Electron-Electron Interaction in Natural Optical Rotation

Yuji KATO*

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Effects of the electron-electron interaction on the natural optical rotation are investigated by a general formula for the Faraday effect expressed in terms of a correlation function of the spatial Fourier components of total electric current. It is proved that, in general, the electron-electron interaction is effective on the natural optical rotation in contrast with that on the Faraday rotation. Furthermore, it is shown as natural and preferable result that calculation of the natural optical rotation is quite complicated in contrast with that of the Faraday rotation, whereas in conventional formula the calculation of the natural optical rotation is easier than that of the Faraday rotation. The electron-electron interactions for the three-dimensional harmonic-oscillator model are also discussed.

1. Introduction

A number of theoretical investigations of natural optical activity has been made from various viewpoints and by various methods.[1-15] The natural optical activity has been able to investigate on the basis of an exciton model and successful results have been obtained by Moffitt,[4] Moffitt et al.,[5] Ando,[8] Kato et al.,[10] Natori,[11] and Kato and Ando.[13,15] Thus, it may be expected that the validity of the exciton model is obtained by making use of a general formula for the Faraday effect[16] encompassing the natural optical activity.

Since excitons originate in the electron-electron interactions, it is required for us calculating effects of the electron-electron interaction on the natural optical rotation.

In the present paper, the electron-electron interactions in the natural optical rotation are investigated and calculations also in a harmonic oscillator model are carried out. It is shown that, in general, the electron-electron interaction is effective on the natural optical rotation in contrast with that on the Faraday rotation.

In sec. 2 the natural optical rotation expressed in terms of the Green functions is formulated from the general formula for the Faraday effect on the basis of the first principle. In sec. 3 the equations for the Green functions are calculated without any model and the electron-electron interactions are discussed. In sec. 4 by making use of a harmonic oscillator model the electron-electron interactions are discussed. Finally in

* Professor, Department of Physics, Faculty of Engineering, Shinshu University, Wakasato, Nagano-shi 380.

sec. 5, summary and discussion are given.

2. Formulation of Natural Optical Rotation

In a previous paper[16] the theory of the Faraday effect was developed and a general formula for the Faraday rotation including the formula for the natural optical rotation has been derived. By making use of this formula the natural optical rotation can be investigated from the same theoretical point of view as in the case of the Faraday effect. The formula for the Faraday rotation in the absence of a constant magnetic field becomes a formula for the natural optical rotation.

The Faraday rotational angle $\phi_F(\omega)$ of the plane of polarized light per unit path length* for an incident monochromatic light with the angular frequency ω propagating to the z-axis in medium is of the form[16]

$$\phi_F(\omega) = -\frac{i}{2c\omega n_F(\omega)} Q_{NF}(q_0, \omega), \tag{1}$$

where $q_0 = \omega/c$, c is the speed of light in vaccum, $n_F(\omega)$ denotes the refractive index in the presence of the constant magnetic field $\boldsymbol{H}$. The expression $Q_{NF}(q, \omega)$ is represented by

$$Q_{NF}(q, \omega) = \frac{4\pi i\omega}{V} \int_{-\infty}^{\infty} dt\ e^{-i\omega t}\ \theta(t) \int_0^\beta d\lambda \langle \mathscr{J}_x(q, t),\ \mathscr{J}_y(-q, i\hbar\lambda)\rangle, \tag{2}$$

where

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

$$\beta = \frac{1}{kT},$$

expression $\mathscr{J}(q, t)$ is the spatial Fourier component of electric current density operator in the presence of $\boldsymbol{H}$, k Boltzmann's constant, T the absolute temperature and V is the volume of the system. The angular brackets denote the canonical ensemble average under the total Hamiltonian.

When the constant magnetic field $H = 0$, the quantity $\mathscr{J}(q, t)$ becomes the spatial Fourier component of electric current density operator $\boldsymbol{j}(q, t)$ expressed as

$$\boldsymbol{j}(q, t) = \sum_i \frac{e}{2m} \{\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_i(t))\,\boldsymbol{p}_i(t) + \boldsymbol{p}_i(t)\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_i(t))\}, \tag{3}$$

where e is the charge of an electron, m the mass of the electron and $\boldsymbol{r}_i(t)$ and $\boldsymbol{p}_i(t)$ the co-ordinate and momentum operators of the ith electron at time t, respectively. The natural optical rotational angle $\phi(\omega)$ reduces to

