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ON NONLINEAR MULTIPOLE MAGNETIZATION

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Synopsis

Starting from the Lorentz microscopic field equations and using a statistical ensemble averaging method and a compact tensor formalism, general equations are derived for the tensors of electric and magnetic permittivity which contain all contributions from the multipole electric and magnetic polarizations of a medium at rest. For the case of an intense DC magnetic field, the multipolar magnetic polarization is calculated by quantum mechanical perturbation theory and Boltzmann statistics to the third-order approximation inclusively. The multipole and nonlinear formalism evolved is effectively applied for calculating the variations in magnetic permeability due to the square of a strong homogeneous magnetic field or to a magnetic field gradient.

§ 1. *Introduction.* The theory of the electrodynamic field is essentially due to Faraday and Maxwell; the latter's well-known equations provide its compact mathematical formulation. Maxwell's theory refrains from inquiring into the structure of matter, which it regards as a continuous medium; thus, it is a phenomenological and macroscopic theory. Lorentz[1]), in his theory of electrons, formulated a microscopic electrodynamics and showed how to make the transition from microscopic to Maxwell's macroscopic field equations by time- and space-averaging of microscopic field quantities over physically infinitesimal regions. The approach of Lorentz was developed by Van Vleck[2]) as well as by Rosenfeld[3]); the latter, in his elegant and modern theory of the electron, showed that if in Maxwell's equations dipolar magnetic polarization is taken into account beside dipolar electric polarization, then a contribution of the same order due to quadrupolar electric polarization has also to be considered. Voisin [3a]) extended the Lorentz-Rosenfeld theory to multipoles of arbitrary order.

Mazur and Nijboer[4]) replaced Lorentz's space-time averageing over physically infinitesimal regions by a statistical ensemble averageing and carried out the transition from microscopic to macroscopic field equation in a consistent way. The statistical-mechanical approach of Mazur and Nijboer was modified by Jansen[5]) and Schram[5a]) on a quantum-mechanical basis. Recently De Groot and Vlieger[6]) developed a general method for deriving the macroscopic Maxwell equations from "atomic field

equations" in a covariant way by an appropriate averaging procedure in a "fluxion-space". They also took into account the retardation of the fields as well as all possible motions of the particles in a medium discussed earlier by Mazur and Nijboer[4]).

In the present paper, applying Mazur and Nijboer's statistical procedure and Jansen's tensor notation, a multipole expansion for the electric charge and current density is derived allowing to obtain general equations for the electric and magnetic permittivity tensors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\mu}$ on the basis of the Maxwell-Lorentz equations. The equations derived contain 2^n-pole tensors of the electric and magnetic polarization, $\boldsymbol{P}_e^{(n)}$ and $\boldsymbol{P}_m^{(n)}$. However, a detailed quantum-mechanical discussion focusses on the magnetic multipole polarization $\boldsymbol{P}_m^{(n)}$ only. The calculations proceed from the multipole expansion of the perturbation Hamiltonian discussed in various approximations by a number of authors (see e.g. refs. 2, 3, and 7–11). Since we are interested mainly in linear as well as non-linear diamagnetic multipole polarization, we recur to the multipole expansion not only of the first-order Hamiltonian, but moreover of that of the second, third and fourth orders. In this way, taking into account also paramagnetic polarization, the results of Langevin[12]) and Van Vleck[2]) are generalized to the case of multipole magnetic polarization, both linear and nonlinear.

For the sake of clarity, the final considerations of this paper are restricted to media sufficiently rarefied for atomic and molecular interactions to be neglected (recently, Kaufman and Soda[13]) proposed a linear, dipolar theory of the magnetic susceptibility of imperfect gases), more stress being laid on the construction of a general multipolar, nonlinear formalism rather than on the physical aspect of the problem already discussed with insight in the monographs of Lorentz[1]), Van Vleck[2]) and Rosenfeld[3]). The formalism evolved is applied to some simple examples of nonlinear variations in magnetic permeability due to the square of a strong homogeneous magnetic field or the gradient of a magnetic field.

§ 2. *Derivation of general equations for the electric and magnetic permittivities.* We consider an assembly of N identical microsystems (atoms, molecules or ions) in statistical equilibrium at the temperature T with average uniform number density at position $\boldsymbol{r}$ and time t defined as[4])

$$\rho(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \delta(\boldsymbol{r}_p - \boldsymbol{r}) \rangle. \tag{1}$$

Here $\delta(\boldsymbol{r}_p - \boldsymbol{r})$ is a three-dimensional Dirac δ-function, $\boldsymbol{r}_p$ is the position vector of the p-th microsystem and the brackets $\langle\ \rangle$ symbolize a suitably defined ensemble average (see e.g. refs 4–6).

Let the p-th microsystem consist of ν_p point particles (nuclei and electrons) with electric charges e_{pi}, masses m_{pi} and positional vectors $\boldsymbol{R}_{pi} (i = 1, 2, \ldots$

... ν_p). For convenience, we introduce the set of independent coordinates

$$\boldsymbol{r}_p = \sum_i m_{pi}\boldsymbol{R}_{pi}/\sum_i m_{pi} \quad \text{and} \quad \boldsymbol{r}_{pi} = \boldsymbol{R}_{pi} - \boldsymbol{r}_p, \tag{2}$$

where $\boldsymbol{r}_{pi}$ is the (relative) position vector of the i-th particle with respect to the center of mass of the microsystem p whose position is $\boldsymbol{r}_p$.

According to Lorentz's[1]) classical theory of the electron, the "microscopic" electromagnetic field equations are of the form

$$\boldsymbol{\nabla} \times \boldsymbol{e} = -\frac{1}{c}\frac{\partial \boldsymbol{h}}{\partial t}, \quad \boldsymbol{\nabla}\cdot\boldsymbol{h} = 0, \tag{3}$$

$$\boldsymbol{\nabla} \times \boldsymbol{h} = \frac{1}{c}\frac{\partial \boldsymbol{e}}{\partial t} + \frac{4\pi}{c}\boldsymbol{j}, \quad \boldsymbol{\nabla}\cdot\boldsymbol{e} = 4\pi\rho'_e, \tag{4}$$

where $\boldsymbol{e}$ and $\boldsymbol{h}$ are the microscopic electric and magnetic field strengths,

$$\rho'_e = \sum_{p=1}^{N}\sum_{i=1}^{\nu_p} e_{pi}\delta(\boldsymbol{R}_{pi} - \boldsymbol{r}) \tag{5}$$

is the electric charge density and

$$\boldsymbol{j} = \sum_{p=1}^{N}\sum_{i=1}^{\nu_p} e_{pi}\dot{\boldsymbol{R}}_{pi}\delta(\boldsymbol{R}_{pi} - \boldsymbol{r}) \tag{6}$$

is the electric current density[4]).

Since the function $\delta(\boldsymbol{R}_{pi} - \boldsymbol{r}) = \delta(\boldsymbol{r}_p + \boldsymbol{r}_{pi} - \boldsymbol{r})$ can be expanded in a series in powers of $\boldsymbol{r}_{pi}$ around $\boldsymbol{r}_p - \boldsymbol{r}$,

$$\delta(\boldsymbol{r}_p + \boldsymbol{r}_{pi} - \boldsymbol{r}) = \sum_{n=0}^{\infty}\frac{1}{n!}\boldsymbol{r}_{pi}^n[n]\,\boldsymbol{\nabla}_p^n\delta(\boldsymbol{r}_p - \boldsymbol{r}), \tag{7}$$

we obtain from (5)($\boldsymbol{\nabla}_p = -\boldsymbol{\nabla}$ is the differential operator at position $\boldsymbol{r}_p$ whereas $\boldsymbol{\nabla}$ operates on $\boldsymbol{r}$)

$$\rho'_e = \sum_{p=1}^{N}\left\{\sum_{i=1}^{\nu_p} e_{pi}\delta(\boldsymbol{r}_p - \boldsymbol{r}) + \sum_{n=1}^{\infty}\frac{2^n n!}{(2n)!}\boldsymbol{M}_{ep}^{(n)}[n]\boldsymbol{\nabla}_p^n\delta(\boldsymbol{r}_p - \boldsymbol{r})\right\}, \tag{8}$$

where we have introduced the 2^n-pole electric moment of the microsystem p defined as[14])

$$\boldsymbol{M}_{ep}^{(n)} = \sum_{i=1}^{\nu_p} e_{pi}r_{pi}^n\boldsymbol{Y}_{pi}^{(n)}. \tag{9}$$

Here, $\boldsymbol{Y}_{pi}^{(n)}$ is the operator of degree n having the properties of spherical harmonics, whereas the symbol $[n]$ according to Jansen's notation[5]) denotes n-fold contraction of two tensors of rank n.

