

# Possibility of electron spin polarization of hydrogenlike atoms in the absence of external magnetic fields

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It is shown within the framework of the Born approximation that if a positively charged particle moving in an optically active medium is transformed via charge exchange into a hydrogenlike atom, this atom should have electron spin polarization. The expected degree of polarization is of the order of  $\kappa(Z\alpha)^2 v_0/v$ , where  $Z$  is the charge of the heaviest of the nuclei of the asymmetric (chiral) center of the material molecule that participates in the charge exchange,  $\kappa$  is the degree of asymmetry of this center,  $v_0$  is the velocity of the valence electrons,  $v$  is the velocity of the charged particle, and  $\alpha$  is the fine-structure constant.

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1. It was recently<sup>1</sup> predicted that when optically active molecules are ionized by fast charged particles the detached electrons should have an electron spin polarization along the momentum of the exciting particles. The expected degree of polarization is of the order of

$$\eta = \kappa(Z\alpha)^2 v_0/v, \quad (1)$$

where  $Z$  is the charge of the heaviest nuclei of the asymmetric (chiral) center of the molecule,  $\kappa$  is the degree of asymmetry of this center,  $v_0$  is the velocity of the valence electrons,  $v$  is the velocity of the incident particle, and  $\alpha$  is the fine-structure constant.

In an optically active molecule we have for some of the electronic transitions<sup>2</sup>

$$R_{0n} = \text{Im}\langle 0 | \mathbf{d} | n \rangle \langle n | \boldsymbol{\mu} | 0 \rangle \neq 0, \quad (2)$$

where  $\mathbf{d}$  and  $\boldsymbol{\mu}$  are the electric and magnetic dipole-moment operators. The quantity  $R_{0n}$  is called the optical rotation force. As a result, a nonzero projection of the orbital angular momentum on the  $z$  axis

$$L_z = \kappa \hbar v_0/v$$

is produced as the detached electron moves along the  $z$  ||  $\mathbf{v}$  axis during the ionization time. On the other hand, owing to the presence of a spin-orbit interaction,<sup>1</sup> the projection  $\sigma_z$  of the detached-electron spin likewise differs from zero. Since the quantity (2) reverses sign on going from the  $L$  to the  $D$  form of the material, the spin polarization also reverses sign.

Let now a heavy charged particle  $A^+$ , with mass much larger than that of the electron, move through an optically active medium. This may be a proton or a singly charged ion from the electron shell of an atom of one of the noble gases, or, e.g., a  $\mu^+$  meson. The hydrogenlike atom  $A$ , produced out of this particle as a result of charge exchange on the molecule  $M$  of the medium

$$A^+ + M \rightarrow A + M^+ \quad (3)$$

should also have an electron spin polarization. Since the physics of its onset is the same as in the case of ionization at velocities  $v \gg v_0$  the degree of polarization will be again of the order of the value given by (1). Using also in this velocity region expression (1) for estimating purposes, we find that  $\eta$  can reach values of the order of

$$\eta \approx \kappa(Z\alpha)^2. \quad (4)$$

If we choose an optically active substance with  $\kappa \approx 1$  (Ref. 3) and place at or near the chiral center of the molecule a nucleus of an element with  $Z \geq 50$ , then the degree of the electron spin polarization of the hydrogenlike atoms  $A$  may turn out to be of the order of ten percent and will reverse sign on going from the  $L$  to the  $D$  form of the material.

In Sec. 2 below the expected effect is estimated within the framework of the first Born approximation of quantum-mechanical collision theory. In Sec. 3 are discussed briefly some of the experimentally observed consequences that can ensue from the presence of the predicted polarization. We note that the effect considered here, and analogously in Ref. 1, can in principle be included among the effects whose existence was predicted in Ref. 4.

