Optical Rotation by a Free Electron
on an Oriented Helix

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The refractive index and optical rotation for a model of free electrons on an oriented helix are investigated on the basis of the first principle, that is, the linear response theory without using the conventional formula. Calculation is made by the method of second quantization under the periodic boundary condition. Expressions for the refractive index and the optical rotation are obtained which are exact for the helicoidal model of arbitrary size relative to the wavelength of incident light.

1. Introduction

The rotation of linearly polarized microwaves by a system of macroscopic helices was measured thirty years ago.[1] To account for the experimental result a number of theoretical investigations of optical activity of a free electron on a helix have been made by the perturbation theory[2-6] and the quantum theory of radiation field.[3,4]

Tinoco and Woody[2] and Leuliette-Devin et al.[6] calculated the optical rotation of an oriented helix with dimensions small compared to the wavelength of polarized light and obtained expressions by using exact wave functions. While Tobias et al.,[3] Balazs et al.[4] and Moore and Tinoco[5] obtained expressions for the rotation of a long helicoidal model with dimensions comparable to the wavelength. Furthermore, Tinoco and Woody,[2] Balazs et al.,[4] Moore and Tinoco[5] and Leuliette-Devin et al.[6] derived expressions for optical rotation by using one-dimensional wave functions of an electron in a box.

In our previous papers,[7-9] a general formula for the Faraday rotation including the natural optical rotation was derived based on the microscopic Maxwell equation and the optical and the magnetic rotatory dispersion of an oriented long helical polymer by an exciton model were obtained.

In the present paper, we calculate the refractive index and natural optical

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rotation for an oriented helicoidal orbital model by applying our theory.[7,9] We limit ourselves to the model which consists of an electron free to move on a long helix.

In sec. 2 we give a description of electric current density of the system, in terms of the second quantization operator, which is induced by an incident polarized light. The periodic boundary condition of the system is used. In sec. 3 formulae for the refractive index and the optical rotation are derived in terms of the current correlation function. In sec. 4 we obtain the correlation function in terms of Green functions. Final section 5 is devoted to summary and discussion.

2. Electric Current Density

The system under cosideration is an electron on an oriented right-handed helix of N turns described by the following equations including the azimuth θ:

$$x = \rho \cos \theta, \quad y = \rho \sin \theta, \quad z = \frac{d}{2\pi}\theta, \tag{1}$$

where ρ is the radius and d is the pitch (the distance between successive turns) of the helix. If s is the length along the helix curve, one can obtain the relation

$$z = s \sin \alpha, \tag{2}$$

where

$$\tan \alpha = \frac{d}{2\pi\rho}. \tag{3}$$

The Hamiltonian $\mathcal{H}$ of an electron constrained to move on this helix is given by

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial s^2}. \tag{4}$$

For an integral number N of turns, solutions of the eigenvalue equation to eq. (4) are

$$\left.\begin{array}{l} \varphi_k(s) = \dfrac{1}{\sqrt{ND}}e^{iks} \\[2mm] \varepsilon(k) = \dfrac{\hbar^2 k^2}{2m} \end{array}\right\} \quad \left(\begin{array}{l} k = \dfrac{2\pi}{ND}l \\[2mm] l = 0, \ \pm 1, \ \pm 2, \ \dots \end{array}\right), \tag{5}$$

where use has been made of the periodic boundary condition

$$\left.\begin{array}{l} \varphi_k(s) = \varphi_k(s + ND) \\[4pt] D = \dfrac{d}{\sin \alpha} \end{array}\right\}. \qquad (6)$$

The orthogonal components of the electric current density $\boldsymbol{j}(r)$ are written as

$$\left.\begin{array}{l} j_x(s) = -j(s) \cos \alpha \sin \theta \\[3pt] j_y(s) = j(s) \cos \alpha \cos \theta \\[3pt] j_z(s) = j(s) \sin \alpha \end{array}\right\}. \qquad (7)$$

