On the energy difference between optical isomers resulting from parity nonconservation

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(Submitted 19 February 1980)
Zh Eksp. Teor. Fiz. 79, 354–360 (August 1980)

A model that demonstrates the appearance of an energy difference between optical isomers as a result of parity nonconservation in the weak interaction of electrons with the nucleus is examined, and the splitting of Mössbauer lines in optically isomeric crystals is discussed.

PACS numbers: 11.30.Er, 12.30. – s, 35.20.Jv, 76.80. + y

1. The discovery of the weak interaction between electrons and nucleons resulting from the neutral currents, which was made at Novosibirsk[1] by observing the optical activity of atomic bismuth vapors, is doubtless only the first positive result to come from the use of the methods of atomic and molecular spectroscopy to investigate the structure of the weak interactions. Research in this direction, both theoretical and experimental, is now being actively pursued by many groups of investigators. One of the most beautiful manifestations of the weak interactions in atomic and molecular physics is the difference between the energies of optical isomers resulting from the violation of space parity. This effect of the neutral currents, which has not yet been observed experimentally, was predicted in Refs. 2–4.[1)]

This phenomenon is so surprising and extraordinary that doubts were being expressed until quite recently as to whether it could occur at all. In this paper a comparatively simple model of the effect, which will make it possible clearly to trace its origin, will be examined. The splitting of Mössbauer lines in crystals that are mirror images of each other will also be discussed.

2. Let us begin with simple estimates of the magnitude of the expected effect. The origin of the effect becomes quite evident when we note that the weak interaction of the electron with the nucleus, which does not conserve parity, leads to the appearance of a helical structure in the orientation of the spin of the atomic electron.[6,7] It is entirely natural that the energy of the molecule should depend on whether the coordinate structure of the molecule has the same handedness as the spin structure, or the opposite one. It can be said that the helical spin structure serves as a peculiar asymmetric probe with the aid of which one can distinguish between right- and left-hand molecules. It is clear from this picture that, among other things, the splitting of the levels must be due to the interaction between the spin and coordinate degrees of freedom, i.e., to the spin-orbit coupling. This fact was first revealed, on the basis of somewhat different considerations, in the work of Gaizago and Marx.[3] However, as will be shown below on the basis of a relatively simple example, the fact that the phenomenon under discussion is related to the spin-orbit interaction does not lead to any additional decrease in the magnitude of the effect in the case of heavy molecules.

The magnitude of the splitting is determined by the matrix element for the parity-violating weak interaction of the electron with the nucleus. This matrix element differs from zero only when it is taken between $s_{1/2}$ and $p_{1/2}$ states; in that case it is given in order of magnitude by the formula[8,9]

$$\delta E \sim \frac{Gm^2\alpha^2 Z^3 R}{\pi}\frac{m\alpha^2}{2}. \tag{1}$$

Here $G=10^{-5}/m_p^2$ is the Fermi weak-interaction constant, m_p and m are the proton and electron masses, $\alpha=1/137$ is the fine structure constant, Z is the nuclear charge, and R is an enhancement factor, which is due to relativistic effects and increases rapidly with increasing Z, reaching values of ~10 at $Z \sim 80$. The factor R is given by the formula

$$R=4(2Z\alpha m r_0)^{2\gamma-2}/\Gamma^2(2\gamma+1)$$

in which r_0 is the nuclear radius and $\gamma=(1-Z^2\alpha^2)^{1/2}$ (we are using units in which $\hbar=c=1$). However, one would naturally expect the relative distortion of the wave function due to the asymmetry of the surroundings to be appreciably smaller than unity. On the whole, the true splitting should evidently be one or two orders of magnitude smaller than the above estimate (1). Taking this into account, we find that δE might reach values of 10^4–10^5 Hz for the case of molecules containing heavy atoms with $Z \sim 80$.

