Magneto-Optical Effects and Paramagnetic Resonance

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INTRODUCTION

LET us consider a material medium in which electromagnetic radiation of two widely different frequencies, for instance, visible radiation and microwave radiation, both approximately monochromatic, is propagated. Concerning the medium, let us assume (as is usual in the dispersion theory) that it may be regarded as an assembly of a very large number of identical "unit systems," such as gas molecules or paramagnetic ions subjected to crystalline electric fields. The medium may or may not be placed in a constant, homogeneous magnetic field, although the former case will usually correspond to actual experimental situations.

In general, the properties of the medium as they show themselves in some observations on either radiation (e.g., observations of the state of polarization or of the Faraday rotation of the plane of polarization) will not be influenced appreciably by the presence of the other. Such an influence may, however, very well occur if the other radiation happens to be in resonance with the unit systems constituting the medium, as has repeatedly been emphasized in recent years.[1] For, in this case, the occupation numbers of the energy levels of the unit systems will, in general, be changed, which, in turn, may lead to modifications of those properties of the medium which determine the results of the observations. Obviously, the occurrence of such modifications implies that the initial energy level for the resonance transition, which may correspond to absorption or induced emission, is occupied, at least intermittently.

The initial level may be occupied for two different reasons, corresponding to two very different kinds of experimental situations. On the one hand, the initial level is occupied because it is, at the same time, the final level for a transition involving the other radiation. Such a "double resonance" case has recently been investigated, experimentally and theoretically, by Bitter and Brossel.[2] They have studied the change in the degree of polarization of the ultraviolet resonance radiation of mercury occurring when mercury vapor placed in a constant magnetic field is subjected to a radiofrequency radiation satisfying the magnetic resonance condition. Double resonance experiments in which the medium is an atomic beam, are also in progress, as reported very recently by Rabi.[3] In this case the changes in the properties of the "medium" are, of course, observed directly.[4]

On the other hand, the initial level is occupied because the temperature of the medium is such that the corresponding Boltzmann factor is not negligible. An experiment involving this kind of situation has recently been proposed by Kastler.[5] He pointed out that the paramagnetic Faraday rotation of visible light will, in general, change considerably under the influence of paramagnetic resonance; in other words, the rotation angle will change if the paramagnetic salt in question is subjected to microwave radiation the frequency of which corresponds to an allowed magnetic dipole transition between the energy levels of paramagnetic ions responsible for the Faraday rotation. Kastler restricted himself to a brief qualitative discussion of this effect. It is the purpose of the present paper to supplement his discussion with a formal quantum-mechanical theory.

Strictly speaking, the initial level may be occupied for both the above stated reasons simultaneously. This case will not, however, be considered here.

GENERAL THEORY

As is well known, the magneto-optical effects depend on the average polarizability tensor of unit atomic systems of which the medium consists ("average" in the sense of statistical mechanics). The average polarizability tensor is, in general, complex, and it can be regarded as composed of a Hermitian part and an anti-Hermitian part. The imaginary and real part of the Hermitian part determine the Faraday rotation and the birefringence, respectively; the anti-Hermitian part determines the absorption. If, besides light, microwave radiation is propagated in the medium, additional terms will appear in the expression for the average polariz-

[1] In particular, F. Bitter, Phys. Rev. **76**, 833 (1949); J. Brossel and A. Kastler, Compt. rend. **229**, 1213 (1949); A. Kastler, Compt. rend. **232**, 953 (1952); See also a review article by A. Kastler, Experientia **8**, 1 (1952).

[2] F. Bitter and J. Brossel, Phys. Rev. **86**, 308 (1952).

[3] I. I. Rabi, Phys. Rev. **87**, 379 (1952).

[4] If unit systems are atomic nuclei rather than atoms, still other experiments very similar in nature to those mentioned above, although involving quite different experimental techniques, become possible. Consider, for instance, an atomic nucleus which emits two gamma-photons in cascade, in the presence of a homogeneous magnetic field. Such a property of the emitted photons as the correlation between their directions of motion will, in general, be modified if a radiofrequency field is switched on, provided its frequency is in resonance with the possible transition frequency between the magnetic sublevels of the intermediate energy level. For these sublevels are final levels for the emission of the first gamma-photon, and initial levels for the emission of the second gamma-photon. *Note added in proof*.—A theory for this case has been developed by B. A. Jacobsohn (University of Washington) and will be published shortly.