Since the electric current density operator of the system is

$$\boldsymbol{j}(\boldsymbol{r}) = \frac{e\hbar}{2mi} \sum_i \left[\delta(\boldsymbol{r} - \boldsymbol{r}_i)\nabla_i + \nabla_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \right],$$

where e and m are the electric charge and mass of electron, respectively, one can express $j_x(s)$ as

$$j_x(s) = -\frac{e\hbar}{2mi} \cos \alpha \sin\frac{2\pi s}{D} \sum_k \sum_{k'} \int ds_i \varphi_{k'}{}^*(s_i)$$

$$\times \left[\delta(s-s_i)\frac{\partial}{\partial s_i} + \frac{\partial}{\partial s_i}\delta(s-s_i) \right] \varphi_k(s_i) a_{k'}{}^\dagger a_k$$

$$= -\frac{1}{ND}\frac{e\hbar}{2m}\cos \alpha \sin\frac{2\pi s}{D}\sum_k\sum_{k'}(k+k')e^{i\,(k-k')\,s} a_{k'}{}^\dagger a_k \qquad (8)$$

and, similarly, $j_y(s)$ as

$$j_y(s) = \frac{1}{ND}\frac{e\hbar}{2m}\cos \alpha \cos\frac{2\pi s}{D}\sum_k\sum_{k'}(k+k')e^{i\,(k-k')\,s} a_{k'}{}^\dagger a_k, \qquad (9)$$

where a_k and $a_k{}^\dagger$ are the annihilation and creation operator for the electron with the wave-number k, respectively, and use has been made of the following relation obtained by eqs. (1), (2) and (6):

$$\theta = \frac{2\pi}{d}z = \frac{2\pi \sin \alpha}{d}s = \frac{2\pi}{D}s.$$

Thus, the Fourier transforms of the electric current density operator of the system are represented in terms of a_k and $a_k{}^\dagger$ by the second quantization as

$$j_x(q) = \int ds e^{iqz} j_x(s) = \int ds e^{iqds/D} j_x(s)$$

$$= i\frac{e\hbar}{2m}\cos \alpha \sum_k \left[\left(k + \frac{d}{2D}q + \frac{\pi}{D}\right) a_{k+\frac{d}{D}q+\frac{2\pi}{D}}{}^\dagger a_k \right.$$

$$- \left(k + \frac{d}{2D}q - \frac{\pi}{D}\right)a_{k+\frac{d}{D}q-\frac{2\pi}{D}}^{\dagger}a_k\right] \tag{10}$$

and

$$j_y(q) = \frac{e\hbar}{2m}\cos\alpha \sum_k \left[\left(k + \frac{d}{2D}q + \frac{\pi}{D}\right)a_{k+\frac{d}{D}q+\frac{2\pi}{D}}^{\dagger}a_k\right.$$

$$\left. + \left(k + \frac{d}{2D}q - \frac{\pi}{D}\right)a_{k+\frac{d}{D}q-\frac{2\pi}{D}}^{\dagger}a_k\right]. \tag{11}$$

3. Formulation of Optical Rotation

The basic equations for refractive index and optical rotation are given from Maxwell's equations in terms of the current correlation functions $Q_D(q, \omega)$ and $Q_N(q, \omega)$[7,9] by

$$q_{\pm}^2 - q_0^2 + \frac{1}{c^2}[Q_D(q_{\pm}, \omega) \mp iQ_N(q_{\pm}, \omega)] = 0, \tag{12}$$

where $q_0 = \omega/c$, c is the speed of light in vaccum and the upper (lower) sign corresponds to left (right) circularly polarized light with frequency ω. The refractive index n and the rotational angle ϕ of the plane of polarization per unit path length* are defined by

$$\left. \begin{array}{c} n = \dfrac{q_- + q_+}{2q_0} \\[2mm] \phi = \dfrac{q_- - q_+}{2} \end{array} \right\} . \tag{13}$$

