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Exciton-Phonon Interaction in Optical Rotation

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Effects of exciton-phonon interaction on optical rotation and refractive index of a polymer are investigated on the basis of the Frenkel exciton model. Exciton-phonon interaction has a little effect on optical rotation and refractive index in comparison with that exerted by electron-electron interaction between monomers, as far as the Frenkel exciton model is concerned. When exciton-phonon interaction is negligible and intermonomeric interaction is much less than exciton energy, the optical rotatory dispersion has the anomalous term; however, the anomalous dispersion disappears in the absorption of light. A relation between rotational angle and refractive index is derived.

1. Introduction

One of the present authors (T. A.)[1] developed the microscopic theory of optical rotation on the basis of the linear response theory and applied it to a long helical polymer by using the Frenkel exciton model. In that theory, vibrations of monomers are neglected, that is, the indirect intermonomeric interaction through phonons is neglected.

In most of the theoretical investigations of optical rotation, temperature-dependent optical rotation formulae have been derived by the perturbation theory through introducing the Boltzmann distribution over energy levels.[2] As in the BCS theory of superconductivity, electron-electron interaction through phonons may give rise to the temperature dependence of optical rotation.

In the present paper, we investigate the effect of exciton-phonon interaction on optical rotation and refractive index in a linear polymer.

In sec. 2 we make the total Hamiltonian of the polymer on the basis of the molecular exciton model by using the second quantization technique. In sec. 3 formulae for optical rotation and refractive index are derived in terms of response function as the commutator of exciton annihilation and creation operators. In sec.

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4 we obtain response functions by the Green function method. It has been proved that exciton-phonon interaction has a little effect on optical rotation and refractive index as far as the Frenkel exciton model is concerned. We have found that rotational angle is closely related to refractive index. Section 5 is devoted to discussion.

2. Hamiltonian

The system under consideration is a polymer composed of similar monomers. The total Hamiltonian $\mathscr{H}$ of the system is expressed as

$$\mathscr{H}=\sum_n \mathscr{H}_n+\frac{1}{2}\sum_{\substack{n\,m\\(n\neq m)}}\sum_i\sum_j V_{nm}(\boldsymbol{r}_{in}-\boldsymbol{r}_{jm})+\sum_{\substack{n\,m\\(n\neq m)}}\sum_i v(\boldsymbol{r}_{in}-\boldsymbol{R}_m), \tag{1}$$

where $\boldsymbol{r}_{in}$ is the co-ordinate of the ith electron in the nth monomer in the polymer, $\boldsymbol{R}_m$ the co-ordinate of the centre of the mth monomer (for example, that of the nucleus of the mth monomer), $\mathscr{H}_n$ the Hamiltonian of the nth isolated monomer, $V_{nm}(\boldsymbol{r}_{in}-\boldsymbol{r}_{jm})$ the interaction between the ith electron in the nth monomer and the jth electron in the mth monomer and $v(\boldsymbol{r}_{in}-\boldsymbol{R}_m)$ is the interaction between the ith electron in the nth monomer and the nucleus of the mth monomer.

In order to derive phonons, taking an average over the positions of electrons in intermonomeric interaction V_{nm}, we obtain

$$V_{nm}^{\alpha\beta\alpha'\beta'}(\boldsymbol{R}_n-\boldsymbol{R}_m)=\int d\boldsymbol{r}_{in}\int d\boldsymbol{r}_{jm}\ \varphi_{n\alpha}^*(\boldsymbol{r}_{in})\varphi_{m\beta}^*(\boldsymbol{r}_{jm})V_{nm}(\boldsymbol{r}_{in}-\boldsymbol{r}_{jm})\times\varphi_{n\alpha'}(\boldsymbol{r}_{in})\varphi_{m\beta'}(\boldsymbol{r}_{jm}), \tag{2}$$

