Effects of parity nonconservation in electronic spectra of molecules

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Effects of parity nonconservation in forbidden magnetic transitions in diatomic molecules are considered. In particular, the effect in the experimentally well investigated $b\,{}^1\Sigma_g^+ \leftarrow X\,{}^3\Sigma_g^-$ atmospheric absorption bands of molecular oxygen is examined. It is shown that Λ the degree of circular polarization in this transition due to electron weak neutral currents should be of the order of 10^{-9}. Possible experiments with solar light or lasers are discussed. It is also shown that doubling leads to effects of considerable magnitude in the radiation from diatomic molecules involving transitions between Π and Σ states. In particular, the degree of circular polarization in the forbidden $a\,{}^3\Pi_2 \rightarrow X\,{}^1\Sigma^+$ transition in the SiS molecule may reach unity if the Λ doublet ($\Delta E \sim 10$Hz) is resolved and amounts to about 10^{-4} if the doublet is not resolved.

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1. One of the most important problems of atomic physics at present is to detect and measure the effects of parity nonconservation in atoms. The importance of this problem stems from the possibility of confirming the presence of weak neutral currents and directly measuring the corresponding coupling constants.[1–3] The first experiments on optical rotation associated with parity nonconservation in atoms have already been performed.[4] It should be emphasized that in all the experiments that have been proposed[1–3] and performed[4] it is a question of weak neutral electron-nucleus currents. It is of no less interest to determine the magnitude of the weak neutral electron-electron currents.[5] In atoms, the latter are usually hidden by the stronger electron-nucleus interactions and in principle can be observed only in special situations.[5] The purpose of the present work is to show that there are also fairly good possibilities of observing neutral electron-electron currents in the electronic spectra of diatomic molecules.

The effects of parity nonconservation in atoms and molecules are similar in nature: they manifest themselves as pseudoscalar terms in the probabilities for various processes. In the case of the absorption or emission of a photon by an atom or a molecule, the only pseudoscalar that can be constructed from the available vectors is $\mathbf{j}\cdot\mathbf{n}$, where $\mathbf{j}$ is the angular momentum of the photon and $\mathbf{n}$ is a unit vector in the photon propagation direction. This pseudoscalar can assume the values ± 1, corresponding to the two circular polarizations of the photon. Specifically, the following mechanism is responsible for the parity violating effects: the weak interaction causes the admixture of a state of opposite parity to a state $\psi_{g,u}$ of definite parity: $\psi_{g,u} \rightarrow \psi_{g,u} + c\psi'_{u,g}$. The mixing coefficient c is given by $c = \langle g|V|u\rangle/\Delta E$, where $\langle g|V|u\rangle$ is the matrix element of the effective weak-interaction potential, and ΔE is the energy separation from the nearest state of opposite parity. As a result of such mixing, the expressions for the amplitudes for various processes assume the form $A = A_0 + cA_1$, where A_0 is the transition amplitude for the main (parity conserving) process (with the weak interaction turned off), and A_1 is the actual transition amplitude in the presence of level mixing.

It is natural to introduce the "degree of parity nonconservation" in a given process by the definition

$$\mathscr{P} = cA_1/A_0 = c\sqrt{W_1/W_0}, \tag{1}$$

in which W_0 and W_1 are the probabilities corresponding to the amplitudes A_0 and A_1. Two possible ways of enhancing the effects in atomic and molecular systems are evident from Eq. (1): 1) to reduce ΔE, and 2) to increase the ratio W_1/W_0. Thus, one must look for a situation in which levels of opposite parity lie as close together as possible and the main transition is forbidden. As a result of interference between the main and admixed transitions, the expression for the probability for a transition involving emission or absorption of a photon takes the form

$$W = W_0(1 + \mathscr{P}(\mathbf{jn})). \tag{2}$$

It follows at once from Eq. (2) that the probabilities $W^{(\pm)}$ for the emission and absorption of right- and left-hand polarized photons will be different, so that the absorption coefficients $k^{(\pm)}$, the absorption cross sections $\sigma^{(\pm)}$, and the refractive indices $n^{(\pm)}$ will also be different. The usual situation in atoms is the interference between a main forbidden $M1$ transition and an admixed allowed $E1$ transition. According to theoretical estimates, $\mathscr{P}$ can attain the maximum value $\mathscr{P} \sim 10^{-4}$ for electron-nucleus interactions[1–3] and $\mathscr{P} \sim 10^{-8}$ for electron-electron interactions.[5] Experiments on the rotation of the plane of polarization of light due to the electron-nucleus interactions, in which $\mathscr{P}$ was measured,[4] gave the result $\mathscr{P} \sim 10^{-8}$, corresponding to the rotation angle $\psi \sim 10^{-7}$ rad/m.