By making use of eq. (12) for the wave-numbers $q_{\pm}$ the refractive index $n(\omega)$ and the rotational angle $\phi(\omega)$ reduce to[9]

$$\left. \begin{array}{c} [n(\omega)]^2 \approx \dfrac{q_-^2 + q_+^2}{2q_0^2} = 1 - \dfrac{1}{\omega^2}Q_D(q_0, \omega) \\[3mm] \phi(\omega) = -\dfrac{i}{2cn(\omega)}\dfrac{1}{\omega}Q_N(q_0, \omega) \end{array} \right\} . \tag{14}$$

Let us take the direction of propagation of an incident monochromatic light of frequency ω to be parallel to the z-axis. The correlation functions $Q_D(q, \omega)$ and $Q_N(q, \omega)$ are expressed in terms of the spatial Fourier transform $j(q, t)$ of the electric current density operator in the forms[7,9]

$$Q_D(q, \omega) = \frac{2\pi i\omega}{V}\int_{-\infty}^{\infty} dt e^{-i\omega t}\theta(t)\int_0^{\beta} d\lambda$$

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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 direction of propagation of the incident light.

$$\times \langle j_x(q,\ t)j_x(-\ q,\ i\hbar\lambda) + j_y(q,\ t)j_y(-\ q,\ i\hbar\lambda)\rangle \qquad (15)$$

and

$$Q_N(q,\ \omega) = \frac{2\pi i\omega}{V}\int_{-\infty}^{\infty} dt e^{-i\omega t}\theta(t)\int_0^{\beta} d\lambda$$

$$\times \langle j_x(q,\ t)j_y(-\ q,\ i\hbar\lambda) - j_y(q,\ t)j_x(-\ q,\ i\hbar\lambda)\rangle, \qquad (16)$$

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

$$\langle \Omega \rangle = \frac{\text{Tr}[\exp(-\ \beta\mathcal{H})\Omega]}{\text{Tr}[\exp(-\ \beta\mathcal{H})]}.$$

The Hamiltonian (4) of the system can be written by the use of the second quantization technique as

$$\mathcal{H} = \sum_k \varepsilon(k)a_k^{\dagger}a_k. \qquad (17)$$

Substitution of eqs. (10) and (11) into eqs. (15) and (16) leads to

$$Q_D(q,\ \omega) = -\ \frac{4\pi\hbar\omega}{V}\left(\frac{e\hbar}{2m}\right)^2\left[1 - \left(\frac{d}{D}\right)^2\right]$$

$$\times \sum_k \sum_{k'} \left\{ \frac{\left(k + \frac{d}{2D}q + \frac{\pi}{D}\right)\left(k' - \frac{d}{2D}q - \frac{\pi}{D}\right)}{\varepsilon\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - \varepsilon(k)} \right.$$

$$\times G\left(k + \frac{d}{D}q + \frac{2\pi}{D},\ k;\ k' - \frac{d}{D}q - \frac{2\pi}{D},\ k';\ \omega\right)$$

$$+ \frac{\left(k + \frac{d}{2D}q - \frac{\pi}{D}\right)\left(k' - \frac{d}{2D}q + \frac{\pi}{D}\right)}{\varepsilon\left(k + \frac{d}{D}q - \frac{2\pi}{D}\right) - \varepsilon(k)}$$

$$\left. \times G\left(k + \frac{d}{D}q - \frac{2\pi}{D},\ k;\ k' - \frac{d}{D}q + \frac{2\pi}{D},\ k';\ \omega\right) \right\} \qquad (18)$$

and

$$Q_N(q,\ \omega) = -\ i\frac{4\pi\hbar\omega}{V}\left(\frac{e\hbar}{2m}\right)^2\left[1 - \left(\frac{d}{D}\right)^2\right]$$

$$\times \sum_k \sum_{k'} \left\{ \frac{\left(k + \frac{d}{2D}q + \frac{\pi}{D}\right)\left(k' - \frac{d}{2D}q - \frac{\pi}{D}\right)}{\varepsilon\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - \varepsilon(k)} \right.$$

