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Theory of Resonance Optical Rotation*

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The theory of optical rotation has been derived by means of the quantum theory of the radiation field with special emphasis on the case where the frequency of the rotated light is in the vicinity of an absorption frequency of the sample that is being studied. It is concluded that for certain frequency ranges optical rotation is not a physically meaningful concept.

I. INTRODUCTION

In a recently proposed theory of resonance fluorescence (*1*) we were forced to base our discussion on an application of the quantum theory of the radiation field (*2*) since it did not seem to be possible to derive the theory by means of semiclassical methods. A special case of this general situation, namely, optical and magnetic rotation spectra (*3*, *4*), had been discussed previously using the same approach. We feel that it should also be possible to derive the Rosenfeld formula (*5*) describing ordinary optical rotation, in a similar way; apparently this formula has only been derived by means of semiclassical arguments so far (*6*). This problem is not entirely trivial and we will discuss it in this paper. Apart from a purely academic significance, inherent in the rederivation of a well-known formula by means of a second method, the following discussion will also have some practical advantages. Our results will be valid also for the case where the frequency of the light that is rotated by a given sample is approximately equal to an absorption frequency of the sample[1], in fact, our discussion will be mainly concerned with this particular situation. Therefore, we are able to determine the conditions under which optical rotation is a physically meaningful concept from a careful analysis of the process of measuring the optical rotation.

The experimental situations that serve as bases for a theoretical discussion of either optical rotation spectra or resonance optical rotation are very similar but the questions that we seek to answer are quite different. It may be helpful to recall the comparison that was made in previous work (*3*). We consider a beam of linearly polarized light which passes through the sample which we are con-

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[1] This case is described here by the term "resonance optical rotation".

cerned with and then, on its way, meets a Nicol prism which permits only the passage of linearly polarized light with a direction of polarization perpendicular to that of the incident light. For a study of the optical rotation spectrum we take the incident light as having a continuous frequency distribution, containing one or more of the absorption frequencies ν_k of the sample, and we determine the optical rotation spectrum by measuring the spectral intensity distribution of the effluent light. The intensities that we measure are due to two different effects: first, the rotation of the plane of polarization and, second, the depolarization or rather the change from linear to elliptical polarization, caused by the sample. However, here we are not particularly interested in these distinctions and all that we seek to determine is the total intensity of the effluent light, since this is the only quantity that is measured. For a study of the optical rotation we take the incident light as monochromatic or, more exactly, as having a spectral intensity distribution that has a sharp maximum around a frequency ν_0 which is close to an absorption frequency ν_k of the sample. Now we rotate the Nicol prism through an angle ϕ and we hope that the intensity of the effluent light as a function of ϕ has a minimum. The angle ϕ_0 for which this minimum is attained is the optical rotation and the minimum intensity of the light at ϕ_0 is a measure of the change in polarization of the light from linear to elliptical. In the ideal situation this minimum intensity is equal to zero or very small; if it becomes comparable with the maximum intensity of the light, it is very difficult to measure optical rotation and the latter is not any more a meaningful physical quantity.

II. GENERAL CONSIDERATIONS

We consider a situation that has been extensively discussed previously (*1*, *3*, *4*), namely, a system of particles that is described by a Hamiltonian $\mathcal{H}_m$, having a set of eigenvalues ϵ_0, ϵ_n, with corresponding eigenfunctions Φ_0, Φ_n, and a radiation field that is described by a Hamiltonian $\mathcal{H}_f$. We take it that before a certain time $t = 0$, the system of particles is in its ground state, corresponding to the eigenvalue ϵ_0 and the eigenfunction Φ_0 and that, simultaneously, the radiation field is in a stationary state described by an eigenvalue ϵ_0' and a state vector ψ_0. At the time $t = 0$ the particles and the radiation field begin to interact and the interaction is described by a Hamiltonian $\mathcal{H}_{\text{int}}$. Obviously the stationary states of the combined system of particles and field (disregarding the interaction) are described by eigenvalues that are sums of the eigenvalues of $\mathcal{H}_m$ and $\mathcal{H}_f$ and by eigenfunctions that are products of the corresponding eigenfunctions of $\mathcal{H}_m$ and $\mathcal{H}_f$. We are interested in the states $(0, 0)$, (n, λ) and $(0, \lambda\mu)$ with the eigenvalues and eigenfunctions

