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Commentationes

Magneto-Optical Rotation in Molecules*

I. General Theory

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A quantum-mechanical theory for the magneto-optical rotation in diamagnetic polyatomic molecules is formulated using the timedependent second-order perturbation theory. The treatment is not restricted to molecules having non-degenerate excited wave functions. The contributions of the induced magnetic moment and the perturbed Boltzmann factor are included. The results are compared with some of the former theories.

Es wird eine quantenmechanische Theorie für die magneto-optische Drehung in diamagnetischen mehratomigen Molekülen unter Anwendung der zeitabhängigen Störungstheorie zweiter Ordnung formuliert. Die Behandlung ist nicht auf Moleküle mit nicht-entarteten angeregten Zuständen beschränkt. Die Beiträge des induzierten magnetischen Moments und des gestörten Boltzmann-Faktors sind eingeschlossen. Die Ergebnisse werden mit denen einiger früherer Theorien verglichen.

La théorie des perturbations dépendantes du temps, limitée au second ordre, est utilisée pour formuler une théorie quantique de la polarisation rotatoire magnétique dans les molécules polyatomiques diamagnétiques. L'étude est étendue aux molécules ayant des fonctions d'onde excitées dégénérées. On tient compte de l'effet du moment magnétique induit et du facteur de Boltzmann perturbé. Les résultats sont comparés à ceux de certaines théories antérieures.

1. Introduction

When linearly polarized radiation is passed through matter placed in a constant magnetic field, it is found that the plane of polarization of the emergent radiation is rotated. This phenomenon is known as the magneto-optical rotation or the Faraday effect. There are two experimental procedures in measuring the magneto-optical rotation for a molecule. One method uses incident radiation in the immediate neighbourhood of an absorption line of the molecule, the other uses incident radiation well removed from resonance with any absorption line of the molecule. A theoretical aspect for the former phenomenon has been demonstrated by HAMEKA [*4*] using a theory of resonance fluorescence, turning his attention to the experimental work done by EBERHARDT et al.

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Experiments of the latter type show that the angle of rotation φ is proportional to the external magnetic field strength $\mathfrak{H}^f$, i.e.

$$\varphi = V\, l\, (\mathfrak{H}^f, \mathfrak{k}) \tag{1}$$

where l is the optical path length through the medium, and $\mathfrak{k}$ a unit vector in the direction of propagation of the radiation. The proportionality constant V is called the Verdet constant. In this paper, an interpretation only for this phenomenon will be discussed.

Quantum mechanical theories of magneto-optical rotation have been developed by Kronig [8], Rosenfeld [10], Kroll [7], Kramers [6], Serber [11], and Carroll [1]. Of these Serber dealt with the magneto-optical rotation in molecules of all symmetry classes, using the first-order perturbation techniques successively, one for the magnetic field (stationary) and the other for the radiation field (time-dependent). More recently, Groenewege [3] treated the magnetic rotation along the same method of deriving natural optical rotation, based on a second-order time-dependent perturbation procedure.

The purpose of the present paper will be to derive more general formulae for the magneto-optical rotation for the case of diamagnetic molecules of all symmetry classes, using the like manner of Groenewege. In these molecules, electronic wave functions for excited states are not always non-degenerate, so that the matrix elements of the induced electric and magnetic moments can be complex. In this paper, the treatment is not restricted to molecules having non-degenerate excited wave functions, unlike the former treatments cited above. The temperature-dependent paramagnetic terms, which are absent in Groenewege's formulae are obtained by expanding the appropriate Boltzmann factor in the ground state of the molecule [5]. The results will be compared with the former theories in the last section.

2. The Time-Dependent Perturbations

Let us consider a molecule subjected to perturbations of a radiation and an external magnetic field. The molecule is assumed to be of diamagnetic so that its ground state wave function is non-degenerate and the total spin angular momentum in the ground state is zero. We restrict our treatment to the case that the frequency of the incident radiation is well removed from resonance with any absorption lines, as mentioned before.

Let the position vector of the j-th electron in the molecule be $\mathfrak{r}_j$, and the canonically conjugate linear momentum $\mathfrak{p}_j$. When the over-all spin-multiplet width and the separations between the rotational levels of the ground state are small compared to kT/h, the spin can be regarded as completely uncoupled from the orbital angular momentum*. In this case, the total Hamiltonian for the molecule may take the form:

$$\mathscr{H} = \sum_j \left[\frac{1}{2\,m}\left(\mathfrak{p}_j - \frac{e}{c}\,\mathfrak{A}_j\right)^2 + e\,\phi_j\right] + U \tag{2}$$

where e and m are the electronic charge and mass, respectively, $U = U\,(\mathfrak{r}_1, \mathfrak{r}_2, \ldots .)$ the internal potential, and ϕ_j the scalar potential acting on electron j. $\mathfrak{A}_j$ is the vector potential at the position of the j-th electron and can be divided into two

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* For more detailed discussions on negligibleness of the spin effect, see ref. [11].

parts; one due to the radiation field and the other due to the external magnetic field. When the incident radiation is a plane wave of frequency ν propagating in the direction of the unit vector $\mathfrak{f}$, the time-dependence of its vector potential $\mathfrak{a}_j$ at the position of the j-th electron may be expressed as

$$\mathfrak{a}_j = \tfrac{1}{2}\left\{\mathfrak{a}_0^0 \operatorname{ixp}\left[\nu\left(t - \frac{n}{c}\,(\mathfrak{r}, \mathfrak{f})\right)\right] + \text{complex conjugate}\right\} \tag{3}$$

where c denotes the velocity of light in vacuo, n the refractive index of the medium, and $\mathfrak{a}_0^0$ the complex amplitude. In Eq. (3), the abbreviation

$$\operatorname{ixp} f \equiv e^{2\pi i f}$$

has been introduced for convenience. On the other side, the vector potential due to the homogeneous external magnetic field is

$$\mathfrak{a}_j^f = \tfrac{1}{2}\,[\mathfrak{H}^f, \mathfrak{r}_j]\,. \tag{4}$$

The total vector potential is then expressed as

$$\mathfrak{A}_j = \mathfrak{a}_j + \mathfrak{a}_j^f\,. \tag{5}$$

In expanding the square in Eq. (2), we must bear in mind that $\mathfrak{p}_j$ and $\mathfrak{A}_j$ commute since we may put div $\mathfrak{A}_j = 0$. Hence the first- and second-order perturbation terms, which have to be added to the unperturbed Hamiltonian $\mathcal{H}_0$, can be written in the forms

$$\mathcal{H}^{(1)} = -\,(e/mc)\sum_j\,((\mathfrak{a}_j + \mathfrak{a}_j^f), \mathfrak{p}_j))\,, \tag{6}$$

$$\mathcal{H}^{(2)} = (e^2/mc^2)\sum_j\,(\mathfrak{a}_j, \mathfrak{a}_j^f)\,. \tag{7}$$