$$\times\, G\Big(k + \frac{d}{D}q + \frac{2\pi}{D},\ k\ ;\ k' - \frac{d}{D}q - \frac{2\pi}{D},\ k'\ ;\ \omega\Big)$$

$$-\, \frac{\Big(k + \frac{d}{2D}q - \frac{\pi}{D}\Big)\Big(k' - \frac{d}{2D}q + \frac{\pi}{D}\Big)}{\varepsilon\Big(k + \frac{d}{D}q - \frac{2\pi}{D}\Big) - \varepsilon(k)}$$

$$\times\, G\Big(k + \frac{d}{D}q - \frac{2\pi}{D},\ k\ ;\ k' - \frac{d}{D}q + \frac{2\pi}{D},\ k'\ ;\ \omega\Big)\bigg\}, \qquad (19)$$

where $G(k_1,\ k_2;\ k_3,\ k_4;\ \omega)$ denotes the Green function for electrons, that is,

$$G(k_1,\ k_2\ ;\ k_3,\ k_4\ ;\ \omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, e^{-i\omega t} G(k_1,\ k_2\ ;\ k_3,\ k_4\ ;\ t) \qquad (20)$$

with

$$G(k_1,\ k_2\ ;\ k_3,\ k_4\ ;\ t) = \frac{i}{\hbar}\theta(t)\langle[a_{k_1}{}^{\dagger}(t)a_{k_2}(t),\ a_{k_3}{}^{\dagger}(0)a_{k_4}(0)]\rangle. \qquad (21)$$

In eqs. (18) and (19), the relation

$$\cos^2\alpha = 1 - \Big(\frac{d}{D}\Big)^2$$

is used.

4. Green Functions

To calculate Green functions, one first considers an equation for $a_k{}^{\dagger}a_{k'}$ and thus the equation

$$-\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}t}(a_{k_1}{}^{\dagger}a_{k_2}) = [\varepsilon(k_2) - \varepsilon(k_1)]a_{k_1}{}^{\dagger}a_{k_2} \qquad (22)$$

is obtained by the use of Hamiltonian (17). By differentiating eq. (21) with respect to time t, the equation of Green function

$$-\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}t}G(k_1,\ k_2\ ;\ k_3,\ k_4\ ;\ t) = -\,\delta(t)[\delta_{k_2 k_3}\langle a_{k_1}{}^{\dagger}a_{k_4}\rangle - \delta_{k_1 k_4}\langle a_{k_3}{}^{\dagger}a_{k_2}\rangle]$$

$$+\, [\varepsilon(k_2) - \varepsilon(k_1)]G(k_1,\ k_2\ ;\ k_3,\ k_4\ ;\ t) \qquad (23)$$

is derived from eq. (22). The exact solution of this equation is transformed by eq. (20) to

$$G(k_1,\ k_2\ ;\ k_3,\ k_4\ ;\ \omega) = \delta_{k_1 k_4}\delta_{k_2 k_3}\frac{f(k_1) - f(k_2)}{\hbar\omega - [\varepsilon(k_1) - \varepsilon(k_2)]}, \qquad (24)$$

where $f(k)$ denotes the Fermi-Dirac distribution function for electrons, that is,

$$f(k) = \langle a_k^\dagger a_k \rangle.$$

Thus, one can find out the correlation functions $Q_D(q, \omega)$ and $Q_N(q, \omega)$ in the forms

$$Q_D(q, \omega) = - \frac{4\pi\hbar\omega}{V}\left(\frac{e\hbar}{2m}\right)^2 \left[1 - \left(\frac{d}{D}\right)^2\right]$$

$$\times \sum_k \left\{ \frac{\left(k + \frac{d}{2D}q + \frac{\pi}{D}\right)^2}{\varepsilon\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - \varepsilon(k)} \frac{f\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - f(k)}{\hbar\omega - \left[\varepsilon\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - \varepsilon(k)\right]} \right.$$

