Borrowed Intensities for Optical Absorption
and Optical Rotation in Helices

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Expressions for borrowed intensities on oscillator strength and rotational strength in a helical polymer are formulated on the basis of a formula in terms of a response function which represents a correlation of electric current densities based on the linear response theory, that is, on the basis of the first principle. The borrowed intensities for optical absorption and optical rotation and f-sum rule in the system of two excited states with the arbitrary strength of interaction between residues are discussed. It is seen that the borrowed intensities for anomalous optical rotation and that for intrinsic optical rotation have close connections with each other.

1. Introduction

Since 1960, the theoretical studies of hypochromism in helical polymer have been made.[1-4] Tinoco[1] and Rhodes[2] have developed equations for the oscillator strength based on the first order degenerate perturbation theory by taking into account the effect of exciton interaction and dispersion force interaction on the oscillator strength of a helical polymer. Hypochromism is attributed mainly to dispersion force interaction between the residues.[2] McLachlan and Ball[3] have shown by the formulae based on the time-dependent self-consistent field theory that the hypochromism for optical absorption spectrum and the anomalous optical rotatory dispersion in helical polymer are interpreted purely as a local field effect. Rhodes and Chase[4] was discussed the optical absorption and the hypochromism in a coupled molecular system by means of generalized susceptibility theory using linear response functions.

In the previous papers, a formula for the natural optical rotation[5] and a general theory of the Faraday effect[6] was developed on the basis of a standpoint of the microscopic Maxwell equation. The formula for the Faraday rotation encompasses

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the theory of natural optical rotation and it is very useful for studying the natural optical rotation from the same points of view.[6] Furthermore, the formula for refractive index was developed in a similar fashion to the formula for the Faraday rotation including the natural optical rotation.[7] It is seen that optical absorption and optical rotation in helices have the close relations with each other in the form of mathematical formulae.[7]

In the present paper, we investigate the oscillator strengths and the rotational strengths in a helical polymer based on the Frenkel exciton model by means of our general theory.[6] The relations between the borrowed intensities for optical absorption and that for optical rotation are discussed.

In sec. 2 the formulae for the refractive index and for the optical rotation in helices are presented by the technique in the previous paper.[7] In sec. 3 the expressions for the borrowed intensities on the oscillator strengths and the rotational strengths are derived in terms of interactions of arbitrary magnitude between residues. The ralations between the borrowed intensities are dincussed. Section 4 is devoted to conclusion.

2. Optical Absorption and Optical Rotation in Helices

In the present section we shall merely express some of the important equations obtained in our previous papers[6,7] which are needed later.

The refractive index $n(\omega)$ and the optical rotational angle $\phi(\omega)$ of the plane of polarization per unit path length* for light with angular frequency ω propagating to the z direction in medium are in the form

$$n(\omega) = 1 - \frac{1}{2c^2 q_0^2} Q_D(q_0, \omega) \qquad (1)$$

and

$$\phi(\omega) = -\frac{i}{2c^2 q_0} Q_N(q_0, \omega), \qquad (2)$$

respectively, where $q_0 = \omega/c$, c is the speed of light in vacuum,

$$Q_D(q, \omega) = \frac{1}{2} [Q_{xx}(q, \omega) + Q_{yy}(q, \omega)] \qquad (3)$$

and

$$Q_N(q, \omega) = \frac{1}{2} [Q_{xy}(q, \omega) - Q_{yx}(q, \omega)] \qquad (4)$$

with the wave-number q and the angular frequency ω. Expressions $Q_{\mu\nu}(q, \omega)$ are given by

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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.

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

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

with

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

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

where $\boldsymbol{j}(q,\ t)$ is the spatial Fourier component of electric current density operator, 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.

