High-frequency asymptotics of circular dichroism

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The circular dichroism of an isotropic medium of chiral molecules, $\mathrm{Im}(n_+-n_-)/\mathrm{Im}(n_++n_-)$, decreases like ω^{-2} at frequencies ω much higher than Ry but much lower than Z^2Ry and like ω^{-3} at frequencies much higher than Z^2Ry, where Z is the charge of the nucleus of the atom characterizing the given chiral group. The electron-spin contribution to the circular dichroism is found to be finite only in the second order of spin–orbit coupling. It is also established that the photoelectron polarization in the absorption of unpolarized light is due to the chiral nature of the molecules and amounts to a fraction $Z^2\alpha^3$ of the degree of geometric asymmetry.

1. INTRODUCTION

Molecules and crystals that are mirror reflections of each other are called optical isomers. When light travels through a medium with an abundance of isomers of definite chirality, along with rotation of the polarization plane the values of absorption coefficients for left- and right-hand polarizations of light differ. This phenomenon is known as circular dichroism (CD). This paper studies CD for $\omega \gg \mathrm{Ry}$, where $\mathrm{Ry}=m\alpha^2/2=13.6$ eV is a characteristic value for atomic and molecular transitions.

Our reason for interest in the high-frequency behavior of CD is twofold. First, according to many hypotheses (see, e.g., Ref. 1), circularly polarized light may be the cause of the optical activity (OA) of biological molecules and the obvious left–right asymmetry in nature. In the ultraviolet range, asymmetric photochemical processes leading to OA were discovered in experiments.[2-5] Second, an interesting question is how correlations in the electron spin and momentum in a chiral molecule, which result from spin–orbit interaction,[6,7] manifest themselves in absorption of light. As is known, the high-frequency behavior of OA is determined by this very interaction.[8] Knowing the angle of rotation of the light's polarization plane in the frequency range $\omega \sim Z^{-3/4}\alpha\mathrm{Ry}$ makes it possible to determine the distance between the energy levels of optical isomers caused by the parity-breaking weak interaction between an electron and the nucleus.[8] In view of this it is natural to study the spin–orbit contribution to the high-frequency asymptotic behavior of CD.

The refractive index of a medium, $n(\omega)$, is related to the amplitude of forward scattering by a single molecule, $f(\omega)$, via the well-known formula

$$n=1+\frac{2\pi N}{\omega^2 V}f(\omega), \tag{1}$$

where N/V is the concentration of molecules. According to the optical theorem, the imaginary part of the refractive index is related to the total cross section of absorption of light by a single molecule by the following formula:

$$\mathrm{Im}\, n(\omega)=\frac{2\pi N}{\omega^2 V}\,\mathrm{Im}\, f(\omega)=\frac{N}{2\omega V}\sigma(\omega). \tag{2}$$

CD emerges as a result of the difference in the cross sections of absorption of photons with different signs of circular polarization λ:

$$\lambda=i(\boldsymbol{\epsilon}\times\boldsymbol{\epsilon}^*)\cdot\mathbf{n}=\pm 1. \tag{3}$$

Here $\boldsymbol{\epsilon}$ is the photon polarization vector and $\mathbf{n}$ the unit vector defining the direction of light propagation.

Quantitatively the CD effect is characterized by the ratio of the difference between the left- and right-hand polarization cross sections to the cross section independent of the photon spin:

$$\eta=\frac{\sigma_+-\sigma_-}{\sigma_++\sigma_-}. \tag{4}$$

Our aim is to study the behavior of $\eta(\omega)$ at high frequencies. As the first step we write (4) in terms of an amplitude ratio. As long as the frequency of the incident light is not too high ($\omega < m\alpha$), we can take into account only the lowest-order multipoles, that is, the first two terms in the expression for the matrix element of light absorption:

$$\langle f|V_{\mathrm{int}}|in\rangle=\langle f|i\omega(\boldsymbol{\epsilon}\cdot\mathbf{d})+i\omega[(\mathbf{n}\times\boldsymbol{\epsilon})\cdot\boldsymbol{\mu}]|in\rangle. \tag{5}$$