$$\begin{aligned}
E_{0,0} &= \epsilon_0 + \epsilon_0' & \Psi_{0,0} &= \Phi_0\psi_0 \\
E_{n,\lambda} &= \epsilon_n + \epsilon_\lambda' & \Psi_{n,\lambda} &= \Phi_n\psi_\lambda \\
E_{0,\lambda\mu} &= \epsilon_0 + \epsilon_{\lambda\mu}' & \Psi_{0,\lambda\mu} &= \Phi_0\psi_{\lambda\mu}
\end{aligned} \tag{1}$$

Here the state vector ψ_λ describes the stationary state where a photon $\mathbf{k}_\lambda$ has been absorbed from the radiation field with respect to ψ_0; its energy is $\epsilon_\lambda' = \epsilon_0' - k_\lambda$. Similarly the state vector $\psi_{\lambda\mu}$ describes the situation where a photon $\mathbf{k}_\lambda$ has been absorbed and a different photon $\mathbf{k}_\mu$ has been emitted with respect to ψ_0; the corresponding energy is $\epsilon_{\lambda\mu}' = \epsilon_0' - k_\lambda + k_\mu$. For our purposes we may now represent the wave function of the total Hamiltonian $\mathcal{H}_m + \mathcal{H}_f + \mathcal{H}_{\text{int}}$ at times $t \geqq 0$ as a linear combination of the functions of Eq. (1):

$$\Psi(t) = b_{0,0}(t)\Psi_{0,0} + \sum_\lambda \sum_n b_{n,\lambda}(t)\Psi_{n,\lambda} + \sum_\lambda \sum_\mu b_{0,\lambda\mu}(t)\Psi_{0,\lambda\mu} \tag{2}$$

The various physical properties related to the interaction between the particles and the radiation may now be expressed in terms of the coefficients b. The calculation of these coefficients b has been discussed elsewhere (*1, 3, 4*); we will comment on these calculations later in this section, but at this point we wish to mention (*2*) that always

$$\lim_{t\to\infty} b_{n,\lambda}(t) = 0 \tag{3}$$

We may recall (*2*) that a photon λ is characterized by a vector $\mathbf{k}_\lambda$, whose direction describes the direction of propagation and whose magnitude is equal to the energy of the photon, and by a unit vector $\mathbf{e}_\lambda$, which denotes the direction of polarization of the photon. The quantum number n_λ represents the number of radiation oscillators λ. Since we wish to study the situation where a beam of linearly polarized light interacts with a given sample, we may take it that the state vector ψ_0 represents a stationary state that contains only photons that are polarized in one particular direction and that all have the same direction of propagation; we will choose the direction of polarization as the X axis and the direction of propagation as the Z axis. We will now distinguish between two classes of photons: (1) photons λ, μ, or σ with a direction of polarization along the X axis, and (2) photons λ', μ', or σ' with a direction of polarization along the Y axis; we only consider photons with a direction of propagation along the Z axis. Apparently in the stationary state described by ψ_0 all quantum numbers $n_{\lambda'}$, $n_{\mu'}$ and $n_{\sigma'}$ are zero.

The component of the radiation field in a particular direction in the XY plane, making an angle ϕ with the Y-axis, is written as

$$A_\phi = \sin\phi \sum_\lambda (q_\lambda A_\lambda + q_\lambda^* A_\lambda^*) + \cos\phi \sum_{\lambda'} (q_{\lambda'} A_{\lambda'} + q_{\lambda'}^* A_{\lambda'}^*) \tag{4}$$

