_c)\} \end{aligned} \quad (50)$$

in which the first term defines the third-order polarization produced in the electric multipole by the third power of the electric field.

3.2. The magnetic and electromagnetic contributions

On replacing in the preceding expressions (37)–(50) the electric multipole moments $\mathbf{M}_e^{(n)}$, ... by the magnetic moments $\mathbf{M}_m^{(n)}$, ... and the electric fields $\mathbf{E}_a^{(n_a)}$, ... by magnetic fields $\mathbf{H}_a^{(n_a)}$, ... we obtain automatically expressions for the induced multipole magnetic moment $\mathbf{P}_m^{(n)}$. Obviously, the same expressions for $\mathbf{P}_m^{(n)}$ can also be derived immediately from the general expressions (11)–(21) on replacing the operator \mathbf{F}_{kl} by $\mathbf{P}_{mkl}^{(n)}$, $\langle k | \mathbf{F} | r \rangle$ by $\langle k | \mathbf{M}_m^{(n)} | r \rangle$, and the first-order perturbation Hamiltonian in (14), (17) and (21) by the magnetic part of equation (31). When aiming at a formalism applicable to the

description of such effects as, for example, optical activity etc., one has to take into consideration in equation (31) both the electric and magnetic parts of the perturbation Hamiltonian. As a result, in addition to the induced moments $\mathbf{P}_e^{(n)}$ and $\mathbf{P}_m^{(n)}$ one obtains, respectively, the additional moments $\mathbf{P}_{em}^{(n)}$ and $\mathbf{P}_{me}^{(n)}$. In general, $\mathbf{P}_{em}^{(n)}$ consists of a part dependent only on the strength of the magnetic fields and of a mixed part dependent on the electric and magnetic fields simultaneously. Thus, for example in a first approximation, $\mathbf{P}_{em}^{(n)}$ consists only of a part depending on the magnetic field and is given as follows:

$$\mathbf{P}_{emkl}^{(1)(n)}(+\omega_a) = \sum_{n_a=1}^{\infty} \frac{2^{n_a} n_a!}{(2n_a)!} {}^{(n)}\mathbf{A}_{emkl}^{(n_a)}(+\omega_a) [n_a] \mathbf{H}_a^{(n_a)+} \exp(it\omega_a) \quad (51)$$

where

$${}^{(n)}\mathbf{A}_{emkl}^{(n_a)}(+\omega_a) = \frac{1}{\hbar} \sum_r \left\{ \frac{\langle k | \mathbf{M}_e^{(n)} | r \rangle \langle r | \mathbf{M}_m^{(n_a)} | l \rangle}{\omega_{rl} + \omega_a} + \frac{\langle k | \mathbf{M}_m^{(n_a)} | r \rangle \langle r | \mathbf{M}_e^{(n)} | l \rangle}{\omega_{rk} - \omega_a} \right\} \quad (52)$$

is the tensor of linear polarization of an electric multipole due to the magnetic field of degree n_a .

Similarly, the expressions for the part of $\mathbf{P}_{em}^{(n)}$ dependent on the magnetic fields in the second and third approximations are obtained immediately from expressions (43)–(50), on replacing therein $\mathbf{M}_e^{(n_a)}$, $\mathbf{M}_e^{(n_b)}$, ... , respectively, by $\mathbf{M}_m^{(n_a)}$, $\mathbf{M}_m^{(n_b)}$, ... and the electric fields $\mathbf{E}_a^{(n_a)}$, $\mathbf{E}_b^{(n_b)}$, ... by the magnetic fields $\mathbf{H}_a^{(n_a)}$, $\mathbf{H}_b^{(n_b)}$, Besides, in the second and third approximations, mixed terms appear in $\mathbf{P}_{em}^{(n)}$; these depend on the electric and magnetic fields simultaneously. For example, in the second approximation the term in question is given by the expressions (44) and (45) on replacing $\mathbf{M}_e^{(n_b)}$ by $\mathbf{M}_m^{(n_b)}$ and $\mathbf{E}_b^{(n_b)}$ by $\mathbf{H}_b^{(n_b)}$. Analogously, one obtains multipolar contributions in the third approximations of perturbation theory. Some of these contributions have been discussed in the dipolar and dipole–quadrupole approximations by Armstrong *et al.* (1962), Franken and Ward (1963), Bloembergen and Shen (1964) and Adler (1964).