Strictly speaking, only parity under the simultaneous inversion of the coordinates of the electrons and the nuclei is valid in diatomic molecules (the corresponding states are called positive or negative). In molecules having like nuclei, parity exists also under the inversion of the electron coordinates alone, the coordinates of the nuclei being held fixed. Such parity is not an exact

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quantum number: because of the spin-spin interaction between the electrons and nuclei, each g or u state will have a small admixture of a state of opposite parity (molecules having spin-zero nuclei, e.g., O_2, are exceptions). Of course parity under complete inversion is not thereby violated. Hence the presence of admixtures of opposite parity in the g and u states leads, in the absence of the weak interactions, only to the appearance of additional terms in the transition problability (but not to interference); such mixing, therefore, can only reduce $\mathscr{P}$. Actually, however, the electron-nucleus spin-spin interaction is so weak that the additional terms are much smaller than the term representing the main transition.

2. Let us first consider the spin-forbidden magnetic dipole transition ${}^1\Sigma_g^+ - {}^3\Sigma_g^-$ in the oxygen molecule. This transition has been thoroughly investigated experimentally, being observable in absorption in the atmosphere and in emission under laboratory conditions. Let us estimate the order of magnitude of the expected effect. In this case the levels ${}^{1,3}\Pi_u$ and ${}^{1,3}\Sigma_u^\pm$ may be mixed with the main-transition levels. These levels lie relatively far from the ${}^{1,3}\Sigma_g^\pm$ levels, so only the second of the two ways mentioned above for increasing $\mathscr{P}$ can be effective. The matrix element $\langle g|V|u\rangle$ (in units in which $\hbar=c=1$) is a small parameter of the following order of magnitude:

$$\langle g|V|u\rangle \sim Gm^3\alpha^4 = 10^{-5} m (m/m_p)^2 \alpha^4,$$

where G is the Fermi constant, m_p is the proton mass, and α is the alpha fine structure constant. The energy separation ΔE is of the order of $m\alpha^2$. Finally, if we estimate the probabilities W_{M1} and W_{E1} on the basis of atomic calculations, we obtain

$$W_{M1} \sim m\alpha^{11}, \quad W_{E1} \sim m\alpha^5.$$

Then formula (1) yields $\mathscr{P} \sim 10^{-9}$.

However, we have not taken into account an additional small numerical factor that may occur in the matrix element $\langle g|V|u\rangle$ because V is a short-range potential. In the case of atoms, this effect leads to an additional factor of $1/32\pi$ in the matrix element for the electron-nucleus weak interaction[2] and to an additional factor of $\sim 10^{-4}$ in the matrix element for the electron-electron interaction.[5] This second factor is as small as it is because the overlap integral between the wave functions of electrons on different spatial orbits in an atom is small. One may suppose, however, that this effect will not arise in the case of the electron-electron weak interactions in molecules since all of the electrons taking part in forming a chemical bond are concentrated in the region between the nuclei. This conclusion is confirmed by estimates, given below, of the matrix elements on the basis of experimental data. Moreover, estimates show that the electron-nucleus contact interaction in diatomic molecules consisting of light atoms is very weak, so that the effects of electron-nucleus neutral currents can be neglected. In estimating the probabilities we also neglected the Franck-Condon factors, which to a considerable extent determine the order of magnitude of transition probabilities in molecules. It will be shown below, however, that these factors cannot significantly affect the magnitude of $\mathscr{P}$ in the situation that we are considering.

According to formula (1), the degree of parity nonconservation in the process under consideration is given by

$$\mathscr{P} = \frac{\langle {}^1\Pi_u|V|{}^3\Sigma_g^-\rangle}{\Delta E_1} \frac{W^{1/2}({}^1\Sigma_g^+ - {}^1\Pi_u)}{W^{1/2}({}^1\Sigma_g^+ - {}^3\Sigma_g^-)} + \frac{\langle {}^1\Sigma_g^+|V|{}^3\Pi_u\rangle}{\Delta E_2} \frac{W^{1/2}({}^3\Pi_u - {}^3\Sigma_g^-)}{W^{1/2}({}^1\Sigma_g^+ - {}^3\Sigma_g^-)}, \quad (3)$$

where

$$\Delta E_1 = E({}^3\Sigma_g^-) - E({}^1\Pi_u), \quad \Delta E_2 = E({}^1\Sigma_g^+) - E({}^3\Pi_u).$$

In Eq. (3) we have neglected the contributions from intermediate Σ states which, as can be seen from symmetry considerations, must contain an additional small factor. The operator V has the following explicit form in the nonrelativistic limit:

$$V = -\frac{G_e}{2m} \sum_{i>j} \{(\mathbf{s}_i - \mathbf{s}_j)[(\mathbf{p}_i - \mathbf{p}_j)\delta^{(3)}(\mathbf{r}_{ij})]_+ - 2i[\mathbf{s}_i\mathbf{s}_j][(\mathbf{p}_i - \mathbf{p}_j)\delta^{(3)}(\mathbf{r}_{ij})]_-\}, \quad (4)$$

where the $\mathbf{p}_i$ and $\mathbf{s}_i$ are the momentum and spin operators of the individual electrons, G_e is the interaction constant, and $[\ldots]_\mp$ denotes the commutator or anticommutator. In Weinberg's model[1-3] $G_e \approx -0.28G$, where G is the usual Fermi constant.

