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Calculation of the Chirality in Solutions

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The chirality parameter of a chiral chemical solution is derived as a new function of the specific rotation analytically. The Maxwell's equations are solved together for an incident linearly polarized wave to find this function. The specific rotation formula found by the measurement is used to find the chirality parameter of chiral solutions. The calculated chirality parameter can be used to simulate the chiral molecule structure in different wavelengths and also to determine the specific rotation and the concentration of a chiral chemical solution.

The interaction of circularly polarized light with the spiral structure of substance—a chiral molecule or an artificial nanostructure—depends on the relative handedness between them naturally. This fact is known as optical activity in chiral solutions such as milk or sugar solutions containing chiral molecules that cause the gradual polarization rotation of an incident linearly polarized wave passing through the medium. It is probable that the microscopic origin of this fact is magnetic dipoles induced by the electric component of the incident wave and vice versa.[1–5] The electric and magnetic vector components in an incident plane wave are perpendicular to each other. While the wave is passing through a chiral medium, an electric dipole parallel to the magnetic field vector is induced by the magnetic component of the incident wave. As a result, a little rotation in the total electric field will be imposed locally. Because of the reciprocity being in a chiral medium, the electric field vector of the incident wave excites the magnetic dipoles parallel to the electric vector component, and consequently, the magnetic field rotates a bit. This rotation is known as the specific rotation.

It should be noted that in the assumed microscopic origin of the optical activity in chiral solutions, the motions of chiral molecules as solute molecules have not been considered. By considering these molecular motions, the induced electric and magnetic dipoles will be in motion. The main effect of this mobility will be a tiny Doppler shift in the frequency of an incident linearly polarized wave passing through a chiral solution. It means that the frequency and bandwidth of the wave are not exactly alike before and after passing through a chiral solution. Also, because of the fact that in a chiral solution, the polarization rotation of an incident linearly polarized wave is not dependent on its propagation direction, it can be found that in spite of solute molecular motions, the chiral structure of solute molecule is not very dependent on the specific direction probably. In this letter, the solute molecular motions have not been considered and a chiral solution will be assumed as a reciprocal chiral medium.

A reciprocal chiral medium, such as numerous chemical solutions, obeys the constitutive relations:[1,3,6]

$$\bar{D} = \varepsilon \bar{E} - j\kappa\sqrt{\mu_0\varepsilon_0}\bar{H} \quad (1)$$

$$\bar{B} = \mu \bar{H} + j\kappa\sqrt{\mu_0\varepsilon_0}\bar{E} \quad (2)$$

Here, $\bar{E}$ is the electric and $\bar{H}$ magnetic field strength, $\bar{D}$ is the electric and $\bar{B}$ magnetic flux density. The material parameters expressing the connection between these quantities are the permittivity $\boldsymbol{\varepsilon}$ and permeability $\boldsymbol{\mu}$ characterizing the electric and magnetic copolarizability of the material, and the chirality parameter κ standing for the magnetoelectric coupling. Also, ε_0 and μ_0 are the permittivity and permeability of free space, respectively. Dimensionless parameter κ shows the degree of chirality in these equations. The refractive index n for right-handed (+) and left-handed (−) circular polarization becomes $n_\pm = \sqrt{\mu\varepsilon} \pm \kappa$. For a glucose solution, both $n_\pm$ are positive and diminutive. Therefore, the difference between them, $n_+ - n_- = 2\kappa$, is tiny. The reason for this fact is the really small quantity of induced magnetic dipoles. Thus, a significant polarization rotation effect will be recognizable after that the wave passes through a glucose solution for several centimeters. This polarization rotation, known as the specific rotation in chiral solutions, has been measured by a polarimeter or the other measurement techniques using cavity ring-down polarimetry[7,8] for several chemical solutions. Also, the specific rotation has been formulated practically, as a function of the concentration of a chiral chemical solution for a variety of temperatures and wavelengths.