Here $\mathbf{d}=e\mathbf{r}$ and $\boldsymbol{\mu}=e(\mathbf{l}+\boldsymbol{\sigma})/2m$ are, respectively, the operators of electric and magnetic dipole moments. The E2-transition is unimportant because its contribution vanishes after averaging over the random orientation of the scatterer. Averaging leads to the following formula for the circular dichroism η in the transition between the "*in*" and "*f*" states:

$$\eta=-\frac{\mathrm{Im}\langle in|\mathbf{l}+\boldsymbol{\sigma}|f\rangle\langle f|\mathbf{r}|in\rangle}{m\langle in|\mathbf{r}|f\rangle\langle f|\mathbf{r}|in\rangle}. \tag{6}$$

At frequencies $\omega \sim \mathrm{Ry}$ the relative CD value is of the order of $\alpha\xi$. The fine-structure constant emerges from the ratio of the $M1$ and $E1$ amplitudes, and the factor $\eta \sim 10^{-2}$ reflects the extent of geometric asymmetry of the molecules.

Further progress requires knowledge of the electron wave functions in chiral molecules.

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2. ELECTRON WAVE FUNCTIONS IN A CHIRAL MOLECULE

Let us consider an external electron moving in the field V of several fixed centers located at points $\mathbf{r}_a$:

$$V=\sum_{a=1}^{N} V_a(|\mathbf{r}-\mathbf{r}_a|). \tag{7}$$

For optical isomerism to occur, the molecules must have at least four centers: $N\geqslant 4$. If the characteristic charges Z of the nuclei of the atoms comprising the chiral group are moderate, $Z^2\alpha^2\ll 1$, the spin-orbit interaction

$$V_{s.o}(\mathbf{r})=-\frac{1}{4m^2}(\sigma\times\mathbf{p})\cdot\nabla V(\mathbf{r}) \tag{8}$$

can be considered a small perturbation. To lowest order in α this interaction can be ignored. It is convenient to assign the origin of coordinates to one of the centers,

$$V=U(r)+\sum_{a=1}^{N-1} V_a(|\mathbf{r}-\mathbf{r}_a|), \tag{9}$$

and use the set of eigenfunctions corresponding to the motion in the field $U(r)$. The distortion of spherical symmetry by the potentials V_a is taken into account perturbatively. To be specific we put $N=4$ and $V_a(|\mathbf{r}-\mathbf{r}_a|)=-\alpha Z_a^{\text{eff}}|\mathbf{r}-\mathbf{r}_a|^{-1}$.

It is clear from the start that there can be no degeneracy in the potential (9) and that the wave functions are real and have no definite parity. Let us first consider two energy levels E_{1s} and E_{2s} corresponding to different s-states with wave functions $s_1(r)$ and $s_2(r)$ in $U(r)$. Here and in what follows the angular-dependence normalization constant $(4\pi)^{-1/2}$ is discarded, with all integrations over angles in matrix elements interpreted as averages. The dipole part of the potential V,

$$\begin{aligned}V_{\text{dip}}&=-\sum_{a=1}^{3}\alpha Z_a^{\text{eff}}(n_a\cdot\mathbf{n})\left[\frac{r}{r_a^2}\theta(r_a-r)+\frac{r_a}{r^2}\theta(r-r_a)\right]\\&\equiv-\sum_{a=1}^{3}\alpha Z_a^{\text{eff}}(\mathbf{n}_a\cdot\mathbf{n})\kappa_a(r),\end{aligned} \tag{10}$$

leads to mixing of p-states into the initial s-states. For our purposes it is sufficient to consider the admixture of two p-waves with different radial dependences $p_1(r)$ and $p_2(r)$ to the lower level and one of them (the closest) to the upper:

$$\begin{aligned}\psi_{in}(\mathbf{r})&=s_1(r)+(\mathbf{A}\cdot\mathbf{n})p_1(r)+(\mathbf{B}\cdot\mathbf{n})p_2(r),\\ \psi_f(\mathbf{r})&=s_2(r)+(\mathbf{C}\cdot\mathbf{n})p_2(r).\end{aligned} \tag{11}$$