Here we have neglected the term $(e/c)^2\,\mathfrak{a}^2$ as usual in most discussions of radiation, and recalled that $(\mathfrak{a}_j^f)^2$ may also be discarded because in calculating the induced moments we are interested only in the terms linear in the external magnetic field. In Eq. (6), the vector potential $\mathfrak{a}_j$ may be expanded into a Taylor's series in terms of the value $\mathfrak{a}$ and its derivatives $\nabla\cdot\mathfrak{a}$ at the origin of a coordinate suitably fixed in the molecule. If we neglect higher terms representing quadrupole moment and more, we obtain

$$\mathcal{H}^{(1)} = -\,(e/mc)\sum_j\,(\mathfrak{p}_j, \mathfrak{a}_0) - (\mathfrak{M}, [\nabla, \mathfrak{a}]_0) - (\mathfrak{M}, \mathfrak{H}^f)\,, \tag{8}$$

$$\mathcal{H}^{(2)} = (e/2\,mc^2)\,(\mathfrak{R}, [\mathfrak{a}_0, \mathfrak{H}^f]) \tag{9}$$

where we have used the following definitions

$$\mathfrak{R} = e\sum_j \mathfrak{r}_j \tag{10}$$

$$\mathfrak{M} = (e/2\,mc)\sum_j\,[\mathfrak{r}_j, \mathfrak{p}_j] \tag{11}$$

and

$$\mathfrak{a}_0 = \tfrac{1}{2}\,\{\mathfrak{a}_0^0 \operatorname{ixp}(\nu t) + \mathfrak{a}_0^{0\dagger} \operatorname{ixp}(-\,\nu t)\}\,, \tag{12}$$

$$[\nabla, \mathfrak{a}]_0 = \tfrac{1}{2}\,\{[\nabla, \mathfrak{a}]_0^0 \operatorname{ixp}(\nu t) + [\nabla, \mathfrak{a}]_0^{0\dagger} \operatorname{ixp}(-\,\nu t)\} \tag{13}$$

The time-dependent Schrödinger equation to be solved has now the form

$$i\,\hbar\,\dot{\Psi}_n = (\mathcal{H}_0 + \mathcal{H}^{(1)} + \mathcal{H}^{(2)})\,\Psi_n \tag{14}$$

the dot being denote the time derivative. Following the usual procedure, one can expand Ψ_n in terms of the unperturbed wave functions Ψ_n^0,

$$\Psi_n = \Psi_n^0 + \sum_{n' \neq n} c_n'(t)\, \Psi_{n'}^0 \,. \tag{15}$$

The set of the unperturbed wave functions satisfies the equation

$$i\,\hbar\,\dot{\Psi}_n^0 = \mathscr{H}_0\, \Psi_n^0 \tag{16}$$

and has the form

$$\Psi_n^0 = \psi_n^0 \exp\left(-\,i\, E_n\, t/\hbar\right) \tag{17}$$

where ψ_n^0 is the unperturbed stationary (time-independent) wave function and E_n denotes its eigenvalue. If we consider up to second-order time-dependent perturbation terms, the time derivative of the coefficient appeared in Eq. (15) comes out to be

$$\begin{aligned} i\,\hbar\, c_n' &= \langle n' \mid \mathscr{H}^{(1)} \mid n\rangle \operatorname{ixp}\{\nu\,(n'\,n)\,t\} + \\ &+ \langle n' \mid \mathscr{H}^{(2)} \mid n\rangle \operatorname{ixp}\{\nu\,(n'\,n)\,t\} + \\ &+ \sum_{n'' \neq n} c_{n''}\, \langle n' \mid \mathscr{H}^{(1)} \mid n''\rangle \operatorname{ixp}\{\nu\,(n'\,n'')\,t\}\,. \end{aligned} \tag{18}$$

Here we have introduced the frequencies

$$\nu\,(n'\,n) = (E_{n'} - E_n)\,/\,\hbar \tag{19}$$

and the matrix elements of the perturbation operator $\mathscr{H}^{(1)}$ and $\mathscr{H}^{(2)}$ defined with respect to the unperturbed time-independent wave functions ψ_n^0,

$$\langle n' \mid \mathscr{H}^{(1)} \mid n\rangle = \int \psi_{n'}^{0*}\, \mathscr{H}^{(1)}\, \psi_n^0\, dv\,. \tag{20}$$

In Eq. (18), the first term determines the perturbed wave function Ψ_n in the first order approximation and the remaining terms give the second order correction.

Substituting Eqs. (8) and (9) into Eq. (18), and integrating with respect to time (the constant of integration is chosen so that $c_{n'} = 0$ at $t = 0$), one obtains

$$\begin{aligned} c_{n'} = \frac{1}{2\,\hbar}\Bigg[& \frac{i\,\nu\,(n'\,n)}{c} \{(\langle n' \mid \mathfrak{R} \mid n\rangle, \mathfrak{a}_0^0)\, F_+(n'\,n) + (\langle n' \mid \mathfrak{R} \mid n\rangle, \mathfrak{a}_0^{0\dagger})\, F_-(n'\,n)\} + \\ & + \frac{1}{2\,\pi} \{(\langle n' \mid \mathfrak{M} \mid n\rangle, [\nabla, \mathfrak{a}]_0^0)\, F_+(n'\,n) + (\langle n' \mid \mathfrak{M} \mid n\rangle, [\Delta, \mathfrak{a}]_0^{0\dagger})\, F_-(n'\,n)\} + \\ & + \frac{1}{\pi}\, \nu^{-1}(n'\,n)\, (\langle n' \mid \mathfrak{M} \mid n\rangle, \mathfrak{H}^f) \operatorname{ixp}\{\nu\,(n'\,n)\,t\} - \\ & - \frac{e}{4\,\pi\, m\, c^2} \{(\langle n' \mid \mathfrak{R} \mid n\rangle, [\mathfrak{a}_0^0, \mathfrak{H}^f])\, F_+(n'\,n) + (\langle n' \mid \mathfrak{R} \mid n\rangle, [\mathfrak{a}_0^{0\dagger}, \mathfrak{H}^f])\, F_-(n'\,n)\}\Bigg] + \\ & + \frac{1}{4\,\pi\, c\,\hbar^2} \sum_{n'' \neq n} [i\,\nu\,(n''\,n)\, \{[\nu\,(n''\,n) + \nu]^{-1} (\langle n'' \mid \mathfrak{R} \mid n\rangle, \mathfrak{a}_0^0)\, F_+(n'\,n) + \\ & + [\nu\,(n''\,n) - \nu]^{-1} (\langle n'' \mid \mathfrak{R} \mid n\rangle, \mathfrak{a}_0^{0\dagger})\, F_-(n'\,n)\} (\langle n' \mid \mathfrak{M} \mid n''\rangle . \mathfrak{H}^f) + \\ & + i\,\nu\,(n'\,n'')\, \nu^{-1}(n''\,n)\, \{(\langle n' \mid \mathfrak{R} \mid n''\rangle, \mathfrak{a}_0^0)\, F_+(n'\,n) + \\ & + (\langle n' \mid \mathfrak{R} \mid n''\rangle, \mathfrak{a}_0^{0\dagger})\, F_-(n'\,n)\} (\langle n'' \mid \mathfrak{M} \mid n\rangle, \mathfrak{H}^f) + \\ & + \frac{c}{2\,\pi} \{[\nu\,(n''\,n) + \nu]^{-1} (\langle n'' \mid \mathfrak{M} \mid n\rangle, [\nabla, \mathfrak{a}]_0^0)\, F_+(n'\,n) + \\ & + [\nu\,(n''\,n) - \nu]^{-1} (\langle n'' \mid \mathfrak{M} \mid n\rangle, [\nabla, \mathfrak{a}]_0^{0\dagger})\, F_-(n'\,n)\} (\langle n' \mid \mathfrak{M} \mid n''\rangle, \mathfrak{H}^f) + \\ & + \frac{c}{2\,\pi}\, \nu^{-1}(n''\,n)\, \{(\langle n' \mid \mathfrak{M} \mid n''\rangle, [\nabla, \mathfrak{a}]_0^0)\, F_+(n'\,n) + \\ & + (\langle n' \mid \mathfrak{M} \mid n''\rangle, [\nabla, \mathfrak{a}]_0^{0\dagger})\, F_-(n'\,n)\} (\langle n' \mid \mathfrak{M} \mid n\rangle, \mathfrak{H}^f)] \end{aligned} \tag{21}$$

