

Spectral exchange in collision broadening of rotational structure

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(Submitted September 11, 1973)

Zh. Eksp. Teor. Fiz. **66**, 894-906 (March 1974)

The rate of spectral exchange between the rotational structure components in isotropic space and in an external field is determined. It is found that spectral exchange is an essentially nonadiabatic phenomenon and that its retention in current classical theory in the elastic collision approximation, and its complete absence in the nonadiabatic quantum theory, is erroneous. After suitable adjustment the two theories have been made consistent with each other. In the course of this it turned out that spectral exchange manifests itself by an unusual transformation (collapse) of the Stark and rotational structure with increasing pressure. Detection of such collapse enables one to establish whether the collisions are "strong" or "weak" and to determine the degree to which they are nonadiabatic.

INTRODUCTION

In the existing literature two different approaches to the problem of the broadening of rotational structure have been established: the quantum and the classical approach. Although both approaches are legitimate, in their present form they are not consistent, and even contradict each other. The majority of the quantum calculations^[1-3] derive from the fundamental paper of Anderson^[4] which laid the foundations of nonadiabatic collision theory. They are all based on a theorem proved by Anderson, according to which the rotational spectrum of molecular gases in the absence of external fields consists of lines which are independently broadened, with each of them, in spite of multiple m-degeneracy of terms which combine in the transition, being characterized by a single relaxation parameter which determines its width and shift. The classical approach has been developed by Gordon^[5-7] who showed that collisions can not only alter the phase of a rotating dipole, thereby giving rise to the usual line broadening, but also can reverse the direction of rotation of the rotator (polarization of the radiation) transforming a P-component of the spectrum into an R-component, and vice versa. A P-R-exchange of this kind, together with the spectral exchange associated with a change in frequency as the result of a collision (j-diffusion), is the cause of a coordinated transformation of all the components of the rotational spectrum which exchange among themselves. The presence in the classical theory of this additional source of broadening of the resolved structure forces one to prefer it in those cases when a considerable discrepancy is discovered between the experimental data and the corresponding quantum estimates of the widths^[7-9].

Such a situation can not be acknowledged to be normal. An exchange between lines of rotational structure ought to be described by quantum theory no worse than by a classical theory, if such a phenomenon has an objective existence. And, conversely, in a situation when Anderson's theorem holds it must disappear in classical theory for the same reasons as in quantum theory. The fact that in quantum theory exchange is always ignored while in classical theory it never disappears merely testifies to the inadequacy of both.

In the present paper both theories, the classical and the quantum theory, are subjected to a revision and are intercompared after the necessary correction. As has been established, spectral exchange within a rotational

structure is absent in quantum theory exclusively due to neglecting the nonadiabatic transitions between different rotational terms. This is well founded if collisions are of an adiabatic nature ($\omega_0\tau_C \gg 1$), and has no justification if they are such as they were taken to be in^[4] on the assumption that $\omega_0\tau_C = 0$ (ω_0 is the rotational frequency, τ_C is the duration of a collision). After a suitable generalization of Anderson's theorem it has been established that also in a not so extreme nonadiabatic situation ($\omega_0\tau_C \ll 1$) all the lines of the rotational spectrum in quantum theory, as in classical theory, are interrelated by j-diffusion, and over and above this pairwise by P-R-exchange. And conversely, under adiabatic conditions, when in accordance with Anderson's theorem all these lines should be broadened independently of one another, exchange between them is exponentially small and can be omitted from consideration. The retention of P-R-exchange in the classical theory of Gordon^[5C] in the case of elastic collisions is a fiction which disappears after an actual averaging of the result of the collision over impact parameters which has not been carried out by the author. Just as in the case of quantum theory, this result is a direct consequence of the rotational isotropy of space which, together with the adiabatic nature of collisions, is a necessary condition for the validity of Anderson's theorem.

