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Effects of Electron-Electron Interaction on the Magneto-Optical Rotation in Coupled Oscillators

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For a system composed of three-dimensional electron harmonic-oscillators, the electron-electron interaction is exactly ineffective on the magneto-optical rotation. It is exactly shown that the Frenkel exciton does not contribute to the magneto-optical rotation and the anomalous optical rotatory dispersion at a helix-coil transition does not occur, being different from the result of natural optical rotation. For a system composed of electron anharmonic-oscillators, the electron-electron interaction has a little effect on the magneto-optical rotation. The magneto-optical rotatory power in the anharmonic oscillators is obtained for the Faraday configuration by using approximation.

1. Introduction

Theories of natural optical rotation have been worked out by a number of authors from various points of view.[1-8] The Faraday effect has long been studied both experimentally and theoretically.[9-13] The expressions for the Faraday rotation[9,10] obtained hitherto are rather complicated in comparison with that for the natural optical rotation. It seems that the calculations of an actual molecule by these formulae are very difficult even by using approximations. On the other hand, the general formula for the Faraday effect[11,12] derived by us is a exact and lucid expression on the basis of the first principle in contrast with the conventional formulae. Furthermore, by making use of our theory the effects of various interactions (for example, electron-phonon interaction[14] or electron-electron interaction[13]) on the magneto-optical rotation can be theoretically investigated by no use of the complicated assumptions as is seen in the conventional calculations. When we calculate these effects on the magneto-optical rotation in a polymer composed of similar monomers using our general formula,[12] it is not necessary for us to have the knowledge of the magneto-optical rotatory power of those monomers. Since our theory of the magneto-optical rotation encompasses that of the natural optical rotation, these effects can be discussed for both phenomena from the same point of view.

Moffitt, Fitts and Kirkwood[2] have theoretically investigated the anomalous

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dispersion in the natural optical rotation by making use of the Frenkel exciton model for a polymer. The Frenkel exciton originates in the electron-electron interaction. For the magneto-optical rotation we have investigated this interaction in the previous paper.[13] It has been seen that the electron-electron interaction hardly contribute, in general, to the magneto-optical rotation.

In the present paper, we investigate the effects of the electron-electron interaction on the magneto-optical rotation in the system composed of coupled oscillators.

In sec. 2 we formulate the theory of the magneto-optical rotation as is shown in the previous paper[12] and in sec. 3 we show calculational procedure for the system composed of the coupled oscillators. In sec. 4 it is proved exactly for the system composed of the three-dimensional electron harmonic-oscillators that there is no effect of the electron-electron interaction on the magneto-optical rotation and that the Voigt effect does not occur as far as only the first order term in the constant magnetic field is considered. In sec. 5 we investigate the effect of the electron-electron interaction for the anharmonic-oscillator system by similar fashion as is demonstrated in the preceding section. The last section is devoted to a sammary and discussion.

2. Formulation

Formerly the general theory of the Faraday effect is developed by us[11,12] from the same viewpoint as the natural optical rotation. The genaral formula for the magneto-optical rotation is expressed in terms of a correlation function of the spatial Fourier components of total electric currents.

Let us take the direction of the propagation of an incident monochromatic light of angular frequency ω to be parallel to the z-axis in medium. As far as only the lowest-order term in the wave-number of light, the magneto-optical rotational angle $\phi(\omega)$ of the plane of polarized light per unit path length* is expressed as[12]

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

where $n_0(\omega)$ is the refractive index in the absence of a constant magnetic field and $\mathscr{J}(t)$ and $\boldsymbol{\mu}(t)$ 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

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

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

* 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.

The rotational angle $\phi(\omega)$ can be represented in terms of the Fourier component $G_{xy}(\omega)$ of the Green function $G_{xy}(t)$ in the form

$$\phi(\omega) = -\frac{2\pi}{Vcn_0(\omega)} G_{xy}(\omega), \tag{2}$$

where

$$G_{xy}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t}\, G_{xy}(t) \tag{3}$$

with

$$G_{xy}(t) = -\frac{\mathrm{i}}{\hbar}\, \theta(t) \langle [\mathscr{J}_x(t),\, \mu_y(0)] \rangle. \tag{4}$$

The system under consideration is a polymer composed of similar monomers in the presence of a constant magnetic field $\boldsymbol{H}$. The total electric current poperator $\mathscr{J}(t)$ and the total electric dipole moment operator $\boldsymbol{\mu}(t)$ at time t are

$$\mathscr{J}(t) = \frac{e}{m} \sum_n \sum_i \left\{ \boldsymbol{p}_{in}(t) - \frac{e}{c} \boldsymbol{A}(\boldsymbol{r}_{in}(t)) \right\} \tag{5}$$

and

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

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

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

When we take an angle α between the directions of the constant magnetic field $\boldsymbol{H}$ and the z-axis, we can assume without loss of generality that the x-, y- and z-components of the constant magnetic field $\boldsymbol{H}$ are $H\sin\alpha$, 0, $H\cos\alpha$, respectively. Hence the components of $\boldsymbol{A}$ are

$$A_x = -\frac{H}{2} y \cos\alpha, \tag{8}$$

$$A_y = \frac{H}{2} (x\cos\alpha - z\sin\alpha), \tag{9}$$

$$A_z = \frac{H}{2} y \sin\alpha. \tag{10}$$

3. Electron-Electron Interaction in Oscillators

In the resent paper, we consider a polymer composed of similar monomers, which are composed of oscillators of electrons in the presence of the constant magnetic field.