where

$$F_{+}(n'\,n) = \operatorname{ixp}\{[\nu(n'\,n)+\nu]\,t\}\,/\,[\nu(n'\,n)+\nu]$$

and

$$F_{-}(n'\,n) = \operatorname{ixp}\{[\nu(n'\,n)-\nu]\,t\}\,/\,[\nu(n'\,n)-\nu]\,. \tag{22}$$

In deriving Eq. (21), all terms containing square powers of the field strenghts of both the light wave and the external magnetic fields have been neglected.

3. Expectation Values of the Induced Electric and Magnetic Moments

Let the general moment operator be $\mathscr{M}$. The expectation value of $\mathscr{M}$ in the perturbed state n

$$\langle\mathscr{M}\rangle_n = \int \Psi_n^{\dagger}\,\mathscr{M}\,\Psi_n\,dv \tag{23}$$

is easily calculated with Eqs. (15) and (21), using the relations of Eqs. (12) and (13) and their time derivatives

$$\dot{\mathfrak{a}}_0 = i\,\pi\,\nu\,\{\mathfrak{a}_0^0\operatorname{ixp}(\nu t) - \mathfrak{a}_0^{0\dagger}\operatorname{ixp}(-\nu t)\} \tag{24}$$

$$[\nabla,\mathfrak{a}]_0^0 = i\,\pi\,\nu\,\{[\nabla,\mathfrak{a}]_0^0\operatorname{ixp}(\nu t) - [\nabla,\mathfrak{a}]_0^{0\dagger}\operatorname{ixp}(-\nu t)\}\,. \tag{25}$$

In this case, it is convenient to express the vector potential in terms of the field strengths $\mathfrak{E}$ and $\mathfrak{H}$: i.e.

$$\begin{gathered} 4\,\pi\,\nu^2\,\mathfrak{a}_0 = c\,\dot{\mathfrak{E}}, \qquad [\nabla,\mathfrak{a}]_0^0 = \mathfrak{H} \\ \dot{\mathfrak{a}}_0 = -\,c\,\mathfrak{E},\ [\nabla,\dot{\mathfrak{a}}]_0^0 = \mathfrak{H}\,. \end{gathered} \tag{26}$$

Then one obtains

$$\begin{aligned} \langle\mathscr{M}\rangle_n = {} & \langle n\,|\,\mathscr{M}\,|\,n\rangle + \frac{1}{\pi h}\,\mathscr{Re}\sum_{n'\neq n}\langle n\,|\,\mathscr{M}\,|\,n'\rangle\,\{\nu^{-2}\,\tau(n'\,n)\,(\langle n'\,|\,\mathfrak{R}\,|\,n\rangle, \\ & 2\,\pi\nu^2\,\nu(n'\,n)\,\mathfrak{E} + i\nu^2(n'\,n)\,\dot{\mathfrak{E}}) + \tau(n'\,n)\,(\langle n'\,|\,\mathfrak{M}\,|\,n\rangle, 2\,\pi\nu(n'\,n)\,\mathfrak{H} + i\,\dot{\mathfrak{H}}) - \\ & - (e/4\,\pi mc)\,\nu^{-2}\,\tau(n'\,n)\,(\langle n'\,|\,\mathfrak{R}\,|\,n\rangle, \nu(n'\,n)\,[\dot{\mathfrak{E}},\mathfrak{H}^f] - 2\,\pi\,i\nu^2\,[\mathfrak{E},\mathfrak{H}^f]) + \\ & + 2\,\pi\nu^{-1}(n'\,n)\,(\langle n'\,|\,\mathfrak{M}\,|\,n\rangle, \mathfrak{H}^f)\} + \\ & + (1/\pi\,h^2)\,\mathscr{Re}\sum_{n'\neq n}\ \sum_{n''\neq n}\langle n\,|\,\mathscr{M}\,|\,n'\rangle\,[(\langle n'\,|\,\mathfrak{M}\,|\,n''\rangle, \mathfrak{H}^f)\,\{\nu^{-2}\,\tau(n'\,n)\,\tau(n''\,n)\times \\ & \times(\langle n''\,|\,\mathfrak{R}\,|\,n\rangle, i\nu(n''\,n)\,[\nu(n'\,n)\,\nu(n''\,n)+\nu^2]\,\dot{\mathfrak{E}} + 2\,\pi\nu^2\,\nu(n''\,n)\ [\nu(n'\,n) + \\ & + \nu(n''\,n)]\,\mathfrak{E}) + \tau(n'\,n)\,\tau(n''\,n)\,(\langle n''\,|\,\mathfrak{M}\,|\,n\rangle, 2\,\pi\,[\nu(n'\,n)\,\nu(n''\,n)+\nu^2]\,\mathfrak{H} + \\ & + i\,[\nu(n'\,n)+\nu(n''\,n)]\,\dot{\mathfrak{H}})\} + \\ & + (\langle n''\,|\,\mathfrak{M}\,|\,n\rangle, \mathfrak{H}^f)\,\{\nu^{-2}\,\nu^{-1}(n''\,n)\,\tau(n'\,n)\,(\langle n'\,|\,\mathfrak{M}\,|\,n''\rangle, 2\,\pi\nu^2\,\nu(n'\,n'')\,\mathfrak{E} + \\ & + i\nu(n'\,n'')\,\nu(n'\,n)\,\dot{\mathfrak{E}}) + \nu^{-1}(n''\,n)\,\tau(n'\,n)\,(\langle n'\,|\,\mathfrak{M}\,|\,n''\rangle, 2\,\pi\nu(n'\,n)\,\mathfrak{H} + i\,\dot{\mathfrak{H}})\}] + \\ & + (1/2\pi\,h^2)\,\mathscr{Re}\sum_{n'\neq n}\ \sum_{n''\neq n}\langle n'\,|\,\mathscr{M}\,|\,n''\rangle\,[(\langle n''\,|\,\mathfrak{M}\,|\,n\rangle, \mathfrak{H}^f)\,\{\nu^{-2}\,\nu^{-1}(n''\,n)\,\tau(n'\,n)\times \\ & \times(\langle n\,|\,\mathfrak{R}\,|\,n'\rangle, 2\,\pi\nu^2\,\nu(n'\,n)\,\mathfrak{E} - i\nu^2(n'\,n)\,\dot{\mathfrak{E}}) + \nu(n'\,n)\,\tau(n'\,n)\times \\ & \times(\langle n\,|\,\mathfrak{M}\,|\,n'\rangle, 2\,\pi\nu(n'\,n)\,\mathfrak{H} - i\dot{\mathfrak{H}})\} + (\langle n\,|\,\mathfrak{M}\,|\,n'\rangle, \mathfrak{H}^f)\,\{\nu^{-2}\nu^{-1}(n'\,n)\,\tau(n''\,n)\times \\ & \times(\langle n''\,|\,\mathfrak{R}\,|\,n\rangle, 2\,\pi\nu^2\,\nu(n''\,n)\,\mathfrak{E} + i\nu^2(n''\,n)\,\dot{\mathfrak{E}}) + \nu^{-1}(n'\,n)\,\tau(n''\,n)\times \\ & \times(\langle n''\,|\,\mathfrak{M}\,|\,n\rangle, 2\,\pi\nu(n''\,n)\,\mathfrak{H} + i\dot{\mathfrak{H}})\}]\,. \end{aligned} \tag{27}$$

