Electron-Electron Interaction in the Faraday Rotation

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It is shown that the electron-electron interaction has a little effect on the magneto-optical rotation, that is, the Frenkel exciton hardly contribute to the Faraday effect. Furthermore, it means that the anomalous magneto-optical dispersion at a helix-coil transition hardly occurs, being different from the result of natural optical rotation. The magneto-optical rotatory power is presented in the case of the Faraday and the Voigt configurations by making use of approximations as far as the electron-electron interaction is negligibly small.

1. Introduction

The natural optical rotation and the Faraday effect (or magneto-optical rotation) are very similar phenomena and there are, on the other hand, essentially different features between them. In the previous papers,[1,2] a general theory of the Faraday effect on the basis of the linear response theory for an external electromagnetic field is developed. By making use of this theory the natural optical rotation and the Faraday effect can be discussed from the same theoretical point of view. The genaral expressions for the Faraday rotation[3,4] hitherto obtained, however, are rather complicated in comparison with those for the natural optical rotation and it seems that the calculation for an actual molecule is very difficult, even by using approximations.

A helix-coil transition of polymers causes an anomalous dispersion in the natural optical rotation. Moffitt[5] has theoretically investigated this phenomenon by making use of the Frenkel exciton model for polymers. In the case of the Faraday effect, any similar studies have not been done yet.

In the present paper, we investigate the effects of the electron-electron interaction on the Faraday rotation in a polymer.

In sec. 2 it is proved by an approximate momentum conservation of the system that in the case of the Faraday effect the anomalous dispersion hardly occurs at the helix-coil transition in contrast with the case of the Moffitt theory in the natural optical rotation. In order to derive this conclusion, it is not necessary for us to have

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the knowldge of the magneto-optical rotatory power of monomers composing a polymer. In sec. 3 the total Hamiltonian of the system is presented in the general form. In sec. 4 we obtain a chain of the equations for coupled Green functions of various types. It has been proved that the electron-electron interaction has a little contribution to the Faraday rotation. In sec. 5, in order to investigate the magneto-optical rotatory dispersion we calculate the response function by using approximations in the cases of the Faraday and the Voigt configurations. Section 6 is devoted to sammary and discussion.

2. Formulation of the Faraday Rotation

In the previous paper,[1,2] a general formula for the Faraday effect was derived by the same method as that for the natural optical rotation, using the linear response theory.[6] The formula for the Faraday effect is represented by a response function between total electric current and electric dipole moment operators of the system.

Let us take the direction of the propagation of an incident monochromatic light of the angular frequency ω to be parallel to the z-axis in medium. Since the Faraday effect is caused by the zeroth-order term in the wave-number of light, the Faraday rotational angle $\phi(\omega)$ of the plane of polarized light per unit path length* is represented in the form[2]

$$\phi(\omega) = \frac{2\pi i}{Vc\hbar n_0(\omega)} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \ \theta(t) \langle [\mathscr{J}_x(t), \ \mu_y(0)] \rangle, \tag{1}$$

where $n_0(\omega)$ is the refractive index in the absence of a constant magnetic field and $\mathscr{J}(t)$ and $\mu(t)$ are the operators for the total electric current and the total electric dipole moment at time t, respectively. The triangular brackets denote the canonical ensemble average under the total Hamiltonian. The symbol $\theta(t)$ is defined by

$$\theta(t) = \begin{cases} 1 & \text{for} \quad t > 0 \\ 0 & \text{for} \quad t < 0, \end{cases}$$

where V is the volume of the system and c is the speed of light in vacuum.

The Faraday rotational angle $\phi(\omega)$ can be expressed in terms of the Fourier component of a Green function:

$$G_{xy}(\omega) = \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \ G_{xy}(t), \tag{2}$$

where

$$G_{xy}(t) = -\frac{i}{\hbar} \theta(t) \langle [\mathscr{J}_x(t), \ \mu_y(0)] \rangle. \tag{3}$$

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* The sense of rotation is defined so that positive ϕ corresponds to counterclockwise rotation as seen by an observer against the z direction of propagation of the incident light.