In the present paper it is shown that in just the same manner in which the nonadiabatic nature of collisions includes exchange between different rotational lines, a violation of isotropy of space, even by a weak field and only over a free path, gives rise to exchange between similarly polarized components of a line split by the field which is brought about by means of adiabatic collisions. An essentially quantum definition of the frequency of P-R-exchange and a quasiclassical estimate of the rate of exchange processes interconnecting components of the structure split by the field has been obtained. The essential generalization and simplification of the theory which made this possible has been achieved by means of decomposing the collision operator in terms of an irreducible tensor representation.

As is well known, every exchange manifests itself by the fact that the lines of the resolved structure which it interconnects are at first broadened and shifted proportionally to the square of the pressure, and then merge at the center of gravity of the spectrum (collapse of the structure) forming at high densities a single homogeneously broadened line. This effect can be easily distin-

guished against the background of the usual broadening and shift linear in terms of the pressure. In accordance with the above, a comparison of the frequency of P-R-exchange with the width of the line enables one to draw conclusions concerning the degree of nonadiabaticity of collisions, while exchange within the Stark or Zeeman structure characterizes the "strength" of the collision, becoming comparable to the width in the case of a weak interaction and disappearing in the case of a complete phase upset.

1. CLASSICAL THEORY

The evolution of the dipole moment of a diatomic molecule which has undergone n collisions at instants $t_1, t_2, \dots, t_k, \dots, t_n$, can be traced from beginning to end in any realization of the process. For this it is sufficient to note that in the system of coordinates whose z' axis is at all times oriented along the rotational angular momentum of the molecule $j(t)$, while the x' axis is oriented along its dipole moment $d(t)$, the latter always has the form $d'(t) = d'(0) = d$. Without restricting the generality of the discussion one can assume that at the initial instant the dipole moment is oriented along the x axis of the laboratory coordinate system: $d(0) = \{d, 0, 0\}$. Its position at the instant t in this system is determined by the transformation of coordinates $R(t)$ which relates it to the moving coordinate system: $d(t) = dR(t)$. It consists of a sequence of rotations which correspond in turn to the free path ($L(t_k - t_{k-1})$) and the collisions (U_k), which in accordance with the sense of the impact approximation are regarded as instantaneous:

$$R(t) = L(t - t_n) U_n \dots L(t_2 - t_1) U_1 L(t_1). \quad (1.1)$$

The operator L rotates the system about the z' axis by an angle $\omega_0(t_k - t_{k-1})$, while the rotation described by U_k depends on the mechanism of the collision and on its impact parameters.

In order to obtain an equation for the average evolution operator $\bar{R}(t)$ it is necessary to carry out an averaging over the stochastic sequence of the instants of collisions and over all possible results of these collisions. For this it is sufficient to utilize the general procedure of summing such realizations which was developed in [10b] and which yields

$$\dot{\bar{R}}(t) = (\omega_0 - \Pi) \bar{R}(t), \quad (1.2)$$

where

$$\omega_0 = \begin{pmatrix} 0 & \omega_0 & 0 \\ -\omega_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \Pi = \langle \tau_0^{-1} (1 - U) \rangle, \quad (1.2a)$$

here τ_0 is the mean duration of a free path, while averaging denoted by angular brackets is performed over different impact parameters of the collision.

From the form of (1.2) it follows that if \bar{R} commutes with $\omega_0 - \Pi$ at the initial instant, then this property is conserved in future. But $\bar{R}(0) = 1$ and, consequently, the operators on the right hand side of (1.2) can have their positions interchanged, and after this multiplication on the left by d leads to the equation

$$\dot{d}(t) = d(\omega_0 - \Pi). \quad (1.3)$$

The symbol indicating averaging above $d(t)$ is omitted both here and in future.