The three vectors $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ are determined by the molecule geometry. Using perturbation theory, we can write them as follows:

$$\begin{aligned}\mathbf{A}&=-\sum_{a=1}^{3}\mathbf{n}_a\left[\frac{\alpha Z_a}{E_{s1}-E_{p1}}\int_0^\infty s_1p_1r^2\kappa_a(r)dr\right],\\ \mathbf{B}&=-\sum_{a=1}^{3}\mathbf{n}_a\left[\frac{\alpha Z_a}{E_{s1}-E_{p2}}\int_0^\infty s_1p_2r^2\kappa_a(r)dr\right],\\ \mathbf{C}&=-\sum_{a=1}^{3}\mathbf{n}_a\left[\frac{\alpha Z_a}{E_{s2}-E_{p2}}\int_0^\infty s_2p_2r^2\kappa_a(r)dr\right].\end{aligned} \tag{12}$$

The calculation of the $E1$–$M1$ interference (12) in the transition between the wave functions is elementary:

$$\begin{aligned}&\operatorname{Im}\langle i|\mathbf{l}|f\rangle\langle f|\mathbf{r}|i\rangle\\ &\quad=-\frac{1}{9}\mathbf{A}\cdot(\mathbf{B}\times\mathbf{C})\int_0^\infty s_2p_2r^3dr\\ &\quad=-\frac{1}{9}\mathbf{n}_1\cdot(\mathbf{n}_2\times\mathbf{n}_3)\epsilon_{abc}\rho_a^A\rho_b^B\rho_c^C\int_0^\infty s_2p_2r^3dr.\end{aligned} \tag{13}$$

Here the ρ_a^A stand for the dimensionless quantities inside the square brackets in (12). As expected, the effect is proportional to $\mathbf{n}_1\cdot(\mathbf{n}_2\times\mathbf{n}_3)$ and vanishes if the molecule is flat. Note that the nontrivial dependence $\kappa_a(r)=\theta(r_a-r)r/r_a^2+\theta(r-r_a)r_a/r^2$ in the formula for the dipole part of the perturbation is mandatory for optical activity to manifest itself in the transition between the wave functions (11). Indeed, the fact that we employ V_{dip} in the form

$$V_{\text{dip}}=-\sum_{a=1}^{3}\alpha Z_a^{\text{eff}}\frac{\mathbf{r}_a\cdot\mathbf{r}}{r_a^2}\equiv\mathbf{r}\cdot\mathbf{D} \tag{14}$$

leads to a situation in which all three vectors $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ are parallel and $\mathbf{A}\cdot(\mathbf{B}\times\mathbf{C})=0$.

On the ordinary physical scale $Z^2\alpha^2\ll 1$ the above model of a chiral molecule closely resembles that developed in Refs. 9 and 10. The constructed wave functions prove useful in analyzing the high-frequency behavior of $\eta(\omega)$.

3. THE ASYMPTOTIC FORMS OF $\eta(\omega)$

When $\omega\gg\text{Ry}$, the final state of an electron lies deep within the continuous spectrum. The electron's energy $E_f=E_i+\omega=k^2/2m$ is close to ω. This imposes the following restriction on the photoelectron's velocity:

$$\frac{\alpha}{v}\ll 1. \tag{15}$$

This condition ensures the validity of the Born approximation, making it possible to consider the potential energy V in the final state a small perturbation. In the leading order this approximation yields the following asymptotic formula for $\sigma_+ + \sigma_-$ (see, e.g., Ref. 11):

$$\sigma_+ + \sigma_- \sim \alpha(m\alpha)^{-2}Z_{\text{eff}}^5(\text{Ry}/\omega)^{7/2}. \tag{16}$$

Here Z_{eff} depends on the subshell from which ionization proceeds.

Now the matrix elements of the $E1$ and $M1$ transitions are integrals of a rapidly oscillating (on the atomic scale $1/m\alpha$) function $\psi_f \sim e^{i\mathbf{k}\cdot\mathbf{r}}$, which implies that the leading contribution to the asymptotic behavior is provided by the lowest multipole components of the wave function ψ_{in}. The plane wave in the final state results in the orthogonality of the $E1$ and $M1$ transitions and, hence, the disappearance of optical activity. A finite effect emerges if we allow for the admixtures to the final-state wave function caused by the potential V_{dip} distorting the spherical symmetry. This means that at high frequencies the CD cross section proves to be suppressed, in comparison to the ordinary photoelectric cross section, by additional powers of the Born parameter $\alpha/v = \sqrt{\mathrm{Ry}/\omega}$. Since all the radial integrals build up at distances r of order $1/k$, the use of V_{dip} in the form (14) is justified.