Substitution of eqs. (2) and (3) into eq. (1) leads to

$$\phi(\omega) = -\frac{2\pi}{Vcn_o(\omega)} G_{xy}(\omega).$$ (4)

The system under consideration is a polymer composed of similar monomers in the presence of a constant magnetic field $\boldsymbol{H}$. The x component of the total electric current operator and the y component of the total electric dipole moment operator at time t are given by

$$\mathscr{J}_x(t) = \frac{e}{m} \sum_n \sum_i \left\{ p_{xin}(t) - \frac{e}{c} A_x(\boldsymbol{r}_{in}(t)) \right\}$$ (5)

and

$$\mu_y(t) = \sum_n \sum_i \mu_y(\boldsymbol{r}_{in}(t)),$$ (6)

respectively, where e is the charge of an electron, m the mass of the electron, $\boldsymbol{r}_{in}$ and $\boldsymbol{p}_{in}$ the co-ordinate and the momentum of the ith electron in the nth monomer in the polymer, respectively, and $A(\boldsymbol{r}_{in})$ is the vector potential satisfying the equation

$$\mathrm{rot}_{in} A(\boldsymbol{r}_{in}) = \boldsymbol{H}.$$ (7)

3. Hamiltonian

The total Hamiltonian $\mathscr{H}$ of the system is expressed as

$$\mathscr{H} = \sum_n \sum_i \left\{ \frac{1}{2m} \left(\boldsymbol{p}_{in} - \frac{e}{c} A(\boldsymbol{r}_{in}) \right)^2 + v_n(\boldsymbol{r}_{in}) \right\} + \frac{1}{2} \sum_n \sum_{\substack{i \\ (i \neq j)}} \sum_j v_n'(\boldsymbol{r}_{in} - \boldsymbol{r}_{jn})$$
$$+ \frac{1}{2} \sum_n \sum_{\substack{m \\ (n \neq m)}} \sum_i \sum_j V_{nm}(\boldsymbol{r}_{in} - \boldsymbol{r}_{jm}) + \sum_n \sum_{\substack{m \\ (n \neq m)}} \sum_i v_m(\boldsymbol{r}_{in}),$$ (8)

where $v_n(\boldsymbol{r}_{in})$ is the interaction between the ith electron in the nth monomer and the nucleus in the nth monomer, $v_n'(\boldsymbol{r}_{in} - \boldsymbol{r}_{jn})$ the interaction between the ith and the jth electrons in the same nth monomer and $V_{nm}(\boldsymbol{r}_{in} - \boldsymbol{r}_{jm})$ is the interaction between the ith electron in the nth monomer and the jth electron in the mth monomer. The last term $v_m(\boldsymbol{r}_{in})$ on the right-hand side of eq. (8) denotes the interaction between the ith electron in the nth monomer and the nucleus in the mth monomer.

4. Green Functions

Let us α be an angle between the directions of the constant magnetic field $\boldsymbol{H}$ and the z-axis. We may assume without loss of generality that the x, y and z components of the constant magnetic field $\boldsymbol{H}$ are $H\sin\alpha$, 0 and $H\cos\alpha$, respectively. In calculating the Green function $G_{xy}(t)$, we take the time derivative of eq. (3) and can obtain the equation

$$-\frac{\hbar}{i}\frac{dG_{xy}(t)}{dt} = -\frac{i}{\hbar}\theta(t)\langle[[\mathscr{J}_x(t),\mathscr{H}],\mu_y(0)]\rangle. \tag{9}$$

By making use of the expression for Hamiltonian (8) and eq. (7),

$$[\mathscr{J}_x(t),\mathscr{H}] = -\frac{\hbar}{i}\frac{e}{mc}(\mathscr{J}(t)\times\boldsymbol{H})_x + \frac{e}{m}\sum_n\sum_i(p_{xin}\,v_n(\boldsymbol{r}_{in}(t)))$$

$$+\frac{e}{m}\sum_n\sum_{\substack{m\\(n\neq m)}}\sum_i(p_{xin}\,v_m(\boldsymbol{r}_{in}(t))). \tag{10}$$