In the same way we obtain from (6) by (7)

$$\boldsymbol{j} = \sum_{p=1}^{N} \left\{ \sum_{i=1}^{\nu_p} e_{pi} \dot{\boldsymbol{r}}_p \delta(\boldsymbol{r}_p - \boldsymbol{r}) + \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \left[\frac{\partial \boldsymbol{M}_{ep}^{(n)}}{\partial t} [n-1] \boldsymbol{\nabla}_p^{n-1} \delta(\boldsymbol{r}_p - \boldsymbol{r}) + \right. \right.$$

$$\left. \left. + c \boldsymbol{\nabla}_p \times (\boldsymbol{M}_{mp}^{(n)} [n-1] \boldsymbol{\nabla}_p^{n-1}) \, \delta(\boldsymbol{r}_p - \boldsymbol{r}) \right] + 0(\dot{\boldsymbol{r}}_p) \right\}, \tag{10}$$

wherein[11])

$$\boldsymbol{M}_{mp}^{(n)} = \frac{n}{(n+1)\, c} \sum_{i=1}^{\nu_p} e_{pi} r_{pi}^n \boldsymbol{Y}_{pi}^{(n)} \times \dot{\boldsymbol{r}}_{pi} \tag{11}$$

is the 2^n-pole magnetic moment of the p-th micro-system.

If now we take the ensemble averaging procedure on both sides of each of the microscopic field equations (3) and (4), we get immediately

$$\boldsymbol{\nabla} \times \boldsymbol{E} = -\frac{1}{c} \frac{\partial \boldsymbol{B}}{\partial t}, \quad \boldsymbol{\nabla} \cdot \boldsymbol{B} = 0, \tag{12}$$

$$\boldsymbol{\nabla} \times \boldsymbol{B} = \frac{1}{c} \frac{\partial \boldsymbol{E}}{\partial t} + \frac{4\pi}{c} \langle \boldsymbol{j} \rangle, \quad \boldsymbol{\nabla} \cdot \boldsymbol{E} = 4\pi \langle \rho_e' \rangle, \tag{13}$$

where $\boldsymbol{E} = \langle \boldsymbol{e} \rangle$ and $\boldsymbol{B} = \langle \boldsymbol{h} \rangle$ are the macroscopic electric and magnetic field strengths.

From the expansions (8) and (10) we obtain for the ensemble average charge and current densities

$$\langle \rho_e' \rangle = \rho_e(\boldsymbol{r}, t) + \sum_{n=1}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \boldsymbol{\nabla}^n [n] \, \boldsymbol{P}_e^{(n)}, \tag{14}$$

$$\langle \boldsymbol{j} \rangle = \boldsymbol{J}(\boldsymbol{r}, t) - \sum_{n=1}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \left\{ \boldsymbol{\nabla}^{n-1} [n-1] \frac{\partial \boldsymbol{P}_e^{(n)}}{\partial t} + \right.$$

$$\left. + c \boldsymbol{\nabla} \times (\boldsymbol{\nabla}^{n-1} [n-1] \, \boldsymbol{P}_m^{(n)}) \right\}, \tag{15}$$

wherein

$$\rho_e(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \sum_{i=1}^{\nu_p} e_{pi} \delta(\boldsymbol{r}_p - \boldsymbol{r}) \rangle, \tag{16}$$

$$\boldsymbol{J}(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \sum_{i=1}^{\nu_p} e_{pi} \dot{\boldsymbol{r}}_p \delta(\boldsymbol{r}_p - \boldsymbol{r}) \rangle, \tag{17}$$

are the average true charge and current densities at position $\boldsymbol{r}$ and time t and

$$\boldsymbol{P}_e^{(n)}(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \boldsymbol{M}_{ep}^{(n)} \delta(\boldsymbol{r}_p - \boldsymbol{r}) \rangle, \tag{18}$$

$$\boldsymbol{P}_m^{(n)}(\boldsymbol{r}, t) = \langle \sum_{p=1}^{N} \boldsymbol{M}_{mp}^{(n)} \, \delta(\boldsymbol{r}_p - \boldsymbol{r}) \rangle \tag{19}$$

define the 2^n-pole electric and magnetic polarization tensors (or moment densities) at $\boldsymbol{r}$ and t, dependent on the thermodynamical state of the medium.

By the expressions (14) and (15) we may write the equations of (13) in Maxwellian form:

$$\nabla \times \boldsymbol{H} = \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t} + \frac{4\pi}{c}\boldsymbol{J}, \quad \nabla \cdot \boldsymbol{D} = 4\pi\rho_e, \tag{20}$$

if the following electric and magnetic displacement vectors are introduced:

$$\boldsymbol{D} = \boldsymbol{E} - 4\pi \sum_{n=1}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\, \boldsymbol{P}_e^{(n)}, \tag{21}$$

$$\boldsymbol{H} = \boldsymbol{B} + 4\pi \sum_{n=1}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\, \boldsymbol{P}_m^{(n)}. \tag{22}$$

The foregoing equations contain all contributions to the vectors $\boldsymbol{D}$ and $\boldsymbol{H}$ arising from the electric and magnetic multipole moment densities of the medium undergoing polarization. In particular, we obtain from (21) the results derived by Rosenfeld[3]) and Mazur and Nijboer[4])

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi\{\boldsymbol{P}_e - \tfrac{1}{3}\nabla \cdot \boldsymbol{Q}_e + \ldots\}, \tag{21a}$$

$$\boldsymbol{H} = \boldsymbol{B} - 4\pi\{\boldsymbol{P}_m - \ldots\}, \tag{22a}$$

where $\boldsymbol{P}_e \equiv \boldsymbol{P}_e^{(1)}$ is the dipole electric polarization vector, $\boldsymbol{Q}_e \equiv \boldsymbol{P}_e^{(2)}$ is the quadrupole electric polarization tensor, etc., and $\boldsymbol{P}_m \equiv \boldsymbol{P}_m^{(1)}$ is the dipole magnetic polarization vector, etc.

On the other hand, the relationships between the vectors $\boldsymbol{D}$ and $\boldsymbol{E}$ and between $\boldsymbol{B}$ and $\boldsymbol{H}$ are expressed by means of the tensors of the electric $\boldsymbol{\varepsilon}$ and magnetic $\boldsymbol{\mu}$ permittivities through the well-known expressions

$$\boldsymbol{D} = \boldsymbol{\varepsilon} \cdot \boldsymbol{E}, \quad \boldsymbol{B} = \boldsymbol{\mu} \cdot \boldsymbol{H}, \tag{23}$$

and we obtain by (21) and (22) the following general equations for the medium at rest:

$$(\boldsymbol{\varepsilon} - \boldsymbol{U}) \cdot \boldsymbol{E} = 4\pi \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\, \boldsymbol{P}_e^{(n)}, \tag{24}$$

$$(\boldsymbol{\mu} - \boldsymbol{U}) \cdot \boldsymbol{H} = 4\pi \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1}[n-1]\, \boldsymbol{P}_m^{(n)}, \tag{25}$$

in which $\boldsymbol{U}$ is the second-rank unit tensor.

In preceding papers[15]) the general equation (24) for the electric permittivity was discussed classically for multicomponent systems consisting of multipolar microsystems. In the present paper, the general equation (25) for the magnetic permeability will be discussed quantum-mechanically on the assumption that the isotropic medium is sufficiently rarefied so that one may use Maxwell-Boltzmann instead of Fermi-Dirac statistics.

§ 3. *Multipole expansion of the perturbation Hamiltonian.* The total Hamiltonian of an assembly is

$$H = \sum_{p=1}^{N} H_p, \tag{26}$$

where in the classical relativistic case*) we have for the Hamiltonian of a p-th microsystem[16])

$$H_p = \sum_{i=1}^{\nu_p} \{[m_{pi}^2 c^4 + (c\boldsymbol{p}_{pi} - e_{pi}\boldsymbol{A}_{pi})^2]^{\frac{1}{2}} + e_{pi}\varphi_{pi}\} \tag{27}$$

in which φ_{pi} and $\boldsymbol{A}_{pi}$ are the scalar and vector potentials at the point of the i-th particle having the momentum operator $\boldsymbol{p}_{pi}$.