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

$$\mathscr{H}=\sum_n\sum_i\sum_\mu\left\{\frac{1}{2m}\left(p_{\mu in}-\frac{e}{c}A_\mu(\boldsymbol{r}_{in})\right)^2+k_\mu(\mu_{in}-M_{in})^{2l}\right\}$$
$$+\frac{1}{2}\sum_n\sum_{\substack{i\ j\\(i\neq j)}}\sum v'_n(\boldsymbol{r}_{in}-\boldsymbol{r}_{jn})+\frac{1}{2}\sum_{\substack{n\ m\\(n\neq m)}}\sum\sum_i\sum_j V_{nm}(\boldsymbol{r}_{in}-\boldsymbol{r}_{jm}), \tag{11}$$
$$(\mu=x,y,z,\qquad M=X,Y,Z,\qquad l=1,2,3,\cdots)$$

where the term $\sum_\mu k_\mu(\mu_{in}-M_{in})^{2l}$ is the potential of the ith electron oscillator in the nth monomer located at $\boldsymbol{R}_{in}(X_{in}, Y_{in}, Z_{in})$, $v'_n(\boldsymbol{r}_{in}-\boldsymbol{r}_{jn})$ the interaction between the ith and the jth oscillators in the same nth monomer and $V_{nm}(\boldsymbol{r}_{in}-\boldsymbol{r}_{jm})$ is the interaction between the ith oscillator in the nth monomer and the jth oscillator in the mth monomer.

By differentiating the Green function (4) with respect to time t the equation for the Green function $G_{xy}(t)$ is presented by making use of the Hamiltonian (11), that is

$$-\frac{k}{\mathrm{i}}\frac{\mathrm{d}G_{xy}(t)}{\mathrm{d}t}=-\frac{\hbar\omega_z}{\mathrm{i}}G_{yy}(t)+2l\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{xy}(t), \tag{12}$$

where

$$G_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\mathscr{J}_\nu(t),\mu_y(0)]\rangle, \tag{13}$$

$$G^1_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu(\nu_{in}(t)-N_{in})^{2l-1},\mu_y(0)]\rangle \tag{14}$$

and

$$\omega_\nu=\frac{eH_\nu}{mc}\quad(\nu=x,y,z\text{ and }N=X,Y,Z) \tag{15}$$

with $H_x=H\sin\alpha$, $H_y=0$, $H_z=H\cos\alpha$. The equations for Green functions $G_{yy}(t)$ and $G^1_{\nu y}(t)$ of new types appeared in eq. (12) can be obtained by similar calculations shown in the previous paper[13] and the successive procedure of the calculations for these new Green functions creates the coupled equations for the Green functions of many various types.

Thus a set of equations for the Green functions is written in the form

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

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{zy}(t)}{\mathrm{d}t}=\frac{\hbar\omega_x}{\mathrm{i}}G_{yy}(t)+2l\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{zy}(t), \tag{17}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^1_{\nu y}(t)}{\mathrm{d}t}=-(2l-1)(2l-2)\left(\frac{\hbar}{\mathrm{i}}\right)^2\frac{1}{2m}G^{21}_{\nu y}(t)-(2l-1)\frac{\hbar}{\mathrm{i}}\frac{1}{e}G^{22}_{\nu y}(t), \tag{18}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^{21}_{\nu y}(t)}{\mathrm{d}t}=-(2l-3)(2l-4)\left(\frac{\hbar}{\mathrm{i}}\right)^2\frac{1}{2m}G^{311}_{\nu y}(t)-(2l-3)\frac{\hbar}{\mathrm{i}}\frac{1}{e}G^{312}_{\nu y}(t), \tag{19}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^{22}_{\nu y}(t)}{\mathrm{d}t}=\delta_{\nu y}\frac{\hbar}{\mathrm{i}}\frac{e^2}{m}\langle\sum_n\sum_i k_y\,(y_{in}-Y_{in})^{2l-2}\rangle\,\delta(t)$$
$$-(2l-2)\frac{\hbar}{\mathrm{i}}\frac{1}{e}G^{321}_{\nu y}(t)-G^{322}_{\nu y}(t)+2l\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^{323}_{\nu y}(t)$$
$$+\frac{e}{2m}G^{324}_{\nu y}(t)+\frac{e}{2m}G^{325}_{\nu y}(t),\qquad(\nu=x,\ y,\ z) \tag{20}$$