Let us choose the initial-state wave function in the form (11). In calculating the $M1$ transition, the orbital angular momentum operator selects the p-wave admixtures with the same radial functions $p_1(r)$ and $p_2(r)$ in the final state. All the other admixtures to the final-state wave function yield only small corrections to the $E1$ transition and can be discarded. Bearing this in mind, we get

$$\psi_f=s_k(r)+\mathbf{D}\cdot\mathbf{r}\left[\frac{p_1(r)}{\omega+E_i-E_{1p}}\int_0^\infty p_1 s_k r^3 dr + \frac{p_2(r)}{\omega+E_i-E_{2p}}\int_0^\infty p_2 s_k r^3 dr\right]. \qquad (17)$$

Over distances r of order $1/m\alpha$ the wave function $s_k(r)$ closely resembles the s-wave free-motion radial function $\sin(kr)/r$. Then the calculation of the $E1$–$M1$ interference in the transition between the wave functions (11) and (17) poses no serious difficulties:

$$\begin{aligned}\mathrm{Im}\langle in|\mathbf{l}|f\rangle\langle f|\mathbf{r}|in\rangle &= \frac{1}{9}(\mathbf{A}\times\mathbf{B})\cdot\mathbf{D}\int_0^\infty p_2 s_k r^3 dr\int_0^\infty p_1 s_k r^3 dr \\ &\quad\times\left(\frac{1}{\omega+E_i-E_{2p}}-\frac{1}{\omega+E_i-E_{1p}}\right) \\ &\simeq \frac{1}{9}(\mathbf{A}\times\mathbf{B})\cdot\mathbf{D}\int_0^\infty p_2 s_k r^3 dr\int_0^\infty p_1 s_k r^3 dr\,\frac{E_{2p}-E_{1p}}{\omega^2}.\end{aligned} \qquad (18)$$

Allowing for the fact that $|\mathbf{D}|$ is of the order of $\alpha(m\alpha)^2$, we arrive at the following estimate for $\eta(\omega)$:

$$\eta(\omega)\sim\alpha\xi\,\frac{\alpha^2 m(E_{1p}-E_{2p})}{\omega^2}\,\frac{\int p_2 s_k r^3 dr\int p_1 s_k r^3 dr}{(\int s_1 p_k r^3 dr)^2}. \qquad (19)$$

Here $p_k(r)$ is a radial p-wave function whose asymptotic behavior coincides with that of the free-motion wave function. Generally, calculating the ratio of the radial integrals in (19) requires knowing the shape of $U(r)$ and the wave functions p_1, p_2, and s_1. In the limiting case of $\omega \gg Z^2\mathrm{Ry}$, the final-state wave functions can be assumed to be rapidly oscillating everywhere, even at very small distances $r \leqslant 1/Zm\alpha$. Then the ratio of radial integrals is determined by the behavior of the wave functions $p_1(r)$, $p_2(r)$, and $s_1(r)$ at zero argument and can be calculated completely:

$$\frac{\int p_2 s_k r^3 dr\int p_1 s_k r^3 dr}{(\int s_1 p_k r^3 dr)^2}=\frac{4p_1''(0)p_2''(0)}{9k^2[s_1'(0)]^2}\sim\frac{Z^2(m\alpha)^2}{k^2}\sim\frac{Z^2\mathrm{Ry}}{\omega}. \qquad (20)$$

Bearing this in mind, we arrive at the following estimate for the asymptotic behavior of the $E1$–$M1$ interference normalized to the square of the $E1$ amplitude:

$$\eta(\omega)\sim\alpha\xi\left(\frac{\mathrm{Ry}}{\omega}\right)^2\times\begin{cases}\mathrm{const}, & \mathrm{Ry}\ll\omega\leqslant Z^2\mathrm{Ry},\\ Z^2\mathrm{Ry}/\omega, & \omega\gg Z^2\mathrm{Ry}.\end{cases} \qquad (21)$$

Note that $(\sigma_+-\sigma_-)/(\sigma_++\sigma_-)$ for $\omega\gg Z^2\mathrm{Ry}$ is Z^2 times smaller than the respective expression in (21) since in this case the photon-spin independent cross section is determined by ionization of the inner electron shell and contains an additional factor Z^2.