The consistent calculation of the optical properties of chiral molecules is a major challenge in electronic structure theory.[7–12] In recent years, substantial progress has been made with the development of quantum chemical models for computing properties such as optical rotation (OR) angles and electronic circular dichroism spectra,[13] but reliable comparison to experimental data remains challenging. The new approach to the calculation of the optical properties of chiral materials is the use of Maxwell's equations with the scattering theory to model these materials as the mixture of known nanostructures embedded in a host medium homogeneously.

The relation between the specific rotation and the chirality parameter κ can be used to find the specific rotation of chemical solution from the reflection coefficient of an incident wave illuminating its interface with the achiral material.[6] Also, the mentioned relation can be applied to present the reliable models such as helices, twisted strips, nonplanar double hooks, irregular tetrahedral, etc. (in nanoscale),[14] for chiral molecules in different wavelengths by using the methods based on the scattering theory.[15]

In this paper, the generalized constitutive relations eqs 1 and 2 with the Maxwell's equations are used to derive the differential equations for the polarization rotation angle of a linearly polarized wave propagating through the chiral medium. These equations are solved analytically, and then the practical specific rotation formula is applied to find the chirality parameter as a function of the concentration of a chiral chemical solution, wavelength, temperature, and the specific rotation.

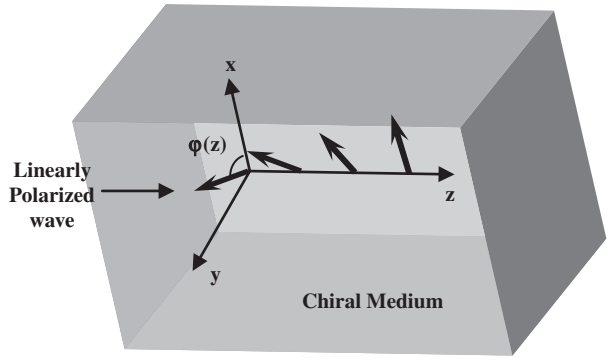

Figure 1. Linearly polarized wave propagating in a chiral medium along z direction with the polarization direction as a function of z.

For homogeneous chiral chemical solutions, combining the generalized constitutive relations eqs 1 and 2 with the Maxwell's equations in the frequency domain ($e^{j\omega t}$ is assumed and suppressed), the reciprocal chiral medium equations can be written as:

$$\nabla \times \bar{E} = -j\omega(\mu \bar{H} + j\kappa\sqrt{\mu_0\varepsilon_0}\bar{E}) \quad (3a)$$

$$\nabla \times \bar{H} = j\omega(\varepsilon \bar{E} - j\kappa\sqrt{\mu_0\varepsilon_0}\bar{H}) \quad (3b)$$

Combining the eqs 3a and 3b, the chiral Helmholtz equation for the electric field E is found as:

$$\nabla^2\bar{E} + 2K_0\kappa\nabla \times \bar{E} + {K_0}^2(\mu_r\varepsilon_r - \kappa^2)\bar{E} = 0 \quad (4)$$

Where, μ_r and ε_r are the relative permeability and permittivity of chiral medium, and K_0 is the wave number of free space. According to the homogeneity and reciprocity of chiral chemical solutions, the polarization rotation of an incident linearly polarized wave, passing through the medium, is independent of the propagation direction. Thus, for the sake of simplicity, the structure showed in Figure 1, is assumed to find the differential equations for the polarization angle ($\varphi(z)$) of an incident linearly polarized wave. In Figure 1, a chiral chemical solution is assumed as a continuous electromagnetic chiral medium. It means that the solute chiral molecules have been distributed homogenously in the chemical solution. To investigate the optical activity in a chiral medium, the plane wave with changeable polarization direction, propagating along z, presented in Figure 1, can be written as:

$$\bar{E} = |\bar{E}|(\cos(\varphi(z))\hat{x} + \sin(\varphi(z))\hat{y})e^{-jK_z z} \quad (5)$$

Here, $|\bar{E}|$ is the magnitude of the electric field and independent of z, K_z is the wave number, and the polarization angle is $\varphi(z)$.

