60

ИНСТИТУТ ЯДЕРНОЙ ФИЗИКИ
им. Г.И. Будкера СО РАН

I.B. Khriplovich and M.E. Pospelov

HIGH-FREQUENCY ASYMPTOTICS OF OPTICAL ACTIVITY AND ENERGY DIFFERENCE OF CHIRAL MOLECULES

BUDKERINP 92-73

НОВОСИБИРСК

High-Frequency Asymptotics of Optical Activity and Energy Difference of Chiral Molecules

I.B. Khriplovich and M.E. Pospelov
Budker Institute of Nuclear Physics,
630090 Novosibirsk, Russia

Abstract

The asymptotics of optical activity $n_+ - n_-$ at $\omega \gg Ry$ is ω^{-5} for oriented chiral molecules and crystals, and ω^{-7} for isotropic media of chiral molecules and policrystals. However, with further increase of ω both fall-offs change to ω^{-3} due to spin-orbit interaction. The expectation value in the numerator of the last asymptotics practically coincides, up to an overall factor, with that of the weak interaction responsible for the P-odd energy difference of right- and left-handed molecules.

1 Introduction

Optical isomers are molecules or crystals that are mirror images of one another. An isotropic medium acquires optical activity (OA) when the concentration of an optical isomer of one sign exceeds in it that of an isomer of the opposite sign. We will investigate the asymptotics of OA, i.e., of the rotation of polarization plane of light, at the frequencies $\omega \gg Ry$ where $Ry = m\alpha^2/2 = 13.6\,eV$ is the characteristic atomic energy.

The refraction index $n(\omega)$ is related to the forward-scattering amplitude $f(\omega)$ through the well-known formula:

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

where N/V is the concentration. The usual asymptotics of the refraction index is determined by the Thomson amplitude $f = -\alpha/m$. Optical activity is caused by the term in $f(\omega)$ linear in the degree of circular polarization

$$\lambda = -i([\vec{e}^{\,*}\vec{e}]\vec{n}) \longrightarrow i\epsilon_{ab}e_a e_b^*. \tag{2}$$

Here $\vec{e}$ is the photon polarization, $\vec{n}$ is the unit vector of its momentum. The last form of this equation corresponds to the choice of the direction $\vec{n}$ along the axis 3. Then $a, b = 1, 2$; $\epsilon_{ab} = -\epsilon_{ba}$; $\epsilon_{12} = 1$.

Substituting the photon density matrix for the product of its polarizations:

$$e_a e_b^* \rightarrow \rho_{ab} = \frac{1}{2}(\delta_{ab} - i\lambda\epsilon_{ab}), \tag{3}$$

one gets easily the λ-dependent scattering amplitude:

$$f_\lambda(\omega) = \frac{\lambda\alpha}{2m^2}i\epsilon_{ab}\sum_k\left[\frac{\langle 1|p_b e^{-i\omega z}|k\rangle\langle k|p_a e^{i\omega z}|1\rangle}{\omega - \omega_{k1}} - \frac{\langle 1|p_a e^{i\omega z}|k\rangle\langle k|p_b e^{-i\omega z}|1\rangle}{\omega + \omega_{k1}}\right]. \tag{4}$$

Here $p_{a,b}$ are the electron momentum operator components, and ω_{k1} is the frequency of the transition from the initial state 1 to the intermediate one k. Obviously, the amplitude f_λ is an odd function of frequency.

At the frequencies $\omega \ll m\alpha$ one can use the multipole expansion for the transition operators restricting to the lowest multipolarities. Since the electron states in a chiral molecule or crystal do not have definite parity, $M1$ and $E2$ matrix elements differ from zero simultaneously with $E1$. OA originates from the interference of the opposite parity amplitudes, $E1$ with $M1$ and $E2$. Let us emphasize that in the anisotropic case $E1$ and $E2$ amplitudes do interfere in the forward scattering.