Here we have used an abbreviated symbol

$$\tau(n'\,n) = 1\,/\,[\nu^2(n'\,n) - \nu^2] \tag{28}$$

and $\mathscr{R}e$ means that we are to take the real part of the terms after each summation sign.

To obtain the average moment per molecule at a given temperature, we have to multiply B_n if B_n is the probability that the molecule will be found in state n with energy E_n at this temperature, and sum over all possible n (n also includes both vibrational and rotational quantum numbers). The Boltzmann factor B_n under the influence of the external magnetic field is

$$\begin{aligned} B_n &= \exp\left(-E_n / kT\right) / \sum_{n'} \exp\left(-E_n' / kT\right) \\ &= \exp\left\{-E_n^0 + (\langle n \mid \mathfrak{M} \mid n\rangle, \mathfrak{H}^f)\right\} / kT / \sum_{n'} \exp\left(-E_n' / kT\right). \end{aligned} \tag{29}$$

Expanding the numerator and taking only the term linear in $\mathfrak{H}^f$, one obtains

$$B_n = B_n^0 \left\{1 + (\langle n \mid \mathfrak{M} \mid n\rangle, \mathfrak{H}^f) / kT\right\} \tag{30}$$

where

$$B_n^0 = \exp\left(-E_n^0 / kT\right) / \sum_{n'} \exp\left(-E_{n'} / kT\right) \tag{31}$$

and B_n^0 corresponds to the probability of state n without any perturbations. The expectation value of the general moment per molecule at a given temperature T then comes out to be

$$\begin{aligned} \langle \mathscr{M} \rangle_{nT} = \sum_n \Big[& \langle \mathscr{M} \rangle_n + (1 / kT) (\langle n \mid \mathfrak{M} \mid n\rangle, \mathfrak{H}^f) \langle n \mid \mathscr{M} \mid n\rangle + \\ & + (1 / \pi h\, kT)\, \mathscr{R}e \sum_{n' \neq n} \{\nu^{-2} \tau (n'\, n) (\langle n' \mid \mathfrak{N} \mid n\rangle, i\nu^2 (n'\, n) \dot{\mathfrak{E}} + \\ & + 2\pi\nu^2 \nu (n'\, n)\, \mathfrak{E}) + (\langle n' \mid \mathfrak{M} \mid n\rangle, 2\pi\nu (n'\, n)\, \mathfrak{H} + i\dot{\mathfrak{H}}) + \\ & + (e / 4\pi mc)\, \nu^{-2} \tau (n'\, n) (\langle n' \mid \mathfrak{N} \mid n\rangle, \nu (n'\, n) [\dot{\mathfrak{E}}, \mathfrak{H}^f] - \\ & - 2\pi\nu^2 [\mathfrak{E}, \mathfrak{H}^f]\} (\langle n \mid \mathfrak{M} \mid n\rangle, \mathfrak{H}^f) \langle n \mid \mathscr{M} \mid n'\rangle \Big] \end{aligned} \tag{32}$$

where the first term $\langle \mathscr{M} \rangle_n$ has the same expression as Eq. (27). Thus the temperature-dependent paramagnetic terms are introduced.

Since we are interested in obtaining the averaged components of moment $\mathscr{M}$ in the directions of the fields $\mathfrak{E}$, $\mathfrak{H}$, and $\mathfrak{H}^f$, we have to average Eq. (32) over all classical orientations of the molecule with respect to the field directions, assuming all orientations to have an equal probability. This procedure is equivalent to taking a summation over all rotational quantum numbers in state functions, as NIESSEN has shown before [*9*]. Let $\mathfrak{A}$, $\mathfrak{B}$, and $\mathfrak{C}$ be vectors rigidly fixed to the freely rotating molecule, such as the electric and magnetic moment vectors. Then the average values of the vector quantities appeared in Eq. (32) take the form

$$\begin{aligned} \overline{\mathfrak{A}\, (\mathfrak{B}, \mathfrak{E})} &= \tfrac{1}{3}\, (\mathfrak{A}, \mathfrak{B})\, \mathfrak{E} \\ \overline{\mathfrak{A}\, (\mathfrak{B}, \mathfrak{H}^f)\, (\mathfrak{C}, \mathfrak{E})} &= \tfrac{1}{6}\, \mathfrak{A}\, \mathfrak{B}\, \mathfrak{C}\, [\mathfrak{H}^f, \mathfrak{E}] \end{aligned} \tag{33}$$

where $\mathfrak{A}\, \mathfrak{B}\, \mathfrak{C}$ denotes the scalar triple product.