By combining the eqs 4 and 5, the differential equations for the polarization angle $\varphi(z)$ will be derived as:

$$\begin{aligned}&(-\cos(\varphi(z))(\varphi'(z))^2 - \varphi''(z)\sin(\varphi(z)) - {K_z}^2\cos(\varphi(z))\\&\quad + {K_0}^2(\mu_r\varepsilon_r - \kappa^2)\cos(\varphi(z)) - 2\kappa K_0\cos(\varphi(z))\varphi'(z))\\&\quad + 2j(K_z\sin(\varphi(z))\varphi'(z) + K_0K_z\kappa\sin(\varphi(z))) = 0 \quad (6a)\\&(-\sin(\varphi(z))(\varphi'(z))^2 + \varphi''(z)\cos(\varphi(z)) - {K_z}^2\sin(\varphi(z))\\&\quad + {K_0}^2(\mu_r\varepsilon_r - \kappa^2)\sin(\varphi(z)) - 2\kappa K_0\sin(\varphi(z))\varphi'(z))\\&\quad - 2j(K_z\cos(\varphi(z))\varphi'(z) + K_0K_z\kappa\cos(\varphi(z))) = 0 \quad (6b)\end{aligned}$$

The solution for $\varphi(z)$ and K_z, satisfying the eq 6, is found as:

$$\varphi(z) = -K_0\kappa z, \quad K_z = K_0\sqrt{\mu_r\varepsilon_r} \quad (7)$$

Considering the solution for polarization angle ($\varphi(z)$) and eq 5, it can be concluded that for chemical solutions with the positive specific rotation such as glucose and sucrose, the chirality parameter is negative ($\kappa < 0$) and vice versa for the materials such as fructose and cholesterol.

The practical formula between the concentration of a chemical solution and the measured polarization rotation of a linearly polarized wave passing through the chiral solution is given by:

$$[\alpha]_\lambda^T = \frac{\alpha_{\text{observed}}}{c \times l} \quad (8)$$

Where $[\alpha]_\lambda^T$ is the specific rotation of a solution at the temperature (T) and the wavelength (λ), c is the concentration of a chemical solution, expressed in $\mathrm{g\,mL^{-1}}$, l is the path length passed by the wave in decimeter (dm), and α_{observed} is the polarization rotation angle. Combining the eqs 7 and 8, the relation between the chirality parameter and the specific rotation of a chemical solution can be found as:

$$\kappa = -(\pi/180) \times \frac{[\alpha]_\lambda^T}{10 \times K_0} \times c \quad (9)$$

As would be expected intrinsically, the chirality of chemical solution is independent of the path length passed by a wave. This fact is observable in eq 9. Also, it can be found that the chirality parameter is dependent on the specific rotation, the concentration of a chemical solution, wavelength, and temperature. The measured specific rotations of some chemical solutions are shown in Table 1.[16–18] Using eq 9, the chirality parameters of solutions presented in Table 1, versus the concentration of a chemical solution are depicted in Figure 2.

Table 1. Measured specific rotations of some chemical solutions

Substance in a solution H_2O solvent	Wavelength/nm	Specific rotation
Sucrose	546.23	+78.41
	589.44	+66.54
	632.99	+57.21
	882.60	+28.54
Glucose	589.44	+52.74
Lactose		+55.3
Maltose		+137.5
Dextrose		+194.8
Fructose		−93.78
Cholesterol		−31.62

According to Figure 2, it can be seen that an increase in the concentration of a chemical solution leads to an increase in the magnitude of chirality parameter. Measuring the reflection or transmission coefficient of the wave interacting with the chemical solution, and then using the scattering properties, it is possible to determine its chirality parameter, and accordingly the specific rotation of every chemical solution in Table 1 by knowing its chemical concentration. Also, using the specific rotation of a chemical solution and the estimation of its chirality parameter from the scattering properties, the concentration of a