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

$$\phi(\omega) = -\frac{i}{2c\omega n(\omega)} Q_{\mathrm{N}}(q_0, \omega), \tag{4}$$

where $n(\omega)$ is the refractive index in the absence of $\boldsymbol{H}$ and the off-diagonal component $Q_{\mathrm{N}}(q, \omega)$ of the current correlation function is given by

$$Q_{\mathrm{N}}(q, \omega) = \frac{4\pi i\omega}{V} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \ \theta(t) \int_0^{\beta} d\lambda \langle j_x(q, t), j_y(-q, i\hbar\lambda)\rangle. \tag{5}$$

When $Q_{\mathrm{N}}(q, \omega)$ is expanded to the first order in the wave-number q of light, the formula for the natural optical rotation is expressed in terms of the Green function $G_{xy}(q, t)$ defined by

$$G_{xy}(q, t) = -\frac{i}{\hbar}\theta(t) \langle [j_x(q, t), \mu_y(0, 0)]\rangle, \tag{6}$$

where $\boldsymbol{\mu}(q, t)$ is the spatial Fourier component of the electric dipole moment operator.

The system under consideration is a polymer composed of similar monomers in the absence of the constant magnetic field. By making use of eq. (3) and by substituting eq. (5) into eq. (4), the natural optical rotational angle $\phi(\omega)$ can be expressed in terms of the Fourier components $G_{\mu\nu}(\omega)$ of the Green functions $G_{\mu\nu}(t)(\mu\nu = xy$ and $yx)$ in the form

$$\phi(\omega) = -\frac{2\pi i e}{Vmc^2 n(\omega)} \{G_{xy}(\omega) - G_{yx}(\omega)\}, \tag{7}$$

where

$$G_{\mu\nu}(\omega) = \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \ G_{\mu\nu}(t) \qquad (\mu\nu = xy, \ yx) \tag{8}$$

with

$$G_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i z_{in}(t)p_{\mu in}(t), \ \mu_\nu(0)]\rangle. \tag{9}$$

Here $\boldsymbol{r}_{in}(t)$ is the co-ordinate operator of the ith electron in the nth monomer at time t and $\boldsymbol{\mu}(t)$ the electric dipole moment operator at time t, that is

$$\boldsymbol{\mu}(t) = \sum_n\sum_i e\boldsymbol{r}_{in}(t). \tag{10}$$

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

$$\mathscr{H} = \sum_n\sum_i \left\{\frac{1}{2m}\boldsymbol{p}_{in}^2 + v_n(\boldsymbol{r}_{in})\right\} + \frac{1}{2}\sum_n\sum_{i\neq j}v_n'(\boldsymbol{r}_{in}-\boldsymbol{r}_{jn})$$
$$+ \frac{1}{2}\sum_{n\neq m}\sum_i\sum_j V_{nm}(\boldsymbol{r}_{in}-\mathbf{r}_{jm}), \tag{11}$$

where $v_n(\boldsymbol{r}_{in})$ is the interaction between the ith electron in the nth monomer and the nucleus in the same 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 $V_{nm}(\boldsymbol{r}_{in}-\mathbf{r}_{jm})$ is the interaction between the ith electron in the nth monomer and the jth electron in the mth monomer.The interactions between the ith electron in the nth monomer and the nucleus in the other

mth monomer $(m \neq n)$ are neglected.

3. Green Functions

In order to obtain the Fourier components $G_{\mu\nu}(\omega)$ of the Green functions, it is necessary for us to have equations of the Green functions $G_{\mu\nu}(t)(\mu\nu = xy$ and $yx)$. Differentiating eq. (9) with respect to time t, we have an equation

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}(t)}{dt} = -\frac{i}{\hbar}\theta(t)\langle[[\sum_n\sum_i z_{in}(t)p_{\mu in}(t), \mathscr{H}], \mu_\nu(0)]\rangle. \tag{12}$$

By making use of Hamiltonian (11) the equation of the Green function $G_{\mu\nu}(t)$ becomes