The average electric and magnetic moments of the molecule in state n can be obtained from Eqs. (32) and (27) by substituting $\mathfrak{N}$ and $\mathfrak{M}$ for $\mathscr{M}$, respectively, and by taking the average through the formulae given in Eq. (33). One may put $\overline{\langle n \mid \mathfrak{N} \mid n\rangle}$ and $\overline{\langle n \mid \mathfrak{M} \mid n\rangle}$ equal to zero for diamagnetic molecules, when the orientating effect of the external field is neglected. Since an actual magnetic moment operator has the form

$$(e / 2\,c) \sum_j [\mathfrak{r}_j, \dot{\mathfrak{r}}_j] = \mathfrak{M} - (e^2 / 2\,mc^2) \sum_j [\mathfrak{r}_j, \mathfrak{A}_j] \tag{34}$$

the second term produces a perturbation and yields a time- and temperature-independent diamagnetic contribution. This procedure was shown by GROENEWEGE [*3*]. For the induced average electric moment per molecule, one finally obtains

$$\begin{aligned}\overline{\langle \mathfrak{R} \rangle}_{nT} = {} & A_1\,\mathfrak{E} + A_2\,\dot{\mathfrak{H}} + A_3\,\mathfrak{H} + A_4\,[\dot{\mathfrak{E}}, \mathfrak{H}^f] + A_5\,[\mathfrak{E}, \mathfrak{H}^f] + \\ & + A_6\,[\dot{\mathfrak{H}}, \mathfrak{H}^f] + A_7\,[\mathfrak{H}, \mathfrak{H}^f]\end{aligned} \tag{35}$$

where

$$A_1 = (2/3\,h) \sum_n B_n^0 \sum_{n' \neq n} \nu\,(n'\,n)\,\tau\,(n'\,n)\,|\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,|^2 \tag{36}$$

$$A_2 = -\,(1/3\,\pi h) \sum_n B_n^0\;\mathscr{I}m \sum_{n' \neq n} \tau\,(n'\,n)\,(\langle n \,|\, \mathfrak{R} \,|\, n' \rangle, \langle n' \,|\, \mathfrak{M} \,|\, n \rangle) \tag{37}$$

$$A_3 = (2/3\,h) \sum_n B_n^0\;\mathscr{R}e \sum_{n' \neq n} \nu\,(n'\,n)\,\tau\,(n'\,n)\,(\langle n \,|\, \mathfrak{R} \,|\, n' \rangle, \langle n' \,|\, \mathfrak{M} \,|\, n \rangle) \tag{38}$$

$$\begin{aligned}A_4 = {} & (1/6\,\pi\,h^2) \sum_n B_n^0\;\mathscr{I}m \sum_{n' \neq n} \sum_{n'' \neq n} [\nu^{-1}\,(n''\,n')\,\{\tau\,(n'\,n) - \tau\,(n''\,n)\}\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\times \\ & \times \langle n' \,|\, \mathfrak{M} \,|\, n'' \rangle\,\langle n'' \,|\, \mathfrak{R} \,|\, n \rangle - 2\,\nu^{-2}\,\nu^{-1}\,(n''\,n)\,\nu^2\,(n'\,n)\,\tau\,(n'\,n)\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\times \\ & \times \langle n' \,|\, \mathfrak{R} \,|\, n'' \rangle\,\langle n'' \,|\, \mathfrak{M} \,|\, n \rangle - \nu^{-2}\,\nu\,(n'\,n)\,\tau\,(n'\,n)\,\{\langle n \,|\, \mathfrak{R} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{M} \,|\, n \rangle + \\ & + \langle n \,|\, \mathfrak{M} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{R} \,|\, n \rangle - (h\,/\,kT)\,\nu^{-2}\,\nu^2\,(n'\,n)\,\tau\,(n'\,n)\,\times \\ & \times \langle n \,|\, \mathfrak{M} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{R} \,|\, n \rangle]\end{aligned} \tag{39}$$

$$\begin{aligned}A_5 = {} & -\,(1/3\,h^2) \sum_n B_n^0\;\mathscr{R}e \sum_{n' \neq n} \sum_{n'' \neq n} [\{\nu\,(n'\,n)\,\nu\,(n''\,n) - \nu^2\}\,\tau\,(n'\,n)\,\tau\,(n''\,n)\,\times \\ & \times \langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{M} \,|\, n'' \rangle\,\langle n'' \,|\, \mathfrak{R} \,|\, n \rangle - \\ & - \nu^{-1}\,(n''\,n)\,\nu\,(n''\,n')\,\tau\,(n''\,n)\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{R} \,|\, n'' \rangle\,\langle n'' \,|\, \mathfrak{M} \,|\, n \rangle - \\ & - \tau\,(n'\,n)\,\{\langle n \,|\, \mathfrak{R} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{M} \,|\, n \rangle + \\ & + \langle n \,|\, \mathfrak{M} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{R} \,|\, n \rangle\} - \\ & - (h/kT)\,\nu\,(n'\,n)\,\tau\,(n'\,n)\,\langle n \,|\, \mathfrak{M} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{R} \,|\, n \rangle]\end{aligned} \tag{40}$$

$$\begin{aligned}A_6 = {} & (1/6\,\pi h^2) \sum_n B_n^0\;\mathscr{I}m \sum_{u' \neq n} \sum_{n'' \neq n} [\nu^{-1}\,(n''\,n)\,\{\nu\,(n'\,n)\,\nu\,(n''\,n) + \nu^2\}\,\tau\,(n'\,n)\,\tau\,(n''\,n)\,\times \\ & \times \langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{M} \,|\, n'' \rangle\,\langle n'' \,|\, \mathfrak{M} \,|\, n \rangle + \\ & + \nu^{-1}\,(n''\,n)\,\tau\,(n'\,n)\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{R} \,|\, n'' \rangle\,\langle n'' \,|\, \mathfrak{M} \,|\, n \rangle - \\ & - (h/kT)\,\tau\,(n'\,n)\,\langle n \,|\, \mathfrak{M} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{M} \,|\, n \rangle]\end{aligned} \tag{41}$$

$$\begin{aligned}A_7 = {} & -\,(1/3\,h^2) \sum_n B_n^0\;\mathscr{R}e \sum_{n' \neq n} \sum_{n'' \neq n} [\nu^{-1}\,(n''\,n)\,\nu^{-1}\,(n''\,n')\,\nu^2\,\{\tau\,(n'\,n) - \tau\,(n''\,n)\}\,\times \\ & \times \langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{M} \,|\, n'' \rangle\,\langle n'' \,|\, \mathfrak{M} \,|\, n \rangle - \\ & - (h/kT)\,\nu\,(n'\,n)\,\tau\,(n'\,n)\,\langle n \,|\, \mathfrak{M} \,|\, n \rangle\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,\langle n' \,|\, \mathfrak{M} \,|\, n \rangle]\,.\end{aligned} \tag{42}$$

Here it should be noted that since one *has to* use complex wave functions (see Introduction), $(\langle n \,|\, \mathfrak{R} \,|\, n' \rangle, \langle n' \,|\, \mathfrak{R} \,|\, n \rangle) = |\,\langle n \,|\, \mathfrak{R} \,|\, n' \rangle\,|^2$ is real but the other vector quantities including the scalar triple products can be complex. We have replaced the $\mathscr{R}e$ symbol to $\mathscr{I}m$ symbol in Eqs. (37), (39), and (41), according to, for example,

$$\mathscr{R}e \sum_{n' \neq u} i\,(\langle n \mid \mathfrak{R} \mid n' \rangle, \langle n' \mid \mathfrak{M} \mid n \rangle) = -\,\mathscr{I}m \sum_{n' \neq n} (\langle n \mid \mathfrak{R} \mid n' \rangle, \langle n' \mid \mathfrak{M} \mid n \rangle)\,.$$

The first coefficient A_1 of Eq. (35) which form is shown in Eq. (36) corresponds to the polarizability of the molecule.