Expanding the Hamiltonian (27) in a power series in $\boldsymbol{A}_{pi}$ we can write

$$H_p = H_p^{(0)} + H_p^{(1)} + H_p^{(2)} + H_p^{(3)} + \ldots = \sum_{s=0}^{\infty} H_p^{(s)}, \tag{28}$$

where $H_p^{(0)}$ is the Hamiltonian of the non-perturbated microsystem p, whereas its perturbation Hamiltonians of the first, second, third and fourth order are of the form

$$H_p^{(1)} = -\tfrac{1}{2} \sum_{i=1}^{\nu_p} \frac{e_{pi}}{m_{pi}c} (\boldsymbol{p}_{pi}\cdot\boldsymbol{A}_{pi} + \boldsymbol{A}_{pi}\cdot\boldsymbol{p}_{pi}) \left\{1 + 0\left(\frac{v_i^2}{c^2}\right)\right\} + \sum_{i=1}^{\nu_p} e_{pi}\varphi_{pi}, \tag{29}$$

$$H_p^{(2)} = \tfrac{1}{2} \sum_{i=1}^{\nu_p} \frac{e_{pi}^2}{m_{pi}c^2} (\boldsymbol{A}_{pi}\cdot\boldsymbol{A}_{pi}) \left\{1 + 0\left(\frac{v_i^2}{c^2}\right)\right\}, \tag{30}$$

$$H_p^{(3)} = \tfrac{1}{4} \sum_{i=1}^{\nu_p} \frac{e_{pi}^3}{m_{pi}^3 c^5} (\boldsymbol{p}_{pi}\cdot\boldsymbol{A}_{pi} + \boldsymbol{A}_{pi}\cdot\boldsymbol{p}_{pi})(\boldsymbol{A}_{pi}\cdot\boldsymbol{A}_{pi}) \left\{1 + 0\left(\frac{v_i^2}{c^2}\right)\right\}, \tag{31}$$

$$H_p^{(4)} = -\tfrac{1}{8} \sum_{i=1}^{\nu_p} \frac{e_{pi}^4}{m_{pi}^3 c^6} (\boldsymbol{A}_{pi}\cdot\boldsymbol{A}_{pi})^2 \left\{1 + 0\left(\frac{v_i^2}{c^2}\right)\right\}. \tag{32}$$

Although the second and higher-order perturbation Hamiltonians of (30)–(32) are usually very small and lead to effects of order comparable to relativistic corrections and retardation effects in the first-order Hamiltonian of (29), there are, nevertheless, cases when they cannot be neglected as e.g. in considering linear as well as nonlinear diamagnetic polarization.

We shall first discuss the consecutive contributions to the perturbation

*) In starting from the classical relativistic Hamiltonian, it was not our intention to construct in this way a nonlinear relativistically correct formalism but we only wanted to show it was possible to derive from it formally perturbations of higher orders in $\boldsymbol{A}$ (see expansion 28). Of course, quite strictly one should start from Dirac's relativistic equation $i\hbar\dot{\psi} = H_D\psi$ with the Hamiltonian of a particle in an electromagnetic field $H_D = \beta mc^2 + \boldsymbol{\alpha}\cdot(c\boldsymbol{p} - e\boldsymbol{A}) + e\varphi$; the latter should then be transformed to the Foldy-Wouthuysen representation $H_{FW} = \beta[m^2c^4 + (c\boldsymbol{p} - e\boldsymbol{A})^2]^{\frac{1}{2}} - e(\boldsymbol{\alpha}\cdot\boldsymbol{A} - \varphi)_{FW}$, which can yield perturbations of order higher than the second with regard to $\boldsymbol{A}$ if appropriate transformations e.g. Eriksen's are recurred to.

Hamiltonian from the potentials $\varphi_{pi}^{\text{ext}}$ and $\boldsymbol{A}_{pi}^{\text{ext}}$ of the external electromagnetic field. In the general case, when the scalar and vector potentials are not constant within the region of the microsystem (the field is generally non-homogeneous throughout the region of a microsystem), one can expand φ_{pi} and $\boldsymbol{A}_{pi}$ in a series in powers of $\boldsymbol{r}_{pi}$ at the point of the microsystem occupied by the i-th particle. Assuming that these potentials vary but slowly in the region of the microsystem, we have the expansions,

$$\varphi_{pi}^{\text{ext}} = \sum_{n=0}^{\infty} \frac{1}{n!} \boldsymbol{r}_{pi}^{n}[n] \nabla^{n} \varphi(\boldsymbol{r}, t), \tag{33}$$

$$\boldsymbol{A}_{pi}^{\text{ext}} = \sum_{n=0}^{\infty} \frac{1}{n!} \boldsymbol{r}_{pi}^{n}[n] \nabla^{n} \boldsymbol{A}(\boldsymbol{r}, t), \tag{34}$$

which by appropriate gauge transformations can be written as follows (see refs 8 and 10):

$$\varphi_{pi}^{\text{ext}} = \varphi(\boldsymbol{r}, t) - \sum_{n=1}^{\infty} \frac{1}{n!} \boldsymbol{r}_{pi}^{n}[n] \boldsymbol{E}^{(n)}, \tag{35}$$

$$\boldsymbol{A}_{pi}^{\text{ext}} = - \sum_{n=1}^{\infty} \frac{n}{(n+1)!} \boldsymbol{r}_{pi}^{n-1}[n-1](\boldsymbol{r}_{pi} \times \boldsymbol{H}^{(n)}). \tag{36}$$

Here, we have introduced the electric and magnetic field strengths of degree n (traditionally we now denote the magnetic field strength by $\boldsymbol{H}$)

$$\boldsymbol{E}^{(n)} = - \nabla^{n-1} \left\{ \frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t} + \nabla \varphi \right\}, \quad \boldsymbol{H}^{(n)} = \nabla^{n} \times \boldsymbol{A}. \tag{37}$$

For $n = 1$, (37) defines first-order or homogeneous fields, for $n = 2$ — second-order fields or field gradients, and for $n = 3, 4$ — higher-order degree space derivatives of the fields.

By the expansions of (35) and (36) the first-order perturbation Hamiltonian (29) can be represented in the form of a multipole expansion (neglecting relativistic corrections)

$$H_{p}^{(1)} = \sum_{i=1}^{\nu_p} e_{pi} \varphi(\boldsymbol{r}, t) - \sum_{n=1}^{\infty} \frac{2^{n} n!}{(2n)!} \{\boldsymbol{M}_{ep}^{(n)}[n] \boldsymbol{E}^{(n)} + \boldsymbol{M}_{mp}^{(n)}[n] \boldsymbol{H}^{(n)}\}, \tag{38}$$

in which the first term represents the potential energy of the total charge of the microsystem in a potential φ, whereas the second and third, respectively, describe interactions between 2^{n}-pole electric or magnetic moments and an electric or magnetic field of degree n.

With respect to (36), the second-order perturbation Hamiltonian is obtained as follows[11])

$$H_{p}^{(2)} = -\tfrac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)! (2n_2)!} \boldsymbol{H}^{(n_1)}[n_1]^{(n_1)} \boldsymbol{A}_{dp}^{(n_2)}[n_2] \boldsymbol{H}^{(n_2)}, \tag{39}$$

where

$$ {}^{(n_1)}A_{dp}^{(n_2)} = -\frac{n_1 n_2}{(n_1+1)(n_2+1)\,c^2}\sum_{i=1}^{\nu_p}\frac{e_{pi}^2}{m_{pi}}\,r_{pi}^{n_1+n_2}\{Y_{pi}^{(n_1)}Y_{pi}^{(n_2)} - Y_{pi}^{(n_1)}\cdot Y_{pi}^{(n_2)}U\} \tag{40} $$

is the diamagnetic multipole polarizability tensor of rank $n_1 + n_2$ of the micro-system p.

