PHYSICAL REVIEW VOLUME 128, NUMBER 2 OCTOBER 15, 1962

Similarity between the Spin-Spin and Spin-Orbit Interactions in the Diatomic Molecules

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(Received May 10, 1962)

It has been shown that the spin-spin and spin-orbit interactions furnish, in the first approximation, expressions of the same form in the multiplet splitting of the Σ and Π terms of higher multiplicity than the doublet, as well as in the case of the Λ-type doubling of the Π terms. The splittings observed experimentally can be attributed to the combined effect of these two interactions.

THE spin-spin as well as the spin-orbit interaction plays an important role in the theoretical interpretation of the fine structure of the diatomic molecules. It has already been pointed out by Hebb[1] that for the multiplet splitting of the $^3\Sigma$ term the second-order perturbations of the spin-orbit interaction lead to exactly the same expressions as have been given by the spin-spin interaction in first-order perturbations introduced earlier by Kramers.[2] Thus, owing to the identical structure of the expressions as a function of the rotational quantum number, the splittings observed experimentally are to be considered as the sum of the two effects. The same results have been obtained by Budó and Kovács[3] in their investigation of the multiplet splittings of the $^4\Sigma$, and by the present author[4] for the $^5\Sigma$, $^6\Sigma$, and $^7\Sigma$ terms, respectively.

Later on it became evident that the spin-spin and spin-orbit interactions play an important part in the case of the multiplet splittings, not only of the Σ terms but of the Π terms as well. For, quite recently, deviations have been observed for a few molecules (such as NH, PH, O_2^+) from the well-known $^3\Pi$ and $^4\Pi$ multiplet term formulas derived for the intermediate case between Hund's cases (a) and (b). In these cases it has been shown by the present author that the "anomalous" multiplet splitting is caused by not taking into account the spin-spin interaction and the spin-orbit interaction of exactly the same structure,[5–7] in the case of the formulas mentioned.

Hence, it can be stated that—with the exception of the doublet terms where spin-spin interaction cannot possibly be assumed because outside the closed shell there exists only one electron—in the case of the Σ and Π terms of higher multiplicity for the theoretical interpretation of the multiplet splitting, both the spin-spin and spin-orbit interactions have to be taken into account; these two entirely different mechanisms furnish in the first approximation results of exactly the same form.

Most recently, Fontana[8] has dealt with the examination of the Λ-type doubling of the $^3\Pi$ term in Hund's case (b). He has pointed out that taking into account the spin-spin interaction supplies new terms, hitherto unknown, for this splitting. Omitting the interaction between the orbital angular moment and the rotation of the nuclei, these terms are the following:

$$h\Delta\nu(^3\Pi_{N=J+1})=\epsilon\frac{N+1}{2N-1},$$
$$h\Delta\nu(^3\Pi_{N=J})=\epsilon, \tag{1}$$
$$h\Delta\nu(^3\Pi_{N=J-1})=\epsilon\frac{N}{2N+3},$$

where

$$\epsilon=\alpha^2(Z^*)^3/80.$$

The same question has been dealt with by the author in one of his earlier works,[9] where, taking into account the spin-orbit interaction as well as the interaction between the orbital angular moment and the rotation of the nuclei, he obtained the following expressions for the Λ-type splitting of the $^3\Pi$ term in Hund's case (b):

$$h\Delta\nu(^3\Pi_{N=J+1})=\tfrac{1}{2}C_0\frac{N+1}{2N-1}+C_1(N+1)+C_2N(N+1),$$
$$h\Delta\nu(^3\Pi_{N=J})=\tfrac{1}{2}C_0-C_1-C_2N(N+1), \tag{2}$$
$$h\Delta\nu(^3\Pi_{N=J-1})=\tfrac{1}{2}C_0\frac{N}{2N+3}-C_1N+C_2N(N+1),$$

where

$$C_0=\sum_k\frac{(-1)^\Sigma|\xi(^3\Pi,{}^3\Sigma_k)|^2}{h\nu(^3\Pi,{}^3\Sigma_k)}-\sum_k\frac{(-1)^\Sigma|\xi(^3\Pi,{}^1\Sigma_k)|^2}{h\nu(^3\Pi,{}^1\Sigma_k)},$$
$$C_1=4\sum_k\frac{(-1)^\Sigma|\xi(^3\Pi,{}^3\Sigma_k)\eta(^3\Pi,{}^3\Sigma_k)|}{h\nu(^3\Pi,{}^3\Sigma_k)};$$
$$C_2=8\sum_k\frac{(-1)^\Sigma|\eta(^3\Pi,{}^3\Sigma_k)|^2}{h\nu(^3\Pi,{}^3\Sigma_k)},$$

and ξ and η are the constants occurring in the matrix elements of the spin-orbit interaction and of the spin-

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rotation interaction, respectively, the Σ appearing in the exponent being 0 or 1 according to whether the Σ term in question is the Σ^+ or Σ^- term.