In order to attain uniformity in the classical and the quantum description of relaxation we go over to the

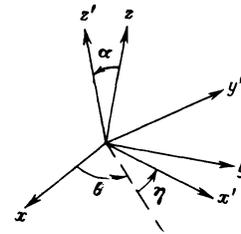


FIG. 1

variables $d_q = d_i A_{iq}$ ($i = x, y, z$; $q = 0, \pm 1$) in such a manner that

$$d_0 = d_z, \quad d_{\pm 1} = \mp 2^{-1/2} (d_x \pm i d_y). \quad (1.4)$$

Then in the kinetic equation obtained from (1.3)

$$\dot{d}_q = (i\omega_0 q \delta_{q'q} - P_{q'q}) d_{q'}, \quad (1.5)$$

the matrix ω_0 is diagonalized, while the collision operator which was initially diagonal now is transformed into

$$P_{q'q} = \langle \tau_0^{-1} [\delta_{q'q} - (A^{-1} \Pi A)_{q'q}] \rangle = \langle \tau_0^{-1} (\delta_{q'q} - D_{q'q}) \rangle, \quad (1.6)$$

where $D_{q'q}(\theta - \pi/2, \alpha, \eta + \pi/2)$ is the matrix of finite rotations [11] the sequence of which is taken to be the same as in [5]: about z by an angle θ , about x by an angle α , about z by an angle η (Fig. 1).

Since a deflection of j in both directions from its initial direction ($\alpha \geq 0$) is brought about by a collision with equal probability, all the elements of the matrix (1.6) odd in α vanish as a result of averaging. In consequence of this it turns out that the relaxation of d_0 is not related to the other $d_{\pm 1}$, and is completely absent in the case of a linear molecule, since from the outset $d_0 = 0$. Thus, (1.5) represents a two-component equation in terms of $d_{\pm 1}$ with

$$P_{q'q} = \begin{pmatrix} \langle \tau_0^{-1} [1 - \cos^2 \frac{\alpha}{2} e^{i(\theta+n)}] \rangle & \langle \tau_0^{-1} \sin^2 \frac{\alpha}{2} e^{i(\theta-n)} \rangle \\ \langle \tau_0^{-1} \sin^2 \frac{\alpha}{2} e^{-i(\theta-n)} \rangle & \langle \tau_0^{-1} [1 - \cos^2 \frac{\alpha}{2} e^{-i(\theta+n)}] \rangle \end{pmatrix}. \quad (1.7)$$

The diagonal elements of this matrix provide for the ordinary broadening and shift of lines of appropriate polarization ($q = \pm 1$), while the nondiagonal elements provide for the exchange between them. The existence of the latter elements was first noted by Gordon [5c], however, in determining the matrix $P_{q'q}$, Gordon unjustifiably assumed that the two angles α and η were quite sufficient to describe the result of the collision. In doing so he assumed that η is nothing other than the jump in the phase of the rotating dipole.

But none of the angles of rotation in (1.7) is superfluous and their connection with the jump in the phase is not so simple. Moreover, not having the aim of actually carrying out the averaging denoted by the angular brackets, Gordon essentially left open the question whether exchange is in reality taking place or not. The point is that the nondiagonal elements of (1.7), and at the same time the effect of exchange can disappear as a result of averaging over the angles.

This is just the situation existing in the case of adiabatic collisions whose only result is a rotation of the pair of vectors j and d by a certain angle δ about an axis whose orientation in the laboratory system is determined by the angles Λ and F . In virtue of the isotropy of space and the loss of memory of the initial

state during the time of collision ($\omega_0 \tau_C \gg 1$) all the orientations of this axis are equally possible, i.e.,

$$dW(\Lambda, F) = \frac{1}{4\pi} \sin \Lambda \, d\Lambda \, dF, \quad dW(\delta) = f(\delta) \, d\delta, \quad (1.8)$$

with $f(\delta)$ being close to a δ -function in the case of weak collisions and degenerating into a constant in the case of strong collisions. The connection between these angles and those which determine the result of a collision in (1.7),

$$\sin \frac{\alpha}{2} = \sin \Lambda \sin \frac{\delta}{2}, \quad \operatorname{tg}(\eta + \theta) = \frac{\cos \Lambda \sin \delta}{\cos \delta + \sin^2 \Lambda \sin^2(\delta/2)} \quad (1.9)$$

$$\operatorname{tg} \left(\frac{\eta - \theta}{2} \right) = \operatorname{tg} F$$

testifies to the fact that they are all needed: if one assumes, as in the case of Gordon^[5c], $\theta = 0$, the system (1.9) becomes inconsistent. But if, taking (1.9) into account one carries out an averaging in (1.7) over the distributions (1.8) then it turns out that all the nondiagonal elements vanish and

$$P_{q'q} = \gamma \delta_{q'q}, \quad (1.10)$$

$$\gamma = \frac{4}{3} \tau_0^{-1} \int_0^{2\pi} \sin^2 \frac{\delta}{2} f(\delta) \, d\delta \leq \frac{2}{3} \frac{1}{\tau_0}.$$