The system under consideration is a helical polymer composed of N similar residues, whose adjacent distance along the helical axis is d and whose pitch angle is φ. By taking the helical axis along the z axis and by using the Frenkel exciton model, the quantity $Q_{\mu\nu}(q,\ \omega)$ is written in terms of correlation functions $C_{nm}(\omega\,;f,f')$ as

$$Q_{\mu\nu}(q,\ \omega) = \frac{4\pi i\omega}{V} \sum_n \sum_m \sum_f \sum_{f'} e^{iq(n-m)d}$$
$$\times (\boldsymbol{T}^n \cdot \boldsymbol{J}(q,f))_\mu (\boldsymbol{T}^m \cdot \boldsymbol{J}(-q,f'))_\nu C_{nm}(\omega\,;f,f'), \tag{6}$$

where n, m denote indices labelling the residues, f, f' indices labelling the energy eigenstates, $\boldsymbol{T}$ a matrix

$$T = \begin{bmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{bmatrix},$$

which makes a rotation of angle φ and $\boldsymbol{J}(q,f)$ denotes the matrix element between the excited state f and the ground state 0 of the electric current density operator of the zeroth residue. By making use of an expression

$$\boldsymbol{j}(q,t) = \sum_{n=0}^{N-1} \sum_f e^{iqnd} \boldsymbol{T}^n \cdot \boldsymbol{J}(q,f)(B_{nf}^\dagger(t) - B_{nf}(t)), \tag{7}$$

the correlation function $C_{nm}(\omega\,;f,f')$ is represented as

$$C_{nm}(\omega\,;f,f') = \int_{-\infty}^{\infty} dt\ e^{-i\omega t}\theta(t)$$
$$\times \int_0^\beta d\lambda \langle \{B_{nf}^\dagger(t-i\hbar\lambda) - B_{nf}(t-i\hbar\lambda)\}\{B_{mf'}^\dagger(0) - B_{mf'}(0)\}\rangle, \tag{8}$$

where $B_{nf}^\dagger$ and B_{nf} are the creation and the annihilation operator of the Frenkel exciton relating to the fth level at the nth residue, respectively. Here use has been made of the assumption without losing its generality that the wave functions $|f\rangle$ and $|0\rangle$ are real. When the Fourier transform is defined by

$$C_k(\omega\,;f,f') = \sum_{n-m=0}^{N-1} e^{ik(n-m)d} C_{nm}(\omega\,;f,f'), \tag{9}$$

$$k = \frac{2\pi}{Nd} l \qquad (l = 0, 1, 2, \cdots, N-1),$$

the expressions $Q_D(q, \omega)$ and $Q_N(q, \omega)$ become

$$Q_D(q, \omega) = \frac{i\pi N\omega}{V} \sum_f \sum_{f'} \{J_0(q; f, f')[C_{q+\varphi/d}(\omega; f, f') + C_{q-\varphi/d}(\omega; f, f')]$$

$$- iJ_1(q; f, f')[C_{q+\varphi/d}(\omega; f, f') - C_{q-\varphi/d}(\omega; f, f')]\} \qquad (10)$$

and

$$Q_N(q, \omega) = \frac{i\pi N\omega}{V} \sum_f \sum_{f'} \{J_1(q; f, f')[C_{q+\varphi/d}(\omega; f, f') + C_{q-\varphi/d}(\omega; f, f')]$$

$$+ iJ_0(q; f, f')[C_{q+\varphi/d}(\omega; f, f') - C_{q-\varphi/d}(\omega; f, f')]\}, \qquad (11)$$

respectively, where

$$J_0(q; f, f') = J_x(q, f)J_x(-q, f') + J_y(q, f)J_y(-q, f') \qquad (12)$$

and

$$J_1(q; f, f') = J_x(q, f)J_y(-q, f') - J_y(q, f)J_x(-q, f'). \qquad (13)$$

By making use of the Hamiltonian of the system the correlation functions are rewritten in terms of the Green functions. The total Hamiltonian $\mathscr{H}$ of the system on the basis of the Frenkel exciton model is described by[8]

$$\mathscr{H} = E_g + \sum_{n=0}^{N-1} \sum_f \varepsilon_f B_{nf}^\dagger B_{nf} + \frac{1}{2} \sum_n \sum_m \sum_f \sum_g V_{nmfg}(B_{nf}^\dagger + B_{nf})(B_{mg}^\dagger + B_{mg}) \qquad (14)$$

and

$$V_{nmfg} = \langle 0f | V_{nm} | g0 \rangle,$$

where E_g is the ground state energy, ε_f the energy eigenvalue of the f-state of residue and V_{nm} the interaction between the nth and the mth residues. Here the assumption that the first excitation energy is much larger than the thermal energy is made. The correlation function $C_{nm}(\omega; f, f')$ given by eq. (8) is written as

$$C_{nm}(\omega; f, f') = \frac{i\hbar}{\varepsilon_f} G_{nm}(\omega; f, f'), \qquad (15)$$

where $C_{nm}(\omega; f, f')$ is the Green function

$$G_{nm}(\omega; f, f') = \int_{-\infty}^{\infty} dt \ e^{-i\omega t}$$

$$\times \frac{i}{\hbar} \theta(t) \langle [B_{nf}^\dagger(t) + B_{nf}(t), B_{mf'}^\dagger(0) - B_{mf'}(0)] \rangle. \qquad (16)$$