At a glance it is clear that formula (1) and the first members of the right side of (2), which then come directly from the spin-orbit interaction, are formally identical; thus, upon the Λ-type splitting of the $^3\Pi$ term in Hund's case (b) the spin-spin interaction again supplies exactly the same expressions as the perturbations transmitted by the spin-orbit interaction. Consequently, it is without doubt that the coefficient of the first term of the formula (2) is correctly: $\beta=\epsilon+\frac{1}{2}C_0$, that is, the Λ splittings observed experimentally can be traced back to the combined effect of these two interactions. Obviously, the same is true of the Λ-type splitting of the $^4\Pi$ terms in Hund's case (b) whose explicit expressions the author, by taking into account the spin-orbit interaction, has formerly given also.[10]

Summarizing, it can be concluded that in the multiplet splittings of the Σ and Π terms of higher multiplicity than the doublet, as well as in the Λ-type doubling of the Π terms in the first approximation, the spin-spin and the spin-orbit interactions give expressions of the same form, and the splittings observed experimentally can be attributed to the combined effect of the two interactions.

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PHYSICAL REVIEW VOLUME 128, NUMBER 2 OCTOBER 15, 1962

Harmonics in the Scattering of Light by Free Electrons

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(Received March 12, 1962; revised manuscript received June 18, 1962)

The presence of harmonics in the scattering of light by free electrons is pointed out. The cross section for the second harmonic is proportional to the energy flux and to the square of the wavelength of the incident light. Thus experiments in which intense monochromatic microwave beams are scattered by plasmas are the most promising for the detection of the effect.

INTRODUCTION

THE author and Punhani[1,2] have recently pointed out that classical electrodynamics predicts the presence of harmonics in the radiation scattered by *free* electrons. The reason for this is simple to understand if we write the equations of motion of the electron in a plane light wave field taking account not only of its electric vector,[3] $\mathbf{E}=\mathbf{E}_0\cos\omega$, but also of the magnetic vector, $\mathbf{H}=\mathbf{H}_0\cos\omega$. Since the velocity, $\mathbf{v}$, of the electron is proportional to $\sin\omega$, the magnetic force, $e\mathbf{v}\times\mathbf{H}$, is proportional to $\sin\omega\cos\omega$, i.e., to $\sin2\omega$. One can therefore at once see that the electron will oscillate not only with frequency k_0 but also with $2k_0$, which, in turn, will give rise to scattered electromagnetic waves of half the incident wavelength. The following calculation shows that if intense monochromatic beams of the same order as those obtained with ruby lasers are available in the microwave region, the cross section for the second harmonic will be comparable with that for the principal mode (the Thomson cross section), but the effect is too small in the optical region to be measurable with the present devices [see Eqs. (14)–(18)].

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[3] $\omega=k_0z_0-\mathbf{k}\cdot\mathbf{z}$; $(z_0,\mathbf{z})$ are the time-space coordinates of the electron; $|\mathbf{H}_0|=|\mathbf{E}_0|=E_0$.

ELECTRON EQUATIONS OF MOTION

It has been shown in reference 2 that the relativistic electron equations of motion,

$$m\dot{v}_\mu=ev^\alpha f_{\alpha\mu}\cos\omega,\quad \mu,\alpha=0,1,2,3, \tag{1}$$

where

$$(f_{01},f_{02},f_{03})=\mathbf{E}_0,\quad (f_{23},f_{31},f_{12})=\mathbf{H}_0,$$
$$v_\mu=dz_\mu/d\tau,\quad \dot{v}_\mu=dv_\mu/d\tau,\quad d\tau=dz_0[1-(d\mathbf{z}/dz_0)^2]^{1/2},$$

(m=electron mass, speed of light=1), can be solved exactly. If we use a coordinate system in which the electron has no translatory motion, the origin is taken at the mean position around which it oscillates, and the clocks are so adjusted that the zero of the observer's time, z_0, coincides with the zero of the electron proper time, τ, the solution of (1) is

$$k_0z_0=k_0'\tau-\tfrac{1}{8}q'\sin(2k_0'\tau), \tag{2a}$$

$$k_0\mathbf{z}=-\mathbf{e}_\mathrm{o}(eE_\mathrm{o}/mk_0')\cos(k_0'\tau)-\mathbf{n}_\mathrm{o}\tfrac{1}{8}q'\sin(2k_0'\tau), \tag{2b}$$

where

$$\mathbf{e}_\mathrm{o}=\mathbf{E}_\mathrm{o}/E_\mathrm{o},\quad \mathbf{n}_\mathrm{o}=\mathbf{k}/k_0,\quad k_0'=k_0(1+\tfrac{1}{2}q)^{1/2},$$
$$q'=(k_0/k_0')^2q,\quad q=e^2E_\mathrm{o}^2/m^2k_0^2. \tag{3}$$

The occurrence of k_0' in (2a) and (2b) does not imply that the frequency of the observed radiation will change. The reason is that the frequency which an observer