MAGNETO-ELECTRIC SUSCEPTIBILITIES OF DEGENERATE STATES. I. GENERAL STRUCTURE OF SUSCEPTIBILITIES, AND LINEAR INTERACTION PROCESSES BETWEEN ATOMS AND ELECTROMAGNETIC FIELDS OF LASER WAVE

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By angular momentum theory, explicit expressions are derived for the tensor of electric, magnetic and magneto-electric susceptibilities of degenerate states. The formulae are well adapted to direct numerical computations for the atoms. The linear atomic susceptibilities analyzed are shown to intervene in the following processes: (*i*) Rayleigh and Raman light scattering; (*ii*) AC Stark effect in intense laser field. Invariant atomic parameters, occurring in the above processes, are calculated numerically in the approximation of the model potential method.

1. Introduction

When considering interaction processes involving a quantal system and the electromagnetic field, complete information on the system is contained in the susceptibility tensors which define the electric and magnetic polarisations, induced therein by the field. Various processes, occurring in systems in the presence of an electric and magnetic field, have been considered in particular in Ref. [1]. We shall be dealing with systems having a centre of inversion: atoms, or the simplest symmetrical molecules. In this case, in the first non-vanishing order of approximation, the electric and magnetic properties are described by the linear electric and magnetic susceptibilities $\chi^{e}_{ij}(-\omega;\omega)$ and $\chi^{m}_{ij}(-\omega;\omega)$ whereas the interferential effects due to the simultaneous action of the oscillating electric and static magnetic fields are described b the third-rank magneto-electric susceptibility tensor $\chi_{ijk}(-\omega;\omega,0)$.

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Inasmuch as the susceptibilities χ are tensors, it is of interest to elucidate explicitly the dependence of χ on its indices $i, j, \ldots$ and to determine the invariant atomic parameters R, dependent solely on the structure of the atom. With regard to the linear susceptibilities, such a procedure is analogous to that applied in the monograph [2] and consisting in a decomposition of the linear scattering tensor into irreducible parts. Since in the general case the state of the atom is degenerate (e.g. with respect to the projection M of its angular momentum on the quantisation axis), the tensor χ depends as well on the quantum numbers M, M' of the initial and final states.

In this work, the general structure of the tensors χ^{e}_{ij}, χ^{m}_{ij} and χ_{ijk} is investigated for degenerate states. A decomposition of these tensors into irreducible parts is derived, their dependence on the tensorial indices and quantum numbers M, M' is resolved, and formulae for the invariant parameters R_{xy} are proposed. Applying the results thus obtained, calculations are performed for Rayleigh and Raman scattering and the dynamical Stark effect in the intense laser field. The atomic parameters defining these processes are calculated numerically for a variety of atoms and various radiation frequencies ω in the approximation of the model potential method, developed in previous papers [3, 4].

2. General structure of linear and non-linear susceptibilities

2.1. General formulae

We shall be considering a quantal system (an atom) in a monochromatic electromagnetic wave with the wave vector $\boldsymbol{k}\left(|\boldsymbol{k}| = \frac{\omega}{c}\right)$ and field vectors:

$$\boldsymbol{E}(t) = \mathrm{Re}\,\{\boldsymbol{E}(\omega)e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}\}, \quad \boldsymbol{H}(t) = \mathrm{Re}\,\{\boldsymbol{H}(\omega)e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}\}, \tag{2.1}$$

with: $\boldsymbol{H} = \frac{c}{\omega}[\boldsymbol{k}\times\boldsymbol{E}]$ and $I = \frac{c}{8\pi}|\boldsymbol{E}|^2$ — the intensity. Moreover, a static magnetic field $H(0)$ exists in the medium. The medium is assumed as sufficiently rarefied for interaction effects between its atoms to be neglected. Our further considerations will bear on the isolated atom.

Effects of interaction between the atom and the external field, of strength small compared with that characterizing intra-atomic fields ($\approx 10^8$ V/cm), are conveniently analyzed in terms of susceptibilities, defining the electric and magnetic moments induced in the atom by the action of the field. The vectors of dipolar electric $\boldsymbol{p}(t)$ and magnetic $\boldsymbol{m}(t)$ polarisation can be calculated in the standard manner as the mean values of the appropriate dipole moment operators:

$$\boldsymbol{p}(t) = \langle\Psi(t)\,|\hat{\boldsymbol{d}}|\Psi(t)\rangle, \quad \boldsymbol{m}(t) = \langle\Psi(t)\,|\hat{\boldsymbol{\mu}}|\Psi(t)\rangle, \tag{2.2}$$

where $\hat{\boldsymbol{d}} = \sum_{i=1}^{N} e_i\boldsymbol{r}_i$, $\hat{\boldsymbol{\mu}} = -\mu_B(\boldsymbol{L}+2\boldsymbol{S})$, $\mu_B = \frac{|e|\hbar}{2mc}$ is Bohr's magneton, N — the number of electrons, $\boldsymbol{r}_i$ — the radius vector of the i-th electron, and $\boldsymbol{L}$, $\boldsymbol{S}$ — the orbital and spin

moment of the atom. $\Psi(t)$ is the solution of the Schrödinger equation of the atom in the field[1]:

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \{\hat{H}_a - \hat{\boldsymbol{d}} \cdot \boldsymbol{E}(t) - \hat{\boldsymbol{\mu}} \cdot [\boldsymbol{H}(t) + \boldsymbol{H}(0)]\}\Psi(t). \tag{2.3}$$

The initial state of the atom at zero field $|0\rangle = |nJM\rangle$ is an eigen-state of the Hamiltonian $\hat{H}_a$, with: n — the principal quantum number, J — the total angular momentum, and M — the projection of J on the quantisation axis. Thus, in the general case, the initial state of the system is $(2J+1)$ — fold degenerate with regard to the projection M. By solving Eq. (2.3) by perturbation theory in the basis of eigen-functions of the operator $\hat{H}_a$, one can obtain $\Psi(t)$ to within the desired order in $\boldsymbol{E}$ and $\boldsymbol{H}$, $\boldsymbol{H}(0)$. Whereas the atomic states possess well-defined parity and the matrix elements of the operator $\hat{\boldsymbol{d}}$ differ from zero only between states of different parity, the perturbation series for $\boldsymbol{p}(t)$ will contain but odd powers of $\boldsymbol{E}$ and that for $\boldsymbol{m}(t)$ — but even powers.

Restricting ourselves to terms linear in the magnetic field, we can write the polarisation vectors at the frequencies 0 and ω as follows:

$$\begin{aligned} \boldsymbol{p}(t) &= \boldsymbol{p}(0) + \{\boldsymbol{p}(\omega)e^{-i\omega t} + \text{h.c.}\} \\ \boldsymbol{m}(t) &= \boldsymbol{m}(0) + \{\boldsymbol{m}(\omega)e^{-i\omega t} + \text{h.c.}\}, \end{aligned} \tag{2.4}$$

where:

$$\begin{aligned} p_i(0) &= \tfrac{1}{2}\chi^{\text{eme}}_{ijk}(0; -\omega, \omega)H^*_j(\omega)E^k(\omega) + \tfrac{1}{2}\chi^{\text{eem}}_{ijk}(0; -\omega, \omega)E^*_j(\omega)H_k(\omega) \\ p_i(\omega) &= \chi^{\text{e}}_{ij}(-\omega; \omega)E_j(\omega) + \chi^{\text{eem}}_{ijk}(-\omega; \omega, 0)E_j(\omega)H_k(0) + \ldots \\ m_i(\omega) &= \chi^{\text{m}}_{ij}(-\omega; \omega)H_j(\omega) + \ldots \\ m_i(0) &= \langle nJM|\hat{\mu}_i|nJM'\rangle + \tfrac{1}{4}\chi^{\text{mee}}_{ijk}(0; \omega, -\omega)E_j(\omega)E^*_k(\omega) + \ldots \end{aligned} \tag{2.5}$$

We shall express the vectorial quantities in the spherical basis $\boldsymbol{e}_0 = \boldsymbol{e}_z$, $\boldsymbol{e}_{\pm 1} = \mp \frac{1}{\sqrt{2}}(\boldsymbol{e}_x \pm i\boldsymbol{e}_y)$. The covariant and contravariant components are related as usual: $A_M = (-1)^M A^{-M}$. For E and H, which are complex vectors if the wave is elliptically polarized, we have $A^*_M = (A^*)^M$. In the formulae (2.5), we omit terms quadratic in $\boldsymbol{H}(\omega)$ and $\boldsymbol{H}(0)$ since they are usually small in systems with a centre of inversion. However, if quadratic terms are taken into account, the operator $\hat{\chi}^{(\text{d})}_{ij}$ of diamagnetic interaction between the atom and the fields $\boldsymbol{H}(\omega)$ and $\boldsymbol{H}(0)$ has to be included in Eq. (2.3) [5].

Since the initial state $|nJ\rangle$ is M-degenerate, in order to take the degeneracy into account the mean values in (2.2) have, in the general case, to be calculated with functions $\Psi(t)$ involving different values of the projection M. For example,

$$\boldsymbol{p}(t) = \langle \Psi_M(t)\,|\hat{\boldsymbol{d}}|\,\Psi_{M'}(t)\rangle,$$

where Ψ_M and $\Psi_{M'}$ are solutions of Eq. (2.3) corresponding, respectively, to the initial

[1] We consider but dipole interaction. Multipole terms will be neglected [5].

and final atomic states $|nJM\rangle$, $|nJM'\rangle$. Consequently, in addition to depending on the tensorial indices $i, j, \ldots$, the dipole moments and susceptibilities in (2.4, 5) depend on the projections M, M' and, from this viewpoint, form a $(2J+1)\times(2J+1)$ matrix. For the sake of conciseness, we shall refrain from stating any dependence of the type $\chi = \chi_{MM'}$ in the formulae. With regard to numerous physical processes, the observables are usually determined as averages over all orientations of the atom in space. Thus, e.g. with regard to processes of spontaneous scattering, averaging bears on the quadratic combinations of χ:

$$\overline{\chi^2} = \frac{1}{(2J+1)^2} \sum_{MM'} |\chi_{MM'}|^2,$$

whereas coherent processes are expressed by the averages

$$\bar{\chi} = \frac{1}{2J+1} \sum_{M} \chi_{MM}.$$

Obviously $\overline{\chi^2} \neq (\bar{\chi})^2$, whereas $\overline{\chi^2}$ equals $(\bar{\chi})^2$ only for the non-degenerate state. Although the direction of the quantisation axis of the atom (the z-axis) is generally arbitrary, and the functions $|nJM\rangle$ for different orientations transform by way of Wigner D-functions [7], the choice of the z-axis is usually dictated by the specific physical situation thus permitting to write the final results in the simplest possible form (cf. e.g. formulae (2.20) and (2.21)).

