EFFECT OF INHOMOGENEOUS FIELD OF CHARGED PARTICLES ON SHIFT OF TERMS IN GAS DISCHARGES

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The theory of Debye [1] and Holstmark [2] applicable to calculations of the intermolecular electric field is limited by homogeneous mean fields. Consequently, the effect of intermolecular fields leads to the homogeneous Stark effect and changes both the intensity of spontaneous lines and the selection rules for the "forced" lines radiating in a homogeneous field. Moreover, the limitation of Holstmark's theory lies in the incapability to explain the results of Bartels [3] for a shift of Na terms in an arc: the assumption made by Bartels that the results of the Stark effect theory are in general applicable only to low states contradicts the results of Olbers [4] who revealed that the theory fits the experiments for high terms as well.

The present work studies the possibility to explain the shift of terms in an arc as a result of the effect of an inhomogeneous electric field. Only the spatial inhomogeneity is considered herein.

1. Let us consider an atom in the external inhomogeneous field $\mathbf{F}(x,y,z)$. We choose the origin of a coordinate system at the mass center of the radiating atom and expand the field strength in a series:

$$\mathbf{F}(x,y,z)=\mathbf{F}(0)+\left(\frac{\partial \mathbf{F}}{\partial x}\right)_0 x+\left(\frac{\partial \mathbf{F}}{\partial y}\right)_0 y+ +\left(\frac{\partial \mathbf{F}}{\partial z}\right)_0 z+\cdots \tag{1}$$

For brevity, we call the first term $\mathbf{F}(0)$ as the "homogeneous" field, and the rest part as the "inhomogeneous" field. If we consider only the "homogeneous" field in (1), then, except for hydrogen, we obtain the square Stark effect for a shift of terms, and the selection rules for the "forced" lines of a one-electron atom are as follows [5]: $\Delta L=0,\ \pm 2$; $\Delta J=0,\ \pm 1,\ \pm 2$. Whereas the "inhomogeneous" field provides the following selection rules for "forced" lines: $\Delta L=\pm 1,\ \pm 3$; $\Delta J=0,\ \pm 1,\ \pm 2,\ \pm 3$. Thus, the existence of 2P–mP series points out the effect of the "homogeneous" field $\mathbf{F}(0)$.

From a general Bartels' indication concerning the intensity of lines of the series 2P–mP, it can be concluded that the "homogeneous" field strength is of the order of 10^2 V/cm, while the strength can be estimated as 10^3-10^4 V/cm from the shift of lines, by assuming the presence of the square Stark effect. The discrepancy between the field strength values estimated from the intensity of "forced" lines and from the shift of lines was also established by Paschen [6] under similar conditions.

2. We choose the coordinate system so that $\left(\frac{\partial F_x}{\partial y}\right)_0=\left(\frac{\partial F_y}{\partial z}\right)_0=\left(\frac{\partial F_z}{\partial x}\right)_0=0$ and take the condition $(\mathrm{div}\mathbf{F})_0=0$ into account. Then the perturbation energy can be written as

$$\Phi=e\left\{\frac{1}{2}[F_x(0)-iF_y(0)](x+iy)+ +\frac{1}{2}[F_x(0)+iF_y(0)](x-iy)+F_z(0)z\right\}+ +\frac{1}{8}e\left\{\left[\left(\frac{\partial F_x}{\partial x}\right)_0-\left(\frac{\partial F_y}{\partial y}\right)_0\right][(x+iy)^2+(x-iy)^2]+ +4\left(\frac{\partial F_z}{\partial z}\right)_0\left[z^2-\frac{1}{2}(x^2+y^2)\right]\right\}+\cdots \tag{2}$$

By assuming, in agreement with the above consideration, that the "homogeneous" field is weak, we can restrict ourselves to the first-order effect.

For a degenerate or quasidegenerate state, the zero approximation of the perturbed eigenfunction takes the form

$$\psi_{k\nu}=\sum_i \alpha_{\nu i}\psi_{ki}, \tag{3}$$

where ψ_{ki} are the unperturbed eigenfunctions corresponding to the eigenvalue E_k or to the eigenvalues $E_{k1},\ E_{k2},\ldots$, whose difference is small in comparison with the splitting of the E_{ki} level in the external field $\mathbf{F}$, and quadrupole transitions can occur between them, according to (2). For the initial eigenfunctions, the following relations are valid:

$$(\psi_{k\nu}, \Phi\psi_{k\mu}) = 0, \qquad \nu \neq \mu. \tag{4}$$

Thus, the first approximation of the eigenvalue can be written as follows:

$$E^{(1)}_{k\nu} = (\psi^{(0)}_{k\nu}, \Phi\psi_{k\nu}) = \sum_i \sum_l \alpha_{\nu i}\alpha_{\nu l}(\psi_{ki}, \Phi\psi_{kl}). \tag{5}$$

It follows from (2) that $(\psi_{ki},\ \Phi\psi_{kl})$ are quadrupole moments. The selection rules for quadrupole moments [7] yield $E^{(1)}_{k\nu} \neq 0$ if $J \geq 1$. Hence, in the "inhomogeneous" field, we can observe the first-order effect, whereas the homogeneous field produces a square Stark effect. Normally, in the intermolecular field, the effects of "homogeneous" and "inhomogeneous" fields superimpose on each other.