2. We shall show that even in the first Born approximation the quantity

$$\eta = [\sigma(+)-\sigma(-)]/[\sigma(+)+\sigma(-)], \quad (5)$$

differs from zero. Here  $\sigma(\pm)$  is the cross section of the reaction (3) with the electron spin of the atom  $A$  parallel or antiparallel to the exciting particle momentum, and that the estimate (1) for  $\eta$  is valid.

For collisions with redistribution of the particles (see Ref. 5, §116), the differential cross section takes the form

$$d\sigma_{ia} = \frac{m_a m_b k_b}{(2\pi\hbar^2)^2 k_a} |\langle \Phi_a | V_b | \Phi_i \rangle|^2 d\Omega_{k_b}, \quad (6)$$

where  $\Phi_a$  and  $\Phi_b$  are the wave functions of the system in the initial (a) and final (b) states;  $m_a$  and  $m_b$  are the reduced masses corresponding to these states;  $k_a$  and  $k_b$  are the wave numbers for the incident and scattered particles, and  $V_b$  is the potential of the interaction in the final state. In the case of the charge-exchange reactions considered by us

$$V_b = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{n,i} \frac{Z_n e^2}{|\mathbf{R}_n - \mathbf{r}_i|} + V_{aL} - \sum_j \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_+|} + \sum_n \frac{Z_n e^2}{|\mathbf{R}_n - \mathbf{r}_+|}. \quad (7)$$

where the subscripts  $i$  and  $j$  number the electrons,  $n$

the nuclei, and + the particle  $A^*$ ;  $V_{\sigma L}$  is the spin-orbit interaction operator; the sum  $\sum_j'$  does not contain the coordinates of the electron that participates in the reaction.

To simplify the analysis we shall assume that only one electron is localized at the chiral center, and it is this electron which participates in the charge-exchange reaction. In the real picture the estimate of  $\sigma_{ba}$  acquires an additional factor of the order of the ratio of the number of valence electrons of the chiral center to the total number of valence electrons of the molecule; this factor cannot affect significantly the order of magnitude of the estimate. We assume also that the reaction products are formed in the ground state (1s for a hydrogenlike atom). The molecule  $M$  is likewise in the ground state. For additional simplification, we assume that its wave function can be represented in the form  $\varphi_0(\mathbf{r})\psi_0(\xi)$ , where  $\psi_0(\mathbf{r})$  describes the initial state of the electron that participates in the reaction, and  $\psi_0(\xi)$  describes the ground state of the molecular remainder  $M^*$ .

We then have in (6)

$$\Phi_b = \frac{1}{(\pi a_0^3)^{1/2}} \psi_0(\xi) \exp\left(-\frac{|\mathbf{r}-\mathbf{r}_+|}{a_0} + i\mathbf{k}_a \cdot \mathbf{r}_+\right),$$

$$\Phi_a = \varphi_0(\mathbf{r}) \psi_0(\xi) \exp(i\mathbf{k}_a \cdot \mathbf{r}_+),$$
(8)

where  $a_0$  is the Bohr radius.

Integrating now in (6) over all the coordinates  $\xi$  of the electrons of the molecular residue we obtain, retaining in the operator  $V_b$  only terms connected with the coordinates of the electron that participates in the reaction, and putting  $m_a \approx m_b \approx m$  (where  $m$  is the mass of the particle  $A^*$ ):

$$d\sigma_{ba} = \frac{m^2}{(2\pi\hbar^2)^2} \frac{k_b}{\pi a_0^3 k_a} \left| \int \exp\left(-i\mathbf{q}\cdot\mathbf{r}_+ - \frac{|\mathbf{r}-\mathbf{r}_+|}{a_0}\right) \times \left(H + \frac{\hbar^2}{2m_a} \Delta\right) \varphi_0(\mathbf{r}) d\mathbf{r}_+ \right|^2 d\Omega_{\mathbf{k}_b},$$
(9)