In the foregoing expressions for the second- and third-order multipole moments we have still to take into consideration the contributions (18), (22) and (23) which result in general with the perturbation Hamiltonians of the second and third orders (27) and (28). Now, since the vector potential can be represented formally as a multipole expansion consisting of an electric and a magnetic part, we can distinguish in equation (27) the purely magnetic part of the second-order perturbation Hamiltonian

$$V_m^{(2)} = -\frac{1}{2} \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} \frac{2^{n+n'} n! n'!}{(2n)!(2n')!} \mathbf{H}^{(n)} [n] {}^{(n')} \mathbf{A}_m^{(n')} [n'] \mathbf{H}^{(n')} \quad (53)$$

where we have the tensor of rank $n+n'$

$${}^{(n)}\mathbf{A}_m^{(n')} = \frac{nn'}{(n+1)(n'+1)c^2} \sum_i \frac{e_i^2}{m_i} r_i^{n+n'} (\mathbf{Y}_i^{(n)} \mathbf{Y}_i^{(n')} - \mathbf{Y}_i^{(n)} \cdot \mathbf{Y}_i^{(n')} \mathbf{U}) \quad (54)$$

determining the multipole (dia)magnetic polarizability operator of a molecule.

In particular, on averaging the Hamiltonian (53) over all classically possible orientations of the molecule, we obtain the result

$$\langle V_m^{(2)} \rangle = -\frac{1}{2} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} a_m^{(2n)} (\mathbf{H}^{(n)} [n] \mathbf{H}^{(n)}) \quad (55)$$

in which

$$a_m^{(2n)} = \frac{2^n n!}{(2n+1)!} \langle {}^{(n)}\mathbf{A}_m^{(n)} [2n] \mathbf{U}^n \rangle = -\frac{2n^2}{(n+1)^2 (2n+1)n! c^2} \left\langle \sum_i \frac{e_i^2}{m_i} r_i^{2n} \right\rangle \quad (56)$$

is the mean diamagnetic multipole polarizability of the molecule, identical in the dipole ($n = 1$) approximation with the well-known Langevin–Pauli diamagnetic polarizability.

By (18) and (53) we obtain one of the more important contributions to the second-order electric multipole moment:

$$\begin{aligned} \mathbf{P}_{emkl}^{(2)(n)}(\pm\omega_a, \pm\omega_b) &= \sum_{n_a=1}^{\infty} \sum_{n_b=1}^{\infty} \frac{2^{n_a+n_b} n_a! n_b!}{(2n_a)!(2n_b)!} \\ &\times {}^{(n)}\mathbf{B}_{emkl}^{(n_a+n_b)}(\pm\omega_a, \pm\omega_b) [n_a+n_b] \overset{\pm}{\mathbf{H}}_a^{(n_a)} \overset{\pm}{\mathbf{H}}_b^{(n_b)} \exp\{\pm i t(\omega_a + \omega_b)\} \end{aligned} \quad (57)$$

where

$$\begin{aligned} {}^{(n)}\mathbf{B}_{emkl}^{(n_a+n_b)}(\pm\omega_a, \pm\omega_b) &= \frac{1}{\hbar} \sum_r \left\{ \frac{\langle k | \mathbf{M}_e^{(n)} | r \rangle \langle r | {}^{(n_a)}\mathbf{A}_m^{(n_b)} | l \rangle}{\omega_{rl} \pm \omega_a \pm \omega_b} \right. \\ &\quad \left. + \frac{\langle k | {}^{(n_a)}\mathbf{A}_m^{(n_b)} | r \rangle \langle r | \mathbf{M}_e^{(n)} | l \rangle}{\omega_{rk} \mp \omega_a \mp \omega_b} \right\} \end{aligned} \quad (58)$$

is the tensor of second-order electric multipole polarizability determining the polarization of the molecule due to the square of the magnetic field of order n_a .