In the same way we obtain formally from expressions (30)–(32) and (36) the higher-order perturbation Hamiltonians given in the following concise form ($s = 1, 2, \ldots$):

$$ H_p^{(s+1)} = -\frac{1}{(s+1)!}\sum_{n=1}^{\infty}\sum_{n_1=1}^{\infty}\cdots\sum_{n_s=1}^{\infty}\frac{2^{n+n_1+\ldots+n_s}\,n!\,n_1!\ldots n_s!}{(2n)!\,(2n_1)!\ldots(2n_s)!}\times $$
$$ \times\, H^{(n)}[n]^{(n)}A_{mp}^{(n_1+\ldots+n_s)}[n_1+\ldots+n_s]\,H^{(n_1)}\ldots H^{(n_s)}, \tag{41} $$

wherein ${}^{(n)}A_{mp}^{(n_1+\ldots+n_s)}$ denotes the multipole magnetic polarizability tensor of order s.

The explicite form of the first-order magnetic multipole polarizability tensor is given by (40), whereas the second- and third-order magnetic multipole polarizability tensors by

$$ {}^{(n)}B_{mp}^{(n_1+n_2)} = \frac{nn_1n_2}{2(n+1)(n_1+1)(n_2+1)\,c^5}\sum_{i=1}^{\nu_p}\frac{e_{pi}^3}{m_{pi}^2}\,r_{pi}^{n+n_1+n_2}\times $$
$$ \times\, S(n, n_1, n_2)(Y_{pi}^{(n)}\times\dot{r}_{pi})(Y_{pi}^{(n_1)}\cdot Y_{pi}^{(n_2)}U - Y_{pi}^{(n_1)}Y_{pi}^{(n_2)}), \tag{42} $$

$$ {}^{(n)}C_{mp}^{(n_1+n_2+n_3)} = \frac{nn_1n_2n_3}{8(n+1)(n_1+1)(n_2+1)(n_3+1)\,c^6}\sum_{i=1}^{\nu_p}\frac{e_{pi}^4}{m_{pi}^3}\,r_{pi}^{n+n_1+n_2+n_3}\times $$
$$ \times\, S(n, n_1, n_2, n_3)(Y_{pi}^{(n)}\cdot Y_{pi}^{(n_1)}U - Y_{pi}^{(n)}Y_{pi}^{(n_1)})(Y_{pi}^{(n_2)}\cdot Y_{pi}^{(n_3)}U - Y_{pi}^{(n_2)}Y_{pi}^{(n_3)}), \tag{43} $$

where $S(n\ n_1, n_2, \ldots)$ is a symmetrizing operator denoting summation over all permutations $n, n_1, n_2, \ldots$

We shall now discuss the perturbation Hamiltonian from internal fields existing in an assembly of interacting microsystems. If we neglect retarded time effects, we have for the scalar and vector potentials

$$ \varphi^{\mathrm{int}}(R_{pi}) = \sum_{\substack{q=1\\ q\neq p}}^{N}\sum_{j=1}^{\nu_q}\frac{e_{qj}}{|R_{pi}-R_{qj}|}, \tag{44} $$

$$ A^{\mathrm{int}}(R_{pi}) = \frac{1}{c}\sum_{\substack{q=1\\ q\neq p}}^{N}\sum_{j=1}^{\nu_q}\frac{e_{qj}\dot{R}_{qj}}{|R_{pi}-R_{qj}|}, \tag{45} $$

where by (2) $|R_{pi} - R_{qj}| = |r_p - r_q + r_{pi} - r_{qj}|$ (see also fig. 1).

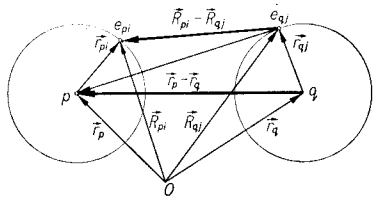

Fig. 1. Schematic diagram of the geometry involved in the interaction of two nonoverlapping microsystems p and q separated by a vector distance $\boldsymbol{r}_p - \boldsymbol{r}_q$.

In the special case of nonoverlapping microsystems when $|\boldsymbol{r}_{pi} + \boldsymbol{r}_{qj}| < |\boldsymbol{r}_p - \boldsymbol{r}_q|$ we can expand $|\boldsymbol{R}_{pi} - \boldsymbol{R}_{qj}|^{-1}$ in the form of a double Taylor series[17])

$$|\boldsymbol{R}_{pi} - \boldsymbol{R}_{qj}|^{-1} = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2+1}}{n_1!\, n_2!}\, \boldsymbol{r}_{pi}^{n_1}[n_1]\, {}^{(n_1)}\boldsymbol{T}_{pq}^{(n_2)}[n_2]\, \boldsymbol{r}_{qj}^{n_2}, \tag{46}$$

wherein the tensor of rank $n_1 + n_2$

$${}^{(n_1)}\boldsymbol{T}_{pq}^{(n_2)} = -\boldsymbol{\nabla}_p^{n_1} \boldsymbol{\nabla}_q^{n_2} \frac{1}{|\boldsymbol{r}_p - \boldsymbol{r}_q|}, \qquad p \neq q \tag{47}$$

describes (2^{n_1}-pole) — (2^{n_2}-pole) – type interactions between microsystems p and q.

By (26), (29), (44)–(46) and the definitions (9) and (11) we obtain for the first-order perturbation Hamiltonian resulting from internal forces

$$H_{\mathrm{int}}^{(1)} = -\tfrac{1}{2} \sum_{p=1}^{N} \left\{ \sum_{n=0}^{\infty} \frac{2^n n!}{(2n)!}\, \boldsymbol{M}_{ep}^{(n)}[n]\, \boldsymbol{F}_{ep}^{(n)} + \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!}\, \boldsymbol{M}_{mp}^{(n)}[n]\, \boldsymbol{F}_{mp}^{(n)} \right\}, \tag{48}$$

where

$$\boldsymbol{F}_{ep}^{(n)} = \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{n_1=0}^{\infty} (-1)^{n_1} \frac{2^{n_1} n_1!}{(2n_1)!}\, {}^{(n)}\boldsymbol{T}_{pq}^{(n_1)}[n_1]\, \boldsymbol{M}_{eq}^{(n_1)}, \tag{49}$$

$$\boldsymbol{F}_{mp}^{(n)} = \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{n_1=1}^{\infty} (-1)^{n_1} \frac{2^{n_1} n_1!}{(2n_1)!}\, {}^{(n)}\boldsymbol{T}_{pq}^{(n_1)}[n_1]\, \boldsymbol{M}_{mq}^{(n_1)}, \tag{50}$$

are the electric and magnetic internal fields of degree n at the centre of the microsystem p due to the electric or magnetic multipoles of all other microsystems of the assembly.

On substituting in (48) the fields of (49) and (50) we obtain in explicite form

$$H_{\mathrm{int}}^{(1)} =$$

$$= -\tfrac{1}{2} \sum_{p=1}^{N} \sum_{\substack{q=1 \\ q \neq p}}^{N} \left\{ \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} (-1)^{n_2} \frac{2^{n_1+n_2} n_1!\, n_2!}{(2n_1)!\, (2n_2)!}\, \boldsymbol{M}_{ep}^{(n_1)}[n_1]\, {}^{(n_1)}\boldsymbol{T}_{pq}^{(n_2)}[n_2]\, \boldsymbol{M}_{eq}^{(n_2)} + \right.$$

$$\left. + \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} (-1)^{n_2} \frac{2^{n_1+n_2} n_1!\, n_2!}{(2n_1)!\, (2n_2)!}\, \boldsymbol{M}_{mp}^{(n_1)}[n_1]\, {}^{(n_1)}\boldsymbol{T}_{pq}^{(n_2)}[n_2]\, \boldsymbol{M}_{mq}^{(n_2)} \right\}. \tag{51}$$

In the case when the spins of the constituent particles are taken into account, the first-order perturbation Hamiltonian of (29) contains the additional term[16]) (the spin-orbit interaction term is omitted)

$$H_p^{(1)}\text{spin} = -\frac{1}{c}\sum_{i=1}^{\nu_p}\frac{e_{pi}}{m_{pi}}\boldsymbol{S}_{pi}\cdot(\boldsymbol{V}\times\boldsymbol{A}_{pi})\left\{1+0\left(\frac{v_i}{c}\right)\right\} \tag{29a}$$

and the 2^n-pole magnetic moment (11) in expansion (38) should be replaced by

$$\boldsymbol{M}_{mp}^{(n)} = \frac{n}{(n+1)\,c}\sum_{i=1}^{\nu_p}\frac{e_{pi}}{m_{pi}}\,r_{pi}^{n}\{\boldsymbol{Y}_{pi}^{(n)}\times\boldsymbol{p}_{pi}+(n+1)\,r_{pi}^{-2}\,\boldsymbol{S}_{pi}(\boldsymbol{r}_{pi}\cdot\boldsymbol{Y}_{pi}^{(n)})\} \tag{52}$$

where $\boldsymbol{S}_{pi}$ is the spin vector operator of the i-th particle.