Let us estimate the matrix elements in (3) from the relevant experimental data. Experimental data on the atmospheric intensities of individual absorption lines in the 0–0 band of the ${}^1\Sigma_g^+ - {}^3\Sigma_g^-$ transition are given in Ref. 6. Since we are regarding this as the main transition, it is natural to choose one of the weakest lines, e.g., the line ${}^PQ(J'=27)$, where J' is the rotational quantum number of the lower state. The intensity of this line in absorption is $S=0.42$ cm^{-1} km^{-1}. Expressed in terms of the intensity, the transition probability is

$$W({}^1\Sigma_g^+ - {}^3\Sigma_g^-) = 4gS/\lambda^2 g'N',$$

where λ is the wavelength in centimeters, g and g' are the statistical weights of the initial and final states, and N' is the concentration of molecules in the initial state. Putting $\lambda = 0.76\times10^{-4}$ cm, $N' = 2.7\times10^{19}$ molecules/cm^3, and $g' \approx g$ in this formula, we obtain $W({}^1\Sigma_g^+ - {}^3\Sigma_g^-) \sim 10^{-16}$ cm^{-1}; this agrees in order of magnitude with the rough estimate given above. This result also shows that the Franck-Condon factor does not play any significant part in this transition.

To estimate the probabilities of the admixed transitions ${}^{1,3}\Sigma_g^+ - {}^{1,3}\Pi_u$ is a more complicated problem. Calculations by the method of molecular orbitals show that the low-lying states of type ${}^{1,3}\Pi_u$ in the O_2 molecule are repulsive.[7] The corresponding energy differences for internuclear distances equal to the equilibrium distances for the ${}^3\Sigma_g^-$ and ${}^1\Sigma_g^+$ states are $\Delta E_1 = 0.74$ Ry and $\Delta E_2 = 0.52$ Ry. In our problem the ${}^{1,3}\Pi_u$ levels are intermediate ones and we may consider transitions to vibrational states in the continuous spectrum. We can accordingly always select a transition for which the Franck-Condon factor will be close to unity. Thus, we can use the previous atomic estimate for the probabilities.

Now let us evaluate the matrix elements $\langle {}^{1,3}\Sigma_g^{\pm} | V | {}^{3,1}\Pi_u \rangle$. Here it is more convenient to use atomic units, in which $\hbar = e = m = 1$. For simplicity we shall consider only part of the interaction operator (4):

$$V' = -G_e \alpha^2 \sum_{i>j} (\mathbf{s}_i - \mathbf{s}_j)(\mathbf{p}_i - \mathbf{p}_j)\delta^{(3)}(\mathbf{r}_{ij}).$$

The O_2 molecule in the ground state has the electron configuration

$$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g^*)^2,$$

where the asterisks mark antibound states.[8] The electron configuration for the ${}^{1,2}\Pi_u$ states differs in having two σ_g and π_u electrons replaced by π_g electrons. As a result, the matrix element

$$\langle g | V' | u \rangle = \langle {}^{1,3}\Sigma_g^{\pm} | V' | {}^{3,1}\Pi_u \rangle$$

takes the form

$$\langle g | V' | u \rangle = -\alpha^2 G_e \langle \sigma_g \pi_u | (\mathbf{s}_1 - \mathbf{s}_2)(\mathbf{p}_1 - \mathbf{p}_2)\delta^{(3)}(\mathbf{r}_{12}) | \pi_g \pi_g \rangle.$$

Treating the operator V' as the product of the operators $-\alpha^2 G_e \delta^{(3)}(\mathbf{r}_{12})$ and $(\mathbf{s}_1 - \mathbf{s}_2)(\mathbf{p}_1 - \mathbf{p}_2)$, we obtain the following approximate expression for the matrix elements:

$$\begin{aligned} &\langle {}^1\Sigma_g^+(\sigma_g\pi_u) | V' | {}^3\Pi_u(\pi_g\pi_g) \rangle \\ &= -G_e\alpha^2 \langle {}^1\Sigma_g^+(\sigma_g\pi_u) | \delta^{(3)}(\mathbf{r}_{12}) | {}^1\Sigma_g^+(\sigma_g\pi_u) \rangle \\ &\times \langle {}^1\Sigma_g^+(\sigma_g\pi_u) | (\mathbf{s}_1 - \mathbf{s}_2)(\mathbf{p}_1 - \mathbf{p}_2) | {}^3\Pi_u(\pi_g\pi_g) \rangle, \end{aligned} \tag{5}$$

and

$$\begin{aligned} &\langle {}^3\Sigma_g^-(\sigma_g\pi_u) | V' | {}^1\Pi_u(\pi_g\pi_g) \rangle \\ &-G_e\alpha^2 \langle {}^3\Sigma_g^-(\sigma_g\pi_u) | \delta^{(3)}(\mathbf{r}_{12}) | {}^3\Sigma_g^-(\sigma_g\pi_u) \rangle \\ &\times \langle {}^3\Sigma_g^-(\sigma_g\pi_u) | (\mathbf{s}_1 - \mathbf{s}_2)(\mathbf{p}_1 - \mathbf{p}_2) | {}^1\Pi_u(\pi_g\pi_g) \rangle. \end{aligned} \tag{6}$$

Here we have neglected the off-diagonal matrix elements of the contact-interaction operator. We also note that the average value of $\delta^3(\mathbf{r}_{12})$ is zero for triplet states of two-electron systems, but that this is not the case for an arbitrary number of electrons.