where $\varphi_{n\alpha}(\boldsymbol{r}_{in})$ is the α-state function of the ith electron in the nth monomer. We consider the linear polymer, composed of N similar monomers spaced a distance d apart on the z-axis, and small vibrations of monomers along the z-axis. Let us define a displacement u_n as the displacement of the nth monomer from its equilibrium position R_n^0, that is, $R_n=R_n^0+u_n$, and then $V_{nm}^{\alpha\beta\alpha'\beta'}$ may be expanded as a power series in displacement u_n around the equilibrium position R_n^0 as follows:

$$V_{nm}^{\alpha\beta\alpha'\beta'}(R_n-R_m)=V_{nm}^{\alpha\beta\alpha'\beta'}(R_n^0-R_m^0)+\frac{1}{2}\left(\frac{\partial^2 V_{nm}^{\alpha\beta\alpha'\beta'}}{\partial R_n^2}\right)_0(u_n-u_m)^2+\cdots. \tag{3}$$

We can derive phonons from the harmonic term in eq. (3) and the kinetic energy part of $\mathscr{H}_n$ in eq. (1) by the operator technique. Introducing a Fourier

transformation to the following set of new operators, derived from operators $u_n(t)$ and $p_n(t)$, the momentum of the nth monomer,

$$\left.\begin{aligned} U_k(t) &= \frac{1}{\sqrt{N}}\sum_n e^{ikrd}u_n(t) \\ P_k(t) &= \frac{1}{\sqrt{N}}\sum_n e^{-ikrd}p_n(t) \end{aligned}\right\} \quad \left(\begin{matrix} k = \dfrac{2\pi}{Nd}m \\ m = 0, 1, 2, \cdots, N-1 \end{matrix}\right), \tag{4}$$

one may diagonalize the Hamiltonian of phonons in the form

$$\mathscr{H}_p = \frac{1}{2M}\sum_k P_k^\dagger P_k + \frac{M}{2}\sum_k (\omega(k))^2 U_k^\dagger U_k, \tag{5}$$

where M denotes the mass of the monomer and

$$\left.\begin{aligned} M(\omega(k))^2 &= \tilde{V}(0) - \tilde{V}(k) \\ \tilde{V}(k) &= \sum_{n-m=0}^{N-1} e^{ik(n-m)d}\sum_\alpha\sum_\beta\sum_{\alpha'}\sum_{\beta'}\left(\frac{\partial^2 V_{nm}^{\alpha\beta\alpha'\beta'}}{\partial R_n^2}\right)_0 \end{aligned}\right\}. \tag{6}$$

Let us define the following annihilation and creation operators for phonons:[3]

$$\left.\begin{aligned} b_k &= \frac{1}{\sqrt{2M\hbar\omega(k)}}(P_k - iM\omega(k)U_k^\dagger) \\ b_k^\dagger &= \frac{1}{\sqrt{2M\hbar\omega(k)}}(P_k^\dagger + iM\omega(k)U_k) \end{aligned}\right\}. \tag{7}$$

Equation (5) can be expressed, by use of eq. (7), as

$$\mathscr{H}_p = \sum_k \hbar\omega(k)\left(b_k^\dagger b_k + \frac{1}{2}\right). \tag{8}$$

It is verified by using the commutation relations for u_n and p_n that the operators b_k and $b_k^\dagger$ satisfy the following commutation relations[3]

$$[b_k,\ b_{k'}^\dagger] = \delta_{kk'}, \quad [b_k,\ b_{k'}] = 0, \quad [b_k^\dagger,\ b_{k'}^\dagger] = 0. \tag{9}$$

The last term in eq. (1) gives rise to exciton-phonon interaction. If we expand $v(\boldsymbol{r}_{in} - \boldsymbol{R}_m)$ in a power series in u_m, we find that

$$v(\boldsymbol{r}_{in} - \boldsymbol{R}_m) = v(\boldsymbol{r}_{in} - \boldsymbol{R}_m^0) - \left(\frac{\partial v}{\partial R_m}\right)_0 u_m + \cdots, \tag{10}$$

and the electron-phonon interaction is obtained from the second term on the right-hand side of eq. (10) in the form