It follows from the calculations for particular cases that, except the terms with $J = 3/2$, the terms are split bidirectionally and asymmetrically, which makes them different both from the linear and square Stark effects. The term $J = 3/2$ is split in a symmetric way.

If the splitting in the "inhomogeneous" field is much bigger than the doublet splitting (in a "strong" field), then the ^{2}P level splitting is asymmetric.

In the case of normal multiplets, quadrupole moments take the form

$$(Q)^{n,L,J,M}_{n',L',J',M'} = A^{n,L}_{n',L'} \cdot \beta^{L,J}_{L',J'} \cdot \alpha^{J,M}_{J',M'};$$

$$Q = (x \pm iy)^2, \quad z^2 - \frac{1}{2}(x^2 + y^2). \tag{6}$$

If E_{k1}, E_{k2},... belong to the same multiplet, relation (5) can be written as

$$E^{(1)}_{k\nu} = A(n,L) \sum_i \sum_l \alpha_{\nu i}\alpha_{\nu l}\overline{\Phi}^{L,J,M}_{L,J',M'};$$

$$\overline{\Phi}^{L,J,M}_{L,J',M'} = \frac{1}{A(n,L)}(\psi_{ki}, \Phi\psi_{kl}), \tag{7}$$

where $A(n,L)$ depends only on the principal and azimuthal quantum numbers. Thus, the splitting increases with the principal quantum number proportionally to $A(n,L)$. If E_{k1} and E_{k2} belong to the same doublet, then, for a one-electron atom, we get

$$A(n,L) = \overline{(r^2)}_{n,L} \tag{8}$$

after simple calculations. Hence, the shift in the "inhomogeneous" field increases proportionally to n^4 in this approximation.

The square Stark effect theory confirmed by the experimental results of Olbers for the Na spectrum gives the growth of a shift proportional to n^7. It was Bartels who discovered the growth of a shift of the P terms proportional to n^3 in a Na arc. With regard for the possible complications on the experimental estimation of a shift of the terms and the uncertainty of the intermolecular "inhomogeneous" field, we can conclude that the agreement between the theory of the effect of "inhomogeneous" field and Bartels' results is very good.

3. Finally, we show that the assumption concerning the effect of the "inhomogeneous" field on atom spectra in gas discharges does not lead to any contradiction. In this case, we restrict ourselves to an elementary consideration which enables us, nevertheless, the opportunity to make some general conclusions and to estimate the order of magnitude of the effect.

a) We assume that the electric field is induced by a single particle with a charge $e_1 = \pm e$. Let the position of the particle be defined by the radius-vector $\mathbf{d}(\xi, \eta, \zeta)$ which is directed along the positive direction of the z axis. Then we obtain

$$\Phi = \mp\frac{e^2}{d^2}z \mp \frac{e^2}{d^3}\left[z^2 - \frac{1}{2}(x^2 + y^2)\right] \mp \ldots \tag{9}$$

The shift for the square Stark effect $\Delta E^{(2)}$ can be calculated from Unsöld's relation [8]. For the shift in the axisymmetric "inhomogeneous" field, we obtain

$$\Delta E^{(1)} = \mp h\mathrm{Ry}\left(\frac{a_0}{d}\right)^3 \frac{n^2}{4z^2(2L-1)(2L+3)} \times$$

$$\times[5n^2 + 1 - 3L(L+1)][L(L+1) - 3M_L^2], \tag{10}$$

where Ry is the Rydberg constant, and a_0 is the radius of the first Bohr orbit.

Thus, the order of the ratio of shifts in the "homogeneous" and "inhomogeneous" fields of one particle is

$$\frac{\Delta E^{(2)}}{\Delta E^{(1)}} \sim \frac{a_0}{d}\frac{h\mathrm{Ry}}{E(n,L) - E(n,L+1)} \tag{11}$$

or

$$\frac{\Delta E^{(2)}}{\Delta E^{(1)}} \sim \frac{a_0}{d}\frac{h\mathrm{Ry}}{E(n,L) - E(n,L-1)}. \tag{12}$$

Hence, in the case of the field induced by one particle, the effect of the "inhomogeneous" field can be stronger for low terms if we take that $a_0/d \sim 10^{-3}$. For higher terms, the main shift in this case is produced by the square "homogeneous" Stark effect.