Now let us estimate the first matrix element in each of Eqs. (5) and (6). To do this we use the following expression for the spin-spin interaction operator:

$$H_{ss} = -\frac{8\pi}{3}\alpha^2 \mathbf{s}_1\mathbf{s}_2\delta^{(3)}(\mathbf{r}_{12}) + \frac{\alpha^2}{r_{12}^3}\left(\mathbf{s}_1\mathbf{s}_2 - \frac{3(\mathbf{s}_1\mathbf{r}_{12})(\mathbf{s}_2\mathbf{r}_{12})}{r_{12}^2}\right). \tag{7}$$

Both terms of this operator are short-range potentials, and the average values of these terms for singlet states are of the same order of magnitude.[9] The average value of the operator (7) for the triplet state corresponding to a given singlet state is also of the same order of magnitude (the average of the first term in (7) over a singlet state vanishes). We therefore use the following sequence of equations to estimate the matrix element $\langle {}^1\Sigma_g^+ | \delta^{(3)}(\mathbf{r}_{12}) | {}^1\Sigma_g^+ \rangle$:

$$\alpha^2 \langle {}^1\Sigma_g^+ | \delta^{(3)}(\mathbf{r}_{12}) | {}^1\Sigma_g^+ \rangle = \frac{1}{2\pi}\langle {}^1\Sigma_g^+ | H_{ss} | {}^1\Sigma_g^+ \rangle \approx \frac{1}{2\pi}\langle {}^3\Sigma_g^- | H_{ss} | {}^3\Sigma_g^- \rangle \approx \frac{1}{2\pi}\delta_s, \tag{8}$$

where δ_s is the spin splitting constant for the ${}^3\Sigma_g^-$ state. On estimating the matrix element $\langle {}^3\Sigma_g^- | \delta^{(3)}(\mathbf{r}_{12}) | {}^3\Sigma_g^- \rangle$ we immediately obtain

$$\alpha^2 \langle {}^3\Sigma_g^- | \delta^{(3)}(\mathbf{r}_{12}) | {}^3\Sigma_g^- \rangle \approx (3/2\pi)\delta_s. \tag{9}$$

We note that such estimates can be made only for Σ states, since only for such states is the multiplet splitting due to the spin-spin interaction, and not to the spin-orbit coupling. The result is the following estimate for the matrix elements $\langle {}^{1,3}\Sigma_g^{\pm} | V | {}^{3,1}\Pi_u \rangle$ on the average:

$$\langle {}^{1,3}\Sigma_g^{\pm} | V | {}^{3,1}\Pi_u \rangle \approx -\frac{1}{\pi} G_e \delta_s \langle {}^{1,3}\Sigma_g^{\pm} | (\mathbf{s}_1 - \mathbf{s}_2)(\mathbf{p}_1 - \mathbf{p}_2) | {}^{3,1}\Pi_u \rangle. \tag{10}$$

The last matrix element in (10) agrees in order of magnitude with the matrix element for an electric dipole transition, i.e., it is of the order of unity. For the constant δ_s we take the value[10] $\delta_s \approx 2\ \text{cm}^{-1}$.

Substituting these estimates for the matrix elements into (3), we obtain the value $\mathcal{P} \sim 10^{-9}$, which agrees with the value obtained above. This shows that atomic calculations can be used to obtain order-of-magnitude estimates for diatomic molecules.

The transition ${}^1\Delta_g - {}^3\Sigma_g^-$, which lies in the infrared, is another magnetic dipole transition that can be used. Although it is more difficult to make estimates for this transition, it is known that it has a considerably lower probability than the ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition.[11] This should lead to a larger value for $\mathcal{P}$. One can also use the magnetic dipole transition ${}^3\Sigma_u^- - {}^1\Sigma_u^+$ between excited states of the oxygen molecule. The ${}^3\Sigma_u^-$ level crosses the ${}^1\Pi_g$ repulsive term near its equilibrium position, and in principle this could increase $\mathcal{P}$ by a factor of $\Delta E/\Gamma \sim 10^6$, where ΔE is the normal term separation and Γ is the level width. Finally, one can also consider transitions in other diatomic molecules, e.g., the $B\,{}^3\Pi_g \leftarrow X\,{}^1\Sigma_g^+$ transition in N_2. Here the weak interaction mixes the $B\,{}^3\Pi_g$ and $a\,{}^1\Pi_u$ levels, for which $\Delta E \approx 0.1$ Ry. We may therefore expect to have $\mathcal{P} \geqslant 10^{-9}$ for this transition.