Introducing the Fourier transforms

$$G_k(\omega; f, f') = \sum_{n-m=0}^{N-1} e^{ik(n-m)d} G_{nm}(\omega; f, f') \qquad (17)$$

and

$$V_{ff'}(k) = \sum_{n-m=0}^{N-1} e^{ik(n-m)d} V_{nmff'} \qquad (18)$$

and considering only the two excited states f and g, one can find out the Green function $G_k(\omega; f, f')$ as follows:

$$G_k(\omega;f,f') = 2\hbar\omega\,\frac{[(\hbar\omega)^2-\tilde{\varepsilon}_g^2(k)]\,\delta_{ff'}+2\varepsilon_f V_{fg}(k)\delta_{gf'}}{[(\hbar\omega)^2-E_f^2(k)]\,[(\hbar\omega)^2-E_g^2(k)]}\,, \tag{19}$$

where

$$\tilde{\varepsilon}_g^2(k) = \varepsilon_g[\varepsilon_g+2\,V_{gg}(k)] \tag{20}$$

and

$$\left.\begin{array}{l}E_f^2(k)\\E_g^2(k)\end{array}\right\} = \frac{\tilde{\varepsilon}_f^2(k)+\tilde{\varepsilon}_g^2(k)}{2}\mp\frac{1}{2}\{[\,\tilde{\varepsilon}_g^2(k)-\tilde{\varepsilon}_f^2(k)]^2+16\varepsilon_f\varepsilon_g|\,V_{fg}(k)|^2\}^{1/2}. \tag{21}$$

By substituting eqs. (9), (15), (17) and (19) into eqs. (10) and (11), one can write down $Q_D(q,\omega)$ and $Q_N(q,\omega)$ in terms of $V_{fg}(k)$, $J_0(q_0;f,g)$ and $J_1(q_0;f,g)$.

3. Borrowed Intensities

In the present section, we consider the system for the two-level exciton and discuss borrowed intensities on the oscillator strengths and the rotational strengths from the other band. In the calculation of the intensities by eqs. (9), (10), (11), (15), (17) and (19), we may deal with the type of function

$$g(\omega;f) = \sum_{f'} J(f,f')G_k(\omega;f,f'), \tag{22}$$

here $J(f,f')$ denotes $J_0(q;f,f')$ or $J_1(q;f,f')$. We obtain from eq. (19)

$$g(\omega;f) = J(f,f)\left[\frac{E_f^2(k)-\tilde{\varepsilon}_g^2(k)}{E_f^2(k)-E_g^2(k)}\,\frac{2\hbar\omega}{(\hbar\omega)^2-E_f^2(k)}-\frac{E_g^2(k)-\tilde{\varepsilon}_g^2(k)}{E_f^2(k)-E_g^2(k)}\,\frac{2\hbar\omega}{(\hbar\omega)^2-E_g^2(k)}\right]$$

$$+J(f,g)\frac{2\varepsilon_f V_{fg}(k)}{E_f^2(k)-E_g^2(k)}\left[\frac{2\hbar\omega}{(\hbar\omega)^2-E_f^2(k)}-\frac{2\hbar\omega}{(\hbar\omega)^2-E_g^2(k)}\right]. \tag{23}$$

When the imaginary part of $g(\omega+i\varepsilon;f)$ $(\varepsilon\to+0)$ is denoted by $\mathrm{Im}g(\omega;f)$, the following relation is confirmed:

$$\int d\omega\,\mathrm{Im}g(\omega;f) = -\frac{\pi}{\hbar}J(f,f), \tag{24}$$

which does not depend on the interaction, and convince us that eq. (23) still keeps the f-sum rules for oscillator strengths and rotational strengths.