where N is the number of electrons in the system and

$$G^{21}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu\,(\nu_{in}(t)-N_{in})^{2l-3},\ \mu_y(0)]\rangle, \tag{21}$$

$$G^{22}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu\,(\nu_{in}(t)-N_{in})^{2l-2}\mathscr{J}_{\nu in}(t),\ \mu_y(0)]\rangle, \tag{22}$$

$$G^{311}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu\,(\nu_{in}(t)-N_{in})^{2l-5},\ \mu_y(0)]\rangle, \tag{23}$$

$$G^{312}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu\,(\nu_{in}(t)-N_{in})^{2l-4}\mathscr{J}_{\nu in}(t),\ \mu_y(0)]\rangle, \tag{24}$$

$$G^{321}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu\,(\nu_{in}(t)-N_{in})^{2l-3}\mathscr{J}_{\nu in}(t)\mathscr{J}_{\nu in}(t),\ \mu_y(0)]\rangle, \tag{25}$$

$$G^{322}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i\Big\{(2l-2)\,(2l-3)\Big(\frac{\hbar}{\mathrm{i}}\Big)^2\frac{1}{2m}k_\nu\,(\nu_{in}(t)-N_{in})^{2l-4}\mathscr{J}_{in}(t)$$
$$+k_\nu\,(\nu_{in}(t)-N_{in})^{2l-2}\Big(\frac{\hbar\boldsymbol{\omega}}{\mathrm{i}}\times\mathscr{J}_{in}(t)\Big)\Big\}_\nu,\ \mu_y(0)]\rangle, \tag{26}$$

$$G^{323}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k^2_\nu\,(\nu_{in}(t)-N_{in})^{4l-3},\ \mu_y(0)]\rangle, \tag{27}$$

$$G^{324}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_{\substack{i\ \ j\\(i\neq j)}}\sum k_\nu\{(\nu_{in}(t)-N_{in})^{2l-2}-(\nu_{jn}(t)-N_{jn})^{2l-2}\}$$
$$\times(p_{\nu in}\,v'_n(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jn}(t))),\ \mu_y(0)]\rangle, \tag{28}$$

$$G^{325}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_{\substack{n\ \ m\\(n\neq m)}}\sum\sum_i\sum_j k_\nu\{(\nu_{in}(t)-N_{in})^{2l-2}-(\nu_{jm}(t)-N_{jm})^{2l-2}\}$$
$$\times(p_{\nu in}\,V_{nm}(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jm}(t))),\ \mu_y(0)]\rangle. \tag{29}$$

In order to solve these equtions it is necessary for us to have the equations for the Green functions defined by eqs. (23)-(29). By a series of calculations of these Green functions, thus, the infinite simultaneous equations are finally obtained. It should be noted that the Green functions $G^{324}_{\nu y}(t)$ and $G^{325}_{\nu y}(t)$ related to the electron-electron interaction have appeared for the first time on only the right-hand side of eq. (20). This implies that there is hardly effect of the electron-electron interaction on the magneto-optical rotation.

For investigation of the magneto-optical rotatory dispersion we calculate the simultaneous equations in the simple models (see also Appendix).

4. Harmonic Oscillator Model

Let us consider a system composed of similar monomers, which consists of the three-dimensional harmonic oscillators. Then, we take $l=1$ in the Hamiltonian (11). By making use of this Hamiltonian, a set of equations for Green functions is found to be

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{xy}(t)}{\mathrm{d}t}=-\frac{\hbar\omega_z}{\mathrm{i}}G_{yy}(t)+2\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{xy}(t), \tag{30}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{yy}(t)}{\mathrm{d}t}=\frac{\hbar}{\mathrm{i}}\frac{Ne^2}{m}\delta(t)+\frac{\hbar\omega_z}{\mathrm{i}}G_{xy}(t)-\frac{\hbar\omega_x}{\mathrm{i}}G_{zy}(t)+2\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{yy}(t), \tag{31}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{zy}(t)}{\mathrm{d}t}=\frac{\hbar\omega_x}{\mathrm{i}}G_{yy}(t)+2\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{zy}(t), \tag{32}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^1_{xy}(t)}{\mathrm{d}t}=-\frac{\hbar}{\mathrm{i}}\frac{k_x}{e}G_{xy}(t), \tag{33}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^1_{yy}(t)}{\mathrm{d}t}=-\frac{\hbar}{\mathrm{i}}\frac{k_y}{e}G_{yy}(t), \tag{34}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^1_{zy}(t)}{\mathrm{d}t}=-\frac{\hbar}{\mathrm{i}}\frac{k_z}{e}G_{zy}(t), \tag{35}$$

where $G_{\nu y}(t)$ $(\nu=x,\ y,\ z)$ are defined by eq. (13) and $G^1_{\nu y}(t)$ now reduced to

$$G^1_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu\,\nu_{in}(t),\ \mu_y(0)]\rangle, \qquad (\nu=x,\ y,\ z) \tag{36}$$