If in equations (57) and (58) $\mathbf{P}_{em}^{(2)(n)}$ is replaced by $\mathbf{P}_m^{(2)(n)}$ and $\mathbf{M}_e^{(n)}$ by $\mathbf{M}_m^{(n)}$, we obtain equations defining the second-order magnetic multipole moment and its magnetic polarizability tensor. Similarly, other mixed contributions to the second-order electric or magnetic multipole moments can be obtained.

An analogous procedure can be applied for performing the multipole expansion of the third-order Hamiltonian (28) and for computing the contributions to the multipole moments of type (23) or, recurring to (31) and (53), of type (22).

4. Tensor of multiharmonic light scattering

We now proceed to show, as an example, how the general formalism derived in the foregoing sections of this paper can be applied to calculate the tensor of the intensity of multipole light scattering.

When considering radiation in a wave zone, we can express the intensities of the electric and magnetic fields at the point of observation \mathbf{R} by the well-known formulae

$$\mathbf{E}_R = \frac{1}{Rc^2} \{ \mathbf{s} \times (\mathbf{s} \times \ddot{\mathbf{Z}}) \}, \quad \mathbf{H}_R = - \frac{1}{Rc^2} (\mathbf{s} \times \dot{\mathbf{Z}}) \quad (59)$$

where \mathbf{s} is the unit vector in the direction of the observation vector, $\mathbf{R} = R\mathbf{s}$, and \mathbf{Z} is Hertz's vector (taken at retarded time $t - R/c$) consisting in general of a part accounting for electric multipole radiation

$$\dot{\mathbf{Z}}_e = \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)! c^{n-1}} \mathbf{s}^{n-1} [n-1] \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_e^{(n)} \quad (60)$$

and a part accounting for magnetic multipole radiation

$$\dot{\mathbf{Z}}_m = - \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)! c^{n-1}} \mathbf{s}^{n-1} [n-1] \left(\mathbf{s} \times \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_m^{(n)} \right) \quad (61)$$

with $\mathbf{P}_e^{(n)}$ and $\mathbf{P}_m^{(n)}$ denoting respectively 2^n -pole electric and magnetic moments defined in analogy with equations (32), (33) and (36); however, in considering scattering,

\mathbf{k}_a has to be given the meaning of the difference between the wave vectors of the incident and scattered waves.

From (59), we obtain Poynting's vector by the usual procedure:

$$\mathbf{S} = \frac{c}{4\pi} \overline{\mathbf{E}_R \times \mathbf{H}_R} = \frac{\mathbf{s}}{4\pi R^2 c^3} \{ \overline{(\dot{\mathbf{Z}} \cdot \dot{\mathbf{Z}})} - \overline{(\mathbf{s} \cdot \dot{\mathbf{Z}})^2} \} \quad (62)$$

and the intensity component of scattered light with oscillations in the direction of \mathbf{u} , a unit vector perpendicular to \mathbf{s} ,

$$I_u = \overline{(\mathbf{E}_R \cdot \mathbf{u})^2} = \frac{1}{R^2 c^4} \overline{(\dot{\mathbf{Z}} \cdot \mathbf{u})^2} \quad (63)$$

where the bar stands for time-averaging.