When the two levels, f and g states, interact mutually, let us arrange many terms coming out in $\varepsilon_f^{-1}g(\omega;f)+\varepsilon_g^{-1}g(\omega;g)$ to look into the intensity for each state as follows:

$$\frac{g(\omega;f)}{\varepsilon_f}+\frac{g(\omega;g)}{\varepsilon_g} = \frac{I(f)\cdot 2\hbar\omega}{(\hbar\omega)^2-E_f^2(k)}+\frac{I(g)\cdot 2\hbar\omega}{(\hbar\omega)^2-E_g^2(k)}, \tag{25}$$

$$I(f) = \frac{J(f,f)}{\varepsilon_f}\left(1+\frac{1}{E_f^2(k)-E_g^2(k)}\left\{(E_g^2(k)-\tilde{\varepsilon}_g^2(k))\right.\right.$$

$$\left.\left.+\frac{\varepsilon_f}{J(f,f)}\left[\frac{J(g,g)}{\varepsilon_g}(E_f^2(k)-\tilde{\varepsilon}_f^2(k))+(J(f,g)+J(g,f))\cdot 2\,V_{fg}(k)\right]\right\}\right), \tag{26}$$

and

$I(g)$ = the term of $(f \hookrightarrow g)$ in eq. (26).

Noticing $I(f) = \varepsilon_f^{-1} J(f, f)$ in the case of $V_{ff}(k) = V_{gg}(k) = V_{fg}(k) = 0$, we can define the oscillator (or rotational) strength including the interactions between the f and g states as $I(f) = \varepsilon_f^{-1} J(f, f)(1 + \Delta R(f))$, where $\Delta R(f)$ is found to be

$$\Delta R(f) = \frac{1}{E_f^2(k) - E_g^2(k)} \left\{ (E_g^2(k) - \tilde{\varepsilon}_g^2(k)) \right.$$
$$\left. + \frac{\varepsilon_f}{J(f, f)} \left[\frac{J(g, g)}{\varepsilon_g} (E_f^2(k) - \tilde{\varepsilon}_f^2(k)) + (J(f, g) + J(g, f)) \cdot 2 V_{fg}(k) \right] \right\}, \quad (27)$$

which represents the effect from the g state.

When the second term in eq. (10) is neglected and the approximation $C_{q+\varphi/d}(\omega; f, f') \approx C_{q-\varphi/d}(\omega; f, f')$ is made, the borrowed intensity $\Delta R(f)$ from the g band on oscillator strength is written in the form

$$\Delta R(f) = \frac{1}{E_f^2(k_0) - E_g^2(k_0)} \left\{ (E_g^2(k_0) - \tilde{\varepsilon}_g^2(k_0)) \right.$$
$$+ \frac{\varepsilon_f}{J_0(q_0; f, f)} \left[\frac{J_0(q_0; g, g)}{\varepsilon_g} (E_f^2(k_0) - \tilde{\varepsilon}_f^2(k_0)) \right.$$
$$\left. \left. + (J_0(q_0; f, g) + J_0(q_0; g, f)) \cdot 2 V_{fg}(k_0) \right] \right\}, \quad (28)$$

where k_0 denotes φ/d. The borrowed intensity $\Delta R(g)$ from the f band can be obtained by interchanging f and g. This expression is slightly different from that of McLachlan and Ball.[3] In their expression corresponding to eq. (28), the energies E_f and E_g appearing in the denominator have been replaced by ε_f and ε_g, respectively. In the present paper the divergency in the borrowed intensities is suppressed even if the interactions between the residues become very large as it is shown later. It should be noted that eq. (28) holds under the arbitrary magnitude of the interaction. If $V_{ff}(k)$, $V_{gg}(k)$ and $V_{fg}(k)$ are very small, eq. (28) leads to

$$\Delta R(f) = \frac{J_0(q_0; f, g) + J_0(q_0; g, f)}{J_0(q_0; f, f)} \frac{2\varepsilon_f V_{fg}(k_0)}{\tilde{\varepsilon}_g^2(k_0) - \tilde{\varepsilon}_f^2(k_0)} \quad (29)$$

and

$$\Delta R(g) = \frac{J_0(q_0; f, g) + J_0(q_0; g, f)}{J_0(q_0; g, g)} \frac{2\varepsilon_g V_{fg}(k_0)}{\tilde{\varepsilon}_g^2(k_0) - \tilde{\varepsilon}_f^2(k_0)}. \quad (30)$$