[5] A. Kastler, Compt. rend. **232**, 953 (1951).

ability tensor for light, provided the frequency of the microwave radiation is such as to give rise to resonance. It is just these additional terms which are to be calculated.

It should be emphasized that, in the theory here given, "light" means a radiation which induces only electric dipole transitions in the medium, and "microwave radiation" means a radiation which induces only magnetic dipole transitions.[6] The values of the frequencies of the two radiations play only a minor role in the theory. If the formulas are, in a rather early stage of theoretical derivations, specialized to the case that the frequencies are those of visible light and microwave radiation, in the usual sense of these terms, it is only because in such a case the effects described by the formulas will, under normal experimental conditions, most easily be observed.

According to the general principles of quantum statistical mechanics, the average $\langle\mathbf{p}\rangle_{\text{Av}}$ of the electric dipole moment $\mathbf{p}$ of a unit system is, at time t,

$$\langle\mathbf{p}(t)\rangle_{\text{Av}}=\text{trace}\,[\mathbf{p}\rho(t)], \tag{1}$$

where ρ is the density matrix of the system. If some system of representation is chosen, Eq. (1) becomes

$$\langle\mathbf{p}(t)\rangle_{\text{Av}}=\sum_m\sum_n\mathbf{p}_{nm}\rho_{mn}(t), \tag{2}$$

where $\mathbf{p}_{mn}$ and ρ_{mn} are the matrix elements of $\mathbf{p}$ and ρ.

The matrix ρ will be, in the approximation here considered, a linear function of the components of the electric vector of the light wave propagated in the medium. Hence, in view of Eq. (2), each component of the average electric dipole moment will be also a linear function of the components of electric vector of the light wave. In other words, Eq. (2) implicitly represents a tensor relation between $\langle\mathbf{p}(t)\rangle_{\text{Av}}$ and the electric vector of the light wave, the tensor in question being by definition, the polarizability tensor, which, as stated before, determines the magneto-optical effects. The problem is thus reduced to that of calculating ρ in the presence of light, microwave radiation and a constant homogeneous magnetic field.

It will be assumed that ρ satisfies the equation

$$\frac{\partial\rho}{\partial t}=-\frac{i}{\hbar}(\mathcal{H}\rho-\rho\mathcal{H})-a(\rho-\rho_0). \tag{3}$$

Here $\mathcal{H}$ is the Hamiltonian of a unit system in the presence of both radiations; ρ_0 is the density matrix for the case in which the thermodynamic equilibrium of the assembly of unit systems would be determined by the instantaneous energy values of the levels of a unit system. In other words, ρ_0 is the solution of the equation

$$\frac{\partial\rho_0}{\partial t}=-\frac{i}{\hbar}(\mathcal{H}\rho_0-\rho_0\mathcal{H}) \tag{4}$$

for the case in which the frequency of the perturbing radiation tends to zero, the assembly being supposed to be in thermodynamic equilibrium in the absence of radiation. The actual density matrix ρ must clearly satisfy an equation which takes into account the fact that the instantaneous equilibrium cannot be reached. The simplest way of taking this fact into account is embodied in the second term on the right-hand side of Eq. (3), where the constant a can be interpreted, in the case of a gas, as the number of collisions per unit time, and, in the case of a paramagnetic salt, as the reciprocal value of the spin-lattice relaxation time. Equation (3) has been used by Karplus and Schwinger[7] and, before them, by Fröhlich,[8] in its classical form, as the starting point for a computation of the shape of microwave absorption lines in a gas, a problem treated previously in a different way by Van Vleck and Weisskopf.[9] Later, Bijl[10] used Eq. (3) in connection with the paramagnetic resonance absorption. These problems are very closely related to the one treated in the present paper.