In special cases we can obtain directly from expansions (38), (39) and (51) the results derived by several authors (see refs 2, 3 and 7–13).

§ 4. *Quantum-mechanical treatment of the multipole magnetic polarization.* We shall now discuss the 2^n-pole magnetic polarization tensor of (19) for the special case of an assembly of non-interacting microsystems subjected to an external static magnetic field. By quantum-mechanical statistics we have

$$\boldsymbol{P}_m^{(n)} = \rho\sum_g \langle g\,|\boldsymbol{M}_m^{(n)}|\,g\rangle_H\,\rho_g, \tag{53}$$

where

$$\langle g\,|\boldsymbol{M}_m^{(n)}|\,g\rangle_H = \int\psi_g^*\,\boldsymbol{M}_m^{(n)}\psi_g\,\mathrm{d}\tau \tag{54}$$

is the diagonal matrix element of the 2^n-pole magnetic operator $\boldsymbol{M}_m^{(n)}$ of the microsystem (for simpler notation the full set of quantum numbers is rendered by the sole quantum state index g) and

$$\rho_g = \frac{\exp\{-\beta E_g\}}{\sum_k \exp\{-\beta E_k\}} \tag{55}$$

is the statistical matrix in the presence of the external magnetic field with $\beta = (kT)^{-1}$.

The eigenfunctions ψ_g and energy eigenvalues E_g of the total Hamiltonian H for the perturbated microsystem satisfy the Schrödinger equation

$$H\psi_g = E_g\psi_g, \tag{56}$$

where we assume, for generality, that the Hamiltonian is given by a power series in the small parameter $\lambda(0<\lambda\leqslant 1)$

$$H = \sum_{n=0}^{\infty}\lambda^n H^{(n)} = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \ldots \tag{57}$$

Analogously we write

$$\psi_g = \sum_{n=0}^{\infty} \lambda^n \sum_k c_{kg}^{(n)} \psi_k^{(0)}, \quad E_g = \sum_{n=0}^{\infty} \lambda^n E_g^{(n)} \tag{58}$$

and obtain finally in the case of perturbations of nondegenerate stationary states

$$\sum_{n=0}^{s} \{\sum_l H_{kl}^{(n)} c_{lg}^{(s-n)} - E_g^{(n)} c_{kg}^{(s-n)}\} = 0. \tag{59}$$

Since in the absence of perturbation $H_{kl}^{(0)} = E_k^0 \delta_{kl}$ one finds from (59) for $k \neq g$,

$$\hbar\omega_{kg}\, c_{kg}^{(s)} = \sum_{n=1}^{s} \{E_g^{(n)}\, c_{kg}^{(s-n)} - \sum_l H_{kl}^{(n)}\, c_{lg}^{(s-n)}\}, \tag{60}$$

and for $k = g$,

$$E_g^{(s)} = \sum_{n=1}^{s} \sum_l H_{gl}^{(n)}\, c_{lg}^{(s-n)}, \tag{61}$$

where $\hbar\omega_{kg} = E_k^0 - E_g^0$ is the difference between the energy eigenvalues of the states g and k in the absence of an external field.

By (38) and (61) the first-order energy of the microsystem perturbated by a magnetic field is

$$E_g^{(1)} = H_{gg}^{(1)} = -\sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \langle g | \overset{(0)}{\boldsymbol{M}}{}_m^{(n)} | g \rangle [n]\, \boldsymbol{H}^{(n)}, \tag{62}$$

where $\langle g | \overset{(0)}{\boldsymbol{M}}{}_m^{(n)} | g \rangle$ is the matrix element ot the zeroth-order magnetic multipole moment (the moment in the absence of an external field).

In second-order perturbation theory we have by (60) and (61)

$$E_g^{(2)} = -\hbar^{-1} \sum_{k \neq g} \omega_{kg}^{-1}\, H_{gk}^{(1)}\, H_{kg}^{(1)} + H_{gg}^{(2)}, \tag{63}$$

which because of (38) and (39) can be written as

$$E_g^{(2)} = -\tfrac{1}{2} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!}\, \boldsymbol{H}^{(n)}\, [n] \langle g | \overset{(1)}{\boldsymbol{M}}{}_m^{(n)} | g \rangle_H, \tag{64}$$

where

$$\langle g | \overset{(1)}{\boldsymbol{M}}{}_m^{(n)} | g \rangle_H = \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} \langle g | {}^{(n)}\boldsymbol{A}_m^{(n_1)} | g \rangle [n_1]\, \boldsymbol{H}^{(n_1)} \tag{65}$$

is the diagonal matrix element of the first-order magnetic multipole moment with

$$\langle g | {}^{(n)}\boldsymbol{A}_m^{(n_1)} | g \rangle = \langle g | {}^{(n)}\boldsymbol{A}_{dm}^{(n_1)} | g \rangle + \langle g | {}^{(n)}\boldsymbol{A}_{pm}^{(n_1)} | g \rangle \tag{66}$$

the diagonal matrix element of the total magnetic multipole polarizability tensor.

The first term in (66) is the diamagnetic part with ${}^{(n)}\boldsymbol{A}_{\delta m}^{(n_1)}$ given by (40), whereas the second

$$\langle g \mid {}^{(n)}\boldsymbol{A}_{\mu m}^{(n_1)} \mid g\rangle = \hbar^{-1} \sum_{k \neq g} \omega_{kg}^{-1} \left(\langle g \mid \boldsymbol{M}_m^{(n)} \mid k\rangle\langle k \mid \boldsymbol{M}_m^{(n_1)} \mid g\rangle + \right.$$
$$\left. + \langle g \mid \boldsymbol{M}_m^{(n_1)} \mid k\rangle\langle k \mid \boldsymbol{M}_m^{(n)} \mid g\rangle\right) \quad (67)$$

is the paramagnetic part of the magnetic multipole polarizability tensor.

In a similar way, one obtains from (41), (60) and (61) the magnetic energies of third-, fourth- and generally $(s+1)$-th-order

$$E_g^{(s+1)} = -\frac{1}{s+1} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \boldsymbol{H}^{(n)}[n] \langle g \mid \overset{(s)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle_H, \quad (68)$$

where

$$\langle g \mid \overset{(s)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle_H = \frac{1}{s!} \sum_{n_1=1}^{\infty} \cdots \sum_{n_s=1}^{\infty} \frac{2^{n_1+\ldots+n_s}\, n_1! \ldots n_s!}{(2n_1)! \ldots (2n_s)!} \times$$
$$\times \langle g \mid {}^{(n)}\boldsymbol{A}_m^{(n_1+\ldots+n_s)} \mid g\rangle [n_1 + \ldots + n_s]\, \boldsymbol{H}^{(n_1)} \ldots \boldsymbol{H}^{(n_s)} \quad (69)$$

is the diagonal matrix element of the s-th order magnetic 2^n-pole moment induced in the microsystem by the external magnetic fields $\boldsymbol{H}^{(n_1)}, \ldots \boldsymbol{H}^{(n_s)}$.

By definition (54) and expressions (53) and (60), the matrix element of the total 2^n-pole magnetic moment can be expanded as follows:

$$\langle g \mid \boldsymbol{M}_m^{(n)} \mid g\rangle_H = \sum_{s=0}^{\infty} \langle g \mid \overset{(s)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle_H, \quad (70)$$

where the moments of consecutive orders are given by

$$\langle g \mid \overset{(s)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle_H = \sum_{r=0}^{s} \sum_{kl} c_{kg}^{(r)*}\, c_{lg}^{(s-r)} \langle k \mid \boldsymbol{M}_m^{(n)} \mid l\rangle, \quad (69a)$$

or, in explicite form, by (69).