These simultaneous equations in sets of six for the Green functions in the form of a finite chain of coupled equations can be exactly solved and the magneto-optical rotational angle $\phi(\omega)$ given by eq. (1) becomes

$$\phi(\omega)=-\frac{2\pi N\hbar^2e^3H\cos\alpha}{Vm^2c^2n_0(\omega)}\frac{\left((\hbar\omega)^2-\frac{\hbar^2k_z}{m}\right)^2-\left(\frac{\hbar^2k_z}{m}\right)^2}{\left[\begin{array}{l}(\hbar\omega)^2\left\{\left((\hbar\omega)^2-\frac{\hbar^2}{m}(k_x+k_y+k_z)\right)^2\right.\\ \left.-\left(\frac{\hbar^2}{m}\right)^2(k_x^2+k_y^2+k_z^2-2k_yk_z-2k_zk_x-2k_xk_y)\right\}\\ -\left(\frac{2\hbar^2}{m}\right)^3k_xk_yk_z\end{array}\right]}. \tag{37}$$

Here it should be noted that the electron-electron interaction is inffective on the magneto-optical rotation and, furthermore, $\phi=0$ in the case of the Voigt configuration (i.e. $\alpha=\frac{\pi}{2}$). It is very important that the results are exact in regard to the electron-electron interactions.

5. Anharmonic Oscillator Model

In order to investigate the effects of the electron-electron interaction on the magneto-optical rotation, we consider now the system in the case of $l=2$ in the

Hamiltonian expressed as eq. (11). By the similar calculations demonstrated in sec. 3, the coupled equations for the Green functions can be written for an anharmonic-oscillator system

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{xy}(t)}{\mathrm{d}t}=-\frac{\hbar\omega_z}{\mathrm{i}}G_{yy}(t)+4\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{xy}(t), \tag{38}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{yy}(t)}{\mathrm{d}t}=\frac{\hbar}{\mathrm{i}}\frac{Ne^2}{m}\delta(t)+\frac{\hbar\omega_z}{\mathrm{i}}G_{xy}(t)-\frac{\hbar\omega_x}{\mathrm{i}}G_{zy}(t)+4\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{yy}(t), \tag{39}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{zy}(t)}{\mathrm{d}t}=\frac{\hbar\omega_x}{\mathrm{i}}G_{yy}(t)+4\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{zy}(t), \tag{40}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^1_{\nu y}(t)}{\mathrm{d}t}=3\frac{\hbar^2}{m}G^{21}_{\nu y}(t)-3\frac{\hbar}{\mathrm{i}}\frac{1}{e}G^{22}_{\nu y}(t), \tag{41}$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^{21}_{\nu y}(t)}{\mathrm{d}t}=-\frac{\hbar}{\mathrm{i}}\frac{k_\nu}{e}G_{\nu y}(t), \tag{42}$$

$$\begin{aligned}-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G^{22}_{\nu y}(t)}{\mathrm{d}t}&=\delta_{\nu y}\frac{\hbar}{\mathrm{i}}\frac{e^2}{m}\langle\sum_n\sum_i k_y(y_{in}-Y_{in})^2\rangle\,\delta(t)\\&\quad-2\frac{\hbar}{\mathrm{i}}\frac{1}{e}G^{321}_{\nu y}(t)-G^{322}_{\nu y}(t)+4\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^{323}_{\nu y}(t)\\&\quad+\frac{e}{2m}G^{324}_{\nu y}(t)+\frac{e}{2m}G^{325}_{\nu y}(t),\qquad(\nu=x,\ y,\ z)\end{aligned} \tag{43}$$

where $G_{\nu y}(t)$ $(\nu=x,\ y,\ z)$ is defined by eq. (13) and

$$G^1_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu(\nu_{in}(t)-N_{in})^3,\ \mu_y(0)]\rangle, \tag{44}$$

$$G^{21}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu(\nu_{in}(t)-N_{in}),\ \mu_y(0)]\rangle, \tag{45}$$

$$G^{22}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu(\nu_{in}(t)-N_{in})^2\mathscr{J}_{\nu in}(t),\ \mu_y(0)]\rangle, \tag{46}$$

$$G^{321}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu(\nu_{in}(t)-N_{in})\mathscr{J}_{\nu in}(t)\mathscr{J}_{\nu in}(t),\ \mu_y(0)]\rangle, \tag{47}$$

$$G^{322}_{\nu y}(t)=-\frac{\hbar^2k_\nu}{m}G_{\nu y}(t)+\left(\frac{\hbar\boldsymbol{\omega}}{\mathrm{i}}\times\boldsymbol{G}^{22}_y\right)_\nu, \tag{48}$$

$$G^{323}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k^2_\nu(\nu_{in}(t)-N_{in})^5,\ \mu_y(0)]\rangle, \tag{49}$$