For an atom in the state $|nJ\rangle$, the expressions for the susceptibilities of (2.5) take the form:

$$\chi^{e}_{ij}(-\omega;\omega) = \langle nJM|d_i G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_j|nJM'\rangle + \langle nJM|d_j G_{E_n+\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_i|nJM'\rangle, \tag{2.6}$$

$$\chi^{m}_{ij}(-\omega,\omega) = \langle nJM|\mu_i G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\mu_j|nJM'\rangle + \langle nJM|\mu_j G_{E_n+\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\mu_i|nJM'\rangle, \tag{2.7}$$

$$\begin{aligned}\chi^{eme}_{ijk}(0,-\omega,\omega) = \langle nJM|\{&d_i G_{E_n}(\boldsymbol{r}_1,\boldsymbol{r}_2)\mu_j G_{E_n+\omega}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_k \\ &+ d_k G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\mu_j G_{E_n}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_i + d_i G_{E_n}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_k G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_3)\mu_j \\ &+ \mu_j G_{E_n+\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_i G_{E_n+\omega}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_k + d_k G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_i G_{E_n-\omega}(\boldsymbol{r}_2,\boldsymbol{r}_3)\mu_j \\ &+ \mu_j G_{E_n+\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_k G_{E_n}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_i\}\,|nJM'\rangle,\end{aligned} \tag{2.8}$$

$$\begin{aligned}\chi^{eem}_{kij}(-\omega,\omega,0) = \langle nJM|\{&d_i G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,[\mu_j - \tfrac{1}{2}(\langle nJM|\mu_j|nJM\rangle \\ &+ \langle nJM'|\mu_j|nJM'\rangle)]G_{E_n-\omega}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_k \\ &+ d_k G_{E_n+\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,[\mu_j - \tfrac{1}{2}(\langle nJM|\mu_j|nJM\rangle + \langle nJM'|\mu_j|nJM'\rangle)]G_{E_n+\omega}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_i \\ &+ d_i G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_k G_{E_n}(\boldsymbol{r}_2,\boldsymbol{r}_3)\mu_j + \mu_j G_{E_n}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_i G_{E_n-\omega}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_k \\ &+ d_k G_{E_n+\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_i G_{E_n}(\boldsymbol{r}_2,\boldsymbol{r}_3)\mu_j \\ &+ \mu_j G_{E_n}(\boldsymbol{r}_1,\boldsymbol{r}_2)d_k G_{E_n+\omega}(\boldsymbol{r}_2,\boldsymbol{r}_3)d_i\}\,|nJM'\rangle,\end{aligned} \tag{2.9}$$

$$\chi^{mee}_{jik}(0;-\omega,\omega) = \chi^{eme}_{ijk}(-\omega;0,\omega). \tag{2.10}$$

Above,

$$G_E(\boldsymbol{r}, \boldsymbol{r}') = \sum_k \frac{\Psi_k(\boldsymbol{r})\Psi_k(\boldsymbol{r}')}{E_k - E} \tag{2.11}$$

is the Green function of the atom replacing summation over intermediate states in the series of perturbation theory. $\sum_k$ denotes summation over the discrete spectrum and integration over the continuous spectrum of the atom. If the energy E in the Green function coincides with one of the eigen-values of the energy of the system, e.g. $E = E_n$, G_{E_n} is given by (2.11) in which the term with $k = n$ is absent.

The susceptibilities (2.8)—(2.10) define various physical processes in which interaction between the atom and field is apparent. Thus, $\chi^{\mathrm{eem}}_{ijk}(-\omega; \omega, 0)$ defines Faraday's effect, light scattering in a magnetic field $\boldsymbol{H}(0)$ and the shifting and splitting of the energy levels of the system in fields $\boldsymbol{E}$ and $\boldsymbol{H}(0)$; likewise, $\chi^{\mathrm{mee}}_{kij}(0; -\omega, \omega)$ defines the inverse Faraday effect; and $\chi^{\mathrm{eme}}_{ijk}(0; -\omega, \omega)$ — that of optical rectification [6]. Besides the preceding magneto-electric susceptibilities, it is of interest to consider the following third-rank susceptibilities at the frequency 2ω:

$$p_i(2\omega) = \chi^{\mathrm{eem}}_{ijk}(-2\omega; \omega, \omega)E_j(\omega)H_k(\omega),$$

$$m_i(2\omega) = \chi^{\mathrm{mee}}_{ijk}(-2\omega; \omega, \omega)E_j(\omega)E_k(\omega),$$

defining scattering of radiation with the frequency 2ω. We shall refrain, however, from detailed calculations of $\chi(-2\omega)$ as a strict analysis of second-harmonic scattering would have to comprise effects of quadrupolar interaction of the field and atom [5].