Considering at first only electric multipole radiation, we have by (60) and (63)

$$\overline{(\dot{\mathbf{Z}}_e \cdot \mathbf{u})^2} = \sum_{n=1}^{\infty} \frac{2^{2n} (n!)^2}{[(2n)!]^2 c^{2(n-1)}} \mathbf{s}^{n-1} \mathbf{u} [n] \overline{\left(\frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_e^{(n)} \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_e^{(n)} \right)} [n] \mathbf{u} \mathbf{s}^{n-1}. \quad (64)$$

By analogy with the above classical expression, we introduce the following tensor:

$$\mathbf{S}_{ekl}^{(2n)} = \overline{\left(\frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_{ekl}^{(n)} \frac{d^{n+1}}{dt^{n+1}} \mathbf{P}_{elk}^{(n)} \right)} \quad (65)$$

which defines electric 2^n -pole light scattering for transition $k \rightarrow l$.

On substituting the expansion (37) as well as the expressions (38)–(50) into equation (65), we can write quite generally

$$\mathbf{S}_{ekl}^{(2n)} = \sum_{r=1}^{\infty} \mathbf{S}_{ekl}^{(r)(2n)} = \mathbf{S}_{ekl}^{(1)(2n)} + \mathbf{S}_{ekl}^{(2)(2n)} + \mathbf{S}_{ekl}^{(3)(2n)} + \dots \quad (66)$$

where the r th-order contribution to the tensor of multipole electric scattering is defined as follows (for the sake of simplicity, only the term in summation frequencies

$$\omega_1 + \omega_2 + \dots + \omega_r$$

for $\omega_1 \neq \omega_2 \neq \dots \neq \omega_r$ is written out):

$$\begin{aligned} \mathbf{S}_{ekl}^{(r)(2n)} &= \frac{1}{2^{2r-1}} (\omega_{kl} + \omega_1 + \dots + \omega_r)^{2n+2} \sum_{n_1=1}^{\infty} \dots \sum_{n_r=1}^{\infty} \frac{2^{2(n_1+\dots+n_r)} (n_1! \dots n_r!)^2}{[(2n_1)! \dots (2n_r)!]^2} \\ &\times {}^{(n)}\mathbf{A}_{ekl}^{(n_1+\dots+n_r)}(+\omega_1, +\dots, +\omega_r) {}^{(n)}\mathbf{A}_{elk}^{(n_1+\dots+n_r)}(-\omega_1, \dots, -\omega_r) \\ &\times [2n_1 + \dots + 2n_r] \mathbf{E}_1^{(n_1)\dagger} \bar{\mathbf{E}}_1^{(n_1)} \dots \mathbf{E}_r^{(n_r)\dagger} \bar{\mathbf{E}}_r^{(n_r)}. \end{aligned} \quad (67)$$

The foregoing expressions describe electric multipolar scattering with multiharmonic frequencies $\omega_{kl} + \omega_1 + \omega_2 + \dots + \omega_r$.

In particular, equation (67) yields for the first-order tensor of multipolar scattering

$$\begin{aligned} \mathbf{S}_{ekl}^{(1)(2n)} &= \frac{1}{2} (\omega_{kl} + \omega_1)^{2n+2} \sum_{n_1=1}^{\infty} \frac{2^{2n_1} (n_1!)^2}{(2n_1)! (2n_1)!} \\ &\times {}^{(n)}\mathbf{A}_{ekl}^{(n_1)}(+\omega_1) {}^{(n)}\mathbf{A}_{elk}^{(n_1)}(-\omega_1) [2n_1] \mathbf{E}_1^{(n_1)\dagger} \bar{\mathbf{E}}_1^{(n_1)} \end{aligned} \quad (68)$$

which can be approximated by

$$\begin{aligned} \mathbf{S}_{ekl}^{(1)(2n)} = & \frac{1}{2}(\omega_{kl} + \omega_1)^{2n+2} \{ {}^{(n)}\mathbf{A}_{ekl}^{(1)}(+\omega_1) {}^0\mathbf{A}_{elk}^{(1)}(-\omega_1) \\ & + \frac{1}{9} {}^{(n)}\mathbf{A}_{ekl}^{(2)}(+\omega_1) {}^{(n)}\mathbf{A}_{elk}^{(2)}(-\omega_1); \mathbf{k}_1 \mathbf{k}_1 + \dots \}; \mathbf{E}_1^0 + \mathbf{E}_1^0. \end{aligned} \quad (69)$$