$$\mathscr{H}_{\text{el-p}}=\sum_k\sum_\alpha\sum_{\alpha'}v^{\alpha\alpha'}(k)\frac{1}{\sqrt{N}}\sum_n e^{-ikrd}\,a_{n\alpha}^{\dagger}\,a_{n\alpha'}(b_k^{\dagger}-b_{-k}),\tag{11}$$

where $a_{n\alpha}$ and $a_{n\alpha}^{\dagger}$ are the annihilation and the creation operator for the α-state electron in the nth monomer, respectively, and

$$v^{\alpha\alpha'}(k)=\frac{1}{i}\sqrt{\frac{1}{2M\omega(k)}}\sum_{n-m}e^{ik(n-m)d}\times\int d\boldsymbol{r}_{in}\varphi_{n\alpha}^{*}(\boldsymbol{r}_{in})(-1)\left(\frac{\partial v}{\partial R_m}\right)_0\varphi_{n\alpha'}(\boldsymbol{r}_{in}).\tag{12}$$

We investigate the effect of phonon on optical rotation by making use of the Frenkel exciton model of polymer. To deriving exciton-phonon interaction, it is convenient to make a Fourier transform

$$\left.\begin{aligned}B_{kf}&=\frac{1}{\sqrt{N}}\sum_n e^{-ikrd}B_{nf}\\ B_{kf}^{\dagger}&=\frac{1}{\sqrt{N}}\sum_n e^{ikrd}B_{nf}^{\dagger}\end{aligned}\right\},\tag{13}$$

where B_{nf} and $B_{nf}^{\dagger}$ are the annihilation and the creation operator for the exciton at the nth monomer and of the fth level, respectively, i.e. $B_{nf}=a_{n0}^{\dagger}a_{nf}$ and $B_{nf}^{\dagger}=a_{nf}^{\dagger}a_{n0}$.[4] Thus, the exciton-phonon interaction is given by

$$\mathscr{H}_{\text{e-p}}=\sum_f\sum_k v_f(k)(B_{-kf}^{\dagger}+B_{kf})(b_k^{\dagger}-b_{-k})\tag{14}$$

with the commutation relations for B_{kf} and $B_{kf}^{\dagger}$

$$[B_{kf},\ B_{k'f'}^{\dagger}]=\delta_{kk'}\delta_{ff'},\quad [B_{kf},\ B_{k'f'}]=0,\quad [B_{kf}^{\dagger},\ B_{k'f'}^{\dagger}]=0,\tag{15}$$

where $v_f(k)=v^{f0}(k)$ with superscript 0 denoting the ground state of electron.

By making use of eq. (13) the Hamiltonian including no phonon part is expressed in terms of B_{kf} and $B_{kf}^{\dagger}$ by second quantization.[1]

Finally, the total Hamiltonian of the polymer becomes

$$\begin{aligned}\mathscr{H}=&\left[E_g+\sum_f\sum_k\Delta_f B_{kf}^{\dagger}B_{kf}+\frac{1}{2}\sum_f\sum_k V_f(k)(B_{-kf}^{\dagger}+B_{kf})(B_{kf}^{\dagger}+B_{-kf})\right]\\&+\sum_f\hbar\omega(k)\left(b_k^{\dagger}b_k+\frac{1}{2}\right)\\&+\sum_f\sum_k v_f(k)(B_{-kf}^{\dagger}+B_{kf})(b_k^{\dagger}-b_{-k})\end{aligned}\tag{16}$$

under the conditions $\langle B_{kf}^{\dagger}B_{kf}\rangle \ll 1$ and $\sum_{f} B_{kf}^{\dagger}B_{kf} = 1$, where E_g is the ground state energy, Δ_f the eigen energy of the f-state of monomer and $V_f(k)$ the Fourier transform of the interaction between monomers[1,4] given by

$$\left.\begin{aligned} V_f(k) &= \sum_{n-m} \mathrm{e}^{\mathrm{i}k(n-m)d} V_{nmf} \\ V_{nmf} &\equiv \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}' \varphi_{nf}^{*}(\boldsymbol{r}) \varphi_{m0}^{*}(\boldsymbol{r}') V(\boldsymbol{r}-\boldsymbol{r}') \varphi_{n0}(\boldsymbol{r}) \varphi_{mf}(\boldsymbol{r}') \end{aligned}\right\}. \tag{17}$$

