

NEW APPROACH TO THE THEORY OF CIRCULAR DICHROISM

Jaroslav ZAMASTIL¹, Lubomir SKALA², Petr PANCOSKA³ and Oldrich BILEK⁴*Faculty of Mathematics and Physics, Charles University, 121 16 Prague 2, Czech Republic;**e-mail : ¹ zamastil@quantum.karlov.mff.cuni.cz, ² skala@quantum.karlov.mff.cuni.cz,**³ pancoska@tigger.uic.edu, ⁴ bilek@quantum.karlov.mff.cuni.cz*

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Using the semiclassical approach for the description of the propagation of the electromagnetic waves in optically active isotropic media we derive a new formula for the circular dichroism parameter. The theory is based on the idea of the time damped electromagnetic wave interacting with the molecules of the sample. In this theory, the Lambert-Beer law need not be taken as an empirical law, however, it follows naturally from the requirement that the electromagnetic wave obeys the Maxwell equations.

Key words: Circular dichroism; Optically active media; CD spectroscopy; Quantum chemistry.

In this paper, we are interested in the theory of the circular dichroism in isotropic media. It is well-known that the propagation of the left or right handed circularly polarized electromagnetic waves (LHCP or RHCP) in optically active media is different. If the molecule absorbs at the frequency of the electromagnetic wave, the absorption of the LHCP and RHCP waves is not equal. This effect is called the circular dichroism (CD) and is characterized by the difference of the corresponding absorption coefficients. This difference is usually denoted as the circular dichroism parameter (see *e.g.* refs^{1,2})

$$\Delta b = b_L - b_R \quad , \quad (I)$$

where b_L and b_R are defined by the Lambert-Beer law

$$\frac{I_L(z)}{I_L(0)} = \exp(-b_L z) \quad , \quad (2)$$

$$\frac{I_R(z)}{I_R(0)} = \exp(-b_R z) \quad . \quad (3)$$

Here, $I(z)$ is the intensity of the wave propagating along the z axis.

The standard theories of the circular dichroism assume the electromagnetic field in the form of the monochromatic plane wave^{1,2}. In case of absorption, such approach is not theoretically justified since the plane wave does not obey the Maxwell equations. The Lambert–Beer law is taken as an empirical law¹.

The aim of this paper is to present a more consistent theory in which we assume a damped electromagnetic wave instead of the plane wave. This approach has two advantages. First, this wave satisfies the Maxwell equations. The second advantage of our approach is that the Lambert–Beer law follows naturally from the damped wave assumption.

In the next section, we summarize the semiclassical approach and introduce the basic physical quantities. We briefly discuss difficulties of the usual approaches and introduce the idea of a damped electromagnetic wave, and then we solve the Maxwell equations and derive the formula for the circular dichroism parameter. In the last section, discussion of the results is presented. The averaging procedure of molecular quantities is described in Appendix A. In Appendix B, an order estimate of the damping constant is performed.

SEMICLASSICAL APPROACH

We assume that the electromagnetic waves are solutions of the Maxwell equations. Assuming further that there are no free charges and currents in the sample the Maxwell equations read

$$\begin{aligned}\nabla \cdot \mathbf{E} &= -\frac{1}{\epsilon_0} \nabla \cdot \mathbf{P} , \\ \frac{1}{\mu_0} \nabla \times \mathbf{B} - \epsilon_0 \frac{\partial}{\partial t} \mathbf{E} &= \nabla \times \mathbf{M} + \frac{\partial}{\partial t} \mathbf{P} , \\ \nabla \cdot \mathbf{B} &= 0 , \\ \nabla \times \mathbf{E} + \frac{\partial}{\partial t} \mathbf{B} &= 0 .\end{aligned}$$

To solve these equations we have to know the material relations

$$\mathbf{P} = \mathbf{P}(\mathbf{E}, \mathbf{B}) , \quad \mathbf{M} = \mathbf{M}(\mathbf{E}, \mathbf{B}) . \quad (4)$$