Thus, an exchange between lines of different polarizations does not take place as a result of adiabatic collisions: they are broadened independently and in the same manner in complete agreement with Anderson's theorem.

It is of interest that no matter how strong are the adiabatic collisions the rate of relaxation of the dipole moment of the rotator does not exceed $2/3$ of the collision frequency $\tau_0^{-1} = n\bar{v}\sigma$ (σ is the cross section for the collision, n is the gas density, \bar{v} is the average thermal velocity). This is explained by the fact that in one of the three orthogonal orientations of the dipole moment (along the axis of rotation resulting from the collision) its phase is unaltered and no broadening results from the collision. In contrast, the two other orientations introduce equal contributions into the phase relaxation each of which at the maximum attains the value $\tau_0^{-1}/3$. In the case of weak collisions the amount of broadening is determined by the disruption in the phase of the dipole moment: $\gamma = \tau_1^{-1} \langle \delta^2 \rangle / 3$, but this phase is specified by δ and certainly not by η as was asserted by Gordon^[5b,c].

The distribution of the angles of rotation arising as a result of nonadiabatic collisions differs essentially from (1.8). In the case of $\omega_0 \tau_C \ll 1$ the axis of the dipole does not have time to shift in the course of a collision and the reorientation of the angular momentum of rotation occurs in the plane perpendicular to this axis, so that

$$\theta = \eta = 0, \quad dW(\alpha) = \varphi(\alpha) \, d\alpha. \quad (1.11)$$

Of course, the absolute value of the angular momentum is also altered at the same time giving rise to j -diffusion, but it is better to postpone taking this circumstance into account until the next section, and to restrict ourselves here to an analysis of only the effect of disorientation of j . The latter is represented by the one-parameter collision matrix obtained from (1.7) and (1.11):

$$P_{q'q} = W \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad (1.12)$$

$$W = \tau_0^{-1} \int_0^\pi \sin^2 \frac{\alpha}{2} \varphi(\alpha) \, d\alpha \leq \frac{1}{2} \frac{1}{\tau_0}.$$

Substituting (1.12) into (1.5) we obtain the balance equations

$$\dot{d}_+ = i\omega_0 d_+ - W d_+ + W d_-, \quad (1.13)$$

$$\dot{d}_- = -i\omega_0 d_- - W d_- + W d_+$$

for the complex amplitudes $d_+ = -\sqrt{2} d_{+1}$ and $d_- = \sqrt{2} d_{-1}$, the meaning of which is clear from (1.4): a rotator with angular momentum oriented along the z axis has on a free path

$$d_+(t) = d e^{i(\omega_0 t + \varphi)}, \quad d_-(t) = d e^{-i(\omega_0 t + \varphi)}.$$

The exchange between them occurring with the frequency W at the same time reverses both the direction of rotation ($\omega_0 \rightarrow -\omega_0$), and also the phase ($\varphi \rightarrow -\varphi$), and together with a reversal of phase there is also a reversal of sign in the work done by the field, the absorption of which gives us an idea of the rotational spectrum of the rotator.

Thus, an exchange of frequencies (polarizations) in (1.13) is accompanied by a replacement of absorption by emission. But in all other respects the situation here is the same as in the well-known problem of averaging the structure of the spectrum by motion^[10a,12,13], the solution of which has the form

$$F(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty dt e^{-i\omega t} d_+(t) = \frac{d}{2\pi} \operatorname{Re} \left[\frac{-i - W/\Omega}{\omega - \Omega - iW} + \frac{-i + W/\Omega}{\omega + \Omega - iW} \right], \quad (1.14)$$

$\Omega = (\omega_0^2 - W^2)^{1/2}$. The resolved structure of this spectrum consists of two weakly asymmetric lines which differ by the sign of the frequency. In a purely rotational spectrum observed only along the positive semiaxis of ω , they correspond to two opposite circular polarizations, while in the vibration-rotational spectrum they correspond to the appropriate P- and R-components^[5].