Thus, with regard to (55), (68) and (70), and since in the case considered

$$\sum_g \langle g \mid \overset{(0)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle \rho_g^0 = \sum_g E_g^{(1)} \rho_g^0 = 0,$$

we can expand the multipole magnetic polarization of (53) as follows:

$$\boldsymbol{P}_m^{(n)} = \overset{(1)}{\boldsymbol{P}}_m^{(n)} + \overset{(2)}{\boldsymbol{P}}_m^{(n)} + \overset{(3)}{\boldsymbol{P}}_m^{(n)} + \ldots, \quad (71)$$

where the first-, second- and third-order contributions are given by

$$\overset{(1)}{\boldsymbol{P}}_m^{(n)} = \rho \sum_g \rho_g^0 \{\langle g \mid \overset{(1)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle_H - \beta \langle g \mid \overset{(0)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle E_g^{(1)}\}, \quad (72)$$

$$\overset{(2)}{\boldsymbol{P}}_m^{(n)} = \rho \sum_g \rho_g^0 \{\langle g \mid \overset{(2)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle_H - \beta(\langle g \mid \overset{(0)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle E_g^{(2)} +$$
$$+ \langle g \mid \overset{(1)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle_H E_g^{(1)}) + \tfrac{1}{2}\beta^2 \langle g \mid \overset{(0)}{\boldsymbol{M}}_m^{(n)} \mid g\rangle E_g^{(1)} E_g^{(1)}\}, \quad (73)$$

$$\overset{(3)}{\boldsymbol{P}}{}_m^{(n)} = \rho \sum_g \rho_g^0 \{\langle g | \overset{(3)}{\boldsymbol{M}}{}_m^{(n)} | g\rangle_H - \beta(\langle g | \overset{(0)}{\boldsymbol{M}}{}_m^{(n)} | g\rangle E_g^{(3)} + \langle g | \overset{(2)}{\boldsymbol{M}}{}_m^{(n)} | g\rangle_H E_g^{(1)}) +$$

$$- \beta(\langle g | \overset{(1)}{\boldsymbol{M}}{}_m^{(n)} | g\rangle_H - \beta\langle g | \overset{(0)}{\boldsymbol{M}}{}_m^{(n)} | g\rangle E_g^{(1)}) [E_g^{(2)} - \sum_k \rho_k^0 E_k^{(2)} +$$

$$- \tfrac{1}{2}\beta(E_g^{(1)} E_g^{(1)} - \sum_k \rho_k^0 E_k^{(1)} E_k^{(1)})] + \tfrac{1}{3}\beta^3 \langle g | \overset{(0)}{\boldsymbol{M}}{}_m | g\rangle E_g^{(1)} E_g^{(1)} E_g^{(1)}\}, \quad (74)$$

wherein $\rho_g^0 = \exp\{-\beta E_g^0\}/\sum_k \exp\{-\beta E_k^0\}$ is the statistical matrix in the absence of an external field.

§ 5. *Tensor of magnetic permeability.* In the case when an intense magnetic field is applied to the isotropic medium, its tensor of magnetic permittivity experiences a nonlinear variation which by (25) and (71) is given as follows in the dipole polarization approximation:

$$(\boldsymbol{\mu} - \boldsymbol{\mu}_0) \cdot \boldsymbol{H} = 4\pi\{\overset{(2)}{\boldsymbol{P}}{}_m^{(1)} + \overset{(3)}{\boldsymbol{P}}{}_m^{(1)} + \ldots\}, \quad (75)$$

wherein

$$(\boldsymbol{\mu}_0 - \boldsymbol{U}) \cdot \boldsymbol{H} = 4\pi \overset{(1)}{\boldsymbol{P}}{}_m^{(1)} \quad (76)$$

is the magnetic permittivity in the absence of the strong magnetic field.

i) Weak magnetic field. We will first compute the first-order multipole magnetic polarization which by (62), (65) and (72) can be represented in the following explicite form:

$$\overset{(1)}{\boldsymbol{P}}{}_m^{(n)} = \rho \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} \sum_g \rho_g^0 \{\langle g | {}^{(n)}\boldsymbol{A}_m^{(n_1)} | g\rangle +$$

$$+ \beta\langle g | \boldsymbol{M}_m^{(n)} | g\rangle\langle g | \boldsymbol{M}_m^{(n_1)} | g\rangle\}[n_1] \boldsymbol{H}^{(n_1)}, \quad (77)$$

or in the special form

$$\overset{(1)}{\boldsymbol{P}}{}_m^{(n)} = \rho \frac{2^n n!}{(2n+1)!} \sum_g \rho_g^0 \{\langle g | {}^{(n)}\boldsymbol{A}_m^{(n)} | g\rangle [2n] \boldsymbol{U}^n +$$

$$+ \beta\langle g | \boldsymbol{M}_m^{(n)} | g\rangle [n] \langle g | \boldsymbol{M}_m^{(n)} | g\rangle\} \boldsymbol{H}^{(n)} \quad (78)$$

hold for the case of spectroscopic stability[2]).

The first part of (78), independent directly of the temperature parameter β, can be written in simpler form

$$\overset{(1)}{\boldsymbol{P}}{}_{m\,\mathrm{I}}^{(n)} = \rho a_m^{(2n)} \boldsymbol{H}^{(n)}, \quad (79)$$

where we have introduced the mean value of the multipole magnetic polarizability of the microsystem

$$a_m^{(2n)} = \frac{2^n n!}{(2n+1)!} \sum_g \rho_g^0 \langle g | {}^{(n)}\boldsymbol{A}_m^{(n)} | g\rangle [2n] \boldsymbol{U}^n \quad (80)$$

consisting the diamagnetic part

$$a_{dm}^{(2n)} = -\frac{2n^2}{(n+1)^2(2n+1)\,n!\,c^2} \sum_g \rho_g^0 \left\langle g \left| \sum_{i=1}^{\nu} \frac{e_i^2}{m_i} r_i^{2n} \right| g \right\rangle \tag{81}$$

and paramagnetic part

$$a_{pm}^{(2n)} = \frac{2^{n+1} n!}{(2n+1)!\,\hbar} \sum_g \sum_{k \neq g} \rho_g^0 \omega_{kg}^{-1} \langle g | \boldsymbol{M}_m^{(n)} | k \rangle [n] \langle k | \boldsymbol{M}_m^{(n)} | g \rangle. \tag{82}$$

If, in particular, the microsystem possesses the axial symmetry, we have[14])

$$\boldsymbol{M}_m^{(n)} [n] \boldsymbol{M}_m^{(n)} = \frac{(2n)!}{2^n (n!)^2} \{M_m^{(n)}\}^2, \tag{83}$$

and expression (82) assumes the simpler form

$$a_{pm}^{(2n)} = \frac{2}{n!(2n+1)\,\hbar} \sum_g \sum_{k \neq g} \rho_g^0 \omega_{kg}^{-1} \langle g | M_m^{(n)} | k \rangle^2, \tag{84}$$

where $M_m^{(n)}$ is the scalar multipole moment of the axially-symmetric microsystem.