In this paper, we assume *linear* material relations. In this case we get from the first Maxwell equation

$$\nabla \cdot \mathbf{E} = 0 \quad .$$

Therefore, we require the gauge conditions

$$\nabla \cdot \mathbf{A}_{\text{mac}} = 0, \quad \varphi = 0 \quad , \quad (5)$$

where \mathbf{A}_{mac} and φ denote the macroscopic vector and scalar potentials. In this way, we get from the Maxwell equations the wave equation

$$-\frac{1}{\mu_0} \nabla^2 \mathbf{A}_{\text{mac}} + \epsilon_0 \frac{\partial^2}{\partial t^2} \mathbf{A}_{\text{mac}} = \frac{\partial}{\partial t} \mathbf{P} + \nabla \times \mathbf{M} \quad . \quad (6)$$

To derive the material relations (4), we proceed as follows. We assume that the optical activity is produced by the interaction of the electromagnetic field with the individual molecules of the sample. We are interested in the electronic states and assume that the interaction among the molecules is weak and the wave functions of the individual molecules are known. For the vibrational states, these assumptions are not justified.

First, we calculate \mathbf{d} and \mathbf{m} , the quantum mechanical average of the electric and magnetic dipole moments of the molecule interacting with the electromagnetic field. These quantities are defined by the equation

$$\langle \mathbf{Q} \rangle = \langle \psi | \hat{\mathbf{Q}} | \psi \rangle \quad , \quad (7)$$

where \mathbf{Q} denotes \mathbf{d} or \mathbf{m} . To calculate (7), we have to know the state vector $|\psi\rangle$. It is the solution of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} | \psi(t) \rangle = (\hat{H}_0 + \hat{W}(t)) | \psi(t) \rangle \quad , \quad (8)$$

where \hat{H}_0 is the Hamiltonian of the free molecule and \hat{W} describes the interaction between the molecule and the local electromagnetic field in the first order of \mathbf{A}_{loc}

$$\hat{W}(t) = -\frac{e}{m} \sum_i \hat{\mathbf{A}}_{\text{loc}}(\mathbf{r}_i) \cdot \hat{\mathbf{p}}_i \quad . \quad (9)$$

Here, $e = -|e|$ and m denote the charge and mass of the electron, respectively, i runs over all electrons in the molecule. Keeping linear terms in \mathbf{A}_{loc} only, we solve Eq. (8) in the first order of the perturbation theory. To solve Eq. (8), we expand $|\psi(t)\rangle$ into the eigenstates $|\psi_m(t)\rangle$ of the free hamiltonian \hat{H}_0 with the energies $E_m = \hbar\omega_m$

$$|\psi(t)\rangle = |\psi_0(t)\rangle + \sum_m c_m(t) |\psi_m(t)\rangle, \quad (10)$$

where

$$|\psi_m(t)\rangle = \exp(i\omega_m t) |m\rangle. \quad (11)$$

Here, $|\psi_0\rangle$ denotes the ground state of the molecule. The sum over stationary states includes the ground state, too. By inserting expansion (10) into Eq. (8) we get in the first order

$$i\hbar \dot{c}_n = \langle \psi_n(t) | \hat{W}(t) | \psi_0(t) \rangle, \quad (12)$$

where the orthonormality relations

$$\langle \psi_m | \psi_n \rangle = \delta_{mn} \quad (13)$$

are used. Integration of Eq. (12) yields

$$c_n = \frac{1}{i\hbar} \int_{t_0}^t dt' \langle \psi_n(t') | \hat{W}(t') | \psi_0(t') \rangle, \quad (14)$$

where t_0 is the initial time of the interaction between the field and the molecule. By inserting expansion (10) into the definition (7) we obtain in the first order of \mathbf{A}_{loc}

$$\langle \psi | \hat{\mathbf{Q}} | \psi \rangle = \mathbf{Q}_{00} + 2\text{Re} \left[\sum_n c_n \mathbf{Q}_{0n} \exp(-i\omega_{n0}t) \right]. \quad (15)$$

Here, Re denotes the real part,

$$\mathbf{Q}_{0n} = \langle 0 | \hat{\mathbf{Q}} | n \rangle \quad (16)$$

and

$$\omega_{n0} = \omega_n - \omega_0 . \quad (17)$$

In the second step, we convert the local electric and magnetic moments \mathbf{d} and \mathbf{m} into the macroscopic polarization \mathbf{P} and magnetization \mathbf{M} . We do it by calculating average over all orientations of the molecules and by multiplying the averaged quantities by the number of the molecules in the unit volume

$$\mathbf{P} = N \overline{\langle \mathbf{d} \rangle}, \quad \mathbf{M} = N \overline{\langle \mathbf{m} \rangle} . \quad (18)$$

Finally, we have to transfer from the local field \mathbf{A}_{loc} to the macroscopic field \mathbf{A}_{mac} . In this paper, we use the usual assumption¹

$$\mathbf{A}_{\text{mac}} = S \mathbf{A}_{\text{loc}} , \quad (19)$$

where S is a phenomenological constant.