3. Now let us discuss the possibility of observing the effect experimentally. We shall first discuss the possibility of determining the difference between the absorption cross sections $\sigma^{(\pm)}$ from atmospheric observations. In this case we have to measure the quantity

$$\varkappa(h) = \frac{I^{(+)}(h) - I^{(-)}(h)}{I^{(+)}(h) + I^{(-)}(h)}, \tag{11}$$

where the $I^{(\pm)}(h)$ are the fluxes of right- and left-hand polarized photons at height h above ground level. Using the barometric formula for the pressure at constant temperature and the relation $k^{(+)} - k^{(-)} = \mathcal{P}k_0$, where $k_0 \approx 3\ \text{km}^{-1}$ is the absorption coefficient for the atmospheric A band $(b\,{}^1\Sigma_g^+ \leftarrow X\,{}^3\Sigma_g^-)$,[6] we obtain

$$\varkappa(h) = {}^1\!/_2\mathcal{P}(k_0/a)e^{-ah}, \tag{12}$$

from Eq. (11), where $a = 1.4 \times 10^{-6}\ \text{cm}^{-1}$. This gives $\varkappa \approx 10^{-8}$ at $h = 0$ and $\varkappa \approx 2 \times 10^{-9}$ at $h = 10$ km.

In an experiment with "ideal" statistics, we should have to record a number $N > 1/\varkappa^2$ of photons in order to bring the difference between the $\sigma^{(\pm)}$ due to the weak interaction above the fluctuation level. In an actual experiment, of course, the total number of photons should be much larger—by several orders of magnitude—because of various losses. If we assume that the total flux of solar radiation throughout the entire visible spectrum is $I_0 \sim 10^{24}$ photons/cm^2 sec and also assume for rough estimates that the photons are distributed uniformly in frequency, we find that the photon flux within a single line (i.e., within its Doppler width) will be $\sim 10^{20}$ cm^{-2} sec^{-1}. Then estimates show that the flux of the photons we are interested in will be $\sim 10^{10}$ cm^{-2} sec^{-1} at ground level and $\sim 10^{17}$ cm^{-2} sec^{-1} at an altitude of 10 km. With a photon-detector area of ~ 1 cm^2, the observing time for the "ideal" experiment would be about 10 days at ground level and about 1 sec at $h = 10$ km.

Now let us consider the possible disturbing factors. Generally speaking, the Zeeman splitting of the levels in an external magnetic field could lead to effects simulating those of parity nonconservation, since the transition frequencies, and therefore also the absorption cross sections, turn out to be different for right- and left-hand polarizations.[1,2] The necessary condition that such effects be insignificant is as follows:

$$\frac{\gamma}{\Delta\omega}\frac{\delta\omega}{\Delta\omega} < \mathscr{P}, \tag{13}$$

where γ is the total (Doppler) line width, $\delta\omega$ is the Zeeman splitting, and $\Delta\omega$ is the band width of the radiation detector (source), which we take equal to the Doppler width: $\Delta\omega \sim \gamma \sim 10^{-5}\,\omega$. This leads to the condition $\mathscr{H} < 10^{-4}$ Oe. Since $\mathscr{H} \sim 0.5$ Oe for the earth's magnetic field, one must take measures to compensate the effect of terrestrial magnetism (by using various orientations of the interuments with respect to the magnetic lines of force, etc.).

Collision-induced transitions are another disturbing factor. If, as a result of collisions, the probability for the ${}^1\Sigma_g^+ - {}^3\Sigma_g^-$ transition becomes larger than that for the main $M1$ transition, $\mathscr{P}$ will fall. However, experimental data indicate that this situation does not obtain at normal pressure.[12]

Finally, there is a special problem: there may be circular polarization in the direct solar radiation itself. This difficulty can be surmounted only by making control measurements beyond the atmosphere.

Now let us consider possible laser experiments. The wavelength region of the A absorption band of molecular oxygen at $\lambda \sim 7600$ Å falls within the range covered by tunable dye lasers. For an absorption experiment in the atmosphere, formula (11) is replaced by

$$\varkappa(l) = \frac{I^{(+)}(l) - I^{(-)}(l)}{I^{(+)}(l) + I^{(-)}(l)}, \tag{14}$$

where $I^{(\pm)}(l) = I_0 \exp(-k^{(\pm)} l)$, l is the absorption path length, and I_0 is the initial beam intensity. Then formula (12) becomes

$$\varkappa(l) = {}^1/_2 \mathscr{P} k_0 l. \tag{15}$$

This gives $\varkappa \sim 10^{-9}$ for $l = 1$ km.

Another laser experiment that is possible in principle is to measure the rotation of the plane of polarization of the laser light.[1,2] The expected rotation angle is roughly $\psi \approx \mathscr{P} k_0 l$, which gives $\psi \approx 10^{-8}$ rad for $l = 3$ km. In this case the beam would be attenuated by a factor of e^{-10}, which is quite acceptable.

4. Another way of observing parity-nonconservation effects in the spectra of diatomic molecules involves making use of the phenomenon of Λ doubling. Now we shall be considering heteronuclear molecules. Each of the Π and Δ levels of such molecules split into two close components, of which one is positive and the other, negative. The weak interaction (4) mixes these components. We note that in the case of two electrons, the operator $V(12)$ does not mix states having the same total spin. In fact, in this case the operator (4) is antisymmetric under exchange of the spin (or spatial) coordinates alone. Hence the two spin functions in the matrix element necessarily have different spin-exchange symmetries. However, this is not the case for an arbitrary number of electrons, i.e., when the interactions of all the bonding electrons in the molecule are taken into account. In the case of dipole transitions from Π or Δ states to a Σ state for which each rotational sublevel is either positive or negative, the transition from one of the Λ sublevels of the Π or Δ state will be of electric type, and that from the other, of magnetic type. Thus, the weak interaction will mix a magnetic transition with an electric transition and the situation discussed in Sec. 2 will arise, but with the difference that here either both transitions will be allowed, or both forbidden.