In light molecules the dependence of the effect on the spin-orbit coupling leads to an additional reduction in the magnitude of the effect by an amount equal to the ratio of the characteristic fine structure splitting to the atomic energy—the Rydberg—which, as is well known (see, e.g., Ref. 10, § 72) is equal in order of magnitude to $Z^2\alpha^2$. The following estimate given in Refs. 11 and 12 is for this case:

$$\delta E \sim \frac{Gm^2\alpha^4 Z^5 R}{\pi}\frac{m\alpha^2}{2}. \tag{2}$$

However, the true magnitude of the splitting must again be considerably reduced. According to numerical calculations,[13] this reduction amounts to three or four orders of magnitude.

The electron-energy splitting δE leads to a difference between the vibrational potential energies of optical isomers, and consequently to a splitting of the vibrational frequencies[4] by the relative amount

$$\delta\omega/\omega \sim \delta E/m\alpha^2. \tag{3}$$

0038-5646/80/080177-04$02.40

This ratio amounts to $\sim 10^{-10}$ for $Z \sim 80$. This deformation of the potential energy alters the equilibrium states and moments of inertia, thereby splitting the rotational frequencies[4] by the same relative amount $\delta E/m\alpha^2$.

The possibility of detecting the effect experimentally in the CHFClBr molecule is discussed in Ref. 5. An experimental search for splitting of the $\lambda \approx 9500$ nm line due to a transition between ground-state vibrational levels in the optical isomers of camphor, which has now been completed, led to an upper bound of 300 kHz on the magnitude of the effect.[14] Since the heaviest atom in the camphor molecule is oxygen, for which $Z = 8$, it follows from the estimates given above that this upper bound is some ten orders of magnitude higher than the expected magnitude of the effect.

3. Now let us explain a specific model for the splitting of the levels of optical isomers as a result of the parity-violating weak interaction. Suppose a heavy atom is surrounded by three other atoms that differ both from it and from one another. It is not difficult to see that the simplest structure that could have optical isomers would be a molecule consisting of four atoms that do not lie in the same plane. Suppose, further, that the outer electron of the heavy atom has the angular momentum $j \geqslant 3/2$, and let us take account of its interaction with one of the neighboring atoms, which we shall call atom 3, by assuming that the levels having different projections μ of the angular momentum onto the axis passing through the heavy atom and atom 3 are not degenerate. The field of atom 3 splits the levels of the heavy atom in this manner—e.g., on account of the tensor polarizability of the latter (see Ref. 10, §76); levels having the same value of $|\mu|$ remain degenerate. In other words, we are speaking of the spin-axis interaction in the molecule (see Ref. 10, §§ 78 and 83), which does not lift the degeneracy in the sign of the angular-momentum projection. We shall assume the field of the other two neighboring atoms (more precisely, ions), atoms 1 and 2, to be the sum of their Coulomb fields:

$$V(\mathbf{r}) = -\frac{Z_1\alpha}{|\mathbf{r}-\mathbf{r}_1|} - \frac{Z_2\alpha}{|\mathbf{r}-\mathbf{r}_2|}. \tag{4}$$

Finally, let us assume that the unperturbed state of the electron in the heavy atom is a $|p_{3/2}, \mu\rangle$ state. In order for the average of the P-odd weak interaction of the electron with the nucleus to be different from zero, the Coulomb interaction (4) must mix at least two new states of types $|s_{1/2}\rangle$ and $|p_{1/2}\rangle$ with the initial state. With the aid of the rules for the addition of angular momenta (including total angular momentum) and the fact that interaction (4) conserves parity, we can see immediately and without difficulty that the mixing of the $|s_{1/2}\rangle$ state to the $|p_{3/2}\rangle$ initial state is due only to the dipole part of the Coulomb interaction, while the mixing of the $|p_{1/2}\rangle$ state is due to the quadrupole part. A direct calculation leads to the following result for the state as perturbed in this way with the $s_{1/2}$ and $p_{1/2}$ admixtures of interest to us taken into account:

$$\begin{aligned} &|p_{3/2}, \mu\rangle + \frac{4}{3}\frac{(4\pi)^{1/2} m\alpha^2}{2E_s}\sum_{i=1,2} Z_i Q_1(r_i)\cdot \\ &\cdot\sum_{q,\mu'} (-1)^{1/2-\mu'} \begin{pmatrix} 3/2 & 1 & 1/2 \\ \mu & q & -\mu' \end{pmatrix} Y^*_{1q}(\mathbf{n}_i)\,|s_{1/2}, \mu'\rangle \\ &+\frac{4}{5}\frac{(4\pi)^{1/2} m\alpha^2}{2E_p}\sum_{i=1,2} Z_i Q_2(r_i) \sum_{q,\mu'} (-1)^{1/2-\mu'} \begin{pmatrix} 3/2 & 2 & 1/2 \\ \mu & q & -\mu' \end{pmatrix} Y^*_{2q}(\mathbf{n}_i)\,|p_{1/2}, \mu'\rangle. \end{aligned} \tag{5}$$

Here $E_s(E_p)$ is the energy of the admixed $s(p)$ state reckoned from the initial $p_{3/2}$ level, the Y_{kq} are spherical functions, the large bracket expressions are 3-j symbols, and

$$\begin{aligned} Q_k(r_i) = \frac{1}{m\alpha}\int_0^\infty dr\, r^2 [f'(r) f(r) + g'(r) g(r)] \\ \times\left[\theta(r-r_i)\frac{r_i^k}{r^{k+1}} + \theta(r_i - r)\frac{r^k}{r_i^{k+1}}\right]; \end{aligned} \tag{6}$$

where $f(r)$ and $g(r)$ [$f'(r)$ and $g'(r)$] are the upper and lower components of the Dirac radial wave functions for the initial (final) state. We note that expression (5) is also valid in the nonrelativistic case, it being sufficient merely to make the substitution $f'f + g'g \to R'R$ in formula (6), where R' and R are the nonrelativistic radial wave functions for the final and initial states. Of course the fine structure of the levels must be taken into account even in the nonrelativistic approximation.

By making use of expression (5) and taking account of the exact value of the matrix element that admixes the $s_{1/2}$ and $p_{1/2}$ states,[8,9] which differs from the estimate (1) by the factor $iq/2^{1/2}(\nu_s \nu_p)^{3/2}$, where ν_s and ν_p are the effective principal quantum numbers of the corresponding states and q is a quantity close to $N/2Z$ (N is the number of neutrons in the nucleus), one can express the energy correction under discussion in the following form:

$$\begin{aligned} &\frac{Gm^2\alpha^2 Z^3 Rq}{2^{1/2}\pi(\nu_s\nu_p)^{3/2}}\frac{(m\alpha^2)^3}{8E_s E_p}\frac{16}{15}4\pi i \sum_{q,q',\mu'} \begin{pmatrix} 3/2 & 1 & 1/2 \\ \mu & q & -\mu' \end{pmatrix}\begin{pmatrix} 3/2 & 2 & 1/2 \\ \mu & q' & -\mu' \end{pmatrix} \\ &\times\sum_{i,j=1,2} Z_i Z_j Q_1(r_i) Q_2(r_j)\,[Y_{1q}(\mathbf{n}_i) Y^*_{2q'}(\mathbf{n}_j) - Y^*_{1q}(\mathbf{n}_i) Y_{2q'}(\mathbf{n}_j)]. \end{aligned} \tag{7}$$

Expression (7) can be reduced to the following simpler form by standard manipulations:

$$\begin{aligned} &\left(\mu^2 - \frac{5}{4}\right)\frac{4}{5} Z_1 Z_2([\mathbf{n}_1\mathbf{n}_2]\mathbf{n}_3)\,([Q_1(r_1)Q_2(r_2)\mathbf{n}_2 \\ &-Q_1(r_2)Q_2(r_1)\mathbf{n}_1]\mathbf{n}_3)\frac{Gm^2\alpha^2 Z^3 Rq}{2^{1/2}\pi(\nu_s\nu_p)^{3/2}}\frac{(m\alpha^2)^3}{8E_s E_p}. \end{aligned} \tag{8}$$

Passing from the right- to the left-hand isomer corresponds to changing the signs of the coordinates of all the atoms, and this also changes the sign of expression (8). Thus, the calculated energy correction actually has opposite signs for right- and left-hand molecules, so that the splitting δE of the isomer levels is equal to twice the value of expression (8). The agreement with estimate (1) is obvious.