In dealing with degenerate states, the investigation of the general structure of the tensors χ and of their dependence on the tensorial indices i, j, k becomes highly complicated in comparison with the non-degenerate case. Thus, for non-degenerate states:

$$\chi_{ijk} \approx a\varepsilon_{ijk}, \qquad \{i, j, k\} = x, y, z$$

where ε_{ijk} is the Levi-Cività tensor, and a — an atomic parameter; in the case of degenerate states, no such simple relation can be written, and χ is a function of several independent atomic parameters and the quantum numbers M, M'. For integration over the angular variables in (2.6)–(2.9), we expand the Green function $G_E(\boldsymbol{r}, \boldsymbol{r}')$ in a series in partial waves:

$$G_E(\boldsymbol{r}, \boldsymbol{r}') = \sum_{JM} g_J(E; \boldsymbol{r}, \boldsymbol{r}')\Phi_{JM}\left(\frac{\boldsymbol{r}}{r}\right)\Phi^*_{JM}\left(\frac{\boldsymbol{r}'}{r'}\right), \tag{2.12}$$

where g_J is a radial Green function, depending only on the absolute values of the radius-vectors $\boldsymbol{r}, \boldsymbol{r}'$, whereas Φ_{JM} is the spin-orbital part of the atomic wave function with total angular momentum J the explicit form of which is given by the type of coupling between

the angular momenta in the atom[2]. The further traansformation of (2.6)–(2.9) is conveniently performed by having recourse to the technique of irreducible tensors and the Wigner–Eckart theorem [7]:

$$\langle JM|\hat{T}_{\kappa\mu}|J'M'\rangle = (-1)^{J-M}\begin{pmatrix} J & \kappa & J' \\ -M & \mu & M' \end{pmatrix}\langle J\|\hat{T}_\kappa\|J'\rangle, \tag{2.13}$$

where $\begin{pmatrix} a\,b\,c \\ \alpha\,\beta\,\gamma \end{pmatrix}$ is a Wigner 3-j symbol, and $\langle J\|T_\kappa\|J'\rangle$ the reduced matrix element of a tensor operator of rank κ.

2.2. The linear electric and magnetic susceptibilities

By (2.12), (2.13) and the well known formula of angular momentum theory [7]:

$$\sum_{\xi}(-1)^{x-\xi}\begin{pmatrix} a & b & x \\ \alpha & \beta & -\xi \end{pmatrix}\begin{pmatrix} x & d & c \\ \xi & \delta & \gamma \end{pmatrix}$$

$$= (-1)^{2a}\sum_{y,\eta}(-1)^{y-\eta}(2y+1)\begin{pmatrix} a & c & y \\ \alpha & \gamma & -\eta \end{pmatrix}\begin{pmatrix} y & d & b \\ \eta & \delta & \beta \end{pmatrix}\begin{Bmatrix} d & c & x \\ a & b & y \end{Bmatrix}, \tag{2.13a}$$

where $\{\}$ is a 6-j symbol, the expression for the linear susceptibility goes over into:

$$\chi_{ij}(-\omega;\omega) = \langle nJM|\{\hat{T}_i G_{E_n+\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\hat{T}_j + \hat{T}_j G_{E_n-\omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\hat{T}_i\}|nJM'\rangle$$

$$= \sum_{\substack{p=0,1,2 \\ m}}(-1)^{J+M'}\sqrt{3(2J+1)}\begin{pmatrix} J & J & p \\ -M & M' & m \end{pmatrix}\begin{pmatrix} p & 1 & 1 \\ -m & i & j \end{pmatrix}\alpha_p, \tag{2.14}$$

where

$$\alpha_p = \frac{(-1)^{2J}(2p+1)}{\sqrt{3(2J+1)}}\sum_{J_1}\begin{Bmatrix} 1 & 1 & p \\ J & J & J_1 \end{Bmatrix}\{M_{J_1}(E_n+\omega)+(-1)^p M_{J_1}(E_n-\omega)\} \tag{2.15}$$

and

$$M_{J_1}(E) = \langle nJ\|\hat{T}g_{J_1}(E;r,r')\hat{T}\|nJ\rangle = \sum_k \frac{\langle nJ\|\hat{T}\|kJ'\rangle\langle kJ'\|\hat{T}\|nJ\rangle}{E_{kJ'}-E}$$

is a reduced compound matrix element, The formulae derived above are valid for χ^e as well as χ^m provided $\hat{T}$ is taken as representing $\hat{\boldsymbol{d}}$ and $\hat{\boldsymbol{\mu}}$, respectively.

The expression (2.14) gives the decomposition of the tensor χ_{ij} into irreducible tensors of rank 0, 1 and 2 corresponding to $p = 0, 1, 2$. The quantities α_p are invariant atomic

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[2] The functions g_J and Φ_{JM} can depend, in addition to J, on other quantum numbers e.g. on the orbital momentum L within LS-coupling, etc. Inasmuch as the general structure of the expansion (2.12) remains unaffected, the indices at g_J and Φ_{JM} are not specified.

parameters. In particular, for the non-degenerate state ($J = 0$) we have: $\alpha_1 = \alpha_2 = 0$,

$$\alpha_0 = \tfrac{1}{3}\,[M_{J_1=1}(E_n+\omega)+M_{J_1=1}(E_n-\omega)]$$

and

$$\chi_{ij}(-\omega;\,\omega) = (-1)^{i+1}\alpha_0\delta_{i,-j}.$$

For the level with $J = \frac{1}{2}$, the two parameters α_0 and α_1 are non-zero.