In the same way, one can obtain the expression for the induced average magnetic moment per molecule:

$$\begin{aligned}\overline{\langle \mathfrak{M} \rangle_{nT}} = {} & B_1\,\mathfrak{H} + B_2\,\dot{\mathfrak{E}} + B_3\,\mathfrak{E} + B_4\,[\dot{\mathfrak{H}}, \mathfrak{H}^f] + B_5\,[\mathfrak{H}, \mathfrak{H}^f] + \\ & + B_6\,[\dot{\mathfrak{E}}, \mathfrak{H}^f] + B_7\,[\mathfrak{E}, \mathfrak{H}^f] + (\chi_p + \chi_d)\,\mathfrak{H}^f\end{aligned} \tag{43}$$

where

$$B_1 = (2/3\,h) \sum_n B_n^0 \sum_{n' \neq n} \nu\,(n'\,n)\,\tau\,(n'\,n)\,|\,\langle n \mid \mathfrak{M} \mid n' \rangle\,|^2 \tag{44}$$

$$B_2 = -\,(1/3\,\pi h) \sum_n B_n^0\ \mathscr{I}m \sum_{n' \neq n} \nu^{-2}\,\nu^2\,(n'\,n)\,\tau\,(n'\,n)\,(\langle n \mid \mathfrak{M} \mid n' \rangle, \langle n' \mid \mathfrak{R} \mid n \rangle) \tag{45}$$

$$B_3 = (2/3\,h) \sum_n B_n^0\ \mathscr{R}e \sum_{n' \neq n} \nu\,(n'\,n)\,\tau\,(n'\,n)\,(\langle n \mid \mathfrak{M} \mid n' \rangle, \langle n' \mid \mathfrak{R} \mid n \rangle) \tag{46}$$

$$\begin{aligned}B_4 = {} & (1/6\,\pi h^2) \sum_n B_n^0\ \mathscr{I}m \sum_{n' \neq n} \sum_{n'' \neq n} [\nu^{-1}\,(n''\,n)\,\{2\,\nu^2 - \\ & - \nu\,(n''\,n)\,\nu\,(n''\,n')\}\,\tau\,(n'\,n)\,\tau\,(n''\,n)\,\langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{M} \mid n'' \rangle \langle n'' \mid \mathfrak{M} \mid n \rangle - \\ & - (h/kT)\,\tau\,(n'\,n)\,\langle n \mid \mathfrak{M} \mid n \rangle \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{M} \mid n \rangle]\end{aligned} \tag{47}$$

$$\begin{aligned}B_5 = {} & -\,(1/3\,h^2) \sum_n B_n^0\ \mathscr{R}e \sum_{n' \neq n} \sum_{n'' \neq n} [\{\nu\,(n'\,n)\,\nu\,(n''\,n) + \nu^2\}\,\tau\,(n'\,n)\,\tau\,(n''\,n) \times \\ & \times \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{M} \mid n'' \rangle \langle n'' \mid \mathfrak{M} \mid n \rangle - (h/kT)\,\nu\,(n'\,n)\,\tau\,(n'\,n) \times \\ & \times \langle n \mid \mathfrak{M} \mid n \rangle \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{M} \mid n \rangle]\end{aligned} \tag{48}$$

$$\begin{aligned}B_6 = {} & (1/6\,\pi h^2) \sum_n B_n^0\ \mathscr{I}m \sum_{n' \neq n} \sum_{n'' \neq n} [\nu^{-1}\,(n''\,n')\,\{\tau\,(n'\,n) - \tau\,(n''\,n)\}\,\langle n \mid \mathfrak{M} \mid n' \rangle \times \\ & \times \langle n' \mid \mathfrak{M} \mid n'' \rangle \langle n'' \mid \mathfrak{R} \mid n \rangle - \nu^{-2}\,\nu^{-1}\,(n''\,n)\,\nu^2\,(n'\,n)\,\tau\,(n'\,n)\,\{\langle n \mid \mathfrak{M} \mid n' \rangle \times \\ & \times \langle n' \mid \mathfrak{R} \mid n'' \rangle \langle n'' \mid \mathfrak{M} \mid n \rangle + \langle n \mid \mathfrak{R} \mid n' \rangle \langle n' \mid \mathfrak{M} \mid n'' \rangle \langle n'' \mid \mathfrak{M} \mid n \rangle\} - \\ & - \nu^{-2}\,\nu\,(n'\,n)\,\tau\,(n'\,n)\,\{\langle n \mid \mathfrak{R} \mid n \rangle \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{M} \mid n \rangle + \\ & + \langle n \mid \mathfrak{M} \mid n \rangle \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{R} \mid n \rangle\} - \\ & - (h/kT)\,\nu^{-2}\,\nu^2\,(n'\,n)\,\tau\,(n'\,n)\,\langle n \mid \mathfrak{M} \mid n \rangle \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{R} \mid n \rangle]\end{aligned} \tag{49}$$

$$\begin{aligned}B_7 = {} & -\,(1/3\,h^2) \sum_n B_n^0\ \mathscr{R}e \sum_{n' \neq n} \sum_{n'' \neq n} [\{\nu^2 + \nu\,(n'\,n)\,\nu\,(n''\,n)\}\,\tau\,(n'\,n)\,\tau\,(n''\,n) \times \\ & \times \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{M} \mid n'' \rangle \langle n'' \mid \mathfrak{R} \mid n \rangle - \nu^{-1}\,(n''\,n)\,\nu\,(n'\,n)\,\tau\,(n'\,n) \times \\ & \times \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{R} \mid n'' \rangle \langle n'' \mid \mathfrak{M} \mid n \rangle - (h/kT)\,\nu\,(n'\,n)\,\tau\,(n'\,n) \times \\ & \times \langle n \mid \mathfrak{M} \mid n \rangle \langle n \mid \mathfrak{M} \mid n' \rangle \langle n' \mid \mathfrak{R} \mid n \rangle]\end{aligned} \tag{50}$$

$$\chi_p = (2/3\,h) \sum_n B_n^0 \sum_{n' \neq n} \nu\,(n'\,n)\,|\,\langle n \mid \mathfrak{M} \mid n' \rangle\,|^2 \tag{51}$$

$$\chi_d = -\,(e^2/6\,mc^2) \sum_n B_n^0 \sum_j \langle n \mid \mathfrak{r}_j^2 \mid n \rangle\,. \tag{52}$$

Here B_1 is the magnetic susceptibility, and χ_p and χ_d are the time- and temperature-dependent paramagnetic and diamagnetic susceptibilities, respectively.