3. Formulation of Optical Rotation

Maxwell's equations give the basic equation for optical rotation

$$q_{\pm}^{2} - q_0^{2} + \frac{1}{c^2}[Q_{\mathrm{D}}(q_{\pm},\omega) \mp \mathrm{i}Q_{\mathrm{N}}(q_{\pm},\omega)] = 0, \tag{18}$$

where $q_0 = \omega/c$ and the upper (lower) sign corresponds to left (right) circularly polarized light. If we take the direction of propagation of an incident monochromatic light of frequency ω to be parallel to the z-axis, correlation functions $Q_{\mathrm{D}}(q,\omega)$ and $Q_{\mathrm{N}}(q,\omega)$ are expressed in terms of the spatial Fourier transform $\boldsymbol{j}(q,t)$ of the electric current density operator in the form[1,5]

$$\begin{aligned} Q_{\mathrm{D}}(q,\ \omega) = \frac{2\pi\mathrm{i}\omega}{V} \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{-\mathrm{i}\omega t}\theta(t) \int_{0}^{\beta} \mathrm{d}\lambda \langle j_x(q,t) j_x(-q, \mathrm{i}\hbar\lambda) \\ + j_y(q,t) j_y(-q, \mathrm{i}\hbar\lambda)\rangle \end{aligned} \tag{19}$$

and

$$\begin{aligned} Q_{\mathrm{N}}(q,\ \omega) = \frac{2\pi\mathrm{i}\omega}{V} \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{-\mathrm{i}\omega t}\theta(t) \int_{0}^{\beta} \mathrm{d}\lambda \langle j_x(q,t) j_y(-q, \mathrm{i}\hbar\lambda) \\ - j_y(q,t) j_x(-q, \mathrm{i}\hbar\lambda)\rangle, \end{aligned} \tag{20}$$

where V denotes the volume of the system, $\theta(t)$ the step function, $\beta = (kT)^{-1}$ and the triangular bracket represents the canonical average, that is,

$$\langle \cdots \rangle = \frac{\mathrm{Tr}[\exp(-\beta\mathscr{H})\cdots]}{\mathrm{Tr}[\exp(-\beta\mathscr{H})]}.$$

When one expands $Q_{\mathrm{D}}(q,\omega)$ and $Q_{\mathrm{N}}(q,\omega)$ as a power series in the wave-number q of light up to the first order in q into

$$\left.\begin{aligned} Q_{\mathrm{D}}(q,\omega) &= Q_{\mathrm{D}}^{(0)}(0,\omega) + qQ_{\mathrm{D}}^{(1)}(0,\omega) \\ Q_{\mathrm{N}}(q,\omega) &= Q_{\mathrm{N}}^{(0)}(0,\omega) + qQ_{\mathrm{N}}^{(1)}(0,\omega) \end{aligned}\right\} \tag{21}$$

and when one defines refractive indices n_+ and n_-, respectively, for left and right circularly polarized lights and the rotational angle ϕ of the plane of polarization per unit path length* by

$$\left.\begin{aligned} \tilde{n} &= \frac{q_- + q_+}{2} = q_0 \frac{n_- + n_+}{2} \\ \phi &= \frac{q_- - q_+}{2} \end{aligned}\right\}, \tag{22}$$

one obtains relations between $\tilde{n}$ and ϕ as follows:

$$\left.\begin{aligned} \tilde{n}^2 - \phi^2 &= {q_0}^2 - \frac{1}{c^2} Q_{\mathrm{D}}^{(0)}(0,\omega) \\ \phi &= -\frac{\mathrm{i}}{2c^2} Q_{\mathrm{N}}^{(1)}(0,\omega) \end{aligned}\right\}, \tag{23}$$

where use has been made of $Q_{\mathrm{D}}^{(1)}(0,\omega) = Q_{\mathrm{N}}^{(0)}(0,\omega) = 0$. It is shown that refractive index relates closely to rotational angle.