In order to prove the advantage of writing χ_{ij} in the form (2.14), we shall now consider two examples: Rayleigh and Raman light scattering, and light shift of atomic levels in a field.

The general cross-section formula for Raman scattering of a photon with the polarisation vector $\boldsymbol{e}$ and frequency ω involving a transition of the atom from the state $|nJ\rangle$ to $|n'J'\rangle$ with emission of a Raman photon having the polarisation $\boldsymbol{e}'$ and frequency $\omega' = E_n+\omega-E_{n'}$ is (cf., e.g. [2]):

$$\frac{d\sigma}{d\Omega_{e'}} = \frac{1}{2J+1}\sum_{M,M'}\Bigg|\sum_{i,j=0,\pm1} e_i'^{*}e^{j}\chi_{ij}^{\mathrm{Ram}}(-\omega';\,\omega)\Bigg|^2\frac{\omega\omega'^3}{c^4}, \tag{2.16}$$

where the Raman susceptibility χ_{ij}^{Ram} is defined similarly to (2.6):

$$\chi_{ij}^{\mathrm{Ram}}(-\omega';\,\omega) = \langle nJM|\,\{d_iG_{E_n+\omega}(\boldsymbol{r}_1,\,\boldsymbol{r}_2)d_j+d_jG_{E_n-\omega}(\boldsymbol{r}_1,\,\boldsymbol{r}_2)d_i\}\,|n'J'M'\rangle$$

and can be put in a form analogical to (2.14):

$$\chi_{ij}^{\mathrm{Ram}}(-\omega',\,\omega) = \sum_{p,m}(-)^{J+M'}\sqrt{3(2J+1)}\begin{pmatrix} J & J' & p\\ -M & M' & m\end{pmatrix}\begin{pmatrix} p & 1 & 1\\ -m & i & j\end{pmatrix}\alpha_p^{\mathrm{Ram}}, \tag{2.17}$$

with:

$$\alpha_p^{\mathrm{Ram}} = \frac{(-1)^{2J}(2p+1)}{\sqrt{3(2J+1)}}\sum_{J_1}\begin{Bmatrix}1 & 1 & p\\ J & J' & J_1\end{Bmatrix}[\langle nJ\|\boldsymbol{d}g_{J_1}(E_n+\omega;\,r_1,\,r_2)\boldsymbol{d}\|n'J'\rangle$$

$$+(-1)^p\langle nJ\|\boldsymbol{d}g_{J_1}(E_n-\omega;\,r_1,\,r_2)\boldsymbol{d}\|n'J'\rangle]. \tag{2.18}$$

By (2.17) and applying spherical tensor technique, $\dfrac{d\sigma}{d\Omega_{e'}}$ can be written as follows:

$$\frac{d\sigma}{d\Omega_{e'}} = \sum_{p=0,1,2}\frac{|\alpha_p^{\mathrm{Ram}}|^2}{(2p+1)^2}(\{\boldsymbol{e}'^{*}\otimes\boldsymbol{e}\}_p\cdot\{\boldsymbol{e}'\otimes\boldsymbol{e}^{*}\}_p)\frac{3\omega\omega'^3}{c^4}$$

$$= [|\alpha_0^{\mathrm{Ram}}|^2|(\boldsymbol{e}'^{*}\cdot\boldsymbol{e})|^2+\tfrac{1}{6}\,|\alpha_1^{\mathrm{Ram}}|^2(1-|(\boldsymbol{e}'\cdot\boldsymbol{e})|^2)$$

$$+\tfrac{3}{50}\,|\alpha_2^{\mathrm{Ram}}|^2(1+|(\boldsymbol{e}'\cdot\boldsymbol{e})|^2-\tfrac{2}{3}\,|(\boldsymbol{e}'^{*}\cdot\boldsymbol{e})|^2)]\,\frac{\omega\omega'^3}{c^4}, \tag{2.19}$$

$\{a \otimes b\}_p$ denoting the irreducible tensor product of the vectors a and b [7]. The above derived expression for $\frac{d\sigma}{d\Omega_{e'}}$ is analogical to formula (61.7) of the monograph [2], and the cross-sections for scalar (G^0), antisymmetric (G^a) and symmetric (G^s) scattering are expressed directly by way of the parameters α_p^{Ram}:

$$G^0 = |\alpha_0^{\mathrm{Ram}}|^2, \quad G^a = |\alpha_1^{\mathrm{Ram}}|^2, \quad G^s = \tfrac{3}{5}\,|\alpha_2^{\mathrm{Ram}}|^2.$$

For Rayleigh scattering, we have $E_n = E_{n'}$, and α_p^{Ram} coincides with (2.15).