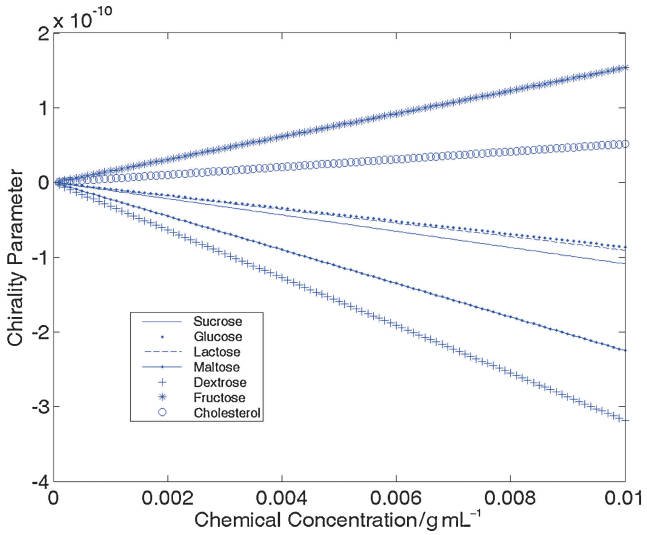

Figure 2. The chirality parameter versus concentration for some chemical solutions.

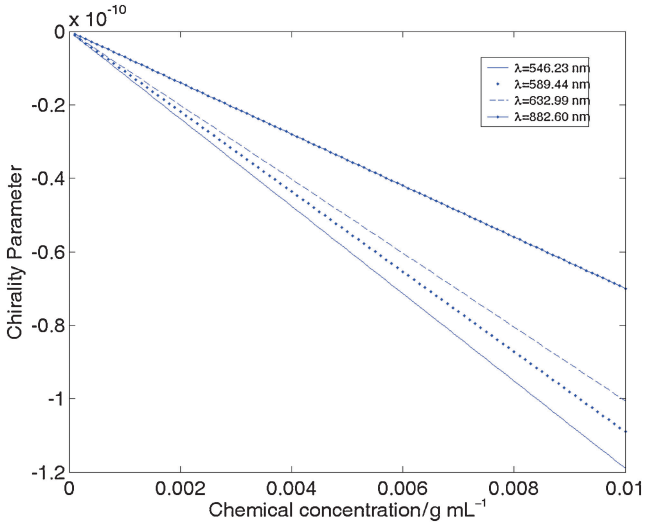

Figure 3. The dependence of chirality parameter on the sucrose concentration and wavelength.

chemical solution can be determined. Figure 3 shows the chirality parameter versus the concentration of sucrose solution for some wavelengths. According to Figure 3, it can be seen that for sucrose, increasing the wavelength decreases the chirality amplitude. Figure 3 can be used to find an appropriate electromagnetic model for chiral molecules of sucrose. In this electromagnetic simulation, the sucrose chiral molecules can be modeled as one of the electromagnetic chiral structures such as helices, twisted strips, nonplanar double hooks, irregular tetrahedral, etc. (in nanoscale). The numerous selected structures will be considered according to the concentration of a sucrose solution. Also, it is assumed that the chiral structures are suspended homogeneously in water as a host medium. After that, the effective chirality parameter of this simulated chiral medium can be found according to the method of ref 15. Finally, an appropriate optimization method must be used to find the best configuration for the selected chiral structure in some wavelengths, so that the calculated chirality parameters of the simulated medium for some concentrations are going to be matched with the chirality parameters presented in Figure 3. As a result, it can be said that the sucrose molecules can be represented by this optimized structure in an electromagnetic analysis.

Finally, it can be concluded that the chirality parameter of a chemical solution was derived analytically as a new function of the specific rotation, the concentration of a chemical solution and wavelength. This parameter can be to determine the specific rotation and the concentration of a chemical solution by the measurement of the reflection/transmission coefficient and using the electromagnetic scattering methods. Also, using different chirality parameters of a chemical solution calculated in some wavelengths and concentrations, it is possible to find a suitable electromagnetic model for its chiral molecules.

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