In the case of electric dipolar scattering ($n = 1$), the first term of this expansion defines normal Raman scattering, whereas the second term accounts for the influence of induced quadrupoles on Raman scattering. Regrettably, this influence is but of the order of $k_1^2 10^{-16} = a^2 k_1^2$ (with a of the order of atomic dimensions) and can play a role solely in the case of short wavelength.

For $n = 2$, the expansion (69) defines quadrupolar electric scattering of order one; with sufficient accuracy, this can be expressed by

$$\mathbf{S}_{ekl}^{(1)(4)} = \frac{1}{2}(\omega_{kl} + \omega_1)^6 {}^{(2)}\mathbf{A}_{ekl}^{(1)}(+\omega_1) {}^{(2)}\mathbf{A}_{elk}^{(1)}(-\omega_1); \mathbf{E}_1^0 + \mathbf{E}_1^0. \quad (70)$$

By (67), the second-order contribution to the tensor of electric multipolar scattering is of the form

$$\begin{aligned} \mathbf{S}_{ekl}^{(2)(2n)} = & \frac{1}{8}(\omega_{kl} + \omega_1 + \omega_2)^{2n+2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{2(n_1+n_2)} (n_1! n_2!)^2}{[(2n_1)!(2n_2)!]^2} {}^{(n)}\mathbf{B}_{eki}^{(n_1+n_2)}(+\omega_1, +\omega_2) \\ & \times {}^{(n)}\mathbf{B}_{elk}^{(n_1+n_2)}(-\omega_1, -\omega_2) [2n_1 + 2n_2] \mathbf{E}_1^{+(n_1)} \mathbf{E}_1^{-(n_1)} \mathbf{E}_2^{+(n_2)} \mathbf{E}_2^{-(n_2)} \end{aligned} \quad (71)$$

whence for the special case of dipolar scattering we have

$$\begin{aligned} \mathbf{S}_{ekl}^{(2)(2)} = & \frac{1}{8}(\omega_{kl} + \omega_1 + \omega_2)^4 \{ {}^{(1)}\mathbf{B}_{ekl}^{(1+1)}(+\omega_1, +\omega_2) {}^{(1)}\mathbf{B}_{elk}^{(1+1)}(-\omega_1, -\omega_2) \\ & + \frac{1}{3} {}^{(1)}\mathbf{B}_{ekl}^{(1+2)}(+\omega_1, +\omega_2) {}^{(1)}\mathbf{B}_{elk}^{(1+2)}(-\omega_1, -\omega_2); \mathbf{k}_2 \mathbf{k}_2 \\ & + \frac{1}{3} {}^{(1)}\mathbf{B}_{ekl}^{(2+1)}(+\omega_1, +\omega_2) {}^{(1)}\mathbf{B}_{elk}^{(2+1)}(-\omega_1, -\omega_2); \mathbf{k}_1 \mathbf{k}_1 + \dots \}; \mathbf{E}_1^0 + \mathbf{E}_1^0 - \mathbf{E}_2^0 + \mathbf{E}_2^0. \end{aligned} \quad (72)$$

From the foregoing expansion, it is seen that non-linear dipolar light scattering with the second harmonic can appear in the first approximation (the first term in equation (72)) only for molecules having no centre of inversion (the tensor ${}^{(1)}\mathbf{B}_0^{(1+1)}$ vanishes for molecules possessing one), whereas in the second approximation it is non-vanishing also for molecules with a centre of inversion, although being regrettably small in normal conditions.