DAMPED WAVE APPROACH

The usual approach to the solution of the wave equation (6) is based on the plane wave assumption^{1,2}. It has two disadvantages. First, this wave does not obey Eq. (6). The second disadvantage is that the Lambert–Beer law does not follow from the theory, however, it must be taken as an empirical law. In this paper, we replace the plane wave assumption by a more accurate damped wave approximation.

To perform the integration in Eq. (14), we have to assume the time dependence of the vector potential $\mathbf{A}_{\text{loc}} = \mathbf{A}_{\text{loc}}(\mathbf{r}, t)$.

In the usual approach^{1,2}, the following time dependence is assumed

$$\mathbf{A}_{\text{loc}}(\mathbf{r}, t) = \mathbf{A}_c(\mathbf{r}) \cos \omega t + \mathbf{A}_s(\mathbf{r}) \sin \omega t . \quad (20)$$

Then, we can write

$$\hat{W}(t) = \hat{W}^+ \exp(i\omega t) + \hat{W}^- \exp(-i\omega t) , \quad (21)$$

where \hat{W}^\pm can be obtained from comparison of Eqs (21), (20) and (9). With this notation, we evaluate the integral in Eq. (14) and get¹⁰

$$c_n = \frac{1}{i\hbar} \left\{ W_{n0}^+ \frac{\exp [i(\omega + \omega_{n0})t]}{i(\omega + \omega_{n0})} + W_{n0}^- \frac{\exp [i(-\omega + \omega_{n0})t]}{i(-\omega + \omega_{n0})} \right\}, \quad (22)$$

where

$$W_{n0}^\pm = \langle n | \hat{W}^\pm | 0 \rangle. \quad (23)$$

It is seen that in case of absorption ($\omega = \omega_{n0}$) the assumption (20) leads to

$$c_n = \frac{1}{i\hbar} \left[W_{n0}^-(t - t_0) + W_{n0}^+ \frac{\exp(2i\omega t)}{2i\omega} \right]. \quad (24)$$

Because of the term proportional to $t - t_0$, this result is in contradiction with the assumption (20). Therefore, this approach cannot be used in case of absorption. This problem can be solved in two ways: either using the Kramers–Kronig relations^{1,3} or taking into account the spontaneous emission^{2,4,5}. However, these approaches are not satisfactory since it is necessary to make rather crude approximations⁶.

In this paper, we find the time dependence of the solution from the heuristic considerations. In case of resonance, molecules are excited to higher energy levels by the absorption of individual photons. After very short times, molecules emit the electromagnetic waves and deexcite. The electromagnetic waves propagate in all directions. Therefore, the amplitude of the wave propagating in one direction is damped.

First we summarize the semiclassical approach. When solving the Schrödinger equation (8) we have to assume some time dependence of \mathbf{A} which must obey the wave equation (6). Therefore, we have to guess the time dependence of the electromagnetic wave in advance. Thus, the wave appearing on the right hand side of Eq. (8) is not the external wave, but the internal wave interacting with individual molecules.

We believe that the picture described above can be obtained by taking into account the nonlinear terms in \mathbf{A} . Therefore, we consider the wave

$$\mathbf{A}_{\text{loc}}(\mathbf{r}, t) = (\mathbf{A}_c(\mathbf{r}) \cos \omega t + \mathbf{A}_s(\mathbf{r}) \sin \omega t) \exp(-\kappa t), \quad (25)$$

where κ is a phenomenological parameter. If we were able to solve the problem of the propagating electromagnetic waves in the matter exactly, we would get the dependence (25) in the limit case of the weak field. In this case, we would get κ as a function of

parameters describing the interaction between the wave and matter. The value of κ is estimated in Appendix B.