Computations of the parameters α_p for atoms are easy to perform when using the analytical expression for the Green function $g_J(E; r, r')$ in the approximation of the model potential method [3, 4]. The technical details of these computations are to be

TABLE I

The cross-section of Rayleigh and Raman scattering for the ground and metastable states of hydrogen atom

ω	σ_{1S-1S}, cm^2	σ_{2S-2S}, cm^2	$\sigma_{2S \to \overline{1S}}$, cm^2
ω_R	2.8×10^{-28}	1.0×10^{-23}	1.3×10^{-22}
ω_N	4.0×10^{-29}	7.5×10^{-26}	1.2×10^{-23}

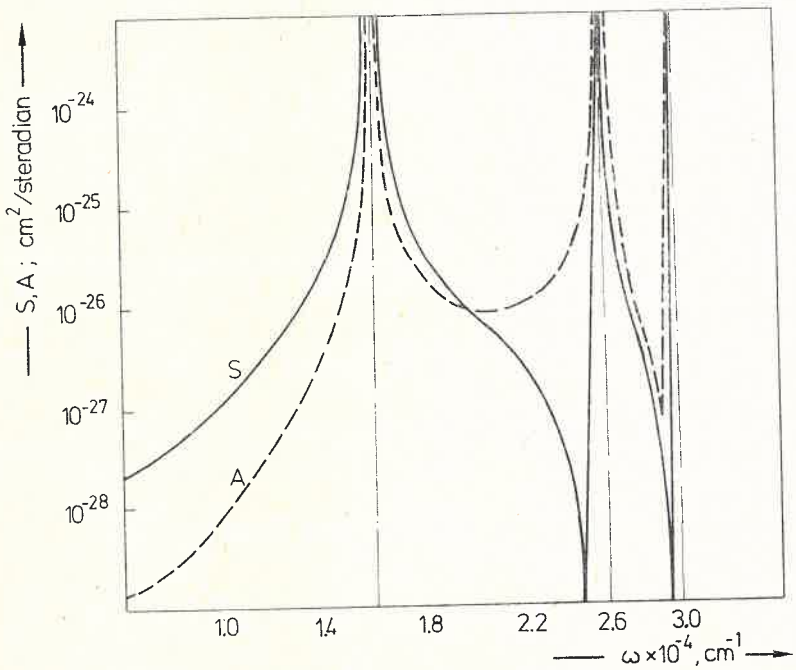

Fig. 1. Dispersion of the symmetric and antisymmetric Raman scattering cross-section for the transition $6^3P_2 \to 6^3P_1$ of the mercury atom

found in Ref. [4]. Numerically, the α_p depend essentially on the light frequency as well as the structure of the atom. Thus, e.g. in the case of the hydrogen atom the cross-sections for Rayleigh and Raman scattering differ strongly for the ground $1S$ and metastable $2S$ states and the ruby laser ($\omega_R = 144000\ \mathrm{cm}^{-1}$) and neodymium laser ($\omega_N = 9440\ \mathrm{cm}^{-1}$) frequencies (Table I).

Fig. 1 shows the dispersion of the quantities $S(\omega)$ and $A(\omega)$ defining the cross-sections for symmetric and antisymmetric scattering

$$S(\omega) = \tfrac{1}{5} r_0^2 \omega\omega'^3 G^s, \quad A(\omega) = \tfrac{1}{6} r_0^2 \omega\omega'^3 G^a.$$

$r_0 = \dfrac{e^2}{mc^2}$ — the classical radius of the electron, for the transition $6^3P_2 \to 6^3P_1$ of the mercury atom (scalar scattering is absent in this case).

Table II gives the values of S and A for Raman scattering by the atoms Tl, J and Hg at some characteristic laser frequencies. It is worth mentioning that our calculations are

TABLE II

Parameters of symmetric (S) and antisymmetric (A) scattering by atoms Tl, J and Hg for laser frequencies (in units of 10^{-28} cm²/sterad)

ω, cm^{-1}	Tl: $6^2P_{1/2} \to 6^2P_{3/2}$		J: $5^2P_{1/2} \to 5^2P_{3/2}$		Hg: $6^3P_2 \to 6^3P_1$	
	$S(\omega)$	$A(\omega)$	$S(\omega)$	$A(\omega)$	$S(\omega)$	$A(\omega)$
9440	0.029	10.0002	10.547	10.006	34.5	1.4
14400	3.84	0.089	2.02	0.042	465	55
18880	42.5	2.45	5.37	0.177	3.7×10^4	1.2×10^4
28800	1460	340	37	2.81	408	700

in good agreement with the experimental data of Refs [8, 9] for the Raman scattering cross-sections of Tl at $\omega = \omega_R$ and J at $\omega = \omega_N$.

The parameters α_p moreover define the change in energy ΔE_{nJM} of the level $|nJ\rangle$ in an intense light field similar to the Stark effect in a static electric field. A general method for the calculation of ΔE_n in a monochromatic wave is to be found e.g. in Ref. [10]. We shall consider the cases of linear and circular polarization separately.

For a linearly polarized field $\boldsymbol{E}(t)$, the expression for ΔE_{nJM} in a system of coordinates with quantisation axis directed along the field vector $\boldsymbol{E}$ is:

$$\Delta E_{nJM} = -\tfrac{1}{4} \chi^e_{0,0}(-\omega; \omega) |\boldsymbol{E}|^2$$

and, with regard to (2.14), can be written in the form:

$$\Delta E_{nJM} = -\tfrac{1}{4} \left\{ \alpha_0 - \alpha_2 \frac{3M^2 - J(J+1)}{[10J(J+1)(2J+3)(2J-1)]^{1/2}} \right\} |\boldsymbol{E}^2|. \tag{2.20}$$

For circularly polarized $E(t)$, the quantisation axis is conveniently chosen in the direction k of wave propagation, and the expression for ΔE takes the form:

$$\Delta E_{nJM} = \tfrac{1}{4}\,\chi^{e}_{+1,-1}(-\omega;\,\omega)\,|E|^2$$

$$= -\tfrac{1}{4}\left\{\alpha_0 - \frac{\alpha_1 M}{[2J(J+1)]^{1/2}} + \alpha_2\,\frac{3M^2 - J(J+1)}{2[10J(J+1)\,(2J+3)\,(2J-1)]^{1/2}}\right\}|E|^2, \qquad (2.21)$$

where $E(t)$ is assumed as right circularly polarized; in the opposite case, the sign at the α_1-term is positive.