$$\begin{aligned}G^{324}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[&\sum_n\sum_i\sum_{j\,(i\neq j)} k_\nu\{(\nu_{in}(t)-N_{in})^2-(\nu_{jn}(t)-N_{jn})^2\}\\&\times(p_{\nu in}\,v'_n(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jn}(t))),\ \mu_y(0)]\rangle,\end{aligned} \tag{50}$$

$$\begin{aligned}G^{325}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[&\sum_n\sum_{m\,(n\neq m)}\sum_i\sum_j k_\nu\{(\nu_{in}(t)-N_{in})^2-(\nu_{jm}(t)-N_{jm})^2\}\\&\times(p_{\nu in}\,V_{nm}(\boldsymbol{r}_{in}(t)-\boldsymbol{r}_{jm}(t))),\ \mu_y(0)]\rangle\end{aligned} \tag{51}$$

with a vector $\boldsymbol{\omega}(\omega_x,\ \omega_y,\ \omega_z)$ and a vector $\boldsymbol{G}^{22}_y(t)$ $(G^{22}_{xy}(t),\ G^{22}_{yy}(t),\ G^{22}_{zy}(t))$.

By making the approximations that the Green functions $G^{321}_{\nu y}(t)$, $G^{323}_{\nu y}(t)$, $G^{324}_{\nu y}(t)$, $G^{325}_{\nu y}(t)$, are replaced by

$$G_{xy}^{321}(t) \approx \left(\frac{e}{m}\right)^2 \left\{ \langle p_{xin}^2 \rangle + \frac{m}{\hbar} \hbar \omega_z \langle y_{in} p_{xin} \rangle + \left(\frac{m}{2\hbar}\right)^2 (\hbar \omega_z)^2 \langle y_{in}^2 \rangle \right\} G_{xy}^{21}(t), \tag{52}$$

$$G_{yy}^{321}(t) \approx \left(\frac{e}{m}\right)^2 \left\{ \langle p_{yin}^2 \rangle - \frac{m}{\hbar} (\hbar \omega_z \langle x_{in} p_{yin} \rangle - \hbar \omega_x \langle z_{in} p_{yin} \rangle) + \left(\frac{m}{2\hbar}\right)^2 ((\hbar \omega_z)^2 \langle x_{in}^2 \rangle + (\hbar \omega_x)^2 \langle z_{in}^2 \rangle - 2 (\hbar \omega_z)(\hbar \omega_x) \langle z_{in} x_{in} \rangle) \right\} G_{yy}^{21}(t), \tag{53}$$

$$G_{zy}^{321}(t) \approx \left(\frac{e}{m}\right)^2 \left\{ \langle p_{zin}^2 \rangle - \frac{m}{\hbar} \hbar \omega_x \langle y_{in} p_{zin} \rangle + \left(\frac{m}{2\hbar}\right)^2 (\hbar \omega_x)^2 \langle y_{in}^2 \rangle \right\} G_{zy}^{21}(t), \tag{54}$$

$$G_{\nu y}^{323}(t) \approx k_\nu \langle (\nu_{in} - N_{in})^4 \rangle G_{\nu y}^{21}(t), \tag{55}$$

$$G_{\nu y}^{324}(t) \approx \langle (\nu_{in} - N_{in}) \sum_{\substack{j \\ (j \neq i)}} (p_{\nu in} (v_n'(\boldsymbol{r}_{in} - \boldsymbol{r}_{jn}) + v_n'(\boldsymbol{r}_{jn} - \boldsymbol{r}_{in}))) \rangle G_{\nu y}^{21}(t), \tag{56}$$

$$G_{\nu y}^{325}(t) \approx \langle (\nu_{in} - N_{in}) \sum_{\substack{m \\ (m \neq n)}} \sum_{j} (p_{\nu in} (V_{nm}(\boldsymbol{r}_{in} - \boldsymbol{r}_{jm}) + V_{mn}(\boldsymbol{r}_{jm} - \boldsymbol{r}_{in}))) \rangle G_{\nu y}^{21}(t), \tag{57}$$

we can solve the simultaneous equations for $G_{xy}(t)$ expressed by eqs. (38)-(43). Since the result is complicated, we confine ourselves considering in the case of the direction of the incident light to be parallel to the constant magnetic field (i.e. for the 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 Fourier components of the Green functions can be written in the form

$$-\hbar \omega G_{xy}(\omega) = -\frac{\hbar \omega_z}{i} G_{yy}(\omega) + 4 \frac{\hbar}{i} \frac{e}{m} G_{xy}^1(\omega), \tag{58}$$

$$-\hbar \omega G_{yy}(\omega) = \frac{\hbar}{i} \frac{Ne^2}{m} + \frac{\hbar \omega_z}{i} G_{xy}(\omega) + 4 \frac{\hbar}{i} \frac{e}{m} G_{yy}^1(\omega), \tag{59}$$