4. CIRCULAR DICHROISM AND SPIN–ORBIT INTERACTION

The rapid decay of CD as the frequency increases suggests that a smoother behavior is caused by effects ignored in our analysis. Below we consider the contribution to the CD asymptotics originating in the electron spin.

In the zeroth order in the spin–orbit interaction the spin and coordinate parts of the wave functions are factorized for any state $|i,\sigma\rangle$ of an electron in a chiral molecule:

$$\psi_i(\mathbf{r};\sigma)=\psi_i(\mathbf{r})\chi, \qquad (22)$$

where χ is a bispinor. All levels in the discrete spectrum are two-fold degenerate. According to the Kramers theorem, this degeneracy remains even after spin–orbit interaction is allowed for in any perturbation order. The first order mixes the initial state $|in,\sigma\rangle$ with arbitrary intermediate states $|n,\sigma'\rangle$:

$$|in,\sigma\rangle+\sum_{n,\sigma'}{}'\,\frac{|n,\sigma'\rangle\langle n,\sigma'|V_{s.o}|in,\sigma\rangle}{E_{in}-E_n}. \qquad (23)$$

Summation over σ' is done via the completeness relation, after which we can use (8) to transform (23) to

$$\left(1-\sum_n{}'\,\frac{|n\rangle\langle n|[\mathbf{p}\nabla V(\mathbf{r})]\boldsymbol{\sigma}}{4m^2(E_{in}-E_n)}\right)|in\chi_{in}. \qquad (24)$$

Now we can write the contribution of the spin part of the $M1$ transition to the $E1$–$M1$ interference. Since $\boldsymbol{\sigma}$ performs transitions between initial states of type (22) only with the same spatial dependence,

$$\langle n,\sigma|\boldsymbol{\sigma}|k,\sigma'\rangle=\chi^{\dagger}\boldsymbol{\sigma}\chi'\delta_{nk}, \qquad (25)$$

when we calculate the electron-spin contribution to the optical activity of the transition the sum over intermediate states disappears to first order in the spin–orbit interaction:

$$\mathrm{Im}\left\langle in\left|\frac{V_{s.o}\boldsymbol{\sigma}}{E_i-E_f}+\frac{\boldsymbol{\sigma}V_{s.o}}{E_f-E_i}\right|f\right\rangle\langle f|\mathbf{r}|in\rangle$$

$$=\frac{1}{\omega}\,\mathrm{Im}\langle in|\boldsymbol{\sigma},V_{s.o}|f\rangle\langle f|\mathbf{r}|in\rangle$$

$$=\frac{1}{2m^2\omega}\,\epsilon_{ijk}\,\mathrm{Re}\langle in|\,L_j\sigma_k|f\rangle\langle f|r_i|in\rangle. \qquad (26)$$

Here we have introduced the notation $\mathbf{L}=\mathbf{p}\times\nabla V(\mathbf{r})$. Since the direction of the electron spin in a chiral molecule is not fixed, we must average over these directions after which (26) vanishes. Thus, it is not sufficient to allow for the spin–orbit interaction in first-order perturbation theory. This conclusion agrees with the fact that the spin–orbit interaction contributes to the high-frequency asymptotic behavior of the real part of the amplitude of optically active scattering only in second-order perturbation theory.[8]

Allowing for relativistic corrections to the optical activity of a transition in second-order perturbation theory requires careful consideration. There are several sources of such corrections. It can be shown, however, that considerable Z-buildup emerges only because of corrections related to additions to the electron wave function caused by the spin–orbit perturbation and is not contained in the contributions related to current modifications, the higher-order terms in the multipole expansion, etc.

Allowing for corrections to the wave function in second-order perturbation theory in conjunction with double counting of first-order corrections leads to the following expression for the electron-spin contribution to the optical activity of the transition:

$$\frac{\epsilon_{ikj}}{8m^4\omega}\,\mathrm{Re}\sum_n\left[\frac{\langle in|L_i|n\rangle\langle n|L_j|f\rangle\langle f|r_k|in\rangle\omega}{(E_{in}-E_n)(E_f-E_n)}+\frac{2\langle in|L_i|n\rangle\langle n|r_j|f\rangle\langle f|L_k|in\rangle}{E_{in}-E_n}+\frac{2\langle in|r_i|n\rangle\langle n|L_j|f\rangle\langle f|L_k|in\rangle}{E_f-E_n}\right]. \qquad (27)$$