Under the assumption that the interaction $v_m(\boldsymbol{r}_{in})$ $(n\neq m)$ between the electron in a monomer and the nucleus in the other monomer is negligibly small in comparison with the interaction $v_n(\boldsymbol{r}_{in})$ between the electron in a monomer and the nucleus in the same monomer, the last term on the right-hand side of eq. (10) can be neglected and eq. (9) reduces to

$$-\frac{\hbar}{i}\frac{dG_{xy}(t)}{dt} = -\frac{\hbar\omega_z}{i}G_{yy}(t) + \frac{e}{m}G^1_{xy}(t), \tag{11}$$

where $\omega_z = eH\cos\alpha/mc$, $G_{yy}(t)$ and a new Green function $G^1_{xy}(t)$ are given by

$$G_{yy}(t) = -\frac{i}{\hbar}\theta(t)\langle[\mathscr{J}_y(t),\mu_y(0)]\rangle \tag{12}$$

and

$$G^1_{xy}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{xin}\,v_n(\boldsymbol{r}_{in}(t))),\mu_y(0)]\rangle. \tag{13}$$

If we take the time derivative of $G_{yy}(t)$ on the right-hand side of eq. (12) in order to obtain $G_{xy}(t)$, it appears Green functions defined by

$$G_{zy}(t) = -\frac{i}{\hbar}\theta(t)\langle[\mathscr{J}_z(t),\mu_y(0)]\rangle \tag{14}$$

and

$$G^1_{yy}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{yin}\,v_n(\boldsymbol{r}_{in}(t))),\mu_y(0)]\rangle \tag{15}$$

and we obtain an equation for $G_{yy}(t)$

$$-\frac{\hbar}{i}\frac{dG_{yy}(t)}{dt} = \frac{\hbar}{i}\frac{Ne^2}{m}\delta(t) + \frac{\hbar\omega_z}{i}G_{xy}(t) - \frac{\hbar\omega_x}{i}G_{zy}(t) + \frac{e}{m}G^1_{yy}(t), \tag{16}$$

where N is the number of electrons in the system and $\omega_x = eH\sin\alpha/mc$. Similarly, the equation for Green function $G_{zy}(t)$ is derived in the form

$$-\frac{\hbar}{i}\frac{dG_{zy}(t)}{dt} = \frac{\hbar\omega_x}{i}G_{yy}(t) + \frac{e}{m}G^1_{zy}(t), \tag{17}$$

where

$$G^1_{zy}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{zin}\,v_n(\boldsymbol{r}_{in}(t))),\mu_y(0)]\rangle. \tag{18}$$

Furthermore, by differentiating eqs. (13), (15) and (18) with respect to time t, the following equations for $G_{\nu y}^1(t)$ ($\nu = x, y, z$) are found to be

$$-\frac{\hbar}{i}\frac{dG_{\nu y}^1(t)}{dt} = -\frac{1}{2m}G_{\nu y}^{21}(t) - \frac{1}{e}G_{\nu y}^{22}(t), \qquad (\nu = x, y, z) \tag{19}$$

where

$$G_{\nu y}^{21}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu (p_{\mu in}\,p_{\mu in}\,p_{\nu in}\,v_n(\mathbf{r}_{in}(t))), \mu_y(0)]\rangle \tag{20}$$

and

$$G_{\nu y}^{22}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu (p_{\mu in}\,p_{\nu in}\,v_n(\mathbf{r}_{in}(t)))\,\mathscr{J}_{\mu in}(t), \mu_y(0)]\rangle. \tag{21}$$

In this way, if we take the series of the time derivative for these Green functions, we obtain the coupled equations for the Green functions of various types. Since the terms $(p_{\nu in}\,v_n(\mathbf{r}_{in}(t)))$ ($\nu = x, y, z$) in eqs. (13), (15) and (18), however, are commutable with the parts of the electron-electron interactions $v_n'(\mathbf{r}_{in} - \mathbf{r}_{jn})$ and $V_{nm}(\mathbf{r}_{in} - \mathbf{r}_{jm})$ in the Hamiltonian $\mathscr{H}$ given by eq. (8), all the equations (i.e. eqs. (11), (16), (17), (19)) for the Green functions obtained in this way do not involve the Green functions for "the electron-electron interaction and the electric dipole moment" response.

If we take an assumption that Green functions $G_{xy}^{21}(t)$, $G_{yy}^{21}(t)$, $G_{zy}^{21}(t)$, $G_{xy}^{22}(t)$, $G_{yy}^{22}(t)$ and $G_{zy}^{22}(t)$ are represented in terms of the Green functions $G_{xy}(t)$, $G_{yy}(t)$, $G_{zy}(t)$, $G_{xy}^1(t)$, $G_{yy}^1(t)$ and $G_{zy}^1(t)$, the Green function $G_{xy}(t)$ is the same solution that we obtain in the case of no electron-electron interaction in the Hamiltonian (8) of the system in the presence of the constant magnetic field $\mathbf{H}$. Therefore, there is only the intrinsic optical rotation in the case of the Faraday effect.