Similarly, as in the case of $n = 2$, equation (71) yields quadrupolar scattering of the second order; in contradistinction to dipolar scattering, the quadrupolar effect in the first approximation can in general exist for all molecules, irrespective of their symmetry (clearly, provided the selection rules are observed). The best chances of detection and experimental investigation are still those of dipolar scattering with the second harmonic as defined by the first term of the expansion (72). This kind of scattering has been discussed in detail in earlier papers (Kielich 1964) for a number of molecules having the point group symmetries D_{2d} , D_{3h} , C_{3v} , C_{4v} , C_{6v} , $C_{\infty v}$ and T_d . The respective numerical evaluation for chloroform yielded a non-linear variation in intensity of scattered light of the order of $10^{-11}(1 + \omega_2/\omega_1)^4 E_2^2$ accessible to detection by means of the high power pulse lasers now in use. As we see, the size of the effect depends, in addition to the intensity E_2^2 of the powerful incident beam, on the judicious choice of the ratio $\omega_2/\omega_1 \geq 1$.

As to the third-order scattering tensor, we give it here for simplicity only in the dipolar approximation defined by (67) as follows:

$$\begin{aligned} \mathbf{S}_{ekl}^{(3)(2)} = & \frac{1}{2}(\omega_{kl} + \omega_1 + \omega_2 + \omega_3)^4 {}^{(1)}\mathbf{C}_{ekl}^{(1+1+1)}(+\omega_1, +\omega_2, +\omega_3) \\ & \times {}^{(1)}\mathbf{C}_{elk}^{(1+1+1)}(-\omega_1, -\omega_2, -\omega_3)::\overset{0}{\mathbf{E}}_1^+ \overset{0}{\mathbf{E}}_1^- \overset{0}{\mathbf{E}}_2^+ \overset{0}{\mathbf{E}}_2^- \overset{0}{\mathbf{E}}_3^+ \overset{0}{\mathbf{E}}_3^-. \end{aligned} \quad (73)$$

Such dipolar scattering with the third harmonic can be caused by molecules of arbitrary symmetry, the spherical symmetry included. However, it will in general present a smaller value than scattering with the second harmonic, and can become of some importance when scattering with the second harmonic is absent.

Change in sign of the frequencies ω_2, ω_3 , etc., allows us to obtain from (67) or (72) and (73) tensors for scattering with difference frequencies, for example

$$\omega_{kl} + \omega_1 \pm \omega_2, \quad \omega_{kl} + \omega_1 \pm \omega_2 \pm \omega_3$$

and the like.

The discussion of magnetic or electromagnetic multipolar light scattering with multiharmonic frequencies proceeds along similar lines.

5. Conclusion

One feels that the detection and experimental investigation of the many hitherto untouched non-linear processes resulting from the theory is at present but a question of further developments in measuring techniques and of appropriate judiciously conceived experiments. Were such measurements to prove feasible in gaseous media, we should obtain immediate information on the non-linear and multipolar properties of atoms and molecules in intense electromagnetic fields. Obviously, it has to be kept in mind that non-linear processes in gases are proportionately smaller than in solids; but then the strict theory of non-linear effects for the case of dense media is highly involved rendering difficult the correct interpretation of the results. In the latter case, one can hardly hope to obtain information relating to the properties of isolated atoms or molecules without making far-reaching simplifications of the theory. More considerable values of non-linear effects in gases are to be awaited in experimental conditions when, for example, one or several oscillation frequencies of the light beams applied lie near an absorption band of the substance investigated.

Indeed, from expressions (45) and (71) or (72), resonance scattering of order two occurs in the following cases: (i) if the sum of frequencies of the incident quanta is equal to the transition frequency, $\omega_1 + \omega_2 = \omega_{jk}$, or (ii) if one of the frequencies ω_1 or ω_2 is equal to the transition frequency ω_{jk} . Similarly, from (49) and (73), resonance scattering of order three can take place if $\omega_1 + \omega_2 + \omega_3 = \omega_{jk}$, or if

$$\omega_1 + \omega_2 = \omega_1 + \omega_3 = \omega_2 + \omega_3 = \omega_{jk}$$

or if one of the frequencies ω_1 or ω_2 or ω_3 is equal to ω_{jk} .