We assume that damping of the monochromatic electromagnetic wave is given by a single damping factor. We note first that $\mathbf{A}_{\text{loc}}(\mathbf{r}, t)$ is multiplied in Eq. (12) by the factor $\exp(i\omega_{n0}t)$. Further, this function of t is integrated in Eq. (14) and divided by $\exp(i\omega_{n0}t)$ (see Eq. (15)). Finally, $S \mathbf{A}_{\text{loc}}(\mathbf{r}, t)$ is inserted into \mathbf{A}_{mac} , \mathbf{P} and \mathbf{M} in Eq. (6) and the derivatives in this equation are performed. It follows from the resulting equation that the time dependence (25) is *the only* dependence which is the solution of the wave equation (6).

CALCULATION OF THE DAMPED WAVE

In case of the time dependence (25) we can write

$$\hat{W}(t) = \exp(-\kappa t) [\hat{W}^+ \exp(i\omega t) + \hat{W}^- \exp(-i\omega t)] . \quad (26)$$

Integration of Eq. (14) with this time dependence yields

$$c_n = \frac{1}{i\hbar} \left\{ W_{n0}^+ \frac{\exp[i(\omega + \omega_{n0} + i\kappa)t]}{i(\omega + \omega_{n0} + i\kappa)} + W_{n0}^- \frac{\exp[i(-\omega + \omega_{n0} + i\kappa)t]}{i(-\omega + \omega_{n0} + i\kappa)} \right\} . \quad (27)$$

By inserting this formula into Eq. (15) we obtain

$$\langle \mathbf{Q} \rangle = \mathbf{Q}_{00} - \frac{2 \exp(-\kappa t)}{\hbar} \times$$

$$\times \text{Re} \left\{ \sum_n \mathbf{Q}_{0n} \left[\frac{W_{n0}^+ \exp(i\omega t)(\omega_{n0} + \omega - i\kappa)}{(\omega_{n0} + \omega)^2 + \kappa^2} + \frac{W_{n0}^- \exp(-i\omega t)(\omega_{n0} - \omega - i\kappa)}{(\omega_{n0} - \omega)^2 + \kappa^2} \right] \right\} . \quad (28)$$

To describe the circular dichroism it is sufficient to consider just two terms of the Taylor expansion of the space dependence of \mathbf{A}_{loc} in the molecule

$$\mathbf{A}_{\text{loc}}(\mathbf{r}, t) = \mathbf{A}_{\text{loc}}(0, t) + \mathbf{r} \cdot \nabla \mathbf{A}_{\text{loc}}(\mathbf{r}, t) \Big|_{\mathbf{r}=0} . \quad (29)$$

Here point $\mathbf{r} = 0$ corresponds to the center of the molecule. Further, we put

$$\mathbf{d} = e \sum_i \mathbf{r}_i \quad (30)$$

and

$$\mathbf{m} = \frac{e}{2m} \sum_i \mathbf{r}_i \times \mathbf{p}_i \quad (31)$$

into \mathbf{Q} , convert these quantities into \mathbf{P} and \mathbf{M} (see Appendix A), convert the local field into the macroscopic one using Eq. (19) and use the well-known relation

$$\mathbf{p}_{n0} = im\omega_{n0} \mathbf{r}_{n0} \quad . \quad (32)$$

Taking the real part of the resulting expression for $\langle \mathbf{Q} \rangle$ we obtain¹¹

$$\begin{aligned} \mathbf{P} = \exp(-\kappa t) [& (\alpha_1 + \omega\alpha_2)(\mathbf{A}_s \cos \omega t - \mathbf{A}_c \sin \omega t) + (\beta_1 + \omega\beta_2)(\mathbf{B}_s \cos \omega t - \mathbf{B}_c \sin \omega t) + \\ & + \kappa\alpha_2(\mathbf{A}_c \cos \omega t + \mathbf{A}_s \sin \omega t) + \kappa\beta_2(\mathbf{B}_c \cos \omega t + \mathbf{B}_s \sin \omega t)] \end{aligned} \quad (33)$$