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{11}(t) + G_{\mu\nu}^{12}(t) + \frac{1}{2}G_{\mu\nu}^{13}(t) + \frac{1}{2}G_{\mu\nu}^{14}(t),$$
$$(\mu\nu = xy, yx) \tag{13}$$

where

$$G_{\mu\nu}^{11}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i p_{\mu in}(t)p_{zin}(t), \mu_\nu(0)]\rangle, \tag{14}$$

$$G_{\mu\nu}^{12}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(z_{in}(t)p_{\mu in}v_n(r_{in}(t))), \mu_\nu(0)]\rangle, \tag{15}$$

$$G_{\mu\nu}^{13}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}(z_{in}(t)-z_{jn}(t))(p_{\mu in}v_n'(r_{in}(t)-r_{jn}(t))), \mu_\nu(0)]\rangle, \tag{16}$$

$$G_{\mu\nu}^{14}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_i\sum_j(z_{in}(t)-z_{jn}(t))(p_{\mu in}V_{nm}(r_{in}(t)-r_{jm}(t))), \mu_\nu(0)]\rangle \tag{17}$$

and it appears four new Green functions $G_{\mu\nu}^{11}(t)$, $G_{\mu\nu}^{12}(t)$, $G_{\mu\nu}^{13}(t)$, $G_{\mu\nu}^{14}(t)$. It should be noted that eq. (13) contains the electron-electron interactions in the Green functions $G_{\mu\nu}^{13}(t)$ and $G_{\mu\nu}^{14}(t)$ defined by eqs. (16) and (17), respectively. It states that, as is shown in the previous paper[17] the electron-electron interactions have a little effect on the Faraday effect,whereas these interactions are effective on the natural optical activity.

Furthermore, when we take the time derivative of $G_{\mu\nu}^{11}(t)$, $G_{\mu\nu}^{12}(t)$, $G_{\mu\nu}^{13}(t)$, $G_{\mu\nu}^{14}(t)$ defined by eqs. (14)-(17), we obtain the equations of these Green functions as follows

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}^{11}(t)}{dt} = G_{\mu\nu}^{211}(t) + G_{\mu\nu}^{212}(t) + G_{\mu\nu}^{213}(t) + G_{\mu\nu}^{214}(t) + G_{\mu\nu}^{215}(t), \tag{18}$$

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}^{12}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{211}(t) - \frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{213}(t) - \frac{1}{2m}G_{\mu\nu}^{221}(t) - \frac{1}{m}G_{\mu\nu}^{222}(t), \tag{19}$$

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}^{13}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{231}(t) - \frac{1}{2m}G_{\mu\nu}^{232}(t) - \frac{1}{m}G_{\mu\nu}^{233}(t) - \frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{234}(t), \tag{20}$$

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}^{14}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{241}(t) - \frac{1}{2m}G_{\mu\nu}^{242}(t) - \frac{1}{m}G_{\mu\nu}^{243}(t) - \frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{244}(t), \tag{21}$$
$$(\mu\nu = xy, yx)$$

where

$$G_{\mu\nu}^{211}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{\mu in}p_{zin}v_n(\boldsymbol{r}_{in}(t))),\ \mu_\nu(0)]\rangle, \tag{22}$$

$$G_{\mu\nu}^{212}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{zin}v_n(\boldsymbol{r}_{in}(t)))p_{\mu in}(t),\ \mu_\nu(0)]\rangle, \tag{23}$$

$$G_{\mu\nu}^{213}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i(p_{\mu in}v_n(\boldsymbol{r}_{in}(t)))p_{zin}(t),\ \mu_\nu(0)]\rangle, \tag{24}$$

$$G_{\mu\nu}^{214}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}(p_{\mu in}p_{zin}v_n'(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jn}(t))),\ \mu_\nu(0)]\rangle, \tag{25}$$

$$G_{\mu\nu}^{215}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_i\sum_j(p_{\mu in}p_{zin}V_{nm}(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jm}(t))),\ \mu_\nu(0)]\rangle, \tag{26}$$

$$G_{\mu\nu}^{221}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_{\mu'}(z_{in}(t)p_{\mu in}p_{\mu'in}p_{\mu'in}v_n(\boldsymbol{r}_{in}(t))),\ \mu_\nu(0)]\rangle, \tag{27}$$

$$G_{\mu\nu}^{222}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i\sum_{\mu'}(z_{in}(t)p_{\mu in}p_{\mu'in}v_n(\boldsymbol{r}_{in}(t)))p_{\mu'in}(t),\ \mu_\nu(0)]\rangle, \tag{28}$$

$$G_{\mu\nu}^{231}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}(p_{\mu in}p_{zin}(v_n'(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jn}(t))$$
$$+ v_n'(\boldsymbol{r}_{jn}(t)-\boldsymbol{r}_{in}(t)))),\ \mu_\nu(0)]\rangle, \tag{29}$$