Here averaging is performed over the initial-spin direction. At $\omega\sim\mathrm{Ry}$ the following appears to be a reasonable estimate of the magnitude of the effect:

$$\eta_{s.o}(\omega)\sim(Z\alpha)^4\alpha\xi. \qquad (28)$$

Considerable Z-buildup emerges because of the singular behavior of the operator

$$\mathbf{L}=\frac{1}{r}\frac{dU}{dr}\mathbf{l}+\sum_a\mathbf{p}\times\nabla V_a(r) \qquad (29)$$

at zero, that is, because of the first term in (29).

With the frequency of the incident light increasing, the expression (27) is nonzero even if no allowance is made for the effect on the final state of the distortion of the spherical symmetry of the potential. Here the main contribution to the sum over the intermediate states n is provided by the levels for which this potential is one hundred percent important. In other words, $E_{in}-E_k\sim\mathrm{Ry}$ and $E_f-E_k\sim\omega$. Then we can ignore the last term in (27), which results in

$$\frac{Z^2\alpha^2\epsilon_{ijk}}{8m^4\omega}\sum_n\frac{1}{E_{in}-E_n}\,\mathrm{Re}\left\langle in\left|\frac{l_i}{r^3}\right|n\right\rangle\times\left(\left\langle n\left|\frac{l_j}{r^3}\right|f\right\rangle\langle f|r_k|in\rangle-2\langle n|r_k|f\rangle\left\langle f\left|\frac{l_j}{r^3}\right|in\right\rangle\right). \qquad (30)$$

We limit our discussion to an estimate of this expression in the frequency range $\mathrm{Ry}\ll\omega\ll Z^2\,\mathrm{Ry}$. Here the matrix elements of the spin–orbit interaction build up at small distances of order $(Z\alpha m)^{-1}$, are independent of the photoelectron velocity, and in order of magnitude are given by the following expression:

$$\langle V_{s.o}\rangle\sim Z^2\alpha^2\,\mathrm{Ry}. \qquad (31)$$

Thus, estimating the high-frequency behavior of (30) normalized to the square of the $E1$ amplitude, we get

$$\eta_{s.o}(\omega)\sim\frac{(Z^2\alpha^2\,\mathrm{Ry})^2}{\omega m\,\mathrm{Ry}\langle r\rangle}\,\xi\sim\frac{(Z\alpha)^4\mathrm{Ry}}{\omega}\frac{k}{m}\,\xi\sim\alpha\xi(Z\alpha)^4\sqrt{\frac{\mathrm{Ry}}{\omega}}. \qquad (32)$$

5. PHOTOELECTRON POLARIZATION

The intramolecular spin–orbit interaction results in a new interesting effect related to photoelectron polarization.

Let us consider ionization of chiral molecules by unpolarized light. The probabilities of finding an electron in the final state with its spin directed along or counter to the direction of light propagation prove to differ. Such effects associated with the passage of electrons through optically active media were discussed earlier in Ref. 12.

The density matrix of the final electrons polarized along $\mathbf{n}$ has the form

$$\rho_f=\tfrac{1}{2}(1+\boldsymbol{\sigma}\cdot\mathbf{n}). \qquad (33)$$

The effect under discussion is characterized by the quantity

$$\zeta=\frac{W(\mathbf{n})-W(-\mathbf{n})}{W(\mathbf{n})+W(-\mathbf{n})}. \qquad (34)$$

Here $W(\mathbf{n})$ is the probability of finding the photoelectron spin directed along $\mathbf{n}$.

The probabilities in (34) are proportional to the square of sum (5) averaged over the polarization of the absorbed photon and the random position of the molecule, with allowance made for the density matrix ρ_f:

$$W(\mathbf{n})-W(-\mathbf{n})\sim i\epsilon_{ijl}\,\mathrm{Im}\langle in|\mu_i|f\rangle\sigma_j\langle f|d_k|in\rangle. \qquad (35)$$