In the limit of small frequencies OA is due to the interference of $E1$ and $M1$ amplitudes and being an odd function of ω can be easily shown to vanish [1], the last fact known already by Boltzmann [2].

At the frequencies $\omega \sim Ry$ the relative magnitude of the OA constitutes $f_\lambda/f \sim \alpha\xi$. The fine structure constant α originates from the ratio of $M1$ (or $E2$) to $E1$ amplitudes. The factor $\xi \sim 10^{-2}$ reflects the degree of the molecule geometrical asymmetry.

2 First asymptotic region

To find the high-frequency behaviour of OA we neither use the multipole expansion, nor make any assumption about the magnitude of ωz. So, our consideration is not restricted to $\omega \ll m\alpha$, but applies to the whole region $\omega \ll m$.

We expand expression (4) in ω_{k1}/ω, substitute commutators with the Hamiltonian for powers of ω_{k1}, and perform the summations over intermediate states by means of the completeness relation.

The zeroth-order term in ω_{k1} in this expansion vanishes trivially since $p_{a,b}$ commute with $e^{\pm i\omega z}$. The numerator of the next term in ω_{k1} reduces to

$$-\,i\epsilon_{ab}\langle[[H,p_b e^{-i\omega z}],p_a e^{i\omega z}]\rangle = i\epsilon_{ab}\langle\nabla_a\nabla_b U\rangle, \tag{5}$$

where H and U are the Hamiltonian and potential energy respectively, and vanishes as well.

The numerator of the second-order term in ω_{k1} transforms to

$$i\epsilon_{ab}\langle[[H,p_b e^{-i\omega z}],[H,p_a e^{i\omega z}]]\rangle = -2\frac{\omega^2}{m}\epsilon_{ab}\langle p_a\nabla_b U(\vec r)\rangle. \tag{6}$$

Together with ω^{-3} from the formal expansion, it leads to the contribution $\sim \omega^{-1}$ to f_λ nonvanishing even for a spherically symmetric potential and leading

to the correlation $\lambda(\vec n\vec l)$. It corresponds in fact to the Faraday rotation in the magnetic field created by the electron orbital angular momentum $\vec l$. Being unrelated to the molecule handedness, such contributions will be omitted in our treatment.

The next orders of the expansion in ω_{k1}/ω also do not lead to the asymptotics ω^{-1} in f_λ (or ω^{-3} in $n_+ - n_-$) due to the molecule handedness (up to negligible relativistic corrections). Curiously enough, such an asymptotics arises at the multipole expansion in the anisotropic case for the contribution originating from the interference between $E1$ and $M1$ amplitudes. It can be easily checked however that this term in the multipole expansion is exactly cancelled by the corresponding contribution from the $E1-E2$ interference.

The first nonvanishing contribution to the asymptotics of f_λ arises to the third order in ω_{k1}:

$$f_\lambda = -\frac{\lambda\alpha}{2m^3\omega^3}\epsilon_{ab}\langle\nabla_a U\nabla_b\nabla_z U\rangle. \tag{7}$$

The corresponding asymptotics of OA, $n_+ - n_-$, is evidently ω^{-5}. To estimate the magnitude of the effect let us note first of all that amplitude (7) does not vanish only if ∇_a and ∇_b are applied to potentials created by different centers. The strongest Z-dependence originates from $\nabla_b\nabla_z U(\vec r) = -Z\alpha(3r_b z/r^5)$. The expectation value of this operator is finite since the contribution of the s-wave components of both bra and ket states vanishes. On the other hand, this interaction is singular enough to consider the nuclear charge Z as unscreened. The wave function squared of the valence electron increases at small distances as Z (see, e.g., Ref. [3], pp. 20, 45). As long as small distances from the Coulomb center discussed dominate, the gradient applied to the potential created by other centers, $\nabla_a U$, reduces to a constant vector. Thus, the OA of oriented media falls off asymptotically as ω^{-5} according to the following relation:

$$n_+ - n_- \sim \frac{N}{V}\frac{2\pi\alpha}{m\omega^2}Z^2\alpha\xi\left(\frac{Ry}{\omega}\right)^3. \tag{8}$$

The factor $(N/V)(2\pi\alpha/m\omega^2)$, singled out in formula (8), corresponds to the Thomson asymptotics of $n-1$.