4. Magneto-Optical Rotation

To complete the discussion of the relation between radiation of the plane of polarization and the field strengths, we consider an isotropic medium containing

N molecules per unit volume. When all molecules in the medium are assumed to be of the same kind and in the same state, the summation over n in the foregoing equations needs not be taken, the value of B_n^0 being put to be equal to unity in the case of diamagnetic molecules. For gases and vapours, we may assume that the effictive field acting on the molecule is set to be equal to the external field. The electric induction $\mathcal{D}$ and magnetic induction $\mathcal{B}$ in the medium may therefore be written as

$$\begin{aligned} \mathcal{D} &= \mathfrak{E} + 4\pi N \overline{\langle \mathfrak{R} \rangle_{nT}}\,, \\ \mathcal{B} &= \mathfrak{H} + 4\pi N \overline{\langle \mathfrak{M} \rangle_{nT}}\,. \end{aligned} \tag{53}$$

Substituting Eqs. (35) and (43) into Eq. (53), and discarding time-independent terms, one obtains

$$\begin{aligned} \mathcal{D} &= \alpha_1 \mathfrak{E} + \alpha_2 \mathfrak{H} + \alpha_3 [\mathfrak{E}, \mathfrak{H}^f] + \alpha_4 [\mathfrak{H}, \mathfrak{H}^f] \\ \mathcal{B} &= \beta_1 \mathfrak{H} + \beta_2 \mathfrak{E} + \beta_3 [\mathfrak{H}, \mathfrak{H}^f] + \beta_4 [\mathfrak{E}, \mathfrak{H}^f] \end{aligned} \tag{54}$$

where

$$\begin{aligned} \alpha_1 &= 1 + 4\pi N A_1 & \beta_1 &= 1 + 4\pi N B_1 \\ \alpha_2 &= 4\pi N (2\pi i\nu A_2 + A_3), & \beta_2 &= 4\pi N (2\pi i\nu B_2 + B_3) \\ \alpha_3 &= 4\pi N (2\pi i\nu A_4 + A_5), & \beta_3 &= 4\pi N (2\pi i\nu B_4 + B_5) \\ \alpha_4 &= 4\pi N (2\pi i\nu A_6 + A_7), & \beta_4 &= 4\pi N (2\pi i\nu B_6 + B_7)\,. \end{aligned} \tag{55}$$

Here it is noted that α_1 is the dielectric constant and β_1 is the permeability of the medium.

Substitution of Eq. (54) into Maxwell's equations

$$n [\mathfrak{k}, \mathfrak{E}] = \mathcal{B}, \quad n [\mathfrak{k}, \mathfrak{H}] = -\mathcal{D} \tag{56}$$

which are derived from his curl equations for the specified plane waves, and elimination of $\mathfrak{H}$ after neglecting higher powers of small quantities α_i and β_i ($i = 2, 3. 4$) yield

$$\begin{aligned} - n^2 [\mathfrak{k}, [\mathfrak{k}, \mathfrak{E}]] - \alpha_1 \beta_1 \mathfrak{E} + \{n (\beta_2 - \alpha_2) + n^2 (\beta_3/\beta_1) (\mathfrak{k}, \mathfrak{H}^f)\} [\mathfrak{k}, \mathfrak{E}] - \\ - \alpha_3 \beta_1 [\mathfrak{E}, \mathfrak{H}^f] - n (\alpha_4 - \beta_4) [\mathfrak{k}, [\mathfrak{E}, \mathfrak{H}^f]] = 0\,. \end{aligned} \tag{57}$$

The vector equation of this kind can be written as a system of homogeneous linear equations in E_x, E_y, and E_z which has non-trivial solutions only for specific values of the refractive index n. When directions of propagations of the radiation $\mathfrak{k}$ and of the external magnetic field $\mathfrak{H}^f$ are both taken to be z-axis, the determinantal equation from which the eigenvalues of n have to be determined is

$$\begin{vmatrix} n^2 - \alpha_1 \beta_1 - n (\alpha_4 - \beta_4) H^f & - n (\beta_2 - \alpha_2) - \{\beta_1 \alpha_3 + n^2 (\beta_3/\beta_1)\} H^f \\ n (\beta_2 - \alpha_2) + \{\beta_1 \alpha_3 + n^2 (\beta_3/\beta_1)\} H^f & n^2 - \alpha_1 \beta_1 - n (\alpha_4 - \beta_4) H^f \end{vmatrix} = 0 \tag{58}$$

where H^f denotes the magnitude of the external magnetic field along the z-axis. In order to obtain approximate eigenvalues of n, let us again retain only first powers of the small quantities α_i and β_i ($i = 2, 3, 4$). The result is

$$\begin{aligned} n_{r,l} = (\alpha_1 \beta_1)^{1/2} + \tfrac{1}{2} (\alpha_4 - \beta_4) H^f \mp \tfrac{1}{2} i (\alpha_2 - \beta_2) \pm \\ \pm \tfrac{1}{2} i (\alpha_3 \beta_1 + \beta_3 \alpha_1) (\alpha_1 \beta_1)^{-1/2} H^f \end{aligned} \tag{59}$$

where n_r and n_l are the refractive indices for right and left circularly polarized waves, respectively, n_r taking the upper sign and n_l the lower.

Hence the rotation of the plane of polarization per unit path length is given by

$$\begin{aligned}\varphi &= (\pi\nu/c)\,(n_l - n_r) = (i\,\pi\nu/c)\,\{\alpha_2 - \beta_2 - (\alpha_3\,\beta_1 + \beta_3\,\alpha_1)\,(\alpha_1\,\beta_1)^{-1/2}\,Hf\} \\ &= (8\,\pi^3\,N\nu^2/c)\,\{B_2 - A_2 + (A_4\,\beta_1 + B_4\,\alpha_1)\,(\alpha_1\,\beta_1)^{-1/2}\,Hf\}\,. \qquad (60)\end{aligned}$$

Since A_2 and B_2 are non-vanishing only for optically active molecules, the Verdet constant for ordinary (optically inactive) molecules can be expressed as

$$V = (8\,\pi^3\,N\nu^2/c)\,(A_4 + B_4) \qquad (61)$$

where α_1 and β_1 have been set equal to unity in accordance with our approximation taken about the effective field. In the absence of the external magnetic field, Eq. (61) leads to the formula for the rotation of the plane of polarization in optically active molecules:

$$\varphi' = (8\,\pi^3\,N\nu^2/c)\,(B_2 - A_2)\,. \qquad (62)$$

Substitution of Eqs. (37) and (45) into Eq. (62), after rewriting Eq. (45) as

$$\begin{aligned}&\mathscr{I}m \sum_{n' \neq n} \nu^{-2}\,\nu^2\,(n'\,n)\,\tau\,(n'\,n)\,(\langle n \mid \mathfrak{M} \mid n'\rangle, \langle n' \mid \mathfrak{R} \mid n\rangle) \\ &= \mathscr{I}m\,\{\nu^{-2}\,[\langle n \mid (\mathfrak{M}, \mathfrak{R}) \mid n\rangle - (\langle n \mid \mathfrak{M} \mid n\rangle, \langle n \mid \mathfrak{R} \mid n\rangle) + \\ &+ \sum_{n' \neq n} \tau\,(n'\,n)\,(\langle n \mid \mathfrak{M} \mid n'\rangle, \langle n' \mid \mathfrak{R} \mid n\rangle) \\ &= \mathscr{I}m \sum_{n' \neq n} \tau\,(n'\,n)\,(\langle n \mid \mathfrak{M} \mid n'\rangle, \langle n' \mid \mathfrak{R} \mid n\rangle) \\ &= -\,\mathscr{I}m \sum_{n' \neq n} \tau\,(n'\,n)\,(\langle n \mid \mathfrak{R} \mid n'\rangle, \langle n' \mid \mathfrak{M} \mid n\rangle)\,,\end{aligned}$$

gives

$$\varphi' = (16\,\pi^2\,N\nu^2/3\,hc) \sum_n B_n \sum_{n' \neq n} \tau\,(n'\,n)\,\mathscr{I}m\,(\langle n \mid \mathfrak{R} \mid n'\rangle, \langle n' \mid \mathfrak{M} \mid n\rangle) \qquad (63)$$

which is the well known formula for the natural optical rotation [2].

Rewriting the second and fourth terms of Eq. (39) and the first term of Eq. (47), and substituting them into Eq. (61), one obtains the final formula for the Verdet constant.

$$\begin{aligned}V = {} & (4\,\pi^2\,N\nu^2/3\,h^2\,c) \sum_n B_n^0\;\mathscr{I}m \sum_{n'} [-\,2\,\nu\,(n'\,n)\,\tau^2\,(n'\,n)\,\langle n' \mid \mathfrak{M} \mid n'\rangle\,\times \\ & \times \langle n \mid \mathfrak{R} \mid n'\rangle\,\langle n' \mid \mathfrak{R} \mid n\rangle - \nu^{-2}\,\nu\,(n'\,n)\,\tau\,(n'\,n)\,\{\langle n \mid \mathfrak{R} \mid n\rangle\,\langle n \mid \mathfrak{R} \mid n'\rangle\,\langle n' \mid \mathfrak{M} \mid n\rangle\,+ \\ & + \langle n \mid \mathfrak{M} \mid n\rangle\,\langle n \mid \mathfrak{R} \mid n'\rangle\,\langle n' \mid \mathfrak{R} \mid n\rangle\}\,+ \\ & + \sum_{n'' \neq n'} \nu^{-1}\,(n''\,n')\,\{\tau\,(n'\,n) - \tau\,(n''\,n)\}\,\langle n \mid \mathfrak{R} \mid n'\rangle\,\langle n' \mid \mathfrak{M} \mid n''\rangle\,\langle n'' \mid \mathfrak{R} \mid n\rangle\,- \\ & - 2 \sum_{n'' \neq n} \nu^{-1}\,(n''\,n)\,\tau\,(n'\,n)\,\langle n \mid \mathfrak{R} \mid n'\rangle\,\langle n' \mid \mathfrak{R} \mid n''\rangle\,\langle n'' \mid \mathfrak{M} \mid n\rangle\,+ \qquad (64) \\ & + \sum_{n'' \neq n} (\nu^{-1}\,(n''\,n')\,\{\tau\,(n'\,n) - \tau\,(n''\,n)\}\,- \\ & - 2\,\nu^{-1}\,(n''\,n)\,\tau\,(n'\,n))\,\langle n \mid \mathfrak{M} \mid n'\rangle\,\langle n' \mid \mathfrak{M} \mid n''\rangle\,\langle n'' \mid \mathfrak{M} \mid n\rangle]\,- \\ & - (4\,\pi^2\,N\nu^2/3\,h\,ckT) \sum_n B_n^0\,\mathscr{I}m \sum_{n' \neq n}\,\sum_{n'' \neq n} \tau\,(n'\,n)\,\times \\ & \times \{\langle n \mid \mathfrak{M} \mid n\rangle\,\langle n \mid \mathfrak{R} \mid n'\rangle\,\langle n' \mid \mathfrak{R} \mid n\rangle + \langle n \mid \mathfrak{M} \mid n\rangle\,\langle n \mid \mathfrak{M} \mid n'\rangle\,\langle n' \mid \mathfrak{M} \mid n\rangle\}\,.\end{aligned}$$

The first term here is the diamagnetic term and is the contribution of the Zeeman effect. As will be seen in a forthcoming paper, this term reduces to the so-called „normal'' Verdet constant

$$V_A = (4\,\pi e\,N\nu^2/3\,h\,mc^2)\sum_{n} B_n^0 \sum_{n'\neq n} \nu\,(n'\,n)\,\tau^2\,(n'\,n)\,|\,\langle n\,|\,\mathfrak{R}\,|\,n'\rangle\,|^2 \tag{65}$$

for linear molecules. The last terms of Eq. (64) are the temperature-dependent paramagnetic terms and are due to the altered distribution of molecules in the ground state caused by the external magnetic field. All other paramagnetic terms arise from the perturbation of the amplitude elements of the electric moment and the magnetic moment by the external magnetic field, and have the same frequency dependence as the temperature-dependent paramagnetic terms. In particular, terms which are proportional to the difference quotient $\nu^{-1}(n''n')\,\{\tau(n'n)-\tau(n''n)\}$ can be expanded in powers of $\nu\,(n''\,n')\,\tau\,(n'\,n)$ when this quantity is small; i.e.

$$\begin{aligned}&\nu^{-1}\,(n''\,n')\,\{\tau\,(n'\,n)-\tau\,(n''\,n)\}\\ &= 2\,\nu\,(n'\,n)\,\tau^2\,(n'\,n)\,\{1-2\,\nu\,(n'\,n)\,\nu\,(n''\,n')\,\tau\,(n'\,n)+\ldots.\}\,.\end{aligned} \tag{66}$$

When terms after the first are neglected, these paramagnetic terms (the third and the fifth terms in Eq. (64)) can be combined together with the first term of Eq. (64), which is diamagnetic. In that case, the Verdet constant can be written in the form

$$V = \nu^2 \sum_{n'} \{\tau^2\,(n'\,n)\,A\,(n'\,n) + \tau\,(n'\,n)\,B\,(n'\,n) + T^{-1}\,\tau\,(n'\,n)\,C\,(n'\,n)\}\,. \tag{67}$$

Eq. (67) agrees with the formula given by SERBER [*11*] except that the scalar triple products $\mathfrak{M}\,\mathfrak{M}\,\mathfrak{M}$ were absent in his formula, since he did not take into consideration the contribution of the induced magnetic moment. It also can be easily shown that the temperature-independent terms in Eq. (64) agree with Groenewege's formula.

The formula given in Eq. (64) is very convenient for actual computations of the Verdet constant of diamagnetic molecules. This will be seen in a forthcoming paper.

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