$$G_{\mu\nu}^{232}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}\sum_{\mu'}(z_{in}(t)-z_{jn}(t))$$
$$\times(p_{\mu in}p_{\mu'in}p_{\mu'in}(v_n'(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jn}(t))+v_n'(\boldsymbol{r}_{jn}(t)-\boldsymbol{r}_{in}(t)))),\ \mu_\nu(0)]\rangle, \tag{30}$$

$$G_{\mu\nu}^{233}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}\sum_{\mu'}(z_{in}(t)-z_{jn}(t))$$
$$\times(p_{\mu in}p_{\mu'in}(v_n'(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jn}(t))+v_n'(\boldsymbol{r}_{jn}(t)-\boldsymbol{r}_{in}(t))))p_{\mu'in}(t),\ \mu_\nu(0)]\rangle, \tag{31}$$

$$G_{\mu\nu}^{234}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}(p_{\mu in}(v_n'(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jn}(t))$$
$$+ v_n'(\boldsymbol{r}_{jn}(t)-\boldsymbol{r}_{in}(t))))p_{zin}(t),\ \mu_\nu(0)]\rangle, \tag{32}$$

$$G_{\mu\nu}^{241}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_i\sum_j(p_{\mu in}p_{zin}(V_{nm}(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jm}(t))$$
$$+ V_{mn}(\boldsymbol{r}_{jm}(t)-\boldsymbol{r}_{in}(t)))),\ \mu_\nu(0)]\rangle, \tag{33}$$

$$G_{\mu\nu}^{242}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_i\sum_j\sum_{\mu'}(z_{in}(t)-z_{jm}(t))$$
$$\times(p_{\mu in}p_{\mu'in}p_{\mu'in}(V_{nm}(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jm}(t))+V_{mn}(\boldsymbol{r}_{jm}(t)-\boldsymbol{r}_{in}(t)))),\ \mu_\nu(0)]\rangle, \tag{34}$$

$$G_{\mu\nu}^{243}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_i\sum_j\sum_{\mu'}(z_{in}(t)-z_{jm}(t))$$
$$\times(p_{\mu in}p_{\mu'in}(V_{nm}(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jm}(t))+V_{mn}(\boldsymbol{r}_{jm}(t)-\boldsymbol{r}_{in}(t))))p_{\mu'in}(t),\ \mu_\nu(0)]\rangle, \tag{35}$$

$$G_{\mu\nu}^{244}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_i\sum_j(p_{\mu in}(V_{nm}(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jm}(t))$$
$$+ V_{mn}(\boldsymbol{r}_{jm}(t)-\boldsymbol{r}_{in}(t))))p_{zin}(t),\ \mu_\nu(0)]\rangle. \tag{36}$$

Here two important results have been found out. The first place, eqs. (18), (20) and (21)

have the terms depending on the electron-electron interactions, while only eq. (19) has no term depending on them. This implies that the phenomenon of the natural optical rotation has close connection with the electron-electron interactions. The second place, there is no constant term in the equations (13), (18)-(21) for the Green functions. In order to solve these simultaneous equations for the Green functions it is necessary for us to have the equations for the Green functions defined by eqs. (22)-(36). The constant terms appear from the equations of the Green functions defined by eqs. (28), (31), (35), which have the commutators for the same Cartesian components of the momentum and the electric dipole moment operators, i.e. $[p_{xin}, \mu_x]$ and $[p_{yin}, \mu_y]$.

For example, we take the time derivative of $G_{\mu\nu}^{222}(t)$ defined by eq. (28), we can write down the equation of the Green function in the form

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}^{222}(t)}{dt} = \frac{\hbar}{i}NeC_1\delta(t) - \frac{1}{2m}G_{\mu\nu}^{3211}(t) - \frac{1}{m}G_{\mu\nu}^{3212}(t) - \frac{\hbar}{i}\frac{1}{m}G_{\mu\nu}^{3213}(t)$$

$$+ G_{\mu\nu}^{3214}(t) + \frac{1}{2}G_{\mu\nu}^{3215}(t) + \frac{1}{2}G_{\mu\nu}^{3216}(t), \qquad (\mu\nu = xy, yx) \quad (37)$$

where N is the number of electrons of the system and

$$C_1 = \left\langle \frac{1}{N}\sum_n\sum_i(z_{in}p_{xin}p_{yin}v_n(r_{in}))\right\rangle, \tag{38}$$