$$-\hbar \omega G_{xy}^1(\omega) = 3 \frac{\hbar^2}{m} G_{xy}^{21}(\omega) - 3 \frac{\hbar}{i} \frac{1}{e} G_{xy}^{22}(\omega), \tag{60}$$

$$-\hbar \omega G_{yy}^1(\omega) = 3 \frac{\hbar^2}{m} G_{yy}^{21}(\omega) - 3 \frac{\hbar}{i} \frac{1}{e} G_{yy}^{22}(\omega), \tag{61}$$

$$-\hbar \omega G_{xy}^{21}(\omega) = -\frac{\hbar}{i} \frac{k_x}{e} G_{xy}(\omega), \tag{62}$$

$$-\hbar \omega G_{yy}^{21}(\omega) = -\frac{\hbar}{i} \frac{k_y}{e} G_{yy}(\omega), \tag{63}$$

$$-\hbar \omega G_{xy}^{22}(\omega) = \frac{\hbar^2 k_x}{m} G_{xy}(\omega) - K_x G_{xy}^{21}(\omega) - \frac{\hbar \omega_z}{i} G_{yy}^{22}(\omega), \tag{64}$$

$$-\hbar \omega G_{yy}^{22}(\omega) = \frac{\hbar}{i} \frac{Ne^2}{m} C + \frac{\hbar^2 k_y}{m} G_{yy}(\omega) - K_y G_{yy}^{21}(\omega) - \frac{\hbar \omega_z}{i} G_{xy}^{22}(\omega), \tag{65}$$

where

$$C = \frac{1}{N} \langle \sum_n \sum_i k_y (y_{in} - Y_{in})^2 \rangle, \tag{66}$$

$$
\begin{aligned}
K_\nu = 4\frac{\hbar}{\mathrm{i}}\frac{e}{m}\Big\{\Big[&\frac{\langle p_{\nu in}^2\rangle}{2m} - k_\nu\langle(\nu_{in}-N_{in})^4\rangle \\
&-\frac{\mathrm{i}}{8\hbar}\langle(\nu_{in}-N_{in})\{\sum_{\substack{j\\(j\neq i)}}(p_{\nu in}(v_n'(\boldsymbol{r}_{in}-\boldsymbol{r}_{jn})+v_n'(\boldsymbol{r}_{jn}-\boldsymbol{r}_{in})))\\
&+\sum_{\substack{m\\(m\neq n)}}\sum_{j}(p_{\nu in}(V_{nm}(\boldsymbol{r}_{in}-\boldsymbol{r}_{jm})+V_{mn}(\boldsymbol{r}_{jm}-\boldsymbol{r}_{in})))\}\rangle\Big]\\
&+\frac{\hbar\omega_z}{2\hbar}\gamma\Big\}, \qquad (\nu = x,\ y)
\end{aligned}
\tag{67}
$$

here $\gamma = \langle y_{in}p_{xin}\rangle$ and $-\langle x_{in}p_{yin}\rangle$ when $\nu = x$ and y, respectively.

For approximate calculations the formula for the Faraday rotation ought to be of the form, instead of eq. (1),

$$
\phi(\omega) = \frac{\pi \mathrm{i}}{Vc\hbar\, n_0(\omega)}\int_{-\infty}^{\infty}\mathrm{d}t\, \mathrm{e}^{-i\omega t}\,\theta(t)\{\langle[\mathscr{J}_x(t),\mu_y(0)]\rangle - \langle[\mathscr{J}_y(t),\mu_x(0)]\rangle\} \tag{68}
$$

because of the loss of the antisymmetry property in respect to x and y by the acceptance of the approximations. As far as we confine ourselves to considering the linear term in the constant magnetic field H, the result becomes

$$
\phi(\omega) = \frac{2\pi N\hbar^2 e^3 H}{Vm^2c^2 n_0(\omega)}\,\frac{6\left(\frac{\hbar^2}{m}\right)^2}{(\hbar\omega)^3}\,\frac{\left[\begin{array}{l}\left\{\hbar\omega + 2\dfrac{K_{x0}-K_{y0}}{k_x-k_y}\right\}^2\\ -\dfrac{4}{k_x-k_y}\left\{\dfrac{3\hbar^2}{m}C_0 + \dfrac{(K_{x0}-K_{y0})^2}{k_x-k_y}\right\}\end{array}\right]}{\left[\begin{array}{l}(\hbar\omega)^4 + (\hbar\omega)\cdot 24\dfrac{\hbar^2}{m}(k_x+k_y)\\ +48\left(\dfrac{\hbar^2}{m}\right)^2(K_{x0}+K_{y0})\end{array}\right]}, \tag{69}
$$

where

$$
C_0 = \frac{1}{N}\langle\sum_n\sum_i(k_x^2(x_{in}-X_{in})^2 - k_y^2(y_{in}-Y_{in})^2)\rangle, \tag{70}
$$