b) Since the field strength and its derivatives decrease very fast with increase in the distance, a noticeable field is induced by charged particles with small distances to the radiating atom. Let us assume that, in the vicinity of the radiating atom, there are $2n$ charged particles with positions determined by the radius-vectors $\mathbf{d}_i(\xi_i, \eta_i, \zeta_i)$. Then, the perturbation energy is as follows:

$$\Phi = -\sum_{i=1}^{2n} \frac{ee_i}{d_i^3}(\mathbf{r}, \mathbf{d}_i) + \frac{1}{2}\sum_{i=1}^{2n} \frac{ee_i}{d_i^5}[r^2 d_i^2 - -3(\mathbf{r}, \mathbf{d}_i)^2] + \dots \quad (13)$$

We assume also that the charged particles are disposed approximately symmetrically so that $\mathbf{d}_k \sim -\mathbf{d}_i$. Then, for particles with equal charges ($e_k = e_i$), the “homogeneous” field vanishes, whereas, for opposite charges ($e_k = -e_i$), the “inhomogeneous” field becomes zero.

Generalizing this conclusion, we can claim that particles with equal charges intensify the “inhomogeneous” field and weaken the “homogeneous” field. On the contrary, particles with opposite charges intensify the “homogeneous” field and weaken the “inhomogeneous” field. Hence, we can prove that, in Bartels’ and Paschen’s works, “homogeneous” fields are weak, and “inhomogeneous” fields are strong.

c) For the purpose of verification, we carried out the approximate calculations of the distances from charged particles to the excited atoms in order to obtain the shifts of terms found by Bartels. Let us suppose that the “inhomogeneous” field is induced by a single charged particle and assume $M_L = \pm 1$ in (10). Then d/a_0 varies from 1140 for $n = 9$ to 1460 for $n = 19$. For $M_L = 0$, d/a_0 increases from 900 at $n = 9$ to 1160 at $n = 19$. If the “inhomogeneous” field is induced by a greater number of charged particles, then d/a_0 will be great. The average atom radius a_n increases from $a_9 = 120a_0$ to $a_{19} = 540a_0$. Hence, the necessary distances between the charged particles are a few times bigger than the atom radius. Found in this way, the order of magnitude of the distances from charged particles to the excited atom coincides with that given by kinetic theory.

Thus, the shift of terms proportional to n^4 proves the existence of the inhomogeneous field effect in gas discharges.

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Vasyl Milianchuk born in Dobrovidka, Ivano-Frankivsk region. He studied at the Mathematics–Natural Sciences Faculty of the Lviv University (1926–1927), as well as at Lviv Polytechnics (1927–1933). In 1933–1939, he was an Assistant at the Department for Theoretical Physics of Lviv University. In 1935, he had a probation at the Institute of Physics of Warsaw University and another probation at the Physics Institute of Leipzig University in 1936, where Heisenberg, Hund, and Debye worked at that time. In 1940, Vasyl Milianchuk became Professor at the Department for Theoretical Mechanics of Lviv University. From 1945 till the end of his life, Milianchuk was Head of the Department for Theoretical Physics there.

The scientific work of Vasyl Milianchuk is rather diverse. First of all, one should mention the calculations of the intensities and polarizations of magnetically split quadrupole doublets and the study of the transverse and longitudinal Zeeman effects and Compton scattering (the 1930s). For these works, Vasyl Milianchuk was elected a Full Member of the Shevchenko Scientific Society (1932), and he became a Doctor of Philosophy in 1935. After the war, his scientific interests included the effect of an inhomogeneous electric field in the gas-discharge plasma on the spectral lines; problems of mesodynamics with higher derivatives; theory of meson-nucleon collisions; theory of slow molecular collisions; selected problems of the theory of self-energy of elementary particles and their radiation scattering. In 1946, as a pre-war Doctor of Philosophy, Vasyl Milianchuk was qualified as a Candidate of Sciences and as a Docent. In 1957, he defended the thesis “The effect of inhomogeneous inter-molecular fields on atomic spectra” and received the degree of Doctor of Sciences and, later on, Professor (1958). Vasyl Milianchuk is one of the founders of the Lviv school of spectroscopy. He was the author of about thirty scientific works, in particular: Zeeman effect of quadrupole lines according to the Dirac theory (Zs. Phys. **74**, 350 (1932)); On the issue of sum rules in “enforced” dipole multiplets (Collection of mathematical, natural sciences and medical section of the Shevchenko Scientific Society **30** (1936)); Effect of inhomogeneous field of charged particles on shift of terms in gas discharges (Dokl. Akad. Nauk SSSR **59**, 667 (1948)); On a possibility of constructing a generalized linear electrodynamics (Dokl. Akad. Nauk SSSR **71**, 871 (1950)); On the issue of the generalized linear electrodynamics (Proceedings of Lviv University, No. 5 (1953)).