Let us first consider the effect in a molecule whose bonding falls under Hund's case a). We write the wave functions for the positive and negative sublevels in the form

$$\psi^{\pm}(n\Lambda\Sigma SJM) = 2^{-1/2}\left(\psi(n\Lambda\Sigma SJM) \pm \psi(n\bar{\Lambda}\bar{\Sigma} SJM)\right), \tag{16}$$

where Λ and Σ are the projections of the electron orbital and spin angular momenta onto the axis of the molecule, S is the electron spin, J and M are the total angular momentum of the molecule and its projection in an arbitrary direction, and n represents the other quantum numbers. We have also used the notation $\bar{A} \equiv -A$. It is not difficult to see that the off-diagonal matrix element of the operator (4) between the states $\psi^{\pm}$ reduces to the matrix element

$$\langle n\Lambda\Sigma SJM | V | n\Lambda\Sigma SJM \rangle,$$

since Λ and Σ change sign under inversion while the operator V cannot couple states with opposite signs of Λ and Σ in the first order. We write V in the form $V = \sum_i \mathbf{s}_i \mathbf{a}_i$, where the $\mathbf{a}_i$ are certain electron orbital vectors. Making use of the fact that the operators $\mathbf{s}_i$ are diagonal in the $n\Lambda JM$ representation, we write the matrix element of V in the form

$$\langle n\Lambda\Omega SJM | V | n\Lambda\Omega SJM \rangle = \sum_i \langle n\Lambda\Omega SJM | \mathbf{s}_i | n\Lambda\Omega SJM \rangle \langle n\Lambda\Omega SJM | \mathbf{a}_i | n\Lambda\Omega SJM \rangle, \tag{17}$$

where we have used $\Omega = \Lambda + \Sigma$ in place of the quantum number Σ. On averaging the vector $\mathbf{a}_i$ over the electron coordinates with the nuclei held fixed, the resulting average vector $\bar{\mathbf{a}}_i$ can obviously be directed only along the axis of the molecule. Hence we can write

$$\begin{aligned}&\langle n\Lambda\Omega SJM|\mathbf{a}_i|n\Lambda\Omega SJM\rangle\\&=a_i(n\Lambda)\langle n\Lambda\Omega SJM|\mathbf{n}|n\Lambda\Omega SJM\rangle,\end{aligned}$$

where $\mathbf{n}$ is a unit vector directed along the axis and the $a_i(n\Lambda)$ are constants calculated for the equilibrium separation between the nuclei.

Introducing the spin vector $\mathbf{U}$ by the definition

$$\mathbf{U}=\sum_i a_i(n\Lambda)\mathbf{s}_i,$$

we reduce the matrix element of V to

$$\langle n\Lambda\Omega SJM|\mathbf{Un}|n\Lambda\Omega SJM\rangle.$$

To calculate this matrix element we use the formula[13]

$$\begin{aligned}&\langle n\Lambda\Omega SJM|\mathbf{Un}|n\Lambda\Omega SJM\rangle\\&=\frac{1}{2J+1}\sum_{J'}\langle n\Lambda\Omega SJ\|U\|n\Lambda\Omega SJ'\rangle\langle n\Lambda\Omega SJ'\|n\|n\Lambda\Omega SJ\rangle.\end{aligned}\tag{18}$$

The reduced matrix element of U can be written[13] as

$$\begin{aligned}&\langle n\Lambda\Omega SJ\|U\|n\Lambda\Omega SJ'\rangle\\&=\langle\Lambda\Omega SJ\|n\|\Lambda\Omega SJ'\rangle\langle S\Sigma|U_\gamma|S\Sigma\rangle,\end{aligned}$$

where U_γ is the projection of the vector U onto the axis of the molecule. Thus,

$$\langle n\Lambda\Omega SJM|V|n\Lambda\Omega SJM\rangle=\frac{1}{2J+1}\langle S\Sigma|U_\gamma(n\Lambda)|S\Sigma\rangle\sum_{J'}|\langle\Lambda\Omega SJ\|n\|\Lambda\Omega SJ'\rangle|^2.\tag{19}$$

Substituting the explicit expressions[13] for the matrix elements of the vector $\mathbf{n}$ into Eq. (19), we obtain

$$\langle n\Lambda\Omega SJM|V|n\Lambda\Omega SJM\rangle=G_e\alpha^2\gamma(\Lambda\Omega S)\frac{[2J^2(J+1)-\Omega^2]}{J(J+1)(2J+1)},\tag{20}$$

where

$$G_e\alpha^2\gamma(\Lambda\Omega S)=\langle S\Sigma|U_\gamma(n\Lambda)|S\Sigma\rangle.$$

It is important that the dependence on the rotational quantum number J is separated out in this expression. Since all the other quantum numbers Λ, Ω, and S are of the order of unity, we can say that $\gamma(\Lambda\Omega S)\sim 1$ (in atomic units). On substituting expression (20) for the matrix element of V into formula (1), we finally obtain the result

$$\mathscr{P}=\frac{2G_e\alpha^2}{\Delta E}\gamma(\Lambda\Omega S)\frac{[2J^2(J+1)-\Omega^2]}{J(J+1)(2J+1)}\sqrt{\frac{W_{E1}}{W_{M1}}}.\tag{21}$$

We note that the transition probabilities W_{E1} and W_{M1} depend on J in the same way, so that this dependence cancels out in Eq. (21).