In order to obtain the exact solution $G_{xy}(t)$ of the coupled equation for the Green functions, it is necessary for us to find the equations for $G_{\nu y}^{21}(t)$ and $G_{\nu y}^{22}(t)$ ($\nu = x, y, z$) defined by eqs. (20) and (21), respectively. By differentiating eqs. (20) and (21) with respect to time t, the equations for the Green functions $G_{\nu y}^{21}(t)$ and $G_{\nu y}^{22}(t)$ are derived being accompanied with the new type Green functions. The equation for $G_{\nu y}^{21}(t)$ becomes

$$-\frac{\hbar}{i}\frac{dG_{\nu y}^{21}(t)}{dt} = -\frac{1}{2m}G_{\nu y}^{311}(t) - \frac{1}{e}G_{\nu y}^{312}(t), \qquad (\nu = x, y, z) \tag{22}$$

where

$$G_{\nu y}^{311}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu\sum_{\mu'}(p_{\mu in}\,p_{\mu in}\,p_{\mu' in}\,p_{\mu' in}\,p_{\nu in}\,v_n(\mathbf{r}_{in}(t))), \mu_y(0)]\rangle, \tag{23}$$

$$G_{\nu y}^{312}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu\sum_{\mu'}(p_{\mu in}\,p_{\mu' in}\,p_{\mu' in}\,p_{\nu in}\,v_n(\mathbf{r}_{in}(t)))\,\mathscr{J}_{\mu in}(t), \mu_y(0)]\rangle \tag{24}$$

and the equation for $G_{\nu y}^{22}(t)$ can be expressed as

$$-\frac{\hbar}{i}\frac{dG_{\nu y}^{22}(t)}{dt} = \frac{\hbar}{i}\frac{e^2}{m}\langle\sum_n\sum_i(p_{yin}\,p_{\nu in}\,v_n(\mathbf{r}_{in}))\rangle\,\delta(t)$$

$$-\frac{1}{e}G_{\nu y}^{321}(t) - G_{\nu y}^{322}(t) + \frac{e}{m}G_{\nu y}^{323}(t) + \frac{e}{2m}G_{\nu y}^{324}(t) + \frac{1}{2m}G_{\nu y}^{325}(t), \tag{25}$$

where

$$G_{\nu y}^{321}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu\sum_{\mu'}(p_{\mu in}\,p_{\mu' in}\,p_{\nu in}\,v_n(r_{in}(t)))\,\mathscr{J}_{\mu in}(t)\,\mathscr{J}_{\mu' in}(t),\mu_y(0)]\rangle,$$

(26)

$$G_{\nu y}^{322}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\left\{\frac{1}{2m}\sum_\mu(p_{\mu in}\,p_{\mu in}\,\boldsymbol{p}_{in}\,p_{\nu in}\,v_n(r_{in}(t)))\right.$$

$$\left.+\frac{\hbar\boldsymbol{\omega}}{i}\times(\boldsymbol{p}_{in}\,p_{\nu in}\,v_n(r_{in}(t)))\right\}\cdot\mathscr{J}_{in}(t),\mu_y(0)]\rangle,$$

(27)

$$G_{\nu y}^{323}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu(p_{\mu in}\,p_{\nu in}\,v_n(r_{in}(t)))(p_{\mu in}\,v_n(r_{in}(t))),\mu_y(0)]\rangle,$$

(28)

$$G_{\nu y}^{324}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{\substack{i\ j\\(i\neq j)}}\sum_\mu\{(p_{\mu in}\,p_{\nu in}\,v_n(r_{in}(t))) - (p_{\mu jn}\,p_{\nu jn}\,v_n(r_{jn}(t)))\}$$

$$\times(p_{\mu in}v_n'(r_{in}(t) - r_{jn}(t))),\ \mu_y(0)]\rangle,$$

(29)

$$G_{\nu y}^{325}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{\substack{m\ i\ j\\(n\neq m)}}\sum_\mu\{(p_{\mu in}\,p_{\nu in}\,v_n(r_{in}(t))) - (p_{\mu jn}\,p_{\nu jn}\,v_n(r_{jn}(t)))\}$$