Let us suppose that the polymer has a pitch angle φ between adjacent monomers. The Fourier transform of the electric current density operator is represented in terms of B_{nf} and $B_{nf}^{\dagger}$, under the assumption—without loss of generality—that the wave function is real, in the form

$$\boldsymbol{j}(q,t) = \sum_f \sum_{n=0}^{N-1} \mathrm{e}^{\mathrm{i}qnd\mathsf{T}^n} \cdot \boldsymbol{J}(q)(B_{nf}^{\dagger}(t) - B_{nf}(t)) \tag{24}$$

with

$$\mathsf{T}^n = \begin{bmatrix} \cos n\varphi & -\sin n\varphi \\ \sin n\varphi & \cos n\varphi \end{bmatrix}$$

and

$$\boldsymbol{J}(q) = (\boldsymbol{J}^{(0)}(q))_{f0},$$

where $(\boldsymbol{J}^{(0)}(q))_{f0}$ is the matrix element of the electric current density operator $\boldsymbol{J}^{(0)}(q)$ for the zeroth monomer.

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

Let us consider only the lowest exciton for the sake of simplicity. Substitution of eq. (24) into eqs. (19) and (20) leads to

$$Q_{\mathrm{D}}(q,\omega)=-\frac{\pi N\hbar\omega}{V\Delta_f}\Big\{J_0(q)[G_{q+\frac{\varphi}{d}f}(\omega)+G_{q-\frac{\varphi}{d}f}(\omega)] - \mathrm{i}J_1(q)[G_{q+\frac{\varphi}{d}f}(\omega)-G_{q-\frac{\varphi}{d}f}(\omega)]\Big\} \tag{25}$$

and

$$Q_{\mathrm{N}}(q,\omega)=-\frac{\pi N\hbar\omega}{V\Delta_f}\Big\{J_1(q)[G_{q+\frac{\varphi}{d}f}(\omega)+G_{q-\frac{\varphi}{d}f}(\omega)] + \mathrm{i}J_0(q)[G_{q+\frac{\varphi}{d}f}(\omega)-G_{q-\frac{\varphi}{d}f}(\omega)]\Big\}, \tag{26}$$

where

$$\left.\begin{aligned} J_0(q)&=J_x(q)J_x(-q)+J_y(q)J_y(-q)\\ J_1(q)&=J_x(q)J_y(-q)-J_y(q)J_x(-q)\end{aligned}\right\} \tag{27}$$

and

$$G_{kf}(\omega)=\sum_{n-m=0}^{N-1}\mathrm{e}^{\mathrm{i}k(n-m)d}\int_{-\infty}^{\infty}\mathrm{d}t\mathrm{e}^{-\mathrm{i}\omega t}\frac{\mathrm{i}}{\hbar}\theta(t) \times\langle[B_{nf}^{\dagger}(t)+B_{nf}(t),\ B_{mf}^{\dagger}(0)-B_{mf}(0)]\rangle. \tag{28}$$

4. Green Functions

Refractive index and optical rotation can be expressed by use of Green functions

$$G_{kf}(\omega)=\int_{-\infty}^{\infty}\mathrm{d}t\mathrm{e}^{-\mathrm{i}\omega t}G_{kf+}(t) \tag{29}$$

with

$$G_{kf\pm}(t)=\frac{\mathrm{i}}{\hbar}\theta(t)\langle[B_{kf}^{\dagger}(t)\pm B_{-kf}(t),\ B_{-kf}^{\dagger}(0)-B_{kf}(0)]\rangle, \tag{30}$$

as has been seen in eqs. (19), (20), (21), (23), (25) and (26). In course of calculating Green functions, one obtains an equation