It is evident from expression (8) that the correction could not arise without the presence of all three of the neighboring atoms. In particular, the fact that the effect disappears on averaging over $|\mu|$ (the quantity $\mu^2 - 5/4$ takes the value $+1$ for $|\mu| = 3/2$ and -1 for $|\mu| = 1/2$) clarifies the importance of the part played by the interaction with the third atom, for it is this interaction that lifts the $|\mu|$ degeneracy of the initial state.

Using the same example, we can easily show how important the spin-orbit interaction is for the level splitting that we are discussing. If there were no spin-orbit interaction, the initial states that differ in spin orientation, e.g., the states $|p, l_z=1\rangle|\uparrow\rangle$ and $|p, l_z=1\rangle|\downarrow\rangle$, would be degenerate. The Coulomb interaction, being independent of the spin, would therefore mix the first of these states with the states $|s\rangle|\uparrow\rangle$ and $|p\rangle|\uparrow\rangle$ just as strongly it would the second of them with the states $|s\rangle|\downarrow\rangle$ and $|p\rangle|\downarrow\rangle$. Concerning the matrix element for the weak interaction, we note that it, being linear in the Pauli matrices σ, changes sign under spin flip;

$$\langle\downarrow|\langle s|H|p\rangle|\downarrow\rangle=-\langle\uparrow|\langle s|H|p\rangle|\uparrow\rangle.$$

Thus, averaging over the spin actually makes the effect disappear.

In a heavy molecule, however, where the spin-orbit interaction is comparable with the electrostatic interaction between the atoms, the magnitude of the effect will not be proportional to the fine structure interval.

4. The splitting of a Mössbauer line in crystals that are mirror images of one another may serve as another manifestation of the same effect. Here the mere existence of a parity-violating weak interaction of the nucleus with the electrons of the crystal is not sufficient to give rise to the effect: it is obviously necessary that the strength of this interaction be different for the upper and lower nuclear levels. This situation obtains for the part of the weak interaction that depends on the nuclear spin. Here, however, not all the nuclear nucleons contribute to the effect, but only one of them, whose angular momentum is unpaired; hence the magnitude of the splitting will be smaller than the previous estimates by roughly a factor of Z.[2)] But if we consider a possible contribution to the effect from an interaction that does not depend on the nuclear spin, we see that such a contribution may differ from zero on account of a change in the nuclear radius on going from the initial to the final state. And again we lose a factor of Z in the magnitude of the effect as compared with the estimates given above. Thus, a simple estimate of the splitting of a Mössbauer line when electrons with unpaired spins are present at the lattice point is as follows [cf. (1)]:

$$\delta E \sim \frac{Gm^2\alpha^2Z^2R}{\pi}\frac{m\alpha^2}{2}.$$

At present, the most suitable nucleus for an experiment on Mössbauer-line splitting seems to be Ta_{73}^{181} (the natural line width Γ is 6.7×10^{-14} keV, the transition energy E is 6.25 keV, and the quantum numbers of the nuclear ground and excited states are $7/2^+$ and $9/2^-$, respectively). In this case the expected magnitude of the splitting is

$$\delta E(\mathrm{Ta}_{73}^{181})\sim10^{-15}-10^{-14}\ \mathrm{keV}.$$

Unfortunately, the effective line width here is about 20 times greater than the natural width and, what is worst of all, the accuracy with which the position of the line is reproduced on going from one specimen to another proves to be no better than 4×10^{-13} keV.

5. In concluding I would like to make a few remarks, as is customary in papers on the present subject, concerning the hypothesis that the reason why optically active biological molecules are encountered in nature in only one of the isomeric forms is to be found in the difference between the energies of the right- and left-hand molecules resulting from the weak neutral currents. Such an explanation of the asymmetry of organic nature was first discussed by Marx,[2] and the same hypothesis has since been persistently promoted by Letokhov.[4] Because the effect concerned is extremely small, however, it seems to me that this hypothesis is clearly less likely to be correct than other possible explanations of the asymmetry of living nature.