As long as the frequency of exchange is small compared to the splitting of the lines ($W \ll \omega_0$), their width is $\Delta\omega_{1/2} = W$, while their shift towards one another

$$\Delta = W^2 / 2\omega_0 \ll \omega_0 \quad (1.15a)$$

is not great. The principal contribution to the broadening is given by the diagonal matrix element $P_{q'q}$, while the correction, quadratic in W , is introduced by the nondiagonal matrix element. At low pressures the effect of the latter is not great and, neglecting the shift of the lines, $P_{q'q}$ can from the outset be secularly simplified. However, with increasing pressure the situation is essentially changed. At $W = \omega_0$ a collapse of the structure occurs: both components of the spectrum merge at its center of gravity (at the middle) forming subsequently a single line of width

$$\Delta\omega_{1/2} = \omega_0^2 / 2W, \quad (1.15b)$$

which diminishes as the pressure increases. As a result of this the distinction between adiabatic and nonadiabatic broadening is manifested with particular degree of contrast in the case of condensation of a gas. The adiabatic spectrum after a smearing out of the structure continues to broaden linearly with increasing density, while the nonadiabatic spectrum, having undergone a collapse, becomes narrowed in the inverse proportion established in (1.15b). The purely rotational spectrum in this case is converted into a spectrum of losses, while the free rotation is converted into the Brownian movement of the dipole moment^[14] which relaxes at the

rate $\tau^{-1} = \langle \omega^2 / 2W \rangle \sim n^{-1}$. In contrast to the adiabatic estimate of it carried out by Anderson^[41] the rate of the non-adiabatic Debye relaxation does not increase, but diminishes with increasing density which is more characteristic of a liquid than of a gas. But in actual fact, apparently, something intermediate takes place, since the real collisions are characterized by moderate nonadiabaticity $\omega_0 \tau_c \approx \hbar b / \sqrt{v} \approx 0.3 M^{-1/2}$ (M is the molecular weight).

2. QUANTUM THEORY

In the case of $\hbar\omega \ll T$ the structure and the form of the absorption spectrum of linearly polarized light (with $\epsilon_x = \epsilon \cos \omega t$, $\epsilon_y = \epsilon_z = 0$)

$$I(\omega) = \frac{\omega^2 N \bar{\mathcal{D}}^2}{3T} \text{Re} \int_0^{\infty} e^{-i\omega t} K(t) dt \quad (2.1)$$

is given by the Fourier transform of the correlation function^[15]

$$K(t) = \frac{1}{2} (-1)^q \rho_j \langle j m | d_q(t) d_{-q} + d_q d_{-q}(t) | j m \rangle, \quad (2.2)$$

where ρ_j is the equilibrium density matrix diagonal in the $|j m\rangle$ -representation (m is the component of the rotational angular momentum j along the z axis of the laboratory system), T is the temperature, N is the density of active molecules.

The temporal evolution of the average dipole moment is described by the kinetic equation of collision theory^[10b]

$$\dot{\bar{d}}_q(t) = \frac{i}{\hbar} [\mathbf{H}, \bar{d}_q(t)] - \langle \dot{d}_q(t) - S \dot{d}_q(t) S^+ \rangle, \quad (2.3)$$

in which \mathbf{H} is the total Hamiltonian of the rotator along a free path, while the result of a collision is given by means of S , the scattering matrix.