Similarly, by (83), the second temperature-dependent part of (78) becomes

$$\overset{(1)}{\boldsymbol{P}}{}_{m\,\mathrm{II}}^{(n)} = \rho \frac{\beta}{n!(2n+1)} \sum_g \rho_g^0 \langle g | M_m^{(n)} | g \rangle^2 \boldsymbol{H}^{(n)}. \tag{85}$$

In the dipole ($n = 1$) approximation, expressions (77)–(85) yield the well-known results of Van Vleck[2]).

ii) Strong magnetic field. By expressions (62)–(69) the explicite form of the second-order multipole polarization of (73) is

$$\begin{aligned} \overset{(2)}{\boldsymbol{P}}{}_m^{(n)} = {} & \tfrac{1}{2}\rho \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n_1+n_2} n_1!\, n_2!}{(2n_1)!\,(2n_2)!} \sum_g \rho_g^0 \{ \langle g | {}^{(n)}\boldsymbol{B}_m^{(n_1+n_2)} | g \rangle + \\ & + \beta(\langle g | \boldsymbol{M}_m^{(n)} | g \rangle \langle g | {}^{(n_1)}\boldsymbol{A}_m^{(n_2)} | g \rangle + 2 \langle g | {}^{(n)}\boldsymbol{A}_m^{(n_1)} | g \rangle \langle g | \boldsymbol{M}_m^{(n_2)} | g \rangle) + \\ & + \beta^2 \langle g | \boldsymbol{M}_m^{(n)} | g \rangle \langle g | \boldsymbol{M}_m^{(n_1)} | g \rangle \langle g | \boldsymbol{M}_m^{(n_2)} | g \rangle \} [n_1 + n_2] \boldsymbol{H}^{(n_1)} \boldsymbol{H}^{(n_2)}. \end{aligned} \tag{86}$$

In the case when the applied magnetic field $\boldsymbol{H}$ is homogeneous ($\boldsymbol{H}^{(n)} = 0$ for $n \geqslant 2$) the second-order dipole magnetic polarization does not contribute to a nonlinear variation of the magnetic permittivity of (75), since the terms on the right-hand side of (86) vanish for $n = n_1 = n_2 = 1$ by averaging over all classical orientations of the microsystems. At the same time the quadrupole magnetic polarization of second-order is nonzero and is given by

$$\begin{aligned} \overset{(2)}{\boldsymbol{P}}{}_m^{(2)} = {} & \tfrac{1}{30}\rho \sum_g \rho_g^0 \{ \boldsymbol{U} : {}^{(2)}\boldsymbol{B}_{mg}^{(1+1)} : \boldsymbol{U} + \beta(\boldsymbol{M}_{mg}^{(2)} : {}^{(1)}\boldsymbol{A}_{mg}^{(1)} + 2\boldsymbol{M}_{mg}^{(1)} \cdot {}^{(2)}\boldsymbol{A}_{mg}^{(1)} : \boldsymbol{U}) + \\ & + \beta^2 \boldsymbol{M}_{mg}^{(1)} \cdot \boldsymbol{M}_{mg}^{(2)} \cdot \boldsymbol{M}_{mg}^{(1)} \} (3\boldsymbol{H}\boldsymbol{H} - \boldsymbol{U}H^2), \end{aligned} \tag{87}$$

wherein ${}^{(2)}\boldsymbol{A}_{mg}^{(1)}$ and ${}^{(2)}\boldsymbol{B}_{mg}^{(1+1)}$ are the matrix elements of the first-order and second-order quadrupole magnetic polarizability tensors due, respectively, to the first and second power of the homogeneous magnetic field.

The explicite form of the third-order multipole magnetic polarization of (74) is, by (68) and (69),

$$\begin{aligned}
\overset{(3)}{\boldsymbol{P}}{}_{m}^{(n)} &= \tfrac{1}{6}\rho \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty} \frac{2^{n_1+n_2+n_3}\, n_1!\, n_2!\, n_3!}{(2n_1)!\,(2n_2)!\,(2n_3)!} \sum_{g} \rho_g^0 \{\langle g|\,{}^{(n)}\boldsymbol{C}_m^{(n_1+n_2+n_3)}|\, g\rangle + \\
&+ \beta(\langle g|\,\boldsymbol{M}_m^{(n)}|\, g\rangle\langle g|\,{}^{(n_1)}\boldsymbol{B}_m^{(n_2+n_3)}|\, g\rangle + 3\langle g|\,{}^{(n)}\boldsymbol{B}_m^{(n_1+n_2)}|\, g\rangle\langle g|\,\boldsymbol{M}_m^{(n_3)}|\, g\rangle) + \\
&+ 3\beta(\langle g|\,{}^{(n)}\boldsymbol{A}_m^{(n_1)}|\, g\rangle + \beta\langle g|\,\boldsymbol{M}_m^{(n)}|\, g\rangle\langle g|\,\boldsymbol{M}_m^{(n_1)}|\, g\rangle)[\langle g|\,{}^{(n_2)}\boldsymbol{A}_m^{(n_3)}|\, g\rangle - \\
&- \sum_k \rho_k^0\langle k|\,{}^{(n_2)}\boldsymbol{A}_m^{(n_3)}|\, k\rangle + \beta(\langle g|\,\boldsymbol{M}_m^{(n_2)}|\, g\rangle\langle g|\,\boldsymbol{M}_m^{(n_3)}|\, g\rangle - \\
&- \sum_k \rho_k^0\langle k|\,\boldsymbol{M}_m^{(n_2)}|\, k\rangle\langle k|\,\boldsymbol{M}_m^{(n_3)}|\, k\rangle)] - 2\beta^3\langle g|\,\boldsymbol{M}_m^{(n)}|\, g\rangle\langle g|\,\boldsymbol{M}_m^{(n_1)}|\, g\rangle\langle g|\,\boldsymbol{M}_m^{(n_2)}|\, g\rangle \times \\
&\times\langle g|\,\boldsymbol{M}_m^{(n_3)}|\, g\rangle\}[n_1 + n_2 + n_3]\, \boldsymbol{H}^{(n_1)}\boldsymbol{H}^{(n_2)}\boldsymbol{H}^{(n_3)}. \qquad (88)
\end{aligned}$$

In the dipole approximation ($n = 1$) and when, as above, the magnetic field is homogeneous ($n_1 = n_2 = n_3 = 1$) the third-order magnetic polarization of (88) is nonzero and finally yields the result

$$\begin{aligned}
\overset{(3)}{\boldsymbol{P}}{}_{m}^{(1)} &= \tfrac{1}{90}\rho \sum_g \rho_g^0\{3\boldsymbol{U} : {}^{(1)}\boldsymbol{C}_{mg}^{(1+1+1)} : \boldsymbol{U} + 6\beta[2\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_{mg}^{(1+1)}\cdot\boldsymbol{M}_{mg}^{(1)} + \\
&+ {}^{(1)}\boldsymbol{A}_{mg}^{(1)} : {}^{(1)}\boldsymbol{A}_{mg}^{(1)} + 2\beta(\boldsymbol{M}_{mg}^{(1)}\cdot{}^{(1)}\boldsymbol{A}_{mg}^{(1)}\cdot\boldsymbol{M}_{mg}^{(1)})] + \\
&+ \beta(\boldsymbol{U} : {}^{(1)}\boldsymbol{A}_{mg}^{(1)} + \beta\boldsymbol{M}_{mg}^{(1)}\cdot\boldsymbol{M}_{mg}^{(1)})[\boldsymbol{U} : (3\,{}^{(1)}\boldsymbol{A}_{mg}^{(1)} - 5\sum_k \rho_k^0\,{}^{(1)}\boldsymbol{A}_{mk}^{(1)}) + \\
&+ \beta(3\boldsymbol{M}_{mg}^{(1)}\cdot\boldsymbol{M}_{mg}^{(1)} - 5\sum_k \rho_k^0\boldsymbol{M}_{mk}^{(1)}\cdot\boldsymbol{M}_{mk}^{(1)})]\}\, \boldsymbol{H}H^2 \qquad (89)
\end{aligned}$$

where ${}^{(1)}\boldsymbol{A}_{mg}^{(1)}$, ${}^{(1)}\boldsymbol{B}_{mg}^{(1+1)}$ and ${}^{(1)}\boldsymbol{C}_{mg}^{(1+1+1)}$ are matrix elements of the tensors of the first-, second- and third-order dipole magnetic polarizabilities produced by the first, second and third power of the uniform magnetic field, respectively.

In general, when the applied magnetic field is inhomogeneous, beside the contribution to $\boldsymbol{\mu} - \boldsymbol{\mu}_0$ from third-order magnetic dipole polarization as discussed above, we obtain an additional nonzero contribution from the second-order magnetic dipole polarization (86); namely, we have,

$$\begin{aligned}
\overset{(2)}{\boldsymbol{P}}{}_{m}^{(1)} &= \tfrac{1}{30}\rho \sum_k \rho_g^0\{\boldsymbol{U} : {}^{(1)}\boldsymbol{B}_{mg}^{(1+2)} : \boldsymbol{U} + \beta(2\boldsymbol{U} : {}^{(1)}\boldsymbol{A}_{mg}^{(2)}\cdot\boldsymbol{M}_{mg}^{(1)} + \\
&+ {}^{(1)}\boldsymbol{A}_{mg}^{(1)} : \boldsymbol{M}_{mg}^{(2)}) + \beta^2\boldsymbol{M}_{mg}^{(1)}\cdot\boldsymbol{M}_{mg}^{(2)}\cdot\boldsymbol{M}_{mg}^{(1)}\}\, \boldsymbol{H}^{(1)}\cdot\boldsymbol{H}^{(2)}, \qquad (90)
\end{aligned}$$

wherein ${}^{(1)}\boldsymbol{A}_{mg}^{(2)}$ is the first-order dipole magnetic polarizability tensor due to the magnetic field gradient $\boldsymbol{H}^{(2)}$ and ${}^{(1)}\boldsymbol{B}_{mg}^{(1+2)}$ is the second-order dipole magnetic polarizability tensor given rise to simultaneously by the fields $\boldsymbol{H}^{(1)}$ and $\boldsymbol{H}^{(2)}$.