In the case of $V_{fg}(k) \to \infty$ (or $\tilde{\varepsilon}_f(k) \approx \tilde{\varepsilon}_g(k)$), eq. (28) can be approximated as

$$\Delta R(f) = -\frac{1}{2} \left\{ 1 - \frac{\varepsilon_f}{J_0(q_0; f, f)} \right.$$
$$\left. \times \left[\frac{J_0(q_0; g, g)}{\varepsilon_g} - \frac{J_0(q_0; f, g) + J_0(q_0; g, f)}{(\varepsilon_f \varepsilon_g)^{1/2}} \frac{V_{fg}(k_0)}{|V_{fg}(k_0)|} \right] \right\} \quad (31)$$

and

$$\Delta R(g) = -\frac{1}{2}\left\{1 - \frac{\varepsilon_g}{J_0(q_0; g, g)}\right.$$

$$\left.\times\left[\frac{J_0(q_0; f, f)}{\varepsilon_f} + \frac{J_0(q_0; f, g) + J_0(q_0; g, f)}{(\varepsilon_f\varepsilon_g)^{1/2}}\frac{V_{fg}(k_0)}{|V_{fg}(k_0)|}\right]\right\}. \qquad (32)$$

Even in the case of optical rotation, if the second term in eq. (11), which represents the anomalous optical rotation, is neglected, the borrowed rotational strength of the f state can be written in the form

$$\Delta R(f) = \frac{1}{E_f^2(k_0) - E_g^2(k_0)}\left\{(E_g^2(k_0) - \tilde{\varepsilon}_g^2(k_0))\right.$$

$$+ \frac{\varepsilon_f}{J_1(q_0; f, f)}\left[\frac{J_1(q_0; g, g)}{\varepsilon_g}(E_f^2(k_0) - \tilde{\varepsilon}_f^2(k_0))\right.$$

$$\left.\left.+ (J_1(q_0; f, g) + J_1(q_0; g, f))\cdot 2V_{fg}(k_0)\right]\right\}. \qquad (33)$$

However, we may introduce the borrowed intensities for intrinsic optical rotation and that for anomalous optical rotation. The borrowed intensity for the latter reduces to

$$\Delta R(f) = \frac{1}{E_f^2(k_0) - E_g^2(k_0)}\left\{(E_g^2(k_0) - \tilde{\varepsilon}_g^2(k_0))\right.$$

$$+ \frac{\varepsilon_f}{J_0(q_0; f, f)}\left[\frac{J_0(q_0; g, g)}{\varepsilon_g}(E_f^2(k_0) - \tilde{\varepsilon}_f^2(k_0))\right.$$

$$\left.\left.+ (J_0(q_0; f, g) + J_0(q_0; g, f))\cdot 2V_{fg}(k_0)\right]\right\}, \qquad (34)$$

which is same as the expression given by eq. (28).

4. Conclusion

In the previous paper,[6] a general formula for the Faraday rotation including the natural optical rotation was derived on the basis of the first principle by no use of the conventional formulae. The formulation for the refractive index was also made in a similar fashion to our theory of the Faraday rotation.[7] It has been seen that the optical absorption and the optical rotation is closely connected with each other in the form of mathematical formulae.

In the present paper, the borrowed intensity has been investigated from the same point of view as is demonstrated in our theory of the Faraday effect and the relationship between the borrowed intensities for optical absorption and for optical rotation have been obtained.

The system under consideration is a helical polymer on the basis of the two-level Frenkel exciton model under the condition that incident light is parallel to the helical

axis.

The f-sum rules for the optical absorption and the optical rotation have been derived.

The expressions for borrowed intensities on oschllator strengths are slightly different from those given by McLachlan and Ball.[3] In the present paper, divergency in the borrowed intensity is suppressed even if the interactions between the residues become very large and our expressions hold under the arbitrary magnitude of the interactions.

It has been shown that the expression for the borrowed intensity for anomalous optical rotation is essentially of the same form as that for intrinsic optical absorption.

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