$$G_{\mu\nu}^{3211}(t) = -\frac{i}{\hbar}\theta(t)\left\langle\left[\sum_n\sum_i\sum_{\mu'}\left\{\sum_{\nu'}(z_{in}(t)p_{\mu in}p_{\mu' in}p_{\nu' in}v_n(r_{in}(t)))\right.\right.\right.$$

$$\left.\left.\left. + 2\frac{\hbar}{i}(p_{\mu in}p_{\mu' in}p_{zin}v_n(r_{in}(t)))\right\}p_{\mu' in}(t), \mu_\nu(0)\right]\right\rangle, \tag{39}$$

$$G_{\mu\nu}^{3212}(t) = -\frac{i}{\hbar}\theta(t)\left\langle\left[\sum_n\sum_i\sum_{\mu'}\sum_{\nu'}(z_{in}(t)p_{\mu in}p_{\mu' in}p_{\nu' in}v_n(r_{in}(t)))p_{\mu' in}(t)p_{\nu' in}(t), \mu_\nu(0)\right]\right\rangle, \tag{40}$$

$$G_{\mu\nu}^{3213}(t) = -\frac{i}{\hbar}\theta(t)\left\langle\left[\sum_n\sum_i\sum_{\mu'}(p_{\mu in}p_{\mu' in}v_n(r_{in}(t)))p_{\mu' in}(t)p_{zin}(t), \mu_\nu(0)\right]\right\rangle, \tag{41}$$

$$G_{\mu\nu}^{3214}(t) = -\frac{i}{\hbar}\theta(t)\left\langle\left[\sum_n\sum_i\sum_{\mu'}(z_{in}(t)p_{\mu in}p_{\mu' in}v_n(r_{in}(t)))(p_{\mu' in}v_n(r_{in}(t))), \mu_\nu(0)\right]\right\rangle, \tag{42}$$

$$G_{\mu\nu}^{3215}(t) = -\frac{i}{\hbar}\theta(t)\left\langle\left[\sum_n\sum_{i\neq j}\sum_{\mu'}\left\{(z_{in}(t)p_{\mu in}p_{\mu' in}v_n(r_{in}(t)))\right.\right.\right.$$

$$\left.\left.\left. - (z_{jn}(t)p_{\mu jn}p_{\mu' jn}v_n(r_{jn}(t)))\right\}(p_{\mu' in}v_n'(r_{in}(t) - r_{jn}(t))), \mu_\nu(0)\right]\right\rangle, \tag{43}$$

$$G_{\mu\nu}^{3216}(t) = -\frac{i}{\hbar}\theta(t)\left\langle\left[\sum_{n\neq m}\sum_i\sum_j\sum_{\mu'}\left\{(z_{in}(t)p_{\mu in}p_{\mu' in}v_n(r_{in}(t)))\right.\right.\right.$$

$$\left.\left.\left. - (z_{jm}(t)p_{\mu jm}p_{\mu' jm}v_m(r_{jm}(t)))\right\}(p_{\mu' in}V_{nm}(r_{in}(t) - r_{jm}(t))), \mu_\nu(0)\right]\right\rangle. \tag{44}$$

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

Here eq. (37) contains the constant C_1. Similarly, the constant terms derived from eqs. (31) and (35) can be obtained in the similar form as in eqs. (38)-(44). Thus, these calculations suggest a more complicated behavior.

Even if any approximation is made, in order to obtain the solution to the equations, twenty simultaneous equations for the Green functions defined by eqs. (9), (14)–(17), (22)–(36) at least ought to be solved. Since this calculation is very complicated and is very difficult to solve, we confine ourselves to considering the three-dimensional oscillator model in the next section. In contrast with the Faraday rotation seen in the previous paper,[17] it should be noted that the calculation of the natural optical rotation is in general more complicated. This result is preferable and reasonable, because the natural optical rotation originates in the first-order terms in the wave-number q of light, whereas the Faraday rotation in the zeroth-order terms in q.

4. Harmonic Oscillator Model

The natural optical rotation is observed only for a very special class of substances (i. e. optically-active substances), while the Faraday rotation can be observed for all substances without exception. The natural optical rotatory power in simple model was studied on the basis of classical theory by Kuhn,[2] whose model was a system composed of only two harmonic oscillators coupled each other, and a discussion of the physical basis has been presented.