§ 6. *Discussion and conclusions.* For micro-systems with centres of inversion (diamagnetic molecules for which $\boldsymbol{M}^{(1)} = {}^{(1)}\boldsymbol{B}_m^{(1+1)} = 0$) we obtain from (75) and (89)

$$\boldsymbol{\mu} - \boldsymbol{\mu}_0 = \frac{2\pi}{45}\rho \sum_g \rho_g^0 \{3\boldsymbol{U} : {}^{(1)}\boldsymbol{C}_{mg}^{(1+1+1)} : \boldsymbol{U} + \beta[6\,{}^{(1)}\boldsymbol{A}_{mg}^{(1)} : {}^{(1)}\boldsymbol{A}_{mg}^{(1)} + \\ + (\boldsymbol{U} : {}^{(1)}\boldsymbol{A}_{mg}^{(1)})\,\boldsymbol{U} : (3\,{}^{(1)}\boldsymbol{A}_{mg}^{(1)} - 5\sum_k \rho_k^0\,{}^{(1)}\boldsymbol{A}_{mk}^{(1)})]\}\,\boldsymbol{HH}, \tag{91}$$

where we have by (40) and (43) on neglecting paramagnetic contributions

$${}^{(1)}\boldsymbol{A}_{mg}^{(1)} = -\frac{1}{4c^2}\left\langle g\left|\sum_{i=1}^{\nu}\frac{e_i^2}{m_i}(r_i^2\boldsymbol{U}_{12} - \boldsymbol{r}_{i1}\boldsymbol{r}_{i2})\right|g\right\rangle, \tag{92}$$

$${}^{(1)}\boldsymbol{C}_{mg}^{(1+1+1)} = \frac{S(1,2,3,4)}{128c^6}\left\langle g\left|\sum_{i=1}^{\nu}\frac{e_i^4}{m_i^3}(r_i^2\boldsymbol{U}_{12} - \boldsymbol{r}_{i1}\boldsymbol{r}_{i2})(r_i^2\boldsymbol{U}_{34} - \boldsymbol{r}_{i3}\boldsymbol{r}_{i4})\right|g\right\rangle, \tag{93}$$

eq. (92) defines the diamagnetic (first-order) dipole polarizability tensor calculated theoretically for some molecules by Tillieu[18]) and others[19]), whereas eq. (93) defines the diamagnetic third-order dipole polarizability tensor.

In the special case of microsystems possessing the spherical symmetry eq. (91) reduces to the simple form

$$\boldsymbol{\mu} - \boldsymbol{\mu}_0 = \frac{2\pi}{3}\rho c_m \boldsymbol{HH}, \tag{94}$$

wherein by (93) we have

$$c_m = \tfrac{1}{5}\sum_g \rho_g^0 \boldsymbol{U} : {}^{(1)}\boldsymbol{C}_{mg}^{(1+1+1)} : \boldsymbol{U} = \frac{3}{20c^6}\sum_g \rho_g^0\left\langle g\left|\sum_{i=1}^{\nu}\frac{e_i^4}{m_i^3}r_i^4\right|g\right\rangle \tag{95}$$

for the scalar third-order dipole magnetic polarizability.

Using the fact that in the absence of a strong magnetic field the magnetic permittivity tensor is isotropic, $\boldsymbol{\mu}_0 = \mu_0\boldsymbol{U}$, expressions (76) and (79) yield

$$(\boldsymbol{\mu}_0 - \boldsymbol{U})\cdot\boldsymbol{H} = (\mu_0 - 1)\,\boldsymbol{H} = 4\pi\rho a_m \boldsymbol{H}, \tag{96}$$

and we obtain from (94) for the relative nonlinear variation of the permeability

$$\frac{\boldsymbol{\mu} - \mu_0\boldsymbol{U}}{\mu_0 - 1} = \frac{1}{6}\left(\frac{c_m}{a_m}\right)\boldsymbol{HH}, \tag{97}$$

where $a_m \equiv a_m^{(2)}$ is the mean dipole Langevin-Pauli diamagnetic polarizability given by (81) for $n = 1$.

Since for atoms the ratio c_m/a_m is at best of the order 10^{-20}, by (97) the nonlinear variation is of the order $10^{-21}H^2$; this is a very small variation, not accessible to observation.

In the case of anisotropic microsystems possessing the axial symmetry we obtain by (91) and (96) in a good approximation

$$\frac{\boldsymbol{\mu} - \mu_0 \boldsymbol{U}}{\mu_0 - 1} = \frac{2\beta}{45 a_m} \sum_g \rho_g^0 (a_{mg}^{//} - a_{mg}^{\perp})^2 \boldsymbol{HH}, \tag{98}$$

where $a_m^{//}$ and $a_m^{\perp}$ denote, respectively, the dipole magnetic polarizabilities in the directions parallel and perpendicular to the molecular axis of symmetry.

Applying the formula of (98) to benzene or nitrobenzene we obtain in normal conditions a nonlinear change in permeability of the order of $10^{-15} H^2$.

Similarly, for paramagnetic microsystems, one obtains from (75), (78) and (89), on neglecting the (in this case) small diamagnetic terms,

$$\frac{\boldsymbol{\mu} - \mu_0 \boldsymbol{U}}{\mu_0 - 1} = \frac{\beta^2}{30} \frac{\sum_g \rho_g^0 \boldsymbol{m}_g^2 (3\boldsymbol{m}_g^2 - 5 \sum_k \rho_k^0 \boldsymbol{m}_k^2)}{\sum_g \rho_g^0 \boldsymbol{m}_g^2} \boldsymbol{HH}, \tag{99}$$

where by (52) for $n = 1$

$$\boldsymbol{m} \equiv \boldsymbol{M}_m^{(1)} = \frac{1}{2c} \sum_{i=1}^{\nu} \frac{e_i}{m_i} (\boldsymbol{r}_i \times \boldsymbol{p}_i + 2\boldsymbol{S}_i) \tag{100}$$

is the dipole magnetic moment.

For a paramagnetic gas of oxygen molecules the formula (99) yields a nonlinear variation in $\boldsymbol{\mu}$ of the order of $10^{-13} H^2$.

As very intense magnetic fields of the order of 10^6 Oe are at present being produced in laboratories applying pulse methods, it is obvious from the preceding evaluations that nonlinear variations in the magnetic permeability of appropriately chosen diamagnetic or paramagnetic substances have become accessible to observation. Such experimental investigation will by no means be easy; nevertheless, in favorable conditions it will be feasible and no doubt will yield important information permitting to gain deeper insight into fine details of microsystems. Hence investigation in this field can be fruitful, providing quite generally data on the multipolar and nonlinear magnetic properties of molecules.

The considerations of sections 4 and 5 can be generalized to dense media by a procedure similar to that applied by Jansen and Mazur[20] for calculating the linear electric polarization. In this case, in addition to the full Hamiltonian of interaction between the microsystems and the external magnetic field, one has, moreover, to apply the Hamiltonian of mutual interaction between the microsystems as defined in a first approximation by the multipolar expansion (51). This problem will be discussed in a separate paper.

The formalism developed in sections 2 and 3 is in general applicable to

the case of time-variable electric and magnetic fields as e.g. conveyed by a light wave. This case is all the more interesting as it is related with the at present highly improved laser techniques which provide an excellent experimental basis for the investigation of various novel nonlinear electro- and magneto-optical effects[11]). Subsequent to some modification (e.g. by applying time-dependent perturbation theory) the formalism proposed above can be employed for calculating e.g. nonlinear variations of the Faraday effect or nonlinear variations of the optical activity.

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