The tensor formalism proposed in this paper can be adapted to the computation of the non-linear variation in optical activity due to an intense electromagnetic field, and to various electro-optical and magneto-optical effects of higher orders.

The effect of molecular interactions on the multipole polarizability tensors of appropriate orders can be calculated, for example, by a method analogous to that elaborated by Mazur and Mandel (1956) for the dipole polarizability. In this case, i.e. when a system of N interacting molecules is considered, the total perturbation Hamiltonian is

composed of two parts, one of which arises from the interaction of all molecules with the electromagnetic fields and is obtained by summation of (31) over all the molecules of the system. The second part of V results from interaction between the molecules in the system and is given in general by (Jansen 1958, Kielich 1965)

$$V' = \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} (-1)^{n_1+1} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)!(2n_2)!} \mathbf{M}_{ep}^{(n_1)}[n_1]^{(n_1)} \mathbf{T}_{pq}^{(n_2)}[n_2] \mathbf{M}_{eq}^{(n_2)} \quad (74)$$

where

$${}^{(n_1)}\mathbf{T}_{pq}^{(n_2)} = -\nabla^{n_1+n_2} \left(\frac{1}{r_{pq}} \right) = (n_1+n_2)! (-r_{pq})^{-(n_1+n_2+1)} \mathbf{Y}_{pq}^{(n_1+n_2)} \quad (75)$$

is a tensor of rank n_1+n_2 describing the interaction between the 2^{n_1} -pole electric moment $\mathbf{M}_{ep}^{(n_1)}$ and the 2^{n_2} -pole electric moment $\mathbf{M}_{eq}^{(n_2)}$ of molecules p and q separated by a distance r_{pq} . The operator $\mathbf{Y}_{pq}^{(n_1+n_2)}$ is given by (34) if n is replaced by n_1+n_2 and \mathbf{r}_i by \mathbf{r}_{pq} . The explicit results for multipole polarizability tensors from calculations with the additional Hamiltonian (74) are highly involved and we refrain from writing them here.

In this case, with ρ denoting the mean number density of molecules of the medium under consideration, its dynamical electric permittivity ϵ is defined in general by the following tensor equation (Kielich 1965):

$$(\epsilon - \mathbf{U}) \cdot \mathbf{E} = 4\pi\rho \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1} [n-1] \mathbf{P}_e^{(n)}(t) \quad (76)$$

in which

$$\mathbf{P}_e^{(n)}(t) = \sum_k \mathbf{P}_{ekk}^{(n)}(t) \rho_{kk} \quad (77)$$

denotes the total electric multipole moment which results on averaging its diagonal matrix element $\mathbf{P}_{ekk}^{(n)}$ as given by expansion (37) for $k=l$ over all occupied quantum states k of the molecule with the density matrix ρ_{kk} in the presence of the electromagnetic fields acting on the medium. A quite analogous equation can be written for the dynamical magnetic permittivity μ , if in (76) \mathbf{E} is replaced by \mathbf{H} and $\mathbf{P}_e^{(n)}$ by $\mathbf{P}_m^{(n)}$. If, on the other hand, in the expressions derived in §§ 3.1 and 3.2 we deal formally with $\mathbf{P}_e^{(n)}$, $\mathbf{P}_m^{(n)}$, ${}^{(n)}\mathbf{A}_e^{(n)}$, ${}^{(n)}\mathbf{B}_e^{(n_a+n_b)}$, etc., as representing multipole operators defining the macroscopic electric or magnetic properties of an isotropic or anisotropic medium, we arrive at a generalization of Pershan's phenomenological formalism (1963) to multipolarity of arbitrary order.

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