More explicitly, $\mathcal{H}$, which is a time-dependent operator, is given by

$$\mathcal{H}(t)=\mathcal{H}_0+P\cos\omega_Pt+M\cos\omega_Mt, \tag{5}$$

$$P=-\mathbf{p}\cdot\mathbf{E},\quad M=-\mathbf{m}\cdot\mathbf{H}; \tag{6}$$

here $\mathbf{p}$ and $\mathbf{m}$ are the electric and the magnetic dipole moment operators; $\mathbf{E}$ and ω_P are the amplitude of the electric vector, and the angular frequency of light; $\mathbf{H}$ and ω_M are, similarly, the amplitude of the magnetic vector and the angular frequency of the microwave radiation. Consequently, $\mathcal{H}_0$ is the Hamiltonian in the absence of both radiations. It is time-independent, and is supposed to include a term that takes into account the presence of the constant homogeneous magnetic field, and also of possible internal perturbations, such as a crystalline field in a paramagnetic salt. Eigenvalues of $\mathcal{H}_0$, which are assumed to be nondegenerate, will be denoted by E_k.

If in the absence of both radiations the medium is in thermal equilibrium, as is assumed here, the density matrix of a unit system will be

$$\rho^0=\exp(-\mathcal{H}_0/kT)/\text{trace}\exp(-\mathcal{H}_0/kT), \tag{7}$$

where k is the Boltzmann constant and T the absolute temperature. In other words, ρ^0 is a diagonal matrix in the system of representation in which $\mathcal{H}_0$ is diagonal, and its matrix elements $\rho_{mn}{}^0$ are the familiar Boltzmann factors

$$\begin{gathered}\rho_{mn}{}^0=\delta_{mn}\rho_m{}^0,\\ \rho_m{}^0=\exp(-E_m/kT)/\textstyle\sum_l\exp(-E_l/kT).\end{gathered} \tag{8}$$

[6] An analogous theory, with merely some minor formal modifications, could easily be developed for the case in which changes in the Faraday effect of microwave radiation are calculated arising from resonance of a radiation inducing electric dipole or quadrupole transitions.

[7] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

[8] H. Fröhlich, Nature **157**, 148 (1946).

[9] J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. **17**, 227 (1945).

[10] D. Bijl, thesis, Leiden, 1950, p. 77.

We now introduce two auxiliary matrices σ_0 and σ,

$$\sigma_0 = \rho_0 - \rho^0, \quad \sigma = \rho - \rho^0. \tag{9}$$

If use is made of Eq. (5), Eq. (3) becomes, in terms of these matrices,

$$\frac{\partial\sigma}{\partial t} + \frac{i}{\hbar}(\mathcal{H}_0\sigma - \sigma\mathcal{H}_0) = -a(\sigma - \sigma_0) - \frac{i}{\hbar}[M(\rho^0+\sigma) - (\rho^0+\sigma)M]\cos\omega_M t + [P(\rho^0+\sigma) - (\rho^0+\sigma)P]\cos\omega_P t, \tag{10}$$

or, in the system of representation in which $\mathcal{H}_0$ is diagonal,

$$\left(\frac{\partial}{\partial t} + i\omega_{mn} + a\right)\sigma_{mn} = a(\sigma_0)_{mn} + \frac{i}{\hbar}(\rho_m{}^0 - \rho_n{}^0)(M_{mn}\cos\omega_M t + P_{mn}\cos\omega_P t) - \frac{i}{\hbar}\sum_k[(M_{mk}\sigma_{kn} - \sigma_{mk}M_{kn})\cos\omega_M t + (P_{mk}\sigma_{kn} - \sigma_{mk}P_{kn})\cos\omega_P t], \tag{11}$$

where

$$\hbar\omega_{mn} = E_m - E_n. \tag{12}$$

A glance at Eqs. (3) and (4) shows that $(\sigma_0)_{mn}$ satisfies the equation which arises from Eq. (11) by setting $a=0$. If the intensity of radiation is not too high, the terms containing the matrix elements of σ_0 on the right-hand side of the equation so obtained may be neglected. In accordance with the above discussed meaning of ρ_0, the appropriate solution of this equation is readily found to be

$$\hbar(\sigma_0)_{mn} = (\rho_m{}^0 - \rho_n{}^0)[(M_{mn}/\omega_{mn})\cos\omega_M t + (P_{mn}/\omega_{mn})\cos\omega_P t]. \tag{13}$$

For paramagnetic ions in crystals, the matrix elements P_{mn} usually vanish if the corresponding transition frequencies belong to microwave or radio regions. For high transition frequencies, $(\sigma_0)_{mn}\approx 0$, because ω_{mn} is then large.