$$\left. + \frac{\left(k + \frac{d}{2D}q - \frac{\pi}{D}\right)^2}{\varepsilon\left(k + \frac{d}{D}q - \frac{2\pi}{D}\right) - \varepsilon(k)} \frac{f\left(k + \frac{d}{D}q - \frac{2\pi}{D}\right) - f(k)}{\hbar\omega - \left[\varepsilon\left(k + \frac{d}{D}q - \frac{2\pi}{D}\right) - \varepsilon(k)\right]} \right\} \qquad (25)$$

and

$$Q_N(q, \omega) = - \mathrm{i}\frac{4\pi\hbar\omega}{V}\left(\frac{e\hbar}{2m}\right)^2 \left[1 - \left(\frac{d}{D}\right)^2\right]$$

$$\times \sum_k \left\{ \frac{\left(k + \frac{d}{2D}q + \frac{\pi}{D}\right)^2}{\varepsilon\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - \varepsilon(k)} \frac{f\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - f(k)}{\hbar\omega - \left[\varepsilon\left(k + \frac{d}{D}q + \frac{2\pi}{D}\right) - \varepsilon(k)\right]} \right.$$

$$\left. - \frac{\left(k + \frac{d}{2D}q - \frac{\pi}{D}\right)^2}{\varepsilon\left(k + \frac{d}{D}q - \frac{2\pi}{D}\right) - \varepsilon(k)} \frac{f\left(k + \frac{d}{D}q - \frac{2\pi}{D}\right) - f(k)}{\hbar\omega - \left[\varepsilon\left(k + \frac{d}{D}q - \frac{2\pi}{D}\right) - \varepsilon(k)\right]} \right\}. \qquad (26)$$

Finally, expressions for the refractive index $n(\omega)$ and the rotational angle $\phi(\omega)$ are obtained by substituting eqs. (25) and (26) into eq. (14).

5. Summary and Discussion

In the present paper we have derived expressions for the refractive index and the optical rotatory power for a free electron constrained to move on an oriented long helix under the periodic boundary condition. The calculation has been made by using a formula in terms of response function which represents a correlation of electric current densities, that is, on the basis of the linear response theory.

Our results have been exactly derived on the basis of the first principle. The situation is quite different from that of Tinoco and Woody[2] and Leuliette-

Devin et al.[6]. Their results also are exact but are based on the Rosenfeld formula[10] which has been derived from an equation expanded in a power series in the wave-number of light. Leuliette-Devin et al.[6] discussed the discontinuity of optical rotation at resonance frequencies. As far as the Rosenfeld formula is used, one cannot avoid the difficulty of the discontinuity of optical rotation.

Our results contain also the temperature dependence of the refractive index and optical rotation through the Fermi-Dirac distribution function for electrons.

References

1) I. Tinoco, Jr. and M. P. Freeman, J. Phys. Chem., **61** (1957), 1196.
2) I. Tinoco, Jr. and R. W. Woody, J. Chem. Phys., **40** (1964), 160.
3) I. Tobias, T. R. Brocki and N. L. Balazs, J. Chem. Phys., **62** (1975), 4181.
4) N. L. Balazs, T. R. Brocki and I. Tobias, Chem. Phys., **13** (1976), 141.
5) D. Moore and I. Tinoco, Jr., J. Chem. Phys., **72** (1980), 3396.
6) E. Leuliette-Devin, R. Locqueneux and J. Tillieu, J. Chem. Phys., **75** (1981), 1239.
7) T. Ando, Prog. Theor. Phys., **40** (1968), 471.
8) T. Ando and Y. Kato, J. Phys. Soc. Jpn., **30** (1971), 1198.
9) T. Ando and Y. Kato, J. Phys. Soc. Jpn., **38** (1975), 509.
10) L. Rosenfeld, Z. Phys., **52** (1928), 161.