Let us now consider a system composed of similar monomers, which consists of the three-dimensional harmonic oscillators of electrons. We introduce a more generalized coupling potential between the oscillators in contrast with Kuhn's model potential[2] as the electron-electron interaction. Thus the Hamiltonian $\mathscr{H}$ of the system under consideration is represented by

$$\mathscr{H} = \sum_n \sum_i \sum_\mu \left\{ \frac{1}{2m} p_{\mu in}^2 + k_\mu (\mu_{in} - M_{in})^2 \right\} + \frac{1}{2} \sum_n \sum_{i \neq j} \sum_{(\lambda\mu\nu)} k_\lambda' (\mu_{in} - M_{in})(\nu_{jn} - N_{jn})$$
$$+ \frac{1}{2} \sum_{n \neq m} \sum_i \sum_j \sum_{(\lambda\mu\nu)} k_\lambda' (\mu_{in} - M_{in})(\nu_{jm} - N_{jm}),$$
$$(\mu = x, y, z \text{ and } M, N = X, Y, Z) \quad (45)$$

where the term $\sum_\mu k_\mu (\mu_{in} - M_{in})^2$ is the potential of the ith electron oscillator in the nth monomer located at $\boldsymbol{R}_{in}(X_{in}, Y_{in}, Z_{in})$, the term $\sum_{(\lambda\mu\nu)} k_\lambda' (\mu_{in} - M_{in})(\nu_{jn} - N_{jn})$ is the interaction between the ith and the jth oscillators in the same nth monomer defined by

$$\sum_{(\lambda\mu\nu)} k_\lambda' (\mu_{in} - M_{in})(\nu_{jn} - N_{jn})$$
$$= k_x' (y_{in} - Y_{in})(z_{jn} - Z_{jn}) + k_y' (z_{in} - Z_{in})(x_{jn} - X_{jn}) + k_z' (x_{in} - X_{in})(y_{jn} - Y_{jn})$$
$$(46)$$

and the term $\sum_{(\lambda\mu\nu)} k_\lambda' (\mu_{in} - M_{in})(\nu_{jm} - N_{jm})$ is the interaction between the ith oscillator in the nth monomer and the jth oscillator in the mth monomer defined by

$$\sum_{(\lambda\mu\nu)} k_\lambda' (\mu_{in} - M_{in})(\nu_{jm} - N_{jm})$$

$$= k'_x(y_{in} - Y_{in})(z_{jm} - Z_{jm}) + k'_y(z_{in} - Z_{in})(x_{jm} - X_{jm}) + k'_z(x_{in} - X_{in})(y_{jm} - Y_{jm}).$$

(47)

From this Hamiltonian (45) the equation of the Green function $G_{\mu\nu}(t)$ defined by eq. (9) can be expressed in the form of the simultaneous equations for the Green functions of various types by making a series of calculations as is shown in the preceding section. The equations for the harmonic oscillator model become of the form

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{m}G^{11}_{\mu\nu}(t) + 2\frac{\hbar}{i}k_\mu G^{12}_{\mu\nu}(t) + \frac{1}{2}\frac{\hbar}{i}G^{13}_{\mu\nu}(t) + \frac{1}{2}\frac{\hbar}{i}G^{14}_{\mu\nu}(t),$$

(48)

$$-\frac{\hbar}{i}\frac{dG^{11}_{\mu\nu}(t)}{dt} = 2\frac{\hbar}{i}k_z G^{211}_{\mu\nu}(t) + 2\frac{\hbar}{i}k_\mu G^{212}_{\mu\nu}(t) + \frac{1}{2}\frac{\hbar}{i}G^{213}_{\mu\nu}(t) + \frac{1}{2}\frac{\hbar}{i}G^{214}_{\mu\nu}(t)$$

$$+ \frac{1}{2}\frac{\hbar}{i}G^{215}_{\mu\nu}(t) + \frac{1}{2}\frac{\hbar}{i}G^{216}_{\mu\nu}(t),$$

(49)

$$-\frac{\hbar}{i}\frac{dG^{12}_{\mu\nu}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{2m}G_{\mu\nu}(t) - \frac{\hbar}{i}\frac{1}{2m}G^{212}_{\mu\nu}(t),$$

(50)

$$-\frac{\hbar}{i}\frac{dG^{13}_{\mu\nu}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{m}G^{214}_{\mu\nu}(t) - \frac{\hbar}{i}\frac{1}{m}G^{231}_{\mu\nu}(t) - \frac{\hbar}{i}\frac{1}{m}G^{232}_{\mu\nu}(t),$$