$$
\begin{aligned}
K_{\nu0} = k_\nu\Big\{&\frac{\langle p_{\nu in}^2\rangle}{2m} - k_\nu\langle(\nu_{in}-N_{in})^4\rangle\\
&-\frac{\mathrm{i}}{8\hbar}\langle(\nu_{in}-N_{in})[\sum_{\substack{j\\(j\neq i)}}(p_{\nu in}(v_n'(\boldsymbol{r}_{in}-\boldsymbol{r}_{jn})+v_n'(\boldsymbol{r}_{jn}-\boldsymbol{r}_{in})))\\
&+\sum_{\substack{m\\(m\neq n)}}\sum_{j}(p_{\nu in}(V_{nm}(\boldsymbol{r}_{in}-\boldsymbol{r}_{jm})+V_{mn}(\boldsymbol{r}_{jm}-\boldsymbol{r}_{in})))]\rangle\Big\}, \qquad (\nu = x,\ y)
\end{aligned}
\tag{71}
$$

and the conditon $k_x \neq k_y$ has been used. It should be noted that there is no effect of k_z on the Faraday rotation $\phi(\omega)$.

When $k_x = k_y \equiv k$, $\phi(\omega)$ is written in the form

$$\phi(\omega)=\frac{2\pi N\hbar^2e^3H}{Vm^2c^2n_0(\omega)}\frac{24\left(\frac{\hbar^2}{m}\right)^2(K_{x0}-K_{y0})}{(\hbar\omega)^3}$$
$$\times\frac{\hbar\omega-3\frac{\hbar^2}{m}\frac{1}{K_{x0}-K_{y0}}C_0}{(\hbar\omega)^4+(\hbar\omega)\cdot 48\frac{\hbar^2}{m}k+48\left(\frac{\hbar^2}{m}\right)^2(K_{x0}+K_{y0})}. \tag{72}$$

For $k_x=k_y\equiv k$ and $K_{x0}=K_{y0}\equiv K_0$, $\phi(\omega)$ can be reduced to a simpler formula,

$$\phi(\omega)=-\frac{2\pi N\hbar^2e^3H}{Vm^2c^2n_0(\omega)}\frac{72\left(\frac{\hbar^2}{m}\right)^3C_0}{(\hbar\omega)^3}\frac{1}{(\hbar\omega)^4+(\hbar\omega)\cdot 48\frac{\hbar^2}{m}k+96\left(\frac{\hbar^2}{m}\right)^2K_0}. \tag{73}$$

6. Summary and Discussion

We have investigated the effects of the electron-electron interaction on the magneto-optical rotation. It has been exactly proved that the electron-electron interaction is ineffective on the magneto-optical rotation for the system composed of the electron harmonic-oscillators. This states that the Frenkel exciton does not contribute to the magneto-optical rotation for the harmonic-oscillator system. Since the Frenkel exciton plays the essential role for the anomalous optical rotatory dispersion in the natural optical rotation, this conclusion also implies that the anomalous magneto-optical rotatory dispersion at a helix-coil transition does not occur for this system in contrast with the case of the natural optical rotatory dispersion discussed by Moffitt, Fitts and Kirkwood.[2]

The calculation to prove no effect of the electron-electron interaction is very difficult by making use of the conventional formula[9,10] instead of ours.[12] For the natural optical rotation, Moffitt, Fitts and Kirkwood have presented theoretically the anomalous dispersion by complicated calculation of a perturbation of the inter-monomeric interaction.

It should be noted that when the constant magnetic field is perpendicular to the direction of the propagation of light (i.e. in the case of the Voigt configuration), the magneto-optical rotatory power is zero as far as we take account of the first order in the constant magnetic field.

For also the system composed of electron anharmonic-oscillators we have discussed the effects of the electron-electron interaction. The formula for the magneto-optical rotation is expressed in terms of the Fourier component of the Green function. By calculating the equations for the Green functions, the Green function with the electron-electron interaction does not appear in the first stage of calculation as is seen in eqs. (38)-(42). It can be considered that the electron-electron interaction has a little effect on the magneto-optical rotation.

In the present paper we have neglected the electron-phonon interaction. This interaction is discussed for the natural optical rotation in the previous paper[14] and hardly contributes to the natural optical rotation.

Appendix

When a potential $v_n(\boldsymbol{r}_{in})$ of the electron oscillator located at $\boldsymbol{R}_{in}(X_{in},\ Y_{in},\ Z_{in})$ is of the form

$$v_n(\boldsymbol{r}_{in})=\sum_{\mu} k_\mu |\mu_{in}-M_{in}|^3, \qquad (\mu=x,\ y,\ z \text{ and } M=X,\ Y,\ Z) \qquad (\mathrm{A}\cdot 1)$$

the equations for the Green functions can also be calcutated similarly by the way as is seen in sec. 3. Although the electron-electron interactions contribute to the magneto-optical rotation, the coupled equations for the Green functions is more simple as compared with the case of the anharmonic-oscillator model ($l=2$). The required equations are found to be