$$\times(p_{\mu in}V_{nm}(r_{in}(t) - r_{jm}(t))),\ \mu_y(0)]\rangle,$$

(30)

here a quantity $\boldsymbol{\omega}$ in eq. (27) denotes a vector whose components are $eH\sin\alpha/mc$, 0, $eH\cos\alpha/mc$, respectively, and use has been made of the relations between the constant magnetic field $\boldsymbol{H}$ and the vector potential $\boldsymbol{A}$ given by

$$A_x = -\frac{H}{2}y\,\cos\alpha,$$

(31)

$$A_y = \frac{H}{2}(x\,\cos\alpha - z\,\sin\alpha),$$

(32)

$$A_z = \frac{H}{2}y\,\sin\alpha.$$

(33)

It should be noted that the electron-electron interactions appear for the first time only in $G_{\nu y}^{324}(t)$ and $G_{\nu y}^{325}(t)$ on the right-hand side of eq. (25), which are defined by eqs. (29) and (30) with terms of the form $(p_{\mu in}v_n'(r_{in}-r_{jn}))$ and $(p_{\mu in}V_{nm}(r_{in}-r_{jm}))$, respectively. It seems to us that the electron-electron interaction has a little effect on the Faraday effect as compared with that exerted by the interactions between the electron and the nucleus in a monomer. Furthermore, the terms related to the electron-electron interaction as seen in eqs. (29) and (30) are of the form multiplied by $(p_{\mu in}p_{\nu in}v_n(r_{in})) - (p_{\mu jn}p_{\nu jn}v_n(r_{jn}))$. It states that the effects of the electron-electron interaction depend on the curvatures of the potential from uncleus.

5. Effects of the Intermonomeric Interaction

In the present section, the contribution of the electron-electron interaction to the Faraday effect is investigated. It is necessary for us to obtain the Green function $G_{xy}(t)$ by solving the coupled equations for the Green functions of various types. In order to solve these simultaneous equations, the equations for $G_{\nu y}^{311}(t)$, $G_{\nu y}^{312}(t)$, $G_{\nu y}^{321}(t)$, $G_{\nu y}^{322}(t)$, $G_{\nu y}^{323}(t)$, $G_{\nu y}^{324}(t)$, $G_{\nu y}^{325}(t)$ $(\nu = x,y,z)$ are necessary for us and those equations yield many Green functions of new types. Thus, such a successive calculation reaches the simultaneous equations of the form as an infinite chain of coupled equations. To investigate the effects of the electron-electron interaction, the calculations to solve the coupled equations are made using the approximation by the decoupling method. For approximate calculations the formula for the Faraday rotational angle ought to be of the form, instead of eq. (1),

$$\phi(\omega) = \frac{\pi i}{Vc\hbar n_0(\omega)} \int_{-\infty}^{\infty} dt e^{-i\omega t} \theta(t) \{\langle [\mathscr{J}_x(t), \mu_y(0)] \rangle - \langle [\mathscr{J}_y(t), \mu_x(0)] \rangle \} \qquad (34)$$

because of the loss of the antisymmetry property under interchange of x with y by acceptance of the approximations.

As far as we confine ourselves to treat no electron-electron interaction, which has a little effect shown in the preceding section, we can obtain the approximate solution by no use of eqs. (29) and (30). Thus, to investigate the magneto-optical rotatory dispersion we calculate the Green function $G_{xy}(t)$ by the approximations to simplify the complicated Green functions in the cases of the Faraday and Voigt configurations.

5. 1. *The case of the direction of the incident light to be parallel to the constant magnetic field (Faraday configuration)*

As the constant magnetic field is parallel to the z-axis (i.e. $\alpha = 0$), $\omega_x = \omega_y = 0$ and $\omega_z = eH/mc$. The simultaneous equations for the system under consideration are of the form

$$-\frac{\hbar}{i} \frac{dG_{xy}(t)}{dt} = -\frac{\hbar\omega_z}{i} G_{yy}(t) + \frac{e}{m} G_{xy}^1(t), \qquad (35)$$

$$-\frac{\hbar}{i} \frac{dG_{yy}(t)}{dt} = \frac{\hbar}{i} \frac{Ne^2}{m} \delta(t) + \frac{\hbar\omega_z}{i} G_{xy}(t) + \frac{e}{m} G_{yy}^1(t), \qquad (36)$$