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}G_{kf+}(t)}{\mathrm{d}t}=2\delta(t)+\Delta_fG_{kf-}(t) \tag{31}$$

by differentiating eq. (30) with respect to time t. If one takes the time derivative of $G_{kf-}(t)$ on the right-hand side of eq. (31) in order to obtain $G_{kf+}(t)$, one will have a Green function $\mathscr{G}_{kf-}(t)$ of new type

$$\mathscr{G}_{kf\pm}(t)=\frac{\mathrm{i}}{\hbar}\theta(t)\langle[b_k^{\dagger}(t)\pm b_{-k}(t),\ B_{-kf}^{\dagger}(0)-B_{kf}(0)]\rangle, \tag{32}$$

which immediately allows $\mathscr{G}_{kf+}(t)$ to be defined. Similarly, if one takes a series of time derivatives for these Green functions, one will obtain coupled equations of Green functions of various types. By solving these simultaneous equations for $G_{kf\pm}(t)$ and $\mathscr{G}_{kf\pm}(t)$, one can obtain

$$G_{kf}(\omega)=\frac{2\hbar\omega}{(\hbar\omega)^2-\Delta_f\left[(\Delta_f+2V_f(k))-\dfrac{4(\hbar\omega(k))(v_f(k))^2}{(\hbar\omega)^2-(\hbar\omega(k))^2}\right]}. \tag{33}$$

Under the condition $\hbar\omega(k)\ll\hbar\omega$, eq. (33) may be rewritten into

$$G_{kf}(\omega)=\frac{2\hbar\omega}{(\hbar\omega)^2-\Delta_f(\Delta_f+2V_f(k))+4\Delta_f(\hbar\omega(k))\left(\dfrac{v_f(k)}{\hbar\omega}\right)^2}. \tag{34}$$

Since $v_f(k)\ll\hbar\omega$, the value of the third term in the denominator in eq. (34) is much less than those of the first and second terms. This states that there is a little effect of the exciton-phonon interaction on refractive index and optical rotation as far as the Frenkel exciton model is concerned.

When one neglects the exciton-phonon interaction, the Green function $G_{kf}(\omega)$ reduces to

$$G_{kf}(\omega)=\frac{2\hbar\omega}{[(\hbar\omega)^2-\Delta_f{}^2]-2\Delta_f V_f(k)}, \tag{35}$$

which has been given in ref. 1. In order to calculate $Q_{\mathrm{D}}(q,\omega)$ and $Q_{\mathrm{N}}(q,\omega)$ represented by eqs. (25) and (26), let us define the sum and remainder of Green functions up to the first order in q as follows:

$$G_{\pm}\equiv G_{q+\frac{\varphi}{d}f}(\omega)\pm G_{q-\frac{\varphi}{d}f}(\omega)=G_{\pm}{}^{(0)}+qG_{\pm}{}^{(1)}. \tag{36}$$

Since $J_0(q)$ in eqs. (25) and (26) has no linear term in q and $J_1(q)$ in those equations has no constant term in q, $Q_{\mathrm{D}}(q,\omega)$ and $Q_{\mathrm{N}}(q,\omega)$ reduce to

$$\left.\begin{aligned}&Q_{\mathrm{D}}(q,\omega)=A[J_0{}^{(0)}G_+{}^{(0)}]\\&Q_{\mathrm{N}}(q,\omega)=Aq[J_1{}^{(1)}G_+{}^{(0)}+\mathrm{i}J_0{}^{(0)}G_-{}^{(1)}]\\&A=-\frac{\pi N\hbar\omega}{V\Delta_f}\end{aligned}\right\}, \tag{37}$$

where $J_0^{(0)} = J_0(0)$ and $J_1(q) = qJ_1^{(1)}$. Consequently, one may say that $Q_D(q, \omega)$ is independent of q and that $Q_N(q, \omega)$ is proportional to q.