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\,G_{xy}(t)}{\mathrm{d}t}=-\frac{\hbar\omega_z}{\mathrm{i}}G_{yy}(t)+3\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{xy}(t), \qquad (\mathrm{A}\cdot 2)$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\,G_{yy}(t)}{\mathrm{d}t}=\frac{\hbar}{\mathrm{i}}\frac{Ne^2}{m}\delta(t)+\frac{\hbar\omega_z}{\mathrm{i}}G_{xy}(t)-\frac{\hbar\omega_x}{\mathrm{i}}G_{zy}(t)+3\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{yy}(t), \qquad (\mathrm{A}\cdot 3)$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\,G_{zy}(t)}{\mathrm{d}t}=\frac{\hbar\omega_x}{\mathrm{i}}G_{yy}(t)+3\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^1_{zy}(t), \qquad (\mathrm{A}\cdot 4)$$

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\,G^1_{\nu y}(t)}{\mathrm{d}t}=-2\frac{\hbar}{\mathrm{i}}\frac{1}{e}G^{22}_{\nu y}(t), \qquad (\mathrm{A}\cdot 5)$$

$$\begin{aligned}-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\,G^{22}_{\nu y}(t)}{\mathrm{d}t}=&\ \delta_{\nu y}\frac{\hbar}{\mathrm{i}}\frac{e^2}{m}\langle\sum_n\sum_i k_y|y_{in}-Y_{in}|\rangle\,\delta(t)\\&-\frac{\hbar}{\mathrm{i}}\frac{1}{e}G^{321}_{\nu y}(t)-G^{322}_{\nu y}(t)+3\frac{\hbar}{\mathrm{i}}\frac{e}{m}G^{323}_{\nu y}(t)\\&+\frac{e}{2m}G^{324}_{\nu y}(t)+\frac{e}{2m}G^{325}_{\nu y}(t), \qquad (\nu=x,\ y,\ z)\end{aligned} \qquad (\mathrm{A}\cdot 6)$$

where

$$G_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\mathscr{J}_\nu(t),\ \mu_y(0)]\rangle, \qquad (\mathrm{A}\cdot 7)$$

$$G^1_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu(\nu_{in}(t)-N_{in})^2\operatorname{sign}(\nu_{in}-N_{in}),\ \mu_y(0)]\rangle, \qquad (\mathrm{A}\cdot 8)$$

$$G^{22}_{\nu y}(t)=-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu|\nu_{in}(t)-N_{in}|\mathscr{J}_{\nu in}(t),\ \mu_y(0)]\rangle, \qquad (\mathrm{A}\cdot 9)$$

$$\begin{aligned}G^{321}_{\nu y}(t)=&-\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_n\sum_i k_\nu(\nu_{in}(t)-N_{in})^0\\&\times\operatorname{sign}(\nu_{in}-N_{in})\mathscr{J}_{\nu in}(t)\,\mathscr{J}_{\nu in}(t),\ \mu_y(0)]\rangle,\end{aligned} \qquad (\mathrm{A}\cdot 10)$$

$$G^{322}_{\nu y}(t)=\left(\frac{\hbar\boldsymbol{\omega}}{\mathrm{i}}\times\boldsymbol{G}^{22}_y\right)_\nu, \qquad (\mathrm{A}\cdot 11)$$

$$G_{\nu y}^{323}(t) = -\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_{n}\sum_{i} k_{\nu}^{2}(\nu_{in}(t) - N_{in})^{3},\ \mu_{y}(0)]\rangle, \tag{A・12}$$

$$G_{\nu y}^{324}(t) = -\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_{n}\sum_{\substack{i\\(i\neq j)}}\sum_{j} k_{\nu}|\nu_{in}(t) - N_{in}| \times (p_{\nu in}(v_{n}'(\boldsymbol{r}_{in}(t) - \boldsymbol{r}_{jn}(t)) + v_{n}'(\boldsymbol{r}_{jn}(t) - \boldsymbol{r}_{in}(t)))),\ \mu_{y}(0)]\rangle, \tag{A・13}$$

$$G_{\nu y}^{325}(t) = -\frac{\mathrm{i}}{\hbar}\theta(t)\langle[\sum_{n}\sum_{\substack{m\\(n\neq m)}}\sum_{i}\sum_{j} k_{\nu}|\nu_{in}(t) - N_{in}| \times (p_{\nu in}(V_{nm}(\boldsymbol{r}_{in}(t) - \boldsymbol{r}_{jm}(t)) + V_{mn}(\boldsymbol{r}_{jm}(t) - \boldsymbol{r}_{in}(t)))),\ \mu_{y}(0)]\rangle, \tag{A・14}$$

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

It should be noted that, as has been shown in sec. 3, the electron-electron interactions are encompassed with $G_{\nu y}^{324}(t)$ and $G_{\nu y}^{325}(t)$ alone on the right-hand side of eq. (A・6) in the first stage of the calculation.

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