The total intensity of the light that is polarized in the ϕ direction, which is the intensity that we would measure in the experiment described in Section I if we were to rotate the Nicol prism though an angle ϕ, is obtained as

$$\begin{aligned} I(\phi) &= \langle \Psi(\infty) \,|\, A_\phi{}^2 \,|\, \Psi(\infty) \rangle \\ A_\phi{}^2 &= \sin^2\phi \sum_\lambda \sum_\mu (q_\lambda q_\mu A_\lambda A_\mu + q_\lambda q_\mu{}^* A_\lambda A_\mu{}^* + q_\lambda{}^* q_\mu A_\lambda{}^* A_\mu \\ &\quad + q_\lambda{}^* q_\mu{}^* A_\lambda{}^* A_\mu{}^*) + 2 \sin\phi \cos\phi \sum_\lambda \sum_{\mu'} , (q_\lambda q_{\mu'} A_\lambda A_{\mu'} \\ &\quad + q_\lambda q_{\mu'}^* A_\lambda A_{\mu'}^* + q_\lambda{}^* q_{\mu'} A_\lambda{}^* A_{\mu'}^* + q_\lambda{}^* q_{\mu'}^* A_\lambda{}^* A_{\mu'}^*) \\ &\quad + \cos^2\phi \textstyle\sum_{\lambda'} \sum_{\mu'} (q_{\lambda'} q_{\mu'} A_{\lambda'} A_{\mu'} + q_{\lambda'} q_{\mu'}^* A_{\lambda'} A_{\mu'}^* \\ &\qquad\qquad + q_{\lambda'}^* q_{\mu'} A_{\lambda'}^* A_{\mu'} + q_{\lambda'}^* q_{\mu'}^* A_{\lambda'}^* A_{\mu'}^*) \end{aligned} \tag{5}$$

where the function $\Psi(t)$ is defined in Eq. (2). Because of Eq. (3) and because of the fact that the first double sum in Eq. (5) will only yield a nonzero result if λ and μ are equal, we may rewrite Eq. (5) as

$$\begin{aligned} I(\phi) = \sum_\lambda n_\lambda [\sin^2\phi + n_\lambda^{-1/2} \sin\phi \cos\phi \sum_{\mu'} \{ b_{0,\lambda\mu'}(\infty) \\ + b_{0,\lambda\mu'}^*(\infty) \} + n_\lambda^{-1} \cos^2\phi \sum_{\mu'} \sum_{\sigma'} b_{0,\lambda\mu'}(\infty) b_{0,\lambda\sigma'}^*(\infty)] \end{aligned} \tag{6}$$

The coefficients $b_{0,\lambda\mu'}$ represent situations where a photon λ with its polarization in the X direction has been absorbed and a photon μ' with its polarization in the Y direction has simultaneously been re-emitted.

The theory of optical rotation will be developed by taking Eq. (6) as a basis and by substituting the results for $b_{0,\lambda\mu'}(\infty)$ that were obtained previously (*1*). We discussed the calculation of $b_{0,\lambda\mu'}$ for the situation where the system of particles, described in Section I by $\mathcal{H}_m$, consists of a large number N of identical molecules. We specifically considered the two cases where the molecules form a dilute gas and where they form a molecular crystal; since the former case is somewhat simpler we will restrict ourselves here to a discussion of the theory of optical rotation of dilute gases only. Before using our previous results for dilute gases (*1*) it is desirable to comment on them.

For the sake of simplicity we will assume that the spectral intensity distribution of the incident light, that is, n_λ as a function of k_λ, has a sharp maximum for $k = k_0$ so that $\sum_\lambda n_\lambda = I_0$; the width of this maximum will be denoted by δ. Now we take it that one individual molecule at rest has a nondegenerate excited state with excitation energy $k_n = \epsilon_n - \epsilon_0$, which is close to k_0, and that the excitation energies of the other states of the molecule at rest are so far removed from k_0 that they may be disregarded. Since the gas will be considered as an assembly of N noninteracting identical molecules, this particular nondegenerate molecular state will give rise to an N-fold degenerate excited state of the gas with excitation energy k_n because the excitation can be on either one of the N molecules.