Taking this into account and eliminating $(\sigma_0)_{mn}$ from Eq. (11), by means of Eq. (13), we obtain

$$\hbar\left(\frac{\partial}{\partial t} + i\omega_{mn} + a\right)\sigma_{mn} = i(\rho_m{}^0 - \rho_n{}^0)[(1 - ia/\omega_{mn})M_{mn}\cos\omega_M t + P_{mn}\cos\omega_P t] - i\sum_k[(M_{mk}\sigma_{kn} - \sigma_{mk}M_{kn})\cos\omega_M t + (P_{mk}\sigma_{kn} - \sigma_{mk}P_{kn})\cos\omega_P t]. \tag{14}$$

If one disregards those terms in σ_{mn} which do not vary with time like $e^{\pm i\omega_M t}$ or $e^{\pm i\omega_P t}$, an approximate solution of Eq. (14) will be of the form[11]

$$\sigma_{mn} = R_{mn} + A_{mn}e^{i\omega_M t} + B_{mn}e^{-i\omega_M t} + C_{mn}e^{i\omega_P t} + D_{mn}e^{-i\omega_P t}. \tag{15}$$

To determine the constants in Eq. (15), we substitute this expression for σ_{mn} in Eq. (14), and so obtain the equations (we neglect $a/(\omega_P - |\omega_{mn}|)$, as the frequency of the visible radiation is supposed not be in the vicinity of resonance)

$$2\hbar aR = -\sum_k[M_{mk}(A_{kn}+B_{kn}) - (A_{mk}+B_{mk})M_{kn} + P_{mk}(C_{kn}+D_{kn}) - (C_{mk}+D_{mk})P_{kn}], \tag{16}$$

$$(\omega_M + \omega_{mn} - ia)A_{mn} = S_{mn}{}^M, \tag{17}$$

$$(-\omega_M + \omega_{mn} - ia)B_{mn} = S_{mn}{}^M, \tag{18}$$

$$(\omega_P + \omega_{mn})C_{mn} = S_{mn}{}^P, \tag{19}$$

$$(-\omega_P + \omega_{mn})D_{mn} = S_{mn}{}^P, \tag{20}$$

$$2\hbar S_{mn}{}^M = (\rho_m{}^0 - \rho_n{}^0)(1 - ia/\omega_{mn})M_{mn} - \sum_k(M_{mk}R_{kn} - R_{mk}M_{kn}), \tag{21}$$

$$2\hbar S_{mn}{}^P = (\rho_m{}^0 - \rho_n{}^0)P_{mn} - \sum_k(P_{mk}R_{kn} - R_{mk}P_{kn}). \tag{22}$$

If both radiations are weak and neither frequency is nearly equal to any ω_{mn}, the matrix R may be put equal to zero. The constants C_{mn} and D_{mn} lead then, using Eqs. (2), (9), (15), to the usual expression for the average polarizability tensor for the frequency ω_P (the Kramers-Heisenberg dispersion formula). The terms in σ_{mn} containing A_{mn} and B_{mn} give no contribution to this tensor. They are proportional to $M_{mn} = -(\mathbf{m}_{mn}\cdot\mathbf{H})$, so that the corresponding terms in Eq. (2) are proportional to $\mathbf{p}_{mn}(\mathbf{m}_{mn}\cdot\mathbf{H})$, which all vanish, because the electric and the magnetic dipole matrix elements are never both different from zero for the same transition (at least, if the two states involved in the transition have definite parities).

Similarly, the constants A_{mn} and B_{mn} lead to an analogous expression for the magnetic susceptibility tensor for the frequency ω_M. The expression is slightly more complicated, owing to the presence of terms containing a, which are responsible for absorption.

If, however, ω_M is nearly equal to one of the ω_{mn}'s and the corresponding magnetic dipole transition is not forbidden, i.e., in the case of magnetic resonance, the sums on the right-hand side of Eqs. (16)–(22) cannot entirely be neglected. For, if $\omega_M \approx (E_u - E_l)/\hbar$ (subscript u refers to the upper level, subscript l to the lower level), A_{lu} and B_{ul} will be much larger than the remaining matrix elements of A and B. Hence, even in the lowest approximation, two of the matrix elements of R, namely, R_{uu} and R_{ll}, will be different from zero.