and

$$\mathbf{M} = \exp(-\kappa t) [(\beta_3 + \omega\beta_1)(\mathbf{A}_c \cos \omega t + \mathbf{A}_s \sin \omega t) - \kappa\beta_1(\mathbf{A}_s \cos \omega t - \mathbf{A}_c \sin \omega t)] \quad , \quad (34)$$

where

$$\mathbf{B}_c = \nabla \times \mathbf{A}_c, \quad \mathbf{B}_s = \nabla \times \mathbf{A}_s, \quad (35)$$

$$\alpha_1 = \frac{N}{3S\hbar} \sum_n \omega_{n0}^2 |\mathbf{d}_{n0}|^2 \left[\frac{1}{(\omega_{n0} + \omega)^2 + \kappa^2} - \frac{1}{(\omega_{n0} - \omega)^2 + \kappa^2} \right], \quad (36)$$

$$\alpha_2 = \frac{N}{3S\hbar} \sum_n \omega_{n0} |\mathbf{d}_{n0}|^2 \left[\frac{1}{(\omega_{n0} + \omega)^2 + \kappa^2} + \frac{1}{(\omega_{n0} - \omega)^2 + \kappa^2} \right], \quad (37)$$

$$\beta_1 = \frac{N}{3S\hbar} \sum_n \omega_{n0} \operatorname{Im} \{ \mathbf{m}_{n0} \cdot \mathbf{d}_{0n} \} \left[\frac{1}{(\omega_{n0} + \omega)^2 + \kappa^2} - \frac{1}{(\omega_{n0} - \omega)^2 + \kappa^2} \right], \quad (38)$$

$$\beta_2 = \frac{N}{3S\hbar} \sum_n \operatorname{Im} \{ \mathbf{m}_{n0} \cdot \mathbf{d}_{0n} \} \left[\frac{1}{(\omega_{n0} + \omega)^2 + \kappa^2} + \frac{1}{(\omega_{n0} - \omega)^2 + \kappa^2} \right], \quad (39)$$

$$\beta_3 = \frac{N}{3S\hbar} \sum_n \omega_{n0}^2 \operatorname{Im} \{ \mathbf{m}_{n0} \cdot \mathbf{d}_{0n} \} \left[\frac{1}{(\omega_{n0} + \omega)^2 + \kappa^2} + \frac{1}{(\omega_{n0} - \omega)^2 + \kappa^2} \right]. \quad (40)$$

Here, we neglected the terms proportional to $\mathbf{m}_{n0} \cdot \mathbf{m}_{0n}$ which are small.

In the limit $\kappa \rightarrow 0$ when the absorption disappears we get

$$\alpha_1 + \omega\alpha_2 = -\omega\alpha, \quad (41)$$

$$\beta_1 + \omega\beta_2 = +\omega\beta, \quad (42)$$

$$\beta_2 + \omega\beta_1 = -\omega^2\beta, \quad (43)$$

where α is the polarizability¹

$$\alpha = \frac{2N}{3S\hbar} \sum_n \frac{\omega_{n0} |\mathbf{d}_{n0}|^2}{\omega_{n0}^2 - \omega^2} \quad (44)$$

and β is the optical rotational parameter¹

$$\beta = \frac{2N}{3S\hbar} \sum_n \frac{\operatorname{Im} \{ \mathbf{m}_{n0} \cdot \mathbf{d}_{0n} \}}{\omega_{n0}^2 - \omega^2}. \quad (45)$$

Using Eq. (33) for \mathbf{P} , Eq. (34) for \mathbf{M} and the time dependence (25) for \mathbf{A} in the wave equation (6) we obtain

$$\begin{aligned} -\frac{1}{\mu_0} \nabla^2 (\mathbf{A}_c \cos \omega t + \mathbf{A}_s \sin \omega t) + \epsilon_0 [(\kappa^2 - \omega^2)(\mathbf{A}_c \cos \omega t + \mathbf{A}_s \sin \omega t) - \\ - 2\kappa\omega (\mathbf{A}_s \cos \omega t - \mathbf{A}_c \sin \omega t)] = -\kappa\alpha_1 (\mathbf{A}_s \cos \omega t - \mathbf{A}_c \sin \omega t) - \\ - [\alpha_2(\kappa^2 + \omega^2) + \alpha_1\omega](\mathbf{A}_c \cos \omega t + \mathbf{A}_s \sin \omega t) - 2\kappa\beta_1 (\mathbf{B}_s \cos \omega t - \mathbf{B}_c \sin \omega t) - \\ - [\beta_2(\kappa^2 + \omega^2) - \beta_3](\mathbf{B}_c \cos \omega t + \mathbf{B}_s \sin \omega t). \end{aligned} \quad (46)$$