where  $m_e$  is of the mass of the electron,  $H$  is its self-consistent Hamiltonian in the field of the molecular residue, and  $\mathbf{q} = \mathbf{k}_b - \mathbf{k}_a$ . Expanding in (8) the ground state of the hydrogenlike atom in a Fourier integral and integrating with respect to  $d\mathbf{r}_+$ , we obtain

$$d\sigma_{ba} = \frac{64\pi a_0^3 m^2}{(2\pi\hbar^2)^2} \frac{k_b}{k_a} \frac{(W - \hbar^2 q^2 / 2m_a)^2}{[1 + (a_0 q)^2]^4} \left| \int e^{-i\mathbf{q}\cdot\mathbf{r}} \varphi_0(\mathbf{r}) d\mathbf{r} \right|^2 d\Omega_{\mathbf{k}_b},$$
(10)

where  $W$  is the molecule ionization potential. It can be seen from (10) that  $d\sigma_{ba}$  decreases rapidly with increasing product  $a_0 q$  at  $a_0 q \gtrsim 1$ , so that the exponential under the integral sign can be expanded in a series.

To estimate the quantity  $\sigma(+) + \sigma(-)$  in the denominator of (5), we replace the exponential by unity and change over in standard fashion from integration with respect to the angle  $\theta$  between the vectors  $\mathbf{k}_b$  and  $\mathbf{k}_a$  to integration with respect to  $q$ :

$$d \cos \theta = q dq / k_a k_b,$$

after which we obtain

$$\sigma_{ba} = \frac{\sigma(+) + \sigma(-)}{2} = \frac{32a_0^3}{(\hbar v)^2} F \left| \int \varphi_0 d\mathbf{r} \right|^2,$$

$$F = \int_0^{q_1} \frac{(W - \hbar^2 q^2 / 2m_a)^2}{[1 + (a_0 q)^2]^4} q dq.$$
(11)

Here  $q_0 = |I - W| / \hbar v$ , where  $I$  is the ionization potential of the hydrogenlike atom;  $q_1 = \gamma / a_1$ ;  $\gamma$  is a certain constant  $\lesssim 1$ , and  $a_1$  is the dimension of the chromophoric center.

We estimate now the numerator of (5). To this end we separate in Eq. (10) for the differential cross section the part that is linear in the spin, taking into account the spin-orbit interaction in the state with the wave function  $\varphi_0$ :

$$\varphi_0 = \varphi_0' + (E_0 - H)^{-1} V_{\sigma L} \varphi_0',$$
(12)

where  $E_0$  is the energy and  $\varphi_0'$  is the wave function of the ground state, but now without allowance for the relativistic effects. Expanding next  $\exp(-i\mathbf{q}\cdot\mathbf{r})$  accurate to terms linear in  $q\mathbf{r}$  and integrating with respect to  $d\Omega_{\mathbf{k}_b}$ , we obtain

$$\sigma_{ba}' = \frac{64a_0^3}{(\hbar v)^2} F \frac{I - W}{\hbar v} \text{Im} \left[ \left( \int \varphi_0' d\mathbf{r} \right)^* \int z \frac{1}{E_0 - H} V_{\sigma L} \varphi_0' d\mathbf{r} - \left( \int z \varphi_0' d\mathbf{r} \right)^* \int \frac{1}{E_0 - H} V_{\sigma L} \varphi_0' d\mathbf{r} \right].$$
(13)

The factor  $(I - W) / \hbar v$  in this expression is the projection of the vector  $q$  on the direction of  $\mathbf{k}_a$ . In fact,

$$q_z = \frac{\mathbf{q}\mathbf{k}_a}{k_a} = \frac{k_b^2 - k_a^2 - q^2}{2k_a} = \frac{m}{\hbar^2 k_a} (I - W) - \frac{q^2}{2k_a} \approx \frac{I - W}{\hbar v}$$
(14)

where  $q \lesssim \gamma / a_1$ .