[11] The calculations which follow are a straightforward generalization of Karplus and Schwinger's calculations, reference 7.

Equations (16)–(22) then reduce to

$$2\hbar i a R_{uu} = M_{ul} A_{lu} - B_{ul} M_{lu}, \tag{23}$$

$$R_{ll} = -R_{uu}, \tag{24}$$

$$2\hbar(\omega_M - \omega_{ul} - ia) A_{lu} = [(\rho_l^0 - \rho_u^0)(1 - ia/\omega_{lu}) - (R_{uu} - R_{ll})] M_{lu}, \tag{25}$$

$$B_{ul} = A_{lu}^*, \tag{26}$$

$$2\hbar(\omega_P + \omega_{mn}) C_{mn} = (\rho_m^0 - \rho_n^0) P_{mn} - (\delta_{nl} P_{ml} - \delta_{ml} P_{ln}) R_{ll} - (\delta_{nu} P_{mu} - \delta_{mu} P_{un}) R_{uu}, \tag{27}$$

$$D_{mn} - C_{nm}^* \tag{28}$$

Changes in the magneto-optical effects arising from paramagnetic resonance are derived from the terms containing R_{uu} and R_{ll} in Eqs. (27) and (28).

From Eqs. (23)–(26), one finds

$$R_{uu} = -R_{ll} = (\rho_l^0 - \rho_u^0) W_{ul},$$
$$W_{ul} = \frac{1}{2} \frac{\omega_M}{\omega_{ul}} \frac{|M_{ul}|^2}{\hbar^2(\omega_{ul} - \omega_M)^2 + |M_{ul}|^2 + \hbar^2 a^2}. \tag{29}$$

This expression for R_{uu} is identical with Karplus and Schwinger's corresponding result if the meaning of symbols is appropriately reinterpreted [see reference 7, Eq. (30)]. Equations (27) and (28) together with Eq. (29) give explicit expressions for C_{mn} and D_{mn}. If one substitutes these expressions in Eq. (15), and uses the expression for σ_{mn} so obtained to calculate, by means of Eqs. (2) and (9), the terms of $\langle \mathbf{p}(t) \rangle_{\text{Av}}$ containing $e^{\pm i\omega_P t}$, which will be denoted by $\langle \mathbf{p}_{\omega_P}(t) \rangle_{\text{Av}}$, one finds after some straightforward but rather lengthy rearrangements

$$\langle \mathbf{p}_{\omega_P}(t) \rangle_{\text{Av}} = \text{Re}[\langle \mathbf{p}(\omega_P) \rangle_{\text{Av}} e^{i\omega_P t}], \tag{30}$$

where

$$\text{Re}\langle \mathbf{p}(\omega_P) \rangle_{\text{Av}} = \frac{1}{\hbar} \sum_n \rho_n^0 \sum_m \frac{2\omega_{nm} \mathbf{P}_{nm}^+}{\omega_P^2 - \omega_{mn}^2} - (\rho_u^0 - \rho_l^0) \frac{W_{ul}}{\hbar} \sum_m \left[\frac{2\omega_{um} \mathbf{P}_{um}^+}{\omega_P^2 - \omega_{um}^2} - \frac{2\omega_{lm} \mathbf{P}_{lm}^+}{\omega_P^2 - \omega_{lm}^2} \right], \tag{31}$$

$$\text{Im}\langle \mathbf{p}(\omega_P) \rangle_{\text{Av}} = \frac{1}{\hbar} \sum_n \rho_n^0 \sum_m \frac{2\omega_P \mathbf{P}_{nm}^-}{\omega_P^2 - \omega_{mn}^2} - (\rho_u^0 - \rho_l^0) \frac{W_{ul}}{\hbar} \sum_m \left[\frac{2\omega_P \mathbf{P}_{um}^-}{\omega_P^2 - \omega_{um}^2} - \frac{2\omega_P \mathbf{P}_{lm}^-}{\omega_P^2 - \omega_{ln}^2} \right]. \tag{32}$$