It seems more natural to suppose that an accidental asymmetry arising spontaneously in a racemic system (i.e., in a system consisting of equal numbers of right- and left-hand molecules) would not tend to die out, but rather to grow, because it ensures a more rapid exchange of matter, i.e., higher chemical-reaction rates.[17,18] As an illustration[3)] let us consider the reaction $A+B\rightarrow AB$ in which each of the molecules A and B has both right- and left-hand isomers. It is clear, generally speaking, that the rate of this reaction will depend on the "helicity" of the reacting molecules. In the limiting case in which the left-hand isomer A_L reacts only with the left-hand isomer B_L and the right-hand isomer A_R reacts only with the right-hand isomer B_R, the number of AB molecules produced per unit time will be proportional to $N(A_L)N(B_L)+N(A_R)N(B_R)$, where N is the concentration of the corresponding isomers. In the racemic mixture, in which $N(A_L)=N(A_R)=N(A)/2$ and $N(B_L)=N(B_R)=N(B)/2$, this quantity is obviously only half as large as the corresponding quantity for a system consisting only of left-hand molecules or only of right-hand ones, in which $N(A_L)=N(A)$, $N(B_L)=N(B)$, $N(A_R)=0$, and $N(B_R)=0$, or $N(A_R)=N(A)$, $N(B_R)=N(B)$, $N(A_L)=0$, and $N(B_L)=0$.

On the other hand, the asymmetry of organic nature might be due to external factors. Thus, it was experimentally established some time ago that circularly polarized light acts differently on right- and left-hand molecules,[19] as is quite natural from a physical point of view. (The sunlight reaching the Earth's surface at a particular place might be circularly polarized to some extent as a result of the dichroism of the atmosphere induced by the Earth's magnetic field.) The hypothesis that the biological asymmetry is due to the action of circularly polarized light goes back to the time of van't Goff.[20]

Finally, the weak interactions might actually take part in producing the asymmetry under discussion without the neutral currents' being involved at all. The hypothesis that the asymmetry of organic molecules is due to parity violation in the β decay of natural radioactive elements was advanced immediately after the discovery of parity nonconservation in the weak interactions.[21] Longitudinally polarized β particles also act differently, generally speaking, on right- and left-hand molecules.

It is not difficult to think of a specific mechanism for this phenomenon. The bremsstrahlung from longitudinally polarized electrons will be partially circularly polarized, and the immediate cause of the effect under consideration turns out again to be the difference between the action of circularly polarized photons on left- and right-hand molecules. Such a selective action on right- and left-hand molecules is being actively sought, using β-decay electrons,[22-25] β-decay positrons,[26-28] and longitudinally polarized electrons from a linear accelerator.[29,30] Unfortunately, the results of these experiments are still contradictory.

I sincerely thank A. I. Vaĭnshteĭn, O. P. Sushkov, and V. V. Flambaum for valuable discussions. I am also deeply indebted to V. K. Voĭtovetskiĭ and V. F. Dmitriev for thorough discussions of matters relating to the Mössbauer effect, and to D. B. Saakyan for useful remarks.

1) The definitions given in Refs. 4 and 5 for the weak charged and neutral currents differ somewhat from those usually adopted.

2) In the unified model for the electromagnetic and weak interactions proposed by Weinberg[15] and Salam,[16] which is confirmed by all the available experimental data, the dimensionless constant characterizing the nuclear-spin-dependent parity-nonconserving interaction is numerically small provided the parameter $\sin^2\theta$ of the theory is given its experimental value $\sin^2\theta\approx0.23$. Here, then, the magnitude of the effect will be further reduced.

3) Although this example was discussed long ago in Gauze's book,[18] I want to present it here, too, since these considerations seem, unfortunately, not to be very well known to the physicists that are discussing these matters.

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Translated by E. Brunner