(51)

$$-\frac{\hbar}{i}\frac{dG^{14}_{\mu\nu}(t)}{dt} = -\frac{\hbar}{i}\frac{1}{m}G^{216}_{\mu\nu}(t) - \frac{\hbar}{i}\frac{1}{m}G^{241}_{\mu\nu}(t) - \frac{\hbar}{i}\frac{1}{m}G^{242}_{\mu\nu}(t),$$

(52)

where

$$G_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i z_{in}(t)p_{\mu in}(t), \ \mu_\nu(0)]\rangle,$$

(53)

$$G^{11}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i p_{\mu in}(t)p_{zin}(t), \ \mu_\nu(0)]\rangle,$$

(54)

$$G^{12}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i z_{in}(t)(\mu_{in}(t) - M_{in}), \ \mu_\nu(0)]\rangle,$$

(55)

$$G^{13}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}\{k'_z z_{in}(t)(\nu_{in}(t) - N_{in})$$

$$+ k'_\nu z_{in}(t)(z_{jn}(t) - Z_{jn})\}, \ \mu_\nu(0)]\rangle,$$

(56)

$$G^{14}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_i\sum_j\{k'_z z_{jm}(t)(\nu_{in}(t) - N_{in})$$

$$+ k'_\nu z_{in}(t)(z_{jm}(t) - Z_{jm})\}, \ \mu_\nu(0)]\rangle,$$

(57)

$$G^{211}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i (z_{in}(t) - Z_{in})p_{\mu in}(t), \ \mu_\nu(0)]\rangle,$$

(58)

$$G^{212}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_i (\mu_{in}(t) - M_{in})p_{zin}(t), \ \mu_\nu(0)]\rangle,$$

(59)

$$G^{213}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}\{k'_\mu(\nu_{jn}(t) - N_{jn}) + k'_\nu(\mu_{jn}(t) - M_{jn})\}p_{\mu in}(t), \ \mu_\nu(0)]\rangle,$$

(60)

$$G^{214}_{\mu\nu}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_n\sum_{i\neq j}\{k'_\nu(z_{jn}(t) - Z_{jn}) + k'_z(\nu_{jn}(t) - N_{jn})\}p_{zin}(t), \ \mu_\nu(0)]\rangle,$$

(61)

$$G_{\mu\nu}^{215}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_{i}\sum_{j}\{k'_{\mu}(\nu_{jm}(t)-N_{jm})+k'_{\nu}(\mu_{jm}-M_{jm})\}p_{\mu in}(t),\ \mu_{\nu}(0)]\rangle,$$
$$\text{(62)}$$

$$G_{\mu\nu}^{216}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_{i}\sum_{j}\{k'_{\nu}(z_{jm}(t)-Z_{jm})+k'_{z}(\nu_{jm}-N_{jm})\}p_{zin}(t),\ \mu_{\nu}(0)]\rangle,$$
$$\text{(63)}$$

$$G_{\mu\nu}^{231}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n}\sum_{i\neq j}\{k'_{z}z_{jn}(t)p_{\nu in}(t),\ \mu_{\nu}(0)]\rangle, \tag{64}$$

$$G_{\mu\nu}^{232}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n}\sum_{i\neq j}k'_{\nu}z_{jn}(t)p_{zin}(t),\ \mu_{\nu}(0)]\rangle, \tag{65}$$

$$G_{\mu\nu}^{241}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_{i}\sum_{j}\{k'_{z}z_{jm}(t)p_{\nu in}(t),\ \mu_{\nu}(0)]\rangle, \tag{66}$$

$$G_{\mu\nu}^{242}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_{i}\sum_{j}k'_{\nu}z_{jm}(t)p_{zin}(t),\ \mu_{\nu}(0)]\rangle. \tag{67}$$

As these eqs. (48)–(52) have no constant term, we ought to continue calculating the Green functions $G_{\mu\nu}^{231}(t)$ and $G_{\mu\nu}^{241}(t)$ defined by eqs. (64) and (66), respectively, from which produce the constant terms. The equation of $G_{\mu\nu}^{231}(t)$ is found to be

$$-\frac{\hbar}{i}\frac{dG_{\mu\nu}^{231}(t)}{dt} = \frac{\hbar}{i}Nek'_{z}C_{1}\delta(t) - \frac{\hbar}{i}\frac{1}{m}k'_{z}G_{\mu\nu}^{3311}(t)$$
$$+ 2\frac{\hbar}{i}k_{\nu}k'_{z}G_{\mu\nu}^{3312}(t) + \frac{1}{2}\frac{\hbar}{i}k'_{z}G_{\mu\nu}^{3313}(t) + \frac{1}{2}\frac{\hbar}{i}k'_{z}G_{\mu\nu}^{3314}(t), \tag{68}$$