The vectors $\mathbf{P}_{mn}^+$ and $\mathbf{P}_{mn}^-$ occurring in Eqs. (32) and (33) are defined by

$$\mathbf{P}_{mn}^+ = \text{Re}[\mathbf{p}_{mn}(\mathbf{p}_{nm} \cdot \mathbf{E})], \tag{33}$$

$$\mathbf{P}_{mn}^- = \text{Im}[\mathbf{p}_{mn}(\mathbf{p}_{nm} \cdot \mathbf{E})]. \tag{34}$$

The tensor relationship between $\langle \mathbf{p}(\omega_P) \rangle_{\text{Av}}$ and $\mathbf{E}$, as given by Eqs. (31)–(34), determines the average polarizability tensor of a unit system. In particular, Eq. (31) determines the real part of this tensor, i.e., the part on which the magnetic birefringence depends. Similarly, Eq. (32) determines its imaginary part, which describes the Faraday effect, as will be discussed below in more detail. The tensor is Hermitian, as may be seen from Eqs. (31)–(34), and from the Hermitian character of the $\mathbf{p}_{mn}$'s. This corresponds to the fact that the absorption of the light wave is here neglected.

THE FARADAY EFFECT

Owing to the Hermitian character of the electric dipole moment matrix $\mathbf{p}_{mn}$, Eq. (34) can be written as follows:

$$\mathbf{P}_{mn}^- = \tfrac{1}{2}(\mathbf{p}_{mn} \times \mathbf{p}_{nm}) \times \mathbf{E}. \tag{35}$$

Making use of this equation and introducing the abbreviation

$$\mathbf{\Omega}_n = \frac{\omega_P}{\hbar} \sum_m \frac{\mathbf{p}_{mn} \times \mathbf{p}_{nm}}{\omega_P^2 - \omega_{mn}^2}, \tag{36}$$

one obtains from Eq. (32)

$$\text{Im}\langle \mathbf{p}(\omega_P) \rangle_{\text{Av}} = \mathbf{\Omega}_{ul} \times \mathbf{E}, \tag{37}$$

where

$$\mathbf{\Omega}_{ul} = \textstyle\sum_n \rho_n^0 \mathbf{\Omega}_n + W_{ul}(\mathbf{\Omega}_l - \mathbf{\Omega}_u)(\rho_u^0 - \rho_l^0). \tag{38}$$

As is well known from the theory of the Faraday effect,[12] the rotation of the plane of polarization θ per centimeter is related to $\mathbf{\Omega}_{ul}$ in a simple way. If the direction of the constant homogeneous magnetic field and that of propagation of the light wave are parallel, θ is proportional to the component of $\mathbf{\Omega}_{ul}$ along the direction of the field. The proportionality constant is

$$G = 8\pi^2 \omega_P N i / c\sqrt{\epsilon}, \tag{39}$$

where N is the number of unit systems per cc, and ϵ is the dielectric constant of the medium (it is assumed that the birefringence is small). Hence the term proportional to W_{ul} in Eq. (38) when multiplied by G represents the contribution of the paramagnetic resonance to the Faraday rotation.

It should be emphasized that the theory has been developed here for the case in which the shape of the paramagnetic resonance line is mainly determined by the spin-lattice relaxation time. If the predominant effects in determining the shape are the dipole-dipole and exchange interactions, the exact calculation of the contribution of the paramagnetic resonance to the Faraday rotation is a problem more or less equivalent to that of computing that shape, so that no straight-

[12] H. A. Kramers, Proc. Acad. Amsterdam **33**, 959 (1930); see also L. Rosenfeld, Z. Physik **57**, 835 (1930); R. Serber, Phys. Rev. **41**, 489 (1932); J. H. Van Vleck and M. H. Hebb, Phys. Rev. **46**, 17 (1934).

forward approach seems to be possible. Of course, the changes in the Faraday effect resulting from the paramagnetic resonance would remain roughly proportional to $(\mathbf{\Omega}_u - \mathbf{\Omega}_l)(\rho_l^0 - \rho_u^0)$.

When one applies the general formula (38) to the case of nickel fluosilicate, which has been considered by Kastler,[5] one easily confirms his qualitative conclusions.

DISCUSSION

A. Abragam, *University of Paris, France:* It might be interesting to generalize slightly this calculation so as to include the dipole magnetic or quadrupole electric transitions for visible light, which may occur in crystals.