Representing the operator  $V_{\sigma L}$  in (13) as  $B\boldsymbol{\sigma} \cdot \mathbf{L}$  ( $B \sim (Z\alpha)^2 R$  and  $R$  is the Rydberg constant [Ref. 6, §72]), and integrating over all the orientations of the molecules, we can transform the expression in the imaginary part into

$$\frac{B}{3} \left[ \int \mathbf{r} \frac{1}{E_0 - H} \mathbf{L} \varphi_0' d\mathbf{r} \left( \int \varphi_0' d\mathbf{r} \right)^* - \int \frac{1}{E_0 - H} \times \mathbf{L} \varphi_0' d\mathbf{r} \left( \int \mathbf{r} \varphi_0' d\mathbf{r} \right)^* \right] \sigma_z.$$
(15)

Using (11), (13), and (15) we readily find that

$$\eta = \frac{2}{3} B \frac{I - W}{\hbar v} \left[ \int \mathbf{r} \frac{1}{E_0 - H} \mathbf{L} \varphi_0' d\mathbf{r} / \int \varphi_0' d\mathbf{r} - \int \frac{1}{E_0 - H} \mathbf{L} \varphi_0' d\mathbf{r} \left( \int \mathbf{r} \varphi_0' d\mathbf{r} \right)^* / \left| \int \varphi_0' d\mathbf{r} \right|^2 \right].$$
(16)

With Condon's model of optical activity<sup>7</sup> as the example, we shall show that the expression in the square brackets of (16) is of the same order as the quantity

$$C = \text{Im} \left\langle 0 \left| \mathbf{r} \frac{1}{E_0 - H} \mathbf{L} \right| 0 \right\rangle = \frac{2m_e c}{e^2} \sum_{n \neq 0} \frac{\text{Im} \langle 0 | \mathbf{d} | n \rangle \langle n | \boldsymbol{\mu} | 0 \rangle}{E_0 - E_n},$$
(17)

which is expressed in terms of the optical rotation forces  $R_{0n}$  [see Eq. (2)].

In Condon's model a chromophoric electron is regarded as an oscillator that moves in a field

$$V = \frac{1}{2} (k_1 x^2 + k_2 y^2 + k_3 z^2) + Axyz, \quad k_1 \neq k_2 \neq k_3.$$
(18)

The term  $Axyz$  is taken into account as a perturbation.

The calculations yield

$$C = \frac{A\hbar(\omega_1 - \omega_2)(\omega_2 - \omega_3)(\omega_3 - \omega_1)}{4m_e^2 \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)(\omega_1 + \omega_2)(\omega_1 + \omega_3)(\omega_2 + \omega_3)},$$

$$\omega_i = (k_i / m_e)^{1/2}, \quad i = 1, 2, 3.$$
(19)

As for the expression in the square brackets of (16), only its first term differs from zero in the Condon model. Its main contribution comes from the intermediate states  $|n_1, n_2, n_3\rangle$  with  $n_i = 0$  or 1. This contribution equals  $2C$ . The remaining intermediate states, when some of the  $n_i$  are equal to 2, yield under the condition  $|\omega_i - \omega_j| \ll \omega_i$  an additional correction  $14C/27 \approx C/2$ , and thus

$$\int r \frac{1}{E_0 - H} L \varphi_0' dr / \int \varphi_0' dr \approx \frac{5}{2} \langle 0 | r \frac{1}{E_0 - H} L | 0 \rangle. \quad (20)$$

Substituting this relation in (16), we obtain ultimately

$$\eta \approx \frac{10}{3} B \frac{I - W}{\hbar v} \frac{m_e c}{e^2} \sum_{n \neq 0} \frac{R_{0n}}{E_0 - E_n}. \quad (21)$$

For some of the electronic transitions in optically active molecules the quantities  $m_e c R_{0n} / e^2$  have an absolute value  $\approx \hbar a_1$ , but their sum over all the states  $|n\rangle$  is zero. Assuming, by way of estimate, that these quantities differ from zero only for certain two transition, and replacing  $B$  in (21) by  $(Z\alpha)^2 R$ , we find that at  $|I - W| \approx E_1 - E_0$

$$\eta \approx \kappa (Z\alpha)^2 \frac{a_1 v_0}{a_0 v} \approx \kappa (Z\alpha)^2 \frac{v_0}{v}. \quad (22)$$

This estimate was obtained under the condition  $v \gg v_0$ . One can expect, however, it to be satisfied also at  $v \approx v_0$ .