Let us average now expression (7) over the scatterer orientations. This is equivalent obviously to the averaging over the directions $\vec n$ of the photon momentum. The last procedure is performed easily after rewriting those expressions in invariant way via the substitutions: $\epsilon_{ab}\nabla_a...\nabla_b \to \epsilon_{ijk}\nabla_i...\nabla_j n_k$,

$\nabla_z \to (\vec{n}\vec{\nabla})$. The averaging leads evidently to vanishing of the effect to this approximation. So, the asymptotics obtained refers to the case of oriented molecules and crystals only.

To obtain the OA asymptotics for isotropic media we have to proceed with the expansion in ω_{k1} up to the fifth order. The calculations are quite straightforward, but tedious. They can be simplified by neglecting systematically all the terms that will vanish anyway at the averaging over $\vec{n}$. The result arising is (in invariant form already)

$$f_\lambda = -\frac{\lambda\alpha}{2m^5\omega^5}\epsilon_{kmn}\langle p_k \nabla_i \nabla_m U \{p_j, \nabla_i \nabla_j \nabla_n U\}\rangle \tag{9}$$

where $\{..., ...\}$ means anticommutator. As above, $\nabla_i\nabla_m U$ and $\nabla_i\nabla_j\nabla_n U$ refer to different centers. Again the strongest Z-dependence originates from the more singular expression $\nabla_i\nabla_j\nabla_n U$, and $\nabla_i\nabla_m U$ can be approximated by a constant symmetric tensor. The expectation value left after separating that tensor can be transformed as follows:

$$\epsilon_{kmn}\langle\{p_j, \nabla_i\nabla_j\nabla_n U p_k\}\rangle = 2im\left\langle\left[\frac{p^2}{2m}, \nabla_i \frac{1}{r}U'(r) l_m\right]\right\rangle \tag{10}$$

$$= -2im\left\langle\left[V(\vec{r}), \nabla_i \frac{1}{r}U'(r) l_m\right]\right\rangle.$$

We have used here the fact that the expectation value of a commutator with the total Hamiltonian vanishes identically. In the last commutator $V(\vec{r})$ is the sum of potentials $V_\alpha(|\vec{r}-\vec{r}_\alpha|)$ created by the centers different from that with the nucleus charge Z and potential $U(r)$ we are interested in at the moment. Anyway $U(r)$ commutes with its own derivatives and orbital angular momentum l_m with respect to the point $r = 0$. It follows in particular from formula (11) that the s-wave component of the electron state does not contribute to the effect. The last commutator equals

$$[V(\vec{r}), l_m] = i\epsilon_{kmn} r_n \sum_\alpha \nabla_k V_\alpha(|\vec{r}-\vec{r}_\alpha|) \tag{11}$$

With our accuracy the sum in this expression reduces at $r \to 0$ again to a constant vector. In the expectation value left $\langle r_n \nabla_i (U'(r)/r)\rangle$ the purely s-wave contribution can be neglected and we come finally to the same Z^2-dependence of the effect as in the oriented case. So, the OA of isotropic media falls off asymptotically as ω^{-7} according to the relation:

$$n_+ - n_- \sim \frac{N}{V}\frac{2\pi\alpha}{m\omega^2} Z^2\alpha\xi\left(\frac{Ry}{\omega}\right)^5. \tag{12}$$

The singled out relative magnitude of the effect is $Z^2\alpha\xi(Ry/\omega)^5$.