In previous work it was found that the calculation of $b_{0,\lambda\mu}$ for the above situation of an N-fold degenerate excited state involves the introduction of a damping matrix. It was shown (*1*) that the off-diagonal elements of this matrix are ordinarily not zero but that they become zero after we average over all possible molecular orientations. Even though this result in itself is correct it does not seem to agree with the theoretical and experimental work by Barrat (*7*) on multiple scattering. Barrat's approach to the problem is somewhat different from ours, but his conclusion that the effective radiative lifetimes are increased by multiple scattering seems to indicate that the off-diagonal elements of the damping matrix are not necessarily zero. We believe that the discrepancy between Barrat's work (*7*) and ours (*1*) may be explained by observing that in calculating $b_{0,\lambda\mu'}$ we should keep all molecular orientations fixed, so that the off-diagonal elements of the damping matrix are nonzero; it is only after the calculation has been performed in this way that we should average over the rotational motion of the molecules. Apparently our procedure, in which we first average the individual off-diagonal elements of the damping matrix over the rotational motion of the molecules and then calculate $b_{0,\lambda\mu'}$, is not quite correct. However if the gas is sufficiently dilute it is known that multiple scattering processes do not play a significant role in optical rotation so that our taking the off-diagonal matrix elements equal to zero may constitute a reasonable approximation. At any rate, this approximation simplified the calculation of the $b_{0,\lambda\mu}$ considerably so that we will assume that it is permissible in our theory of optical rotation.

If we use the above approximation we obtain $b_{0,\lambda\mu'}$ as a sum of terms, each one of which refers to the excitation being on one of the N molecules. This sum is again evaluated by averaging over all molecular orientations but this procedure is not subject to the objection raised in the previous section, since now we average over the different orientations of all molecules at any one time and not over the orientations of one molecule at different times.

In our previous work we did not consider the motion of the molecules so that we neglected the Doppler effect and the collision broadening. We will show that the Doppler effect may be accounted for by introducing a suitable convolution integral. We will assume that the density of the gas is so small that the collision broadening is negligible.

III. CALCULATIONS

In order to evaluate Eq. (6) further it is profitable to write $b_{0,\lambda\mu'}(\infty)$ as

$$b_{0,\lambda\mu'}(\infty) = [k_{\mu'} - k_\lambda + \tfrac{1}{2}i\hbar\Gamma]^{-1} n_\lambda^{1/2} Q_{\lambda\mu'} \tag{7}$$

with

$$
\begin{aligned}
Q_{\lambda\mu'} &= n_\lambda^{-1/2} U_{0,\lambda\mu';0,0}(E_{0,\lambda\mu'}) \\
\Gamma &= \Re\Gamma(E_{0,\lambda\mu'})
\end{aligned}
\tag{8}
$$

The definitions and calculations of the functions U and of the damping constant Γ have been discussed previously (*1, 3, 4*). It is worth noting that $Q_{\lambda\mu'}$ no longer depends on n_λ and also that Γ is very small, not only with respect to unity, but also with respect to the damping constants γ that will be introduced later. Substitution of Eq. (7) into Eq. (6) yields

$$
\begin{aligned}
I(\phi) = \sum_\lambda n_\lambda [\sin^2\phi &+ \sin\phi\cos\phi \sum (k_{\mu'} - k_\lambda + \tfrac{1}{2}i\hbar\Gamma)^{-1}Q_{\lambda\mu'} \\
&+ (k_{\mu'} - k_\lambda - \tfrac{1}{2}i\hbar\Gamma)^{-1}Q^*_{\lambda\mu'} \\
&+ \tfrac{1}{2}\cos^2\phi \sum_{\mu'}\sum_{\sigma'} \{(k_{\mu'} - k_\lambda + \tfrac{1}{2}i\hbar\Gamma)^{-1}(k_{\sigma'} - k_\lambda - \tfrac{1}{2}i\hbar\Gamma)^{-1}Q_{\lambda\mu'}Q^*_{\lambda\sigma'} \\
&+ (k_{\mu'} - k_\lambda - \tfrac{1}{2}i\hbar\Gamma)^{-1}(k_{\sigma'} - k_\lambda + \tfrac{1}{2}i\hbar\Gamma)^{-1}Q^*_{\lambda\mu'}Q_{\lambda\sigma'}\}]
\end{aligned}
\tag{9}
$$

If we introduce the real and imaginary parts, $R_{\lambda\mu'}$ and $S_{\lambda\mu'}$, respectively, of $Q_{\lambda\mu'}$:

$$
Q_{\lambda\mu'} = R_{\lambda\mu'} + iS_{\lambda\mu'} \tag{10}
$$

we obtain after straightforward integration of Eq. (9)

$$
I(\phi) = \sum_\lambda n_\lambda[\{\sin\phi + (S_{\lambda\lambda'}/\hbar c)\cos\phi\}^2 + \{(R_{\lambda\lambda'}/\hbar c)\cos\phi\}^2] \tag{11}
$$

It follows that the optical rotation will generally be proportional to $S_{\lambda\lambda'}$, whereas the depolarization, or rather the change from linear to elliptical polarization, is determined by $R_{\lambda\lambda'}$.