**3.** We now point out several examples in which, from our viewpoint, the discussed electron spin polarization can manifest itself.

1) Let the irradiation be by  $\mu^+$  mesons obtained in the decay of mesons. In this case the particles are practically completely polarized in a direction opposite to their emission velocity (the helicity is  $-1$ ). When a  $\mu^+$  meson is stopped in a diamagnetic medium its polarization can be neglected. The polarization begins if a hydrogenlike atom—muonium—is produced and stops when the muonium reacts with a molecule of the medium to produce a diamagnetic complex.<sup>8</sup>

We denote by  $\tau$  the average dwell time of the  $\mu^+$  meson in the muonium, by  $\omega$  the cyclic frequency of the hyperfine splitting of the muonium in the medium ( $\omega \leq \omega_0 = 2.8 \cdot 10^{10} \text{ sec}^{-1}$ ), and by  $\tau_s$  the relaxation time of the electron spin in the medium. Then, if  $\tau \ll \tau_s$ , the degree  $P$  of the depolarization in a racemic mixtures (the  $L$  and  $D$  forms of the molecules are on a par) equals<sup>8</sup>

$$P = \frac{1}{2} \left[ 1 + \frac{1}{1 + (\tau\omega)^2} \right], \quad (23)$$

whereas at the antipodes

$$P_{L,D} = P \pm \frac{\eta}{2} \left[ 1 - \frac{1}{1 + (\tau\omega)^2} \right], \quad (24)$$

and the order of  $\eta$  is given by the estimate (22), while the increment itself has opposite signs for the  $L$  and  $D$  forms of the material. At  $\omega\tau \gg 1$  the difference between the depolarization degrees in the  $L$  and  $D$  forms is found to be equal to  $\eta$ . The degree of depolarization itself is determined from the asymmetry of the  $\mu^+$ -meson decay.

2) Let a positron  $e^+$  from a radioactive source, say  $^{22}\text{Na}$ , enter an optically active medium. Immediately after emission it is again practically completely polarized (the helicity equals 1). During the initial section of its stopping path,  $e^+$  can transfer the greater part of its energy to several electrons of the medium and then, becoming thermalized, it lands in the trail of one of these electrons. In an optically active medium, the electrons of the trail should be partially polarized either parallel or antiparallel to the momentum of the fast electron that produces them, depending on the form of the material (see Sec. 1). This direction is close to the direction of the emission of  $e^+$  from the source, i.e., to the direction of its spin polarization. Becoming thermalized, the  $e^+$  can capture an electron from the trail,<sup>9</sup> producing a hydrogenlike atom—positronium (Ps). If the medium is not magnetic, the positron hardly undergoes any depolarization during its lifetime.<sup>10</sup> One can expect therefore in the  $L$  and  $D$  forms of the material differences in the yield of ortho-positronium ( $^3\text{Ps}$ ) with equality of the Ps yield with allowance for the parapositronium. This difference can manifest itself in the spectra of the positron-lifetime distribution,<sup>11</sup> and in particular in the intensities of the long-lived components  $I_3$ . It can be easily shown that

$$|(I_{3L} - I_{3D}) / (I_{3L} + I_{3D})| = \eta/3. \quad (25)$$

We note in conclusion that to obtain an electron spin polarization on the order of 10% in diamagnetic substances at room temperature it would be necessary to apply magnetic fields of the order of  $5 \times 10^5$  Oe.

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<sup>1)</sup> It leads to the appearance of a factor  $(Z\alpha)^2$  in Eq. (1).

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