Now let us consider a molecule whose bonding falls under Hund's case b). As before we start with Eq. (17) and perform the subsequent operations, but now we use the following formula[13] in place of Eq. (18):

$$\langle n\Lambda SKJ|\mathbf{Un}|n\Lambda SKJ\rangle=(-1)^{K+S+J}\begin{Bmatrix}JSK\\1KS\end{Bmatrix}\langle\Lambda K\|n\|\Lambda K\rangle\langle S\|U(n\Lambda)\|S\rangle,\tag{22}$$

where K is the eigenvalue of the total orbital angular momentum of the molecule. Substituting the explicit expressions[13] for the $6j$ symbol and the matrix element of $\mathbf{n}$, we obtain

$$\mathscr{P}=\frac{2G_e\alpha^2}{\Delta E}\gamma(\Lambda S)\frac{[J(J+1)-K(K+1)-S(S+1)]}{K(K+1)}\sqrt{\frac{W_{E1}}{W_{M1}}},\tag{23}$$

where now

$$G_e\alpha^2\gamma(\Lambda S)=\Lambda\langle S\|U(n\Lambda)\|S\rangle.$$

We note that for singlet states the matrix element (22) vanishes and the effect is not present.

5. Let us use various examples to estimate the order of magnitude of the effect and the possibilities of observing it. The main thing to pay attention to in selecting the transitions is the fact that a magnetic transition always falls within the wing of a stronger electric transition from a neighboring Λ sublevel. In the general case one cannot avoid the effect of this wing in emission by means of a time delay, because for this it would be necessary that no allowed electric transitions to other states be possible from the sublevel on which the magnetic transition originates.

The above situation may be encountered in the case of a $^3\Pi_0(J=0)\to{}^3\Sigma^\pm(J=1)$ transition in which the Σ state is the ground state and the Π state is the first excited triplet state. Then the $^3\Pi_0(J=0)\to{}^3\Sigma^\pm(J=1)$ transition is strictly forbidden and one of the sublevels of the Λ doublet is metastable. The desired delay might be effected, for example, by using molecular beams.[14] Suitable molecules would by NH and PH,[12] but the Λ splitting of the $^3\Pi_0$ state is relatively large and $\mathscr{P}$ turns out to be small: $\mathscr{P}\sim 10^{-9}$.

Another way to avoid the effect of the wing of the electric transition is to use forbidden transitions with narrow lines. The condition that the wing of the electric transition will not reduce $\mathscr{P}$ is as follows:

$$\frac{W_{E1}}{W_{M1}}\frac{W_{E1}\Delta\omega}{(\Delta E)^2}\leqslant 1.\tag{24}$$

For this, however, it is absolutely necessary to resolve the Λ doublet, and this may not be possible in the case of metastable states; if the doublet is not resolved, the degree of circular polarization is reduced to

$$(W_{M1}/W_{E1})\mathscr{P}\sim 10^{-4}\mathscr{P}.$$

As the first example let us consider the forbidden transition $a\,{}^3\Pi_1 - X\,{}^1\Sigma^+$ in the CO molecule. According to Van Vleck[15]

$$\Delta E(^3\Pi_1)=\frac{4B^2}{\omega}J(J+1).\tag{25}$$

Taking $\omega\approx 5\times 10^4$ cm^{-1}, $B\approx 2$ cm^{-1} (Ref. 12), and $J=1$, we find $\Delta E\sim 10^{-3}$ cm^{-1}. Using the atomic estimates $\langle g|V|u\rangle\sim 10^{-16}$ Ry and $W_{E1}/W_{M1}\sim 10^4$ for the weak-interaction matrix element and the ratio of the transition probabilities for the forbidden transitions, we obtain $\mathscr{P}\sim 10^{-6}$.

A still more favorable situation should obtain for a $^3\Pi_2$ sublevel. Let us estimate the Λ splitting in this case. According to Van Vleck[15] the splitting $\Delta E(^3\Pi_2)$ is equal to the matrix element of the operator coupling the $\Lambda=1$, $\Omega=2$ and $\Lambda=-1$, $\Omega=-2$ states:

$$\Delta E(^3\Pi_2)=\langle\Lambda=1,\ \Sigma=1,\ \Omega=2|W|\Lambda=-1,\ \Sigma=-1,\ \Omega=-2\rangle.$$