The calculation of the functions $U_{0,\lambda\mu';0,0}(E_{0,\lambda\mu'})$, and consequently of the quantities $Q_{\lambda\mu'}$, $R_{\lambda\mu'}$ and $S_{\lambda\mu'}$, has been discussed previously (*1, 3, 4*) for dilute gases and molecular crystals. Our present calculation will be concerned with dilute gases since here the results are somewhat simpler. We found (*1, 3*) that

$$
Q_{\lambda\lambda'} = \frac{e^2}{m^2}\,\frac{2\pi\hbar^2}{k_\lambda} \sum_\tau \frac{\langle\phi_0^\tau \mid \Omega_x^\tau \mid \phi_n^\tau\rangle\langle\phi_n^\tau \mid \Omega_y^{\tau*} \mid \phi_0^\tau\rangle}{k_\lambda - k_n + \tfrac{1}{2}i\hbar\gamma} \tag{12}
$$

if we neglect all off-diagonal elements of the damping matrix, as we discussed in the previous section. Here the summation is to be performed over all molecules; the functions ϕ_0^τ and ϕ_n^τ are the wave functions of the ground and excited states of molecule τ and the operators are defined as

$$
\begin{aligned}
\Omega_x^\tau &= \sum_j p_{jx} \exp(ik_\lambda z_j/\hbar c) \\
\Omega_y^{\tau*} &= \sum p_{jy} \exp(-ik_\lambda z_j/\hbar c)
\end{aligned}
\tag{13}
$$

where the summations are to be performed over all electrons in molecule τ and where the coordinates and momenta are defined with respect to a coordinate system that is fixed in space and has the same orientation for all molecules. The damping constants γ were discussed in previous work.

The sum of Eq. (12) may be evaluated by averaging over all possible molecular orientations and by simultaneously multiplying by the total number of molecules. For a cubic centimeter, containing N molecules, we found (*3*)

$$\begin{aligned} Q_{\lambda\lambda'} &= (4\pi k_\lambda N/3i)\,(k_\lambda - k_n + \tfrac{1}{2}i\hbar\gamma)^{-1}U_n \\ U_n &= \mathcal{I}\,(\langle\phi_0 \mid \mathbf{P} \mid \phi_n\rangle\cdot\langle\phi_n \mid \mathbf{M} \mid \phi_0\rangle) \end{aligned} \tag{14}$$

where $\mathcal{I}$ means that we have to take the imaginary part. The operators are defined as the electric and magnetic moments

$$\begin{aligned} \mathbf{p} &= e\sum_j \mathbf{r}_j \\ \mathbf{M} &= (e/2mc)\sum_j [\mathbf{r}_j \times \mathbf{p}_j] \end{aligned} \tag{15}$$

The summations are again performed over all electrons in one molecule and the coordinates and momenta are now defined with respect to a coordinate system that is attached to the molecule. It follows after substitution into Eq. (11) that

$$\begin{aligned} I(\phi) = \sum_\lambda n_\lambda \Bigg[\bigg(\sin\phi &- \frac{4\pi\omega_\lambda N}{3c}\,\frac{(k_\lambda - k_n)U_n}{(k_\lambda - k_n)^2 + \frac{1}{4}\hbar^2\gamma^2}\cos\phi \bigg)^2 \\ &+ \bigg(\frac{4\pi\omega_\lambda N}{3c}\,\frac{\frac{1}{2}\hbar\gamma U_n}{(k_\lambda - k_n)^2 + \frac{1}{4}\hbar^2\gamma^2}\cos\phi \bigg)^2 \Bigg] \end{aligned} \tag{16}$$