Furthermore, when we expand the Green function (35) in a power series in $V_f(k)$ as in ref. 1, then using eq. (17) and the expression

$$\frac{1}{\left[(\hbar\omega)^2 - \Delta_f^2 - 2\Delta_f \sum_{n-m} e^{i(n-m)\varphi} V_{nmf}\right]^2}$$

$$\approx \frac{1}{\left[(\hbar\omega)^2 - \Delta_f^2\right]^2}\left[1 + \frac{4\Delta_f \sum_{n-m} e^{i(n-m)\varphi} V_{nmf}}{(\hbar\omega)^2 - \Delta_f^2}\right]$$

we find out an expression

$$\frac{\partial G_+^{(0)}}{\partial(\varphi/d)} = G_-^{(1)}. \tag{38}$$

By making use of this equation one can derive the relation between refractive index and optical rotation

$$\tilde{n}\frac{\partial \tilde{n}}{\partial(\varphi/d)} + C(\tilde{n}^2 - q_0^2) = \phi\frac{\partial \phi}{\partial(\varphi/d)} + C\phi^2 - \phi, \tag{39}$$

where

$$C = -\frac{i}{2}\frac{J_1^{(1)}}{J_0^{(0)}}. \tag{40}$$

This shows a close relationship between refractive index and optical rotation.

5. Discussion and Summary

We have investigated the exciton-phonon interaction of linear polymer on the basis of the molecular exciton theory of second quantization. The total Hamiltonian of the polymer in terms of exciton annihilation and creation operators is written as eq. (16), and then it is shown that the Hamiltonian satisfies the condition of exciton momentum conservation.

The refractive index and the optical rotational angle are expressed in terms of response functions, which are shown in eqs. (23), (25), (26) and (28). In order to obtain Green function (i.e. response function) we have had a set of four equations for $G_{kf\pm}(t)$ and $\mathscr{G}_{kf\pm}(t)$, and then we have obtained the exact solutions of these four simultaneous equations with a finite chain of coupled equations, without using the decoupling method. It should be noted that one of these exact solutions, given by eq. (33), could be obtained because of the relevant Hamiltonian

in the form of eq. (16) on the basis of the Frenkel exciton model.

In the optical frequency region it may be satisfied that $\hbar\omega(k) \ll \hbar\omega$, hence the Green function may be allowed to reduce to the form of eq. (34). Since the exciton-phonon interaction energy is much less than photon energy, the value of the third term in the denominator on the right-hand side of eq. (34) is negligibly small as compared with those of the other terms. This means that the exciton-phonon interaction has a little effect on refractive index and optical rotation.

As has been seen in eqs. (25) and (26), $Q_{\mathrm{D}}(q,\omega)$ and $Q_{\mathrm{N}}(q,\omega)$ are expressed in terms of $G_{\pm}$ defined by eq. (36), $J_0(q)$ and $J_1(q)$. In these expressions the roles of $J_0(q)$ and $J_1(q)$ are interchanged with each other in $Q_{\mathrm{D}}(q,\omega)$ and $Q_{\mathrm{N}}(q,\omega)$ that is, the anomalous dispersion relates to $J_1(q)$ in the absorption of light and to $J_0(q)$ in the optical rotation. When the effect of exciton-phonon interaction can be neglected, $Q_{\mathrm{D}}(q,\omega)$ has no anomalous dispersion, whereas $Q_{\mathrm{N}}(q,\omega)$ has the anomalous dispersion, because the anomalous dispersion term arises from the first order term of q, i.e. $G_{-}^{(1)}$ in eq. (37).

By expanding the Green function of eq. (35) in a power series in $V_f(k)$, we have found a relation between refractive index and optical rotational angle as expressed by eq. (39). Therefore, it has been seen that the optical rotation is in close connection with the refractive index or the absorption of light. The constant C in eq. (39) corresponds to the gyration constant or the rotatory parameter g_0 given by the classical phenomenological theory of optical rotation developed in ref. 6.

References

1) T. Ando, Prog. Theor. Phys., **40** (1968), 471.
2) See, for example, Ying-Nan Chiu, J. Chem. Phys., **52** (1970), 1042.
3) J. M. Ziman, *Elements of Advanced Quantum Theory*, Chap. 1, Cambridge Univ. P., Cambridge, 1969.
4) R. Hoffmann, Radiat. Res., **20** (1963), 140.
5) T. Ando and Y. Kato, J. Phys. Soc. Jpn., **38** (1975), 509.
6) Y. Kato, J. Fac. Eng., Shinshu Univ., No. 56 (1984), 1.