It can be shown along the same lines that both asymptotics, ω^{-5} and ω^{-7}, for oriented and nonoriented media, respectively, change neither by going beyond the one-electron approximation, nor by relativistic corrections to the dispersion law and to electron-electron interaction. In the next section they will be shown however to change by including the spin-orbit interaction and spin current.

After having derived the asymptotics ω^{-7} for the optical activity of isotropic media, we came across Ref. [4] where the sum rules for the $E1 - M1$ interference in the multipole expansion were obtained leading in fact to the same result, but restricted to the lowest multipole contribution.

The OA asymptotics was also discussed without multipole expansion in Ref. [5]. However, the conclusion $n_+ - n_- \sim \omega^{-3}$ made in that paper is obviously a result of the wrong relative sign of the two terms in the expression analogous to ours (4) for the scattering amplitude.

In the conclusion of this section let us note that the OA asymptotics ω^{-7} refers not only to a gas or solution of chiral molecules, but to optically active policrystals as well.

3 Optical activity and spin-orbit interaction

Let us consider now the influence of the intramolecular spin-orbit interaction on OA. The general expression for this interaction

$$V(\vec{r}) = -\frac{1}{4m^2}([\vec{\sigma}\vec{p}]\nabla U(\vec{r})) \tag{13}$$

does not depend on whether the charge distribution creating the Coulomb potential $U(\vec{r})$ is spherically-symmetric (as in an atom) or not. The current operator is modified now both by this interaction directly, and by including the spin current. So, besides adding V to H in the commutators, we have to make the following substitution in formula (4):

$$p_a e^{\pm i\omega z} \to P_a e^{\pm i\omega z} = (p_a + \frac{1}{4m}w_a \pm \frac{i\omega}{2}\epsilon_{ac}\sigma_c)e^{\pm i\omega z}. \tag{14}$$

where $\vec{w} = \vec{\sigma} \times \vec{\nabla} U$.

We proceed again with the expansion of the scattering amplitude in ω_{k1}. The term of the zeroth order in ω_{k1} produces the correlations of the type $\lambda(\vec{\sigma}\vec{n})$ only, nonvanishing even in a spherically-symmetric case and therefore of no interest for our problem. The first-order contribution is

$$f_\lambda = \frac{\lambda\alpha}{2m^2\omega^2}(-i)\epsilon_{ab}\langle[[H+V, P_b e^{-i\omega z}], P_a e^{i\omega z}]\rangle. \tag{15}$$

The term in this expression quadratic in the spin-orbit interaction induces only a correction $\sim \omega^2/m^2$ to the amplitude (7) which can be neglected in the region $\omega \ll m$ we are interested in. The linear contributions transform to

$$f_\lambda^1 = \frac{\lambda\alpha}{2m^3\omega}\frac{1}{2m}\langle\epsilon_{ab}(\{p_a, \nabla_b w_z\} - \{p_z, \nabla_a w_b\} - \{p_a, \nabla_z w_b\}) \tag{16}$$
$$-\frac{1}{2}\{\vec{p}, \vec{\sigma}\nabla_a\nabla_a U\} + \frac{1}{2}\{p_a, \vec{\sigma}\vec{\nabla}\nabla_a U\}\rangle.$$

The first term in $\langle ... \rangle$ is induced by V directly, the second and third are due to the spin-orbit contributions $w_{a,b}$ to $P_{a,b}$, the last two contributions originate from the spin currents.

Now, however, due to the ω-dependence of the spin currents we have to proceed further with the expansion in ω_{k1}. The second-order terms of the expansion result in contributions to the amplitude of too high order in α which should be neglected. So, let us consider the third order, $\sim \omega_{k1}^3$. The only contribution of interest originates here from retaining the spin current in one of the operators and the usual $p_{a,b}$ in another. So, the resulting effective operator in the amplitude

$$f_\lambda^3 = -\frac{\lambda\alpha}{2m^3\omega}\frac{1}{2m}\langle\{p_a, \sigma_a\nabla_z^2 U\} + 3\{p_z, \sigma_a\nabla_a\nabla_z U\}\rangle. \tag{17}$$

by itself is not related to the spin-orbit interaction.