$$-\frac{\hbar}{i} \frac{dG_{xy}^1(t)}{dt} = -\frac{1}{2m} G_{xy}^{21}(t) - \frac{1}{e} G_{xy}^{22}(t), \qquad (37)$$

$$-\frac{\hbar}{i} \frac{dG_{yy}^1(t)}{dt} = -\frac{1}{2m} G_{yy}^{21}(t) - \frac{1}{e} G_{yy}^{22}(t), \qquad (38)$$

where

$$G_{\nu y}(t) = -\frac{i}{\hbar} \theta(t) \langle [\mathscr{J}_\nu(t), \mu_y(0)] \rangle, \qquad (39)$$

$$G^1_{\nu y}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{\nu in}\,v_n(\boldsymbol{r}_{in}(t))),\,\mu_y(0)]\rangle, \tag{40}$$

$$G^{21}_{\nu y}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu(p_{\mu in}\,p_{\mu in}\,p_{\nu in}\,v_n(\boldsymbol{r}_{in}(t))),\,\mu_y(0)]\rangle, \tag{41}$$

$$G^{22}_{\nu y}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{xin}\,p_{\nu in}\,v_n(\boldsymbol{r}_{in}(t)))\,\mathcal{A}_{xin}(t),\,\mu_y(0)]\rangle,$$
$$-\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{yin}\,p_{\nu in}\,v_n(\boldsymbol{r}_{in}(t)))\,\mathcal{A}_{yin}(t),\,\mu_y(0)]\rangle. \tag{42}$$
$$(\mu,\ \nu = x,\ y,\ z)$$

If we assume that $G^{21}_{\nu y}(t)$ and $G^{22}_{\nu y}(t)$ are expressed in terms of $G_{\nu y}(t)$ and $G^1_{\nu y}(t)$, we can obtain $G_{xy}(t)$ by solving the simultaneous equations given by eqs. (35)–(38). Then, we approximate the Green functions $G^{21}_{\nu y}(t)$ and $G^{22}_{\nu y}(t)$ defined by eqs. (41) and (42) to the form

$$G^{21}_{\nu y}(t) \approx \langle\sum_\mu p_{\mu in}\,p_{\mu in}\rangle G^1_{\nu y}(t) \tag{43}$$

and

$$G^{22}_{\nu y}(t) \approx \langle(p_{xin}\,p_{\nu in}\,v_n(\boldsymbol{r}_{in}))\rangle G_{xy}(t) + \langle(p_{yin}\,p_{\nu in}\,v_n(\boldsymbol{r}_{in}))\rangle G_{yy}(t), \tag{44}$$
$$(\mu,\ \nu = x,\ y,\ z)$$

respectively. Under these assumptions the rotational angle $\phi(\omega)$, which represents the magneto-optical rotatory dispersion, can be written as

$$\phi(\omega) = -\frac{2\pi N\hbar^2 e^3 H}{Vm^2c^2n_0(\omega)}\,\frac{\left(\hbar\omega - \frac{\langle p^2\rangle}{2m}\right)^2}{\left[\begin{array}{c}\left\{\left(\hbar\omega - \frac{\langle p^2\rangle}{4m}\right)^2 + \left(\frac{\langle p_x^2 v\rangle}{2m} + \frac{\langle p_y^2 v\rangle}{2m} - \frac{1}{4}\left(\frac{\langle p^2\rangle}{2m}\right)^2\right)\right\}^2 \\ -\left\{\left(\frac{\langle p_x^2 v\rangle}{2m} - \frac{\langle p_y^2 v\rangle}{2m}\right)^2 + \left(\frac{\langle p_x p_y v\rangle}{m}\right)^2\right\}\end{array}\right]}, \tag{45}$$

where

$$\langle p^2\rangle = \langle\sum_\mu p_{\mu in}\,p_{\mu in}\rangle, \tag{46}$$

$$\langle p_\nu^2 v\rangle = \langle(p_{\nu in}\,p_{\nu in}\,v_n(\boldsymbol{r}_{in}))\rangle, \tag{47}$$

$$\langle p_x p_y v\rangle = \langle(p_{xin}\,p_{yin}\,v_n(\boldsymbol{r}_{in}))\rangle. \tag{48}$$

5. 2. *The case of the direction of the incident light to be perpendicular to the constant magnetic field (Voigt configuration)*