where

$$C_{1} = \langle\frac{1}{N}\sum_{n}\sum_{i\neq j}z_{jn}\rangle, \tag{69}$$

$$G_{\mu\nu}^{3311}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n}\sum_{i\neq j}p_{\nu jn}(t)p_{zin}(t),\ \mu_{\nu}(0)]\rangle, \tag{70}$$

$$G_{\mu\nu}^{3312}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n}\sum_{i\neq j}z_{jn}(t)(\nu_{in}(t)-N_{in}),\ \mu_{\nu}(0)]\rangle, \tag{71}$$

$$G_{\mu\nu}^{3313}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n}\sum_{i\neq j}\sum_{j'}z_{j'n}(t)\{k'_{\mu}(z_{jn}(t)-Z_{jn})+k'_{z}(\mu_{in}(t)-M_{in})\},\ \mu_{\nu}(0)]\rangle, \tag{72}$$

$$G_{\mu\nu}^{3314}(t) = -\frac{i}{\hbar}\theta(t)\langle[\sum_{n\neq m}\sum_{i}\sum_{j}\sum_{j'}z_{j'm}(t)\{k'_{\mu}(z_{jm}(t)-Z_{jm})$$
$$+ k'_{z}(\mu_{in}(t)-M_{in})\},\ \mu_{\nu}(0)]\rangle. \tag{73}$$

Similarly, the equation of $G_{\mu\nu}^{241}(t)$ is presented in the similar form.

Thus, when the Green functions of new types induced from the equations of the Green functions defined by eqs. (58)–(67) are expressed in terms of the Green function defined by eqs. (53)–(67) by approximations, the Fourier component of $G_{\mu\nu}(t)$ can be obtained in principle by solving fifteen simultaneous equations composed of eqs. (48)–(52) and of the equations of the Green functions defined by eqs. (58)–(67). Even if any such approximation for the harmonic oscillator model is made, the calculations for

solving these simultaneous equations are still quite complicated.

5. Summary and Discussion

The formulation of the natural optical rotation has been made from the general formula for the Faraday effect derived by us[16] formerly. By making use of this formula for the Faraday effect, the natural optical activity can be investigated from the same point of view as in the case of the Faraday effect.

In the previous paper,[17] it has been shown that the electron-electron interaction has a little effect in general on the Faraday rotation and is ineffective exactly in the harmonic oscillator model. In the present paper, it is proved that the electron-electron interaction is effective on the natural optical activity. It implies that the natural optical rotation can be successfully discussed by the Frenkel exciton model which originates in the electron-electron interaction. Since the Frenkel exciton model plays an essential role in the anomalous rotational dispersion for the natural optical rotation as it has been shown by Moffitt[4] and Moffitt et al.,[5] the electron-electron interaction is very important for the natural optical rotation in contrast with that for the Faraday rotation.

In the previous paper[13] it has been proved that the electron-phonon interaction has a little effect on the natural optical rotation. In the present paper, the electron-phonon interaction and the interaction between the electron in a monomer and the nucleus in the other monomer are neglected as it is seen in eqs. (11) and (45). These interactions have been also neglected in Moffitt's work[4] on the anomalous rotational dispersion at the helix-coil transition in the natural optical rotation.

One of the important results obtained by us is that calculations of the natural optical rotation is in general quite complicated in comparison with those of the Faraday rotation. This is an inevitable result from the fact that the natural optical rotation is caused by the first-order terms in the wave-number q of light, whereas the Faraday rotation by the zeroth-order terms in q. Even if the simple system, for example a harmonic oscillator model, is considered, the calculation of the natural optical rotation is still complicated in contrast with that of the Faraday rotation as is demonstrated in the preceding section. The natural optical rotation is caused by the terms more higher-order in q than the terms causing the Faraday rotation, nevertheless there is an unexpected result in conventional theories that the calculation of the natural optical rotation is easier than that of the Faraday rotation.

Finally, it should be noted that the various effects on the natural optical activity and the Faraday effect can be discussed from the same point of view for both the phenomena by a general formula for the Faraday effect, which is derived on the basis of the first principle and constantly from the microscopic viewpoints by us.[16] Thus, a comparison between both the phenomena can be precisely made by our formula.

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