The spin-dependent amplitude $f_\lambda^1 + f_\lambda^3$ could be expected to increase with the nucleus charge as Z^3. An extra Z as compared to the spin-independent amplitude (7) arises since here in the expectation values there is an extra momentum which increases as Z near unscreened nucleus. However, the expectation values in expressions (16) and (17) depend on the electron spin and do not vanish only if the spin-orbit interaction is taken into account in the electron state as well. Its relative magnitude is $Z^2\alpha^2$ [6]. Since the operators themselves in (16) and (17) are of the relativistic origin, the discussed OA

asymptotics, although falls off more slowly than (8), but is suppressed as compared to it by the factor $Z^3\alpha^4$:

$$n_+ - n_- \sim \frac{N}{V}\frac{2\pi\alpha}{m\omega^2}Z^5\alpha^5\xi\frac{Ry}{\omega}. \tag{18}$$

Therefore, the OA asymptotics for oriented molecules and crystals switches from ω^{-5} to ω^{-3} at $\omega \sim mZ^{-3/2}$. For organic substances where Z is not large these frequencies are very high.

Let us go over now to isotropic media. Averaging $f_\lambda^1 + f_\lambda^3$ over the orientations we get the following expression for the scattering amplitude:

$$f_\lambda = -\frac{7\lambda\alpha}{60m^3\omega}\frac{1}{2m}\langle\{\vec{\sigma}\vec{p}, \Delta U\} - \{p_i, \sigma_j\nabla_i\nabla_j U\}\rangle. \tag{19}$$

In fact, the second operator in the expectation value does not work and can be omitted. Indeed, as it was mentioned above, for the spin-dependent matrix element not to vanish, the electron state itself should be perturbed by the spin-orbit interaction. Due to the identity

$$\{p_i, \sigma_j\nabla_i\nabla_j U\} = 2im[H, \sigma_j\nabla_j U] \tag{20}$$

the expectation value of that operator, to the first order in the spin-orbit interaction, transforms as follows:

$$2im\sum_n \frac{\langle 1|[H, \vec{\sigma}\vec{\nabla}U]|n\rangle\langle n|V|1\rangle + \langle 1|V|n\rangle\langle n|[H, \vec{\sigma}\vec{\nabla}U]|1\rangle}{E_1 - E_n} \tag{21}$$
$$= 2im\langle 1|[\vec{\sigma}\vec{\nabla}U, \frac{1}{4m^2}[\vec{p}\times\vec{\sigma}]\vec{\nabla}U]|1\rangle.$$

With our accuracy we have now to average the last expression over the spins, i.e., to make the substitution $\sigma_i\sigma_j \to \delta_{ij}$. After it the commutator obtained vanishes.

Finally, the amplitude of interest simplifies to

$$f_\lambda = -\frac{7\lambda\alpha}{60m^3\omega}\frac{1}{2m}\langle\{\vec{\sigma}\vec{p}, \Delta U\}\rangle. \tag{22}$$

In this case the same estimate (18) holds evidently for the OA. However, due to the different ω-dependence of (12) as compared to (8), the asymptotics changes here at much lower frequencies

$$\omega \sim m\alpha Z^{-3/4}. \tag{23}$$

4 Discussion

Even the first asymptotics ω^{-5} and especially ω^{-7} seem to be amusing enough to become objects of experimental investigation. However, the most interesting problem would be to observe the change of the asymptotics to ω^{-3} due to the spin-orbit interaction and spin current. Unfortunately, for usual organic compounds with $Z \sim 6-8$ this transition even for isotropic media occurs at high photon energies $\sim 1KeV$. The optical path cannot exceed essentially the absorption length which is extremely small here. The observation of the resulting optical rotation angles $\psi \sim 10^{-11}$ is far from being realistic at such photon energies. However, if the compound contains a heavy atom, the critical photon energy can fall down to $\sim 100\,eV$. Here the strong Z-dependence of the OA, Z^5, is not accompanied by as strong Z-dependence of the absorption, and the rotation angles can reach 10^{-8}. It should be noted however that all those estimates are of very crude nature. In particular, the onset of the ω^{-3} asymptotics may well occur earlier, which would lead to better prospects for the observation of the effect. These problems can be reliably cleared up by experiment only.