We will use this equation as a basis for our discussion of optical rotation. It seems that for a further evaluation it is necessary to know how sharp the maximum is for n_λ as a function of k_λ, since we will obtain different results for the two cases that $\delta < \frac{1}{2}\hbar\gamma$ and $\delta \geqq \frac{1}{2}\hbar\gamma$, where δ is the width of this maximum. However, it is pointless to consider the situation that $\delta < \frac{1}{2}\hbar\gamma$ since the Doppler effect, which we have disregarded so far, causes the lines to be always broader than γ. The intensity distribution due to the Doppler effect is given by (*2*)

$$\begin{aligned} I(k)\,dk &= \text{const.}\,dk \exp\,[-(k - k_0)^2/(\delta')^2] \\ \delta' &= (2k_0^2/Mc^2\beta)^{1/2} \end{aligned} \tag{17}$$

where $(1/\beta)$ is the product of the Boltzmann constant and the absolute temperature and M is the mass of the molecule. Apparently we should amend Eq. (16) in order to include the Doppler effect; we may rewrite the equation then as

$$I(\phi) \propto \iint \exp\,[-(k_\mu - k_\lambda)^2/(\delta')^2] \exp\,[-(k_\lambda - k_0)^2/\delta^2] W_\phi(k_\lambda)\,dk_\lambda\,dk_\mu \tag{18}$$

where, for the sake of brevity, we have denoted the expression between square brackets of Eq. (16) by $W_\phi(k_\lambda)$ and, for the sake of simplicity, we have taken the intensity distribution of n_λ to be Gaussian. In effect, we may replace Eq. (18) by

$$I(\phi) \propto \int \exp\,[-\delta_>(k_\lambda - k_0)^2] W_\phi(k_\lambda)\, dk_\lambda \tag{19}$$

where $\delta_>$ is the larger of δ and δ' if δ and δ' are very different and $\delta_>$ is of the order of magnitude of δ and δ' if they are about equal. In general, the line width $\delta_>$ is significantly larger than γ.

From the considerations in Section I it follows that optical rotation is only a meaningful concept if the intensity as a function of the angle ϕ has a measurable minimum. This is only the case if

$$| k_0 - k_n | > \delta_> \tag{20}$$

or, substituting Eq. (17),

$$| k_0 - k_n | > (2k_0^2/Mc^2\beta)^{1/2}, \delta \tag{21}$$

Only if the Doppler line breadth δ' is very small do we then have to impose the condition

$$| k_0 - k_n | > \tfrac{1}{2}\hbar\gamma \tag{22}$$

IV. DISCUSSION

The considerations in the previous sections are subject to a serious restriction: they are only valid for situations where the amplitude of the radiation field is approximately constant throughout the sample that we consider. This means that they are only valid for samples where the rotation is extremely small and that they are not applicable to most situations where the rotations are more than a few degrees. However, we can remove this limitation by means of the following procedure: The sample that we wish to study is subdivided into many thin slices with their surfaces perpendicular to the beam of light so that in each slice the rotation is very small and simultaneously each slice contains a large number of molecules. For each slice separately the considerations of the previous sections are applicable and the total rotation of the sample may be obtained macroscopically by adding the successive rotations due to each slice. We find then from Eq. (16) that the total rotation ϕ_0 is given by

$$\phi_0 = \frac{4\pi\omega_0 Nl}{3c} \frac{(k_0 - k_n)U_n}{(k_0 - k_n)^2 + \tfrac{1}{4}\hbar^2\gamma^2} \approx \frac{4\pi\omega_0 NlU_n}{3c(k_0 - k_n)} \tag{23}$$

where l is the total length of the sample through which the beam of light travels and N is again the number of molecules per unit volume. This expression is equivalent to the old Rosenfeld formula (*5*, *6*).

In previous work we also evaluated the quantity $Q_{\lambda\lambda'}$ for a molecular crystal (*1*). It was found that $|Q_{\lambda\lambda'}|$ for a crystal may be significantly larger than for a gas; however, it also followed that the analogue of U_n for a molecular crystal then has a leading term which is imaginary instead of real. Apparently the relatively large intensities that may occur in the optical rotation spectra of molecular crystals are due to changes in polarization rather than to optical rotation.

We may conclude that it is possible to describe resonance optical rotation by means of quantum field theory. If we neglect multiple scattering we find that our results agree with previous results (*5, 6*), derived by means of semiclassical methods, if the conditions (21) and (22) are satisfied, otherwise optical rotation is not a physically meaningful concept.

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