Comparing terms with the same $\cos \omega t$ and $\sin \omega t$ dependence on both sides of Eq. (46) we obtain two equations. By putting $\mathbf{A}_s = \pm i\mathbf{A}_c$ we can reduce these two equations into one equation

$$-\frac{1}{\mu_0} \nabla^2 \mathbf{A}_c + \epsilon_0(\kappa^2 - \omega^2) \mathbf{A}_c - 2i\epsilon\kappa\omega \mathbf{A}_c = \\ -i\kappa\alpha_1 \mathbf{A}_c - [\alpha_2(\kappa_2 + \omega_2) + \alpha_1\omega] \mathbf{A}_c - 2i\kappa\beta_1 \mathbf{B}_c - [\beta_2(\kappa^2 + \omega^2) - \beta_3] \mathbf{B}_c . \quad (47)$$

Now we search for the solution in the form

$$\mathbf{A}_c = \mathbf{A}_0 \exp(i\mathbf{k} \cdot \mathbf{r}) , \quad (48)$$

where

$$|\mathbf{k}| = \frac{\omega n}{c} . \quad (49)$$

Here, n is a refraction index, ω is a circular frequency, c is the velocity of the propagation of the electromagnetic waves and \mathbf{A}_0 is the complex amplitude of the vector potential. From the gauge condition (5) we obtain

$$\mathbf{k} \cdot \mathbf{A}_0 = 0 . \quad (50)$$

Therefore, we can put the z axis along the direction of the \mathbf{k} vector. Then we can write

$$\mathbf{A}_0 = (A_1, A_2, 0) . \quad (51)$$

From Eq. (47) we get a system of two linear algebraic homogenous equations

$$(\epsilon_0 n^2 + a_{\text{Re}} + ia_{\text{Im}})A_1 = i(b_{\text{Re}} + ib_{\text{Im}})nA_2 , \quad (52)$$

$$(\epsilon_0 n^2 + a_{\text{Re}} + ia_{\text{Im}})A_2 = -i(b_{\text{Re}} + ib_{\text{Im}})nA_1 , \quad (53)$$

where

$$a_{\text{Re}} = \frac{\epsilon_0 (\kappa^2 - \omega^2) + \alpha_2 (\omega^2 + \kappa^2) + \alpha_1 \omega}{\omega^2}, \quad (54)$$

$$a_{\text{Im}} = \frac{\kappa \alpha_1 - 2\epsilon_0 \kappa \omega}{\omega^2}, \quad (55)$$

$$b_{\text{Re}} = \frac{\beta_2 (\omega^2 + \kappa^2) - \beta_3}{\omega c} \quad (56)$$

and

$$b_{\text{Im}} = \frac{2\kappa \beta_1}{\omega c}. \quad (57)$$

To solve Eqs (52) and (53), the determinant of this system of equations for A_1 and A_2 must equal zero. The solution of this condition with respect to n is

$$n_{1,2} = \frac{b_{\text{Re}} + i b_{\text{Im}} \pm \sqrt{4\epsilon_0 (a_{\text{Re}} + i a_{\text{Im}})}}{2\epsilon_0}, \quad (58)$$

$$n_{3,4} = \frac{-b_{\text{Re}} - i b_{\text{Im}} \pm \sqrt{4\epsilon_0 (a_{\text{Re}} + i a_{\text{Im}})}}{2\epsilon_0}. \quad (59)$$

Here, we neglected the term $(b_{\text{Re}} + i b_{\text{Im}})^2$ in the discriminant which is quadratic in \mathbf{m}_{n0} . The solutions with the minus sign in front of the discriminant in Eqs (58) and (59) are unphysical since the amplitude of the corresponding wave would increase.