The effects of such an operator appear only in the fourth order of perturbation theory in the small axis-orbit coupling H_{or}:

$$\begin{aligned}&\langle\Lambda=1,\Sigma=1,\Omega=2|W|\Lambda=-1,\Sigma=-1,\Omega=-2\rangle\\&=\langle\Lambda=1,\Sigma=1,\Omega=2|H_{or}|\Lambda=1,\Sigma=0,\Omega=1\rangle\frac{1}{\Delta E_1}\\&\times\langle\Lambda=1,\Sigma=0,\Omega=1|H_{or}|\Lambda=1,\Sigma=-1,\Omega=0\rangle\frac{1}{\Delta E_2}\\&\times\langle\Lambda=1,\Sigma=-1,\Omega=0|H_{or}|\Lambda=0,\Sigma=-1,\Omega=-1\rangle\frac{1}{\Delta E_3}\\&\times\langle\Lambda=0,\Sigma=-1,\Omega=-1|H_{or}|\Lambda=-1,\Sigma=-1,\Omega=-2\rangle.\end{aligned}\tag{26}$$

The matrix elements of H_{or} have the form[13]

$$\langle\Lambda,\ \Sigma,\ \Omega,\ J|H_{or}|\Lambda',\ \Sigma',\ \Omega-1,\ J\rangle=B\gamma(\Lambda\Sigma\Lambda'\Sigma')[(J+\Omega)(J+1-\Omega)]^{1/2}.\tag{27}$$

The energy denominators ΔE_1 and ΔE_2 in (26) are of the order of the intramultiplet splittings $\Delta E_1\sim\Delta E_2\sim A$, while ΔE_3 is of the order of the intermultiplet separations $\Delta E_3\sim\omega$. Therefore, using formula (27), we obtain

$$\Delta E(^3\Pi_2)\sim\frac{B^2}{\omega}\left(\frac{B}{A}\right)^2(J-1)J(J+1)(J+2).\tag{28}$$

Using the same values of ω and B as for the $^3\Pi_1$ level together with the estimate $A\sim\alpha^2(\mathrm{Ry}/\omega)\mathrm{Ry}\sim10^2$ cm^{-1}, we obtain $\Delta E\sim10^{-6}$ cm^{-1} and $\mathscr{P}\sim10^{-3}$ for $J=2$.

Analogous $a\,^3\Pi-X\,^1\Sigma^+$ transitions can also be considered in the SiO and SiS molecules, in which transitions from the $^3\Pi_1$ level have recently been observed.[16,17] For SiO we have[16] $\omega\approx3.5\times10^4$ cm^{-1}, $A\approx73$ cm^{-1}, and $B\approx0.7$ cm^{-1}; this gives

$$\begin{aligned}&\Delta E(^3\Pi_1)\sim10^{-4}\ \mathrm{cm}^{-1},\quad \mathscr{P}(^3\Pi_1)\sim10^{-5},\\&\Delta E(^3\Pi_2)\sim2\cdot10^{-8}\ \mathrm{cm}^{-1},\quad \mathscr{P}(^3\Pi_2)\sim5\cdot10^{-2}.\end{aligned}$$

For SiS we have[17] $\omega\approx3\times10^4$ cm^{-1} and $B\approx0.3$ cm^{-1}; then using the estimate $A\sim10^2$ cm^{-1} again, we obtain

$$\begin{aligned}&\Delta E(^3\Pi_1)\sim3\cdot10^{-6}\ \mathrm{cm}^{-1},\quad \mathscr{P}(^3\Pi_1)\sim3\cdot10^{-4},\\&\Delta E(^3\Pi_2)\sim10^{-9}\ \mathrm{cm}^{-1},\quad \mathscr{P}(^3\Pi_2)\sim1.\end{aligned}$$

Condition (24) is satisfied for all the cases listed above except the last one. In the last case, however, we do not have to resolve the Λ doublet, since $\mathscr{P}\sim1$: the degree of circular polarization will be $\sim10^{-4}$ even if the doublet is not resolved.

Finally, we shall give the limitation on the electric fringe fields that might be present in the apparatus, which could reduce $\mathscr{P}$ because of Stark broadening. The necessary condition that this effect is negligible is

$$\mathscr{E}\langle d\rangle/\Delta E<\sqrt{W_{M1}/W_{E1}}\sim10^{-2},\tag{29}$$

where $\mathscr{E}$ is the electric field strength, $\langle d\rangle$ is the Stark matrix element, and ΔE is the level splitting. For the $^3\Pi_2-{}^1\Sigma^+$ transitions in CO and SiS, this condition reduces to $\mathscr{E}<10^{-4}$ V/cm and $\mathscr{E}<10^{-7}$ V/cm, respectively.

In concluding, let us once again emphasize the reasons why certain of the experiments described above seem realistic to us. First, by now the technique for measuring the rotation of the plane of polarization of light in laser experiments through angles of the order of 10^{-8}–10^{9} rad has been virtually mastered. This makes it possible seriously to discuss the experiment on molecular oxygen described in Sec. 3. Second, modern methods of laser spectroscopy make it possible to resolve lines with separations of ~10 kHz, and this is adequate for observing the $^3\Pi_1-{}^1\Sigma^+$ magnetic transition in SiS. Finally, an attempt to detect the $^3\Pi_2-{}^1\Sigma^+$ transition in SiS and to measure its comparatively high degree of circular polarization also seems to be fairly realistic.

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