But what will we learn from all those experiments? Let us note first that nonvanishing expectation value of the operator $\{\vec{\sigma}\vec{p}, \Delta U\}$ leading to the OA of isotropic media, means evidently that the electron in a chiral molecule has nonvanishing helicity, i.e., its spin and momentum are correlated. It would be certainly interesting to observe experimentally this correlation predicted in Refs. [7], [8].

However, the most interesting is perhaps the fact that the OA of isotropic media is directly related to the intriguing problem of the energy difference of right- and left-handed molecules due to parity nonconservation in weak interactions (see, e.g. Ref. [3]). Indeed, with good accuracy, especially for high Z, one can substitute $4\pi Z\alpha\delta(\vec{r})$ for $\Delta U(r)$ in the effective operator $\{\vec{\sigma}\vec{p}, \Delta U\}$. But after it this operator coincides up to an overall factor with that of the P-odd weak interaction. Therefore, the measurement of OA in the region $\omega > m\alpha Z^{-3/4}$ may constitute an essential preliminary stage of an experiment aimed at the discovery of the mentioned P-odd energy difference. In the case of the success of such an experiment the knowledge of the OA would allow one to extract from it a reliable quantitative information on the weak interactions. At least, the OA measurement would be a reliable test of the accuracy of the theoretical calculations of P-odd effects in chiral molecules.

One should have in mind however that for high Z, in particular at $Z \sim 80$, the spin-orbit interaction cannot be treated as a perturbation anymore, and the ω^{-3} asymptotics of the OA should be calculated within the relativistic approach. This problem deserves special consideration.

We are extremely grateful to R. Conti and D. Gidley for the interest to this work and useful discussions, and to J. Babb for attracting our attention to Refs.[4],[5]. We highly appreciate the warm hospitality extended to us at the Randall Laboratory of Physics, University of Michigan where part of the work has been done.

References

[1] L.D. Landau and E.M. Lifshitz, Electrodynamics of continuous media (Nauka, Moscow, 1982).

[2] L. Boltzmann, Ann.Phys.Chem. (Pogg.Ann., Jubelband) 153 (1874) 128.

[3] I.B. Khriplovich, Parity nonconservation in atomic phenomena (Gordon and Breach, London, 1991).

[4] A. Hansen, Mol.Phys. 33 (1977) 483.

[5] R.A. Harris, Chem.Phys.Lett. 45 (1977) 477.

[6] L.D. Landau and E.M. Lifshitz, Quantum mechanics (Nauka, Moscow, 1974).

[7] A. Garay and P. Hrasko, J.Mol.Evolut. 6 (1975) 77.

[8] R. Hegstrom, Nature 297 (1982) 643.

I.B. Khriplovich and M.E. Pospelov

High-Frequency Asymptotics of Optical Activity and Energy Difference of Chiral Molecules

И.Б. Хриплович, М.Э. Поспелов

Высокочастотная асимптотика оптической активности и разность энергий каральных молекул

BUDKERINP 92-73

Ответственный за выпуск С.Г. Попов

Работа поступила 5 августа 1992 г.
Подписано в печать 18.09.1992 г.
Формат бумаги 60×90 1/16 Объем 0,8 печ.л., 0,7 уч.-изд.л.
Тираж 150 экз. Бесплатно. Заказ N 73

Обработано на IBM PC и отпечатано на
ротапринте ИЯФ им. Г.И. Будкера СО РАН,
Новосибирск, 630090, пр. академика Лаврентьева, 11.