As the constant magnetic field is parallel to the x-axis (i.e. $\alpha = \frac{\pi}{2}$), $\omega_x = eH/mc$, $\omega_y = \omega_z = 0$. The simultaneous equations are of the form

$$-\frac{\hbar}{i}\frac{dG_{xy}(t)}{dt}=\frac{e}{m}G_{xy}^1(t), \tag{49}$$

$$-\frac{\hbar}{i}\frac{dG_{yy}(t)}{dt}=\frac{\hbar}{i}\frac{Ne^2}{m}\delta(t)-\frac{\hbar\omega_x}{i}G_{zy}(t)+\frac{e}{m}G_{yy}^1(t), \tag{50}$$

$$-\frac{\hbar}{i}\frac{dG_{zy}(t)}{dt}=\frac{\hbar\omega_x}{i}G_{yy}(t)+\frac{e}{m}G_{zy}^1(t), \tag{51}$$

$$-\frac{\hbar}{i}\frac{dG_{xy}^1(t)}{dt}=-\frac{1}{2m}G_{xy}^{21}(t)-\frac{1}{e}G_{xy}^{22}(t), \tag{52}$$

$$-\frac{\hbar}{i}\frac{dG_{yy}^1(t)}{dt}=-\frac{1}{2m}G_{yy}^{21}(t)-\frac{1}{e}G_{yy}^{22}(t), \tag{53}$$

$$-\frac{\hbar}{i}\frac{dG_{zy}^1(t)}{dt}=-\frac{1}{2m}G_{zy}^{21}(t)-\frac{1}{e}G_{zy}^{22}(t), \tag{54}$$

where $G_{\nu y}(t)$, $G_{\nu y}^1(t)$, $G_{\nu y}^{21}(t)$ ($\nu=x, y, z$) are defined by eqs. (39), (40), (41), respectively, and $G_{\nu y}^{22}(t)$ is now defined by

$$G_{\nu y}^{22}(t)=-\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_\mu(p_{\mu in}p_{\nu in}v_n(r_{in}(t)))\mathscr{J}_{\mu in}(t), \mu_y(0)]\rangle. \tag{55}$$

$$(\mu, \nu=x, y, z)$$

We now assume by the similar fashion in the case of the Faraday configuration that $G_{\nu y}^{21}(t)$ is expressed as eq. (43) and $G_{\nu y}^{22}(t)$ is now of the form

$$G_{\nu y}^{22}(t)\approx\sum_\mu\langle(p_{\mu in}p_{\nu in}v_n(r_{in}))\rangle G_{\mu y}(t). \tag{56}$$

The calculations of eqs. (49)-(54) under these approximations lead to the rotational angle $\phi(\omega)$ which is slightly more complicated in comparison with that in the case of the Faraday configuration, that is

$$\phi(\omega)=-\frac{2\pi N\hbar^2e^3H}{Vm^2c^2n_0(\omega)}\frac{K\left(\hbar\omega-\frac{\langle p^2\rangle}{2m}\right)^2}{\left(\hbar\omega-\frac{\langle p^2\rangle}{4m}\right)^6+A\left(\hbar\omega-\frac{\langle p^2\rangle}{4m}\right)^4+B\left(\hbar\omega-\frac{\langle p^2\rangle}{4m}\right)^2+C}, \tag{57}$$

where

$$K=\frac{\langle p_z p_x v\rangle}{m}, \tag{58}$$

$$A=-3\left(\frac{\langle p^2\rangle}{4m}\right)^2+\frac{\langle p^2 v\rangle}{m}, \tag{59}$$

$$B = 3\left(\frac{\langle p^2 \rangle}{4m}\right)^4 - 2\left(\frac{\langle p^2 \rangle}{4m}\right)^2 \frac{\langle p^2 v \rangle}{m} + \frac{1}{3}\left(\frac{\langle p^2 v \rangle}{m}\right)^2$$

$$- \left\{ \left(\frac{\langle p_y p_z v \rangle}{m}\right)^2 + \left(\frac{\langle p_z p_x v \rangle}{m}\right)^2 + \left(\frac{\langle p_x p_y v \rangle}{m}\right)^2 \right\}, \tag{60}$$

$$C = -\left(\frac{\langle p^2 \rangle}{4m}\right)^6 + \left(\frac{\langle p^2 \rangle}{4m}\right)^4 \frac{\langle p^2 v \rangle}{m}$$