As a result, we get the left handed polarized wave

$$A_2 = i A_1 \quad (60)$$

corresponding to n_1 and the right handed polarized wave

$$A_2 = -i A_1 \quad (61)$$

corresponding to n_3 .

Calculating $I_L = |\mathbf{A}_L|^2$ and $I_R = |\mathbf{A}_R|^2$ we get the Lambert–Beer law, Eqs (2) and (3). Rather complex expressions for b_L and b_R will not be given explicitly here.

The ratio of the intensities I_L and I_R equals

$$\frac{I_L}{I_R} = \frac{|\mathbf{A}_L|^2}{|\mathbf{A}_R|^2} = \exp(-\Delta b z) \quad (62)$$

where

$$\Delta b = -\frac{2\omega b_{\text{Im}}}{\epsilon_0 c} =$$

$$\frac{4\kappa\mu_0 N}{3S\hbar} \sum_n \omega_{n0} \text{Im} \{ \mathbf{m}_{n0} \cdot \mathbf{d}_{0n} \} \left[\frac{1}{(\omega_{n0} - \omega)^2 + \kappa^2} - \frac{1}{(\omega_{n0} + \omega)^2 + \kappa^2} \right] \quad (63)$$

is the final formula for the circular dichroism parameter.

In contrast to ref.², Eq. (63) takes into account the summation over all states. We note also that the second term in the brackets is not considered in ref.². However, for ω closed to ω_{n0} this term can be neglected. We emphasize that, in contrast to ref.², κ does not describe the natural line width but the effective line width resulting from the absorption of the electromagnetic wave by the medium.

In the usual approximate approach to the theory of circular dichroism¹, the expression for Δb reads

$$\Delta b = \frac{4\mu_0 N}{3S\hbar\kappa} \omega \text{Im} \{ \mathbf{m}_{k0} \cdot \mathbf{d}_{0k} \} \quad (64)$$

for $\omega = \omega_{k0}$ and $\Delta b = 0$ otherwise. We see that this formula can be obtained from our Eq. (63) as an approximation for $\omega = \omega_{k0}$ if the second term in the brackets in Eq. (63) is neglected and the summation in this equation is reduced to just one k -th term. It is obvious that the approximate formula (64) can be used only if the energy levels of the molecule are sufficiently distant. In contrast to Eq. (64) where the spectral lines have δ -like character our equation (63) yields more realistic Lorentzian shape of spectral lines. It is obvious that for achiral molecules with the center of symmetry the scalar product $\text{Im} \{ \mathbf{m}_{k0} \cdot \mathbf{d}_{0k} \}$ is equal to zero (compare with ref.²). Therefore, the circular dichroism parameter Δb equals zero for such molecules.

CONCLUSIONS

In this paper, we have used the semiclassical approach to derive a new formula (63) for the circular dichroism parameter Δb . The standard expressions for the circular dichroism parameter follow from our more general formula as a special case.

In our approach, we do not have to take the Lambert–Beer law as an empirical law, however, this law follows naturally from the discussion of the possible forms of the solutions of the Maxwell equations.

APPENDIX A

In this Appendix, we describe the averaging procedure in more detail. We follow the procedure introduced in ref.⁷. We assume that the matter is isotropic. It means that the molecules have all possible spatial orientations. We limit our attention to the vector character of Eq. (28)

$$\langle Q_i \rangle \propto Q_i + A_j p_j Q_i + \nabla_j r_j A_l p_l Q_i , \quad (65)$$

where the summation convention is used. An arbitrary rotation of the vector α_i is given by

$$\alpha'_\lambda = R_{\lambda i} \alpha_i , \quad (66)$$

where α'_λ is the rotated vector, $R_{\lambda i}$ is the matrix of rotation in the three dimensional space expressed in terms of the Euler angels. The explicit form of the rotation matrix is not necessary for our purposes. Rotating the expression in Eq. (65) we get

$$\langle Q'_\lambda \rangle \propto Q'_\lambda + A_\mu p'_\mu Q'_\lambda + \nabla_\mu r'_\mu A_\nu p'_\nu Q'_\lambda . \quad (67)$$