Taking into account the initial condition $\bar{d}_q(0) = d_q$ one can easily obtain from (2.3) the following matrix equation for the Fourier-transformed components of the dipole moment

$$\begin{aligned} \bar{d}_q(\omega) &= \int_0^{\infty} e^{-i\omega t} \dot{d}_q(t) dt: \\ \langle j m | i(\omega - \hbar^{-1}[\mathbf{H}, d_q(\omega)]) | l n \rangle &+ \langle j' m' | d_q(\omega) | l' n' \rangle \\ &\times \mathbf{P} \begin{pmatrix} j' m' & | & l' n' \\ j m & | & l n \end{pmatrix} = \langle j m | d_q | l n \rangle. \end{aligned} \quad (2.4)$$

The quantum relaxation operator

$$\begin{aligned} \mathbf{P} \begin{pmatrix} j' m' & | & l' n' \\ j m & | & l n \end{pmatrix} &= n \int v f(v) dv b db d\Omega \\ &\times [\delta_{j' m' m} \delta_{l' n' l} - \langle j m | S | j' m' \rangle \langle l n | S | l' n' \rangle^*] \end{aligned} \quad (2.5)$$

in contrast to the classical one is in an evident manner diagonal with respect to q . Its other properties are established after averaging over the impact parameters b and the relative velocities of the colliding particles v ($d\Omega = \sin \beta d\beta d\alpha d\gamma$, where α and β are the polar angles of v , γ is the azimuthal angle of b in the plane perpendicular to v).

The averaging over the angles can be carried out in a general form^[16] if the external fields are so weak that they do not affect the result of a collision. In such a case in the system of coordinates rigidly connected to b and v it is given by the scattering matrix \tilde{S} , which in virtue of the spatial isotropy depends only on the absolute values b and v . The same result is expressed in the laboratory system in terms of \tilde{S} by means of matrices of finite rotations^[11]:

$$\langle j m | S | j' m' \rangle = D_{\alpha m}^{j*}(\Omega) D_{\alpha' m'}^j(\Omega) \langle j \alpha | \tilde{S} | j' \alpha' \rangle. \quad (2.6)$$

After averaging over Ω the operator \mathbf{P} assumes the following form:

$$\begin{aligned} \mathbf{P} \begin{pmatrix} j' m' & | & l' n' \\ j m & | & l n \end{pmatrix} &= (-1)^{m+m'} (2\alpha+1) \begin{pmatrix} j & \alpha & l \\ -m & q & n \end{pmatrix} \\ &\times \begin{pmatrix} j' & \alpha' & l' \\ -m' & q & n' \end{pmatrix} \langle j l | \mathbf{p}(\kappa) | j' l' \rangle, \end{aligned} \quad (2.7)$$

where

$$\langle j l | \mathbf{p}(\kappa) | j' l' \rangle = (-1)^{\alpha+\alpha'} \begin{pmatrix} j & \alpha & l \\ -\alpha & q & \beta \end{pmatrix} \begin{pmatrix} j' & \alpha' & l' \\ -\alpha' & q & \beta' \end{pmatrix} \tilde{\mathbf{P}} \begin{pmatrix} j' \alpha' & | & l' \beta' \\ j \alpha & | & l \beta \end{pmatrix} \quad (2.8)$$

are the matrix elements of the reduced operator \mathbf{p} , while

$$\begin{aligned} \tilde{\mathbf{P}} \begin{pmatrix} j' \alpha' & | & l' \beta' \\ j \alpha & | & l \beta \end{pmatrix} &= 8\pi^2 n \int v f(v) dv b db [\delta_{j' j} \delta_{\alpha \alpha'} \delta_{l' l} \delta_{\beta \beta'} \\ &- \langle j \alpha | \tilde{S} | j' \alpha' \rangle \langle l \beta | \tilde{S} | l' \beta' \rangle^*] \end{aligned} \quad (2.9)$$

is the relaxation operator in the coordinate system of the collision.

From the properties of the $3j$ -symbols the following selection rules emerge for the nonvanishing elements of the operator \mathbf{P} : $m+n' = m'+n$, while from the unitary nature of the S -matrix follows the property: $\langle j l | \mathbf{p}(\kappa) | j' l' \rangle = \langle j l | \mathbf{p}(\kappa) | l' j' \rangle^*$.