Here the σ-matrix arose from ρ_f. For ζ to be finite we must allow for the effect of spin–orbit interaction on the electron state in the chiral molecule. Now the first-order perturbation theory (24) proves sufficient. The final formula for the asymmetry of polarization is

$$\zeta=\frac{2\,\mathrm{Im}\langle in|\mathbf{r}|f\rangle\langle f|\mathbf{L}|in\rangle}{m^3\omega\langle in|\mathbf{r}|f\rangle\langle f|\mathbf{r}|in\rangle}+\epsilon_{ijk}\sum_n\left[\frac{\langle in|L_i|n\rangle\langle n|r_j|f\rangle\langle f|l_k|in\rangle+\langle in|L_i|n\rangle\langle n|l_k|f\rangle\langle f|r_j|in\rangle}{2(E_{in}-E_n)m^3\omega\langle in|\mathbf{r}|f\rangle\langle f|\mathbf{r}|in\rangle}\right.$$

$$\left.-\epsilon_{ijk}\sum_n\frac{\langle in|r_i|n\rangle\langle n|L_j|f\rangle\langle f|l_k|in\rangle+\langle in|r_i|f\rangle\langle f|L_j|n\rangle\langle n|l_k|in\rangle}{2(E_f-E_n)m^3\omega\langle in|\mathbf{r}|f\rangle\langle f|\mathbf{r}|in\rangle}\right]. \qquad (36)$$

In the frequency range $\omega\sim\mathrm{Ry}$, where the photoelectron velocity is of the order of α, the ratio ζ is given in order of magnitude by the following expression:

$$\zeta\sim\alpha\xi(Z\alpha)^2. \qquad (37)$$

This result is smaller by α than the estimate made in Ref. 12 of the helicity acquired by slow electrons ($v\sim\alpha$) in their passage through a medium of molecules of definite chirality.

6. DISCUSSION AND CONCLUSIONS

In this paper we arrived at (21) because we used a model of chiral molecules in which the potential distorting the spherical symmetry was taken into account by perturbation techniques. It is clear, however, that qualitatively the result will be the same if we step outside the scope of this approximation. Indeed, the condition for perturbation theory to be applicable in deriving the wave functions (11) is only that $|\mathbf{A}|$, $|\mathbf{B}|$, and $|\mathbf{C}|$ be much less than unity. Nowhere in our further discussion have we employed this fact.

Let us now discuss the contributions to the asymptotic behavior provided by the multipole components of the wave functions of higher order than the *s*- and *p*-components, which were ignored in (11). For $\omega\gg Z^2$ Ry the asymptotic form is determined by the behavior of the wave functions at zero, with the result that the contributions are suppressed in comparison to the *s–p* effect owing to the additional powers of Ry/ω. In the frequency range $\mathrm{Ry}\ll\omega\ll Z^2$ Ry, the higher-order multipole components of the wave function can, apparently, provide contributions to the CD that are similar in their frequency behavior. In our discussion we ignore these contributions because they possess a different and more complicated geometric structure than $\mathbf{n}_1\cdot(\mathbf{n}_2\times\mathbf{n}_3)$ and *a priori* have a smaller geometric factor ξ.

For organic molecules the characteristic charges Z of the nuclei of atoms comprising a chiral group lie in range 6–8. Hence, the frequency at which $\eta(\omega)$ begins to behave like ω^{-3} is below the limit of applicability of the multipole expansion used to obtain (21). Here the spin–orbit contributions to CD are negligible. These effects may prove important and lead to a smoother frequency behavior in chiral compounds containing elements with higher values of Z. Comparison of (21) and (32) shows that the spin contribution to CD becomes important when $\omega\geqslant(Z\alpha)^{-8/3}$ Ry. This frequency satisfies the condition $\omega\leqslant m\alpha$ for $Z>22$. In exotic compounds with very heavy elements in the chiral group the spin–orbit interaction cannot be considered small in comparison to the effect of the surrounding atoms. In this situation it is clear that separating the contribution to the asymptotic behavior of CD into the spin contribution and the "ordinary" is clearly unjustified.

The effect of the emission electrons acquiring polarizations parallel or antiparallel to the direction in which the incident light propagates is interesting because it can serve as the measure of spin–momentum correlations inside chiral molecules. Here the spin–orbit interaction is present in first-order perturbation theory, which gives some hope that the asymmetry of polarization will be discovered in experiments. For compounds containing heavy atoms the effect being discussed can amount to one part in a hundred from the extent of the geometric asymmetry of a molecule.

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