Here, we do not rotate the field quantities. The electromagnetic wave propagates through the matter, where it interacts with different rotating electric and magnetic moments of the molecules. Using Eq. (66) we obtain

$$\langle Q'_\lambda \rangle \propto R_{\lambda i} Q_i + A_\mu R_{\mu j} R_{\lambda i} p_j Q_i + \nabla_\mu A_\nu R_{\lambda i} R_{\nu l} R_{\mu j} r_j p_l Q_i . \quad (68)$$

Averaging over all spatial orientations means the integration of the terms containing the matrices $R_{\lambda i}$ over the Euler angels. Here, we can use the identities^{3,7,8}

$$\overline{R_{\lambda i}} = 0 \quad , \quad (69)$$

$$\overline{R_{\lambda i} R_{\mu j}} = \frac{1}{3} \delta_{\lambda \mu} \delta_{ij} \quad (70)$$

and

$$\overline{R_{\lambda i} R_{\mu j} R_{\nu l}} = \frac{1}{6} \epsilon_{\lambda \mu \nu} \epsilon_{ijl} \quad (71)$$

Using these equations we get from Eq. (68)

$$\langle \overline{Q_{\lambda}} \rangle \propto A_{\mu} \frac{1}{3} \delta_{\lambda \mu} \delta_{ij} p_j Q_i + \nabla_{\mu} A_{\nu} \frac{1}{6} \epsilon_{\lambda \mu \nu} \epsilon_{ijl} Q_i r_j p_l \quad (72)$$

This formula is used in the transition from Eq. (28) to Eqs (33) and (34).

APPENDIX B

In this Appendix, we make an order estimate of κ .

By using the estimates

$$N \approx 10^{24} \text{ m}^{-3}, \quad \mu_0 \approx 10^{-6} \text{ N C}^{-2} \text{ s}^2,$$

$$\omega \approx \frac{c}{\lambda} \approx 10^{15} \text{ s}^{-1}, \quad \text{Im } \mathbf{m}_{k0} \cdot \mathbf{d}_{0k} \approx 10^{-56} \text{ C}^2 \text{ m}^3 \text{ s}^{-1}, \quad \hbar \approx 10^{-34} \text{ Js}$$

in Eq. (64) we get

$$\Delta b \approx \frac{10^{11}}{S\kappa} \text{ m}^{-1}.$$

In the case of a box of the length $z \approx 10^{-2} \text{ m}$ we have

$$\Delta bz \approx \frac{10^9}{S\kappa}.$$

A typical experimental value of Δb_z for the considered molecular concentration and length of the box⁹ is

$$\Delta b_z \approx 10^{-5} \ln 10 .$$

Comparison of the last two estimates yields the order estimate of the product $S\kappa$

$$S\kappa \approx 10^{14} \text{ s}^{-1} .$$

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REFERENCES AND NOTES

1. Caldwell D. J., Eyring H.: *The Theory of Optical Activity*. Wiley, New York 1971.
2. Barron L. D.: *Molecular Light Scattering and Optical Activity*. Cambridge University Press, Cambridge 1982.
3. Healy W.: *J. Phys. B: At., Mol. Opt. Phys.* **1974**, 7, 13.
4. Davydov A. S.: *Quantum Mechanics*. Gosizdat, Moscow 1963.
5. Heitler W.: *The Quantum Theory of Radiation*. Clarendon Press, Oxford 1936.
6. Zamastil J.: *M.S. Thesis*. Charles University, Praha 1997.
7. Power E. A., Thirunamachandran T.: *J. Chem. Phys.* **1974**, 60, 9.
8. Weyl H.: *The Classical Groups*. Princeton University Press, Princeton 1946.
9. Easman G. D., Ed.: *Circular Dichroism and the Conformational Analysis of Biomolecules*. Plenum Press, New York 1996.
10. The molecules in the sample are excited at different times t_0 . The macroscopic polarization and magnetization are given by an average over a large number of the molecules. Due to the oscillating form of c_n , we can assume that the contributions of the lower bounds in Eq. (14) cancel so that the lower bounds need not be considered.
11. Since the Hamiltonian H_0 describing the molecule is real, both the real and imaginary parts of the wave function have to obey the stationary Schrodinger equation. Hence, we may assume that the wave function is real. It follows from this assumption that we can take real \mathbf{d}_{n0} and purely imaginary \mathbf{m}_{n0} .