The concrete form of the relaxation operator achieved in (2.7) essentially simplifies the solution of the kinetic equations. In the absence of external fields when \mathbf{H} is nothing other than the Hamiltonian of the free rotator \mathbf{H}_0 it is natural to seek a solution of (2.4) in a spherically symmetric form

$$\langle j m | d_q(\omega) | l n \rangle = (-1)^{j+m} \langle j | d(\omega) | l \rangle \begin{pmatrix} j & 1 & l \\ -m & q & n \end{pmatrix}, \quad (2.10)$$

assuming that only the reduced matrix elements of the dipole moment $\langle j | d(t) | l \rangle$ vary with time. Contracting (2.4) with the aid of (2.7) and (2.10) we obtain the equation for the reduced elements

$$i(\omega - \omega_j) \langle j | d(\omega) | l \rangle + \langle j l | \mathbf{p}(1) | j' l' \rangle \langle j' | d(\omega) | l' \rangle = \langle j | d | l \rangle, \quad (2.11)$$

the formal solution of which $\langle j' | d(\omega) | l' \rangle = \langle j l | \mathbf{G}^{-1} | j' l' \rangle \langle j | d | l \rangle$ is obtained by an inversion of the fundamental matrix

$$\langle j l | \mathbf{G} | j' l' \rangle = i(\omega - \omega_j) \delta_{j' j} \delta_{l' l} + \langle j l | \mathbf{p}(1) | j' l' \rangle. \quad (2.12)$$

Substituting it into (2.10) and utilizing the result in (2.2) we obtain from (2.1)

$$I(\omega) \sim \text{Re} \rho_j [\langle j | d | l \rangle \langle j' | d | l' \rangle \langle j' l' | \mathbf{G}^{-1} | j l \rangle + \langle l | d | j \rangle \langle l' | d | j' \rangle \langle l' j' | \mathbf{G}^{-1} | l j \rangle]; \quad (2.13)$$

$$\begin{aligned} \langle j | d | l \rangle &= d \langle j | n_0 | l \rangle = d (-1)^{j+(j+l)/2} [\max(j, l)]^{\frac{1}{2}}, \\ \rho_j &= \frac{1}{z} \exp \left[-\frac{\hbar^2 j(j+1)}{2IT} \right]. \end{aligned} \quad (2.14)$$

Since the nonadiabatic processes have been taken into account in (2.13) on the same basis as the adiabatic ones all the lines of that spectrum which differ in magnitude or in the sign of the frequency are in principle interrelated by means of the nondiagonal elements $\langle j l | \mathbf{p}(1) | j' l' \rangle$ which specify the frequency of exchange. Only if the collisions (as a result of adiabaticity) are unable to induce transitions between different j -terms $\langle j \alpha | \tilde{S} | j' \alpha' \rangle = \delta_{j j'} \tilde{S}_{\alpha \alpha'}^j$, the operator \mathbf{p} , and together with it the \mathbf{G} -matrix are diagonalized and the spectrum (2.13) in complete agreement with Anderson's theorem degenerates into a sum of independently broadened Lorentz lines

$$I(\omega) \sim \text{Re} \rho_j \langle j | d | l \rangle^2 \left[\frac{1}{i(\omega - \omega_0) + \Gamma} + \frac{1}{i(\omega + \omega_0) + \Gamma} \right], \quad (2.15)$$

for which $\Gamma = \langle j | \mathbf{p} | l \rangle$. The resonance term in (2.15) corresponds to absorption of circularly polarized light by a rotator rotating in the same direction; while the nonresonance term corresponds to absorption of circularly polarized light by a rotator rotating in the opposite direction. It is not superfluous to note this, since the presence at the same time of both terms is necessary only in the case of a rotator. In the case of a two-level system, just as in the case of a harmonic oscillator, the sign of the frequency does not alternate ($\omega_0 > 0$) and the correctly polarized light is always absorbed and emitted only in a resonant manner (Fig. 2a). Both terms are present in this case only when the light is linearly polarized, i.e., when in addition to the correctly polarized component ($\omega_0 > 0$) it also contains the incorrectly polarized component ($\omega_0 < 0$), and certainly not because the resonant term should be identified with absorption while the nonresonant term should be identified with emission