$$- \left(\frac{\langle p^2 \rangle}{4m}\right)^2 \left\{ \frac{1}{3}\left(\frac{\langle p^2 v \rangle}{m}\right)^2 - \left(\left(\frac{\langle p_y p_z v \rangle}{m}\right)^2 + \left(\frac{\langle p_z p_x v \rangle}{m}\right)^2 + \left(\frac{\langle p_x p_y v \rangle}{m}\right)^2\right)\right\}$$

$$+ \frac{1}{27}\left(\frac{\langle p^2 v \rangle}{m}\right)^3 + 2\frac{\langle p_y p_z v \rangle}{m}\frac{\langle p_z p_x v \rangle}{m}\frac{\langle p_x p_y v \rangle}{m}$$

$$- \frac{1}{3}\frac{\langle p^2 v \rangle}{m}\left(\left(\frac{\langle p_y p_z v \rangle}{m}\right)^2 + \left(\frac{\langle p_z p_x v \rangle}{m}\right)^2 + \left(\frac{\langle p_x p_y v \rangle}{m}\right)^2\right) \tag{61}$$

and use has been made of

$$\langle p_x^2 v \rangle = \langle p_y^2 v \rangle = \langle p_z^2 v \rangle = \frac{1}{3}\langle p^2 v \rangle \equiv \frac{1}{3}\left\langle \sum_\mu \left(p_{\mu in}\, p_{\mu in}\, v_n(r_{in})\right)\right\rangle. \tag{62}$$

6. Summary and Discussion

It has been seen that the Frenkel exciton, which originates in the electron-electron interaction, has a little effect on the Faraday rotation. If we calculate the Faraday rotation by using the conventional formula,[3,4] instead of our general one, it seems to be very difficult to prove that the Frenkel exciton has a little effect on the Faraday rotation. The validity of our results is clear by the reason that eq. (1) is given by the response functions of the total currents and the total electric dipole moments. It is an unexpected result that the Frenkel exciton has a little effect on the Faraday rotation in contrast with playing the essential role of the Frenkel exciton for the anomalous dispersion in the natural optical rotation.

In the present paper, we have neglected the electron-phonon interaction and the interaction between the electron in a monomer and the nucleus in the other monomer as it has been seen in eq. (11). These effects have been neglected in Moffitt's work[5] on the anomalous dispersion at the helix-coil transition in the natural optical rotation.

In the case of the helical homopolymers composed of the DNA-bases, it seems that the Frenkel exciton model is accepted. Although the theoretical result by Deutsche[7] has shown that the anomalous dispersion is not observed in the helical polymer which is exposed to the light travelling parallel to the helical axis, his result is not experimentally confirmed as far as we know.[8]

Although our results seem to be trivial, it is very important that the results are exact in regard to the intermonomeric interaction in the polymer. If we write eq. (1) using the representation in which the total Hamiltonian of the system is diagonalized and if we calculate it by the first order perturbation with respect to the intermonomeric interaction, we may obtain the term corresponding to that of the anomalous dispersion in natural optical rotation, in particular, in the case of the helical polymer oriented perpendicular to the direction of the propagation of light. The formulae for anomalous dispersion given theoretically by Moffitt[5] are calculated by means of a perturbation of the intermonomeric interaction.

One of the important differences between the Faraday effect and the natural optical rotation is that the former is caused by the zeroth-order term in the wave-number q of light, whereas the latter by the first-order term in q. If we take account of the first order in q, the formula for the natural optical rotation also will be expressed by the response functions of the total currents and any other physical quantities (for example, magnetic moments or electric quadrupole moments).[9] More presisely speaking, we suspect that the differences of our result in the Faraday effect and Moffitt's one in the natural optical rotation do not originate in the difference of q dependence on two phenonena as far as the anomalous dispersion is discussed.

Finally, the expressions for magneto-optical rotatory dispersion are presented by making use of the approximations, in the case of the Faraday and the Voigt configurations, when the effects of the electron-electron interaction are negligibly small. These approximations that the complicated Green functions are replaced by the simple one are somewhat ambiguous, because there is no first principle of the decoupling method for the Green functions. The expressions for the magneto-optical rotatory dispersion obtained by these approximations, however, can be considered to be reasonable.

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