At $\omega = 0$, Eq. (2.20) describes the static Stark effect and α_0, α_2 are related with the scalar (α^S) and tensorial (α^T) polarizabilities of the level $|nJ\rangle$ [11]:

$$\alpha^S = \alpha_0, \quad \alpha^T = -\alpha_2\left[\frac{J(2J-1)}{10(J+1)\,(2J+3)}\right]^{1/2}.$$

The parameter α_1 vanishes at $\omega = 0$, as follows directly from the definition (2.15); consequently, α_1 is a supplementary characteristic of the level $|nJ\rangle$ in a field with non-zero degree of circular polarisation. By analogy with α^S and α^T, the quantity α_1 is naturally referred to as a vectorial (or antisymmetric) polarizability as defining the antisymmetric part of the cross-section for Rayleigh scattering in (2.19).

Numerical computations of α^S and α^T for a variety of atoms at laser frequencies are to be found in Ref. [4]. Table III gives the values of α_1 for some excited states of the xenon

TABLE III

Vectorial (or antisymmetric) polarizability α_1 for some excited states of the xenon atom at neodymium laser frequency ($\omega_N = 9440\ \mathrm{cm}^{-1}$)

State	Re α_1; in atomic units	Im α_1; in atomic units
$5d\ [0\ \frac{1}{2}]_1$	3521.8	0
$5d\ [1\ \frac{1}{2}]_1$	13653.4	0
$5d\ [1\ \frac{1}{2}]_2$	3824.54	0
$5f\ [1\ \frac{1}{2}]_1$	−499.34	78.2
$5f\ [1\ \frac{1}{2}]_2$	−433.4	66.4
$5f\ [3\ \frac{1}{2}]_3$	−642.9	48.8
$5f\ [3\ \frac{1}{2}]_4$	−785.6	47.6
$5f\ [4\ \frac{1}{2}]_4$	−494.7	57.5
$5f\ [4\ \frac{1}{2}]_5$	−420.7	56.6

atom at neodymium laser frequency calculated in the approximation of the model potential method [3, 4]. The imaginary part of α_1 is related with the photoionization cross-section of the level $|nJ\rangle$, when the frequency ω exceeds the ionization potential $|E_n|$.

Thus, the measurement of the parameters α_p in experiment is feasible in processes of light scattering as well as in studies of the shifts in spectral line frequencies of the atom in a field. In the latter case, not only the absolute value but also the sign of α_p can be determined.

2.3. The magneto-electric susceptibilities

The investigation of the general structure of the susceptibilities χ_{ijk} is more highly complicated than in the case of χ_{ij}, since the decomposition of a third-rank tensor into irreducible parts is not unique [7]. As an example, we shall consider $\chi^{\mathrm{eme}}_{ijk}(-\omega; 0, \omega)$; the other tensor χ_{ijk} can then be dealt with similarly. With regard to (2.12, 13) and the summation formulae for 3j-Wigner symbols (12.1.7) of Ref. [7], we re-write (2.9) in a form similar to (2.14):

$$\chi^{\mathrm{eme}}_{kji}(-\omega; 0, \omega) = (-1)^{J+M+j+1} \sum_{x,\xi;y,\eta} [3(2J+1)(2x+1)]^{1/2} \begin{pmatrix} J & J & x \\ -M & M' & \xi \end{pmatrix} \begin{pmatrix} x & 1 & y \\ -\xi & j & -\eta \end{pmatrix} \begin{pmatrix} y & 1 & 1 \\ \eta & i & k \end{pmatrix} R_{xy}. \tag{2.22}$$

Here, the R_{xy} are combinations of reduced compound matrix elements, and are analogical to the parameters α_p of Subsection 2.2:

$$\begin{aligned} R_{xy} = (2y+1)\left[\frac{2x+1}{3(2J+1)}\right]^{1/2} \Bigg\{ \sum_{J_1,J_2} (-1)^{J_1-J} \Bigg[\begin{Bmatrix} 1 & J_1 & J \\ 1 & J_2 & J \\ y & 1 & x \end{Bmatrix} \\ \times (\langle nJ \| dg_{J_1}(E_n-\omega; \boldsymbol{r}_1, \boldsymbol{r}_2) \mu g_{J_2}(E_n-\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) \boldsymbol{d} \| nJ \rangle + (-1)^y \langle nJ \| dg_{J_1}(E_n+\omega; \boldsymbol{r}_1, \boldsymbol{r}_2)\, \mu \\ \times g_{J_2}(E_n+\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) \boldsymbol{d} \| nJ \rangle) + \{1-(-1)^{x+y}\} \begin{Bmatrix} 1 & 1 & y \\ J & J_1 & J_2 \end{Bmatrix} \begin{Bmatrix} J & J & x \\ y & 1 & J_1 \end{Bmatrix} \\ \times (\langle nJ \| \mu g_{J_1}(E_n; \boldsymbol{r}_1, \boldsymbol{r}_2) dg_{J_2}(E_n-\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) \boldsymbol{d} \| nJ \rangle + (-1)^y \langle nJ \| \mu g_{J_1}(E_n; \boldsymbol{r}_1, \boldsymbol{r}_2) \boldsymbol{d} \\ \times g_{J_2}(E_n+\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) \boldsymbol{d} \| nJ \rangle) \Bigg] + \tfrac{1}{2} [1-(-1)^{x+y}] (-1)^{y+2J} \\ \times \langle nJ \| \mu \| nJ \rangle \begin{Bmatrix} x & y & 1 \\ J & J & J \end{Bmatrix} \sum_{J_1} \begin{Bmatrix} 1 & 1 & y \\ J & J & J_1 \end{Bmatrix} (\langle nJ \| dg_{J_1}(E_n+\omega; \boldsymbol{r}_1, \boldsymbol{r}_2) g_{J_2}(E_n+\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) \boldsymbol{d} \| nJ \rangle \\ + (-1)^y \langle nJ \| dg_{J_1}(E_n-\omega; \boldsymbol{r}_1, \boldsymbol{r}_2) g_{J_1}(E_n-\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) \boldsymbol{d} \| nJ \rangle) \Bigg\}. \end{aligned} \tag{2.23}$$

It follows from the selection values for the 3-j symbols of (2.22) that, in the general case, 7 distinct parameters R_{xy} can occur corresponding to different combinations of the indices x, y. This, moreover, is in agreement with the general statement (see Subsection 3.2 of Ref. [7]) that an arbitrary third-rank tensor can be decomposed into 7 irreducible tensors; from the latter point of view, the parameters R_{xy} are their invariants. From the form of (2.23), however, the terms of R_{xy} with $x = y$ can be shown to vanish. With regard to the second and third group of terms in (2.23) this is obvious because of the factor $\{1-(-1)^{x+y}\}$. For the first terms, this follows from the properties of the 9-j symbol: at

$J_1 = J_2$, the 9-j symbol contains 2 identical rows and is equal to zero, if $(x+y+1)$ is odd; at $J_1 = J_2 \pm 1$ and fixed J_2, the respective 9-j symbols are identical if $(x+y)$ is even, but with regard to the phase $(-1)^{J_1-J}$ the matrix elements with the momenta $J_1 = J_2+1$ and $J_1 = J_2-1$ cancel out.

Hence, the susceptibility χ_{ijk} is characterized by 5 mutually independent atomic paramaters R_{xy}, corresponding to the sets

$$(x, y) = (0,1), (1,0), (1,2), (2,1), (3,2).$$

With regard to the "triangle relationship" for the 3j-symbols of (2.22) it is easy to check that, for the non-degenerate state with $J = 0$, the only non-zero parameter is R_{01}, and (2.22) becomes:

$$\chi^{\text{eme}}_{ijk}(-\omega; 0, \omega) = \begin{pmatrix} 1 & 1 & 1 \\ i & j & k \end{pmatrix} R_{01}, \tag{2.24}$$

$$R_{01} = \tfrac{1}{3} \langle n, J = 0 \| \boldsymbol{d} \{ g_1(E_n+\omega; \boldsymbol{r}_1, \boldsymbol{r}_2) \mu g_1(E_n+\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) - g_1(E_n-\omega; \boldsymbol{r}_1, \boldsymbol{r}_2)$$

$$\times \mu g_1(E_n-\omega; \boldsymbol{r}_2, \boldsymbol{r}_3) \} \boldsymbol{d} \| n, J = 0 \rangle.$$

Above, the 3-j symbol $\begin{pmatrix} 1 & 1 & 1 \\ i & j & k \end{pmatrix}$ has antisymmetry properties like those of the Levi-Cività tensor ε_{ijk} and is zero if $(i+j+k) \neq 0$.

For states with $J = \frac{1}{2}$ (twice degenerate level) the following 3 parameters are non-zero: R_{01}, R_{10} and R_{12}. In states with $J = 1$ only R_{32} is zero. Finally, in the general case at $J \geqslant \frac{3}{2}$ all 5 parameters R_{xy} differ from zero.

It should be noted that the decomposition (2.22) for χ is not unique. By applying the relation (2.13a) to the product

$$\begin{pmatrix} x & 1 & y \\ -\xi & j & -\eta \end{pmatrix} \begin{pmatrix} y & 1 & 1 \\ \eta & i & k \end{pmatrix},$$

χ_{ijk} can be transformed to a form similar to (2.22) albeit with the interchange $i \rightleftarrows j$ and differently defined R_{xy}, the number of independent R_{xy}'s remaining unchanged. This, in fact, is the expression of the previously mentioned non uniqueness characterizing the decomposition of a third-rank tensor into irreducible parts.

A detailed account of the numerical calculation of the parameters α_p and R_{xy} for specific atoms, as well as discussions of various magneto-electric processes described by these parameters, will be given in a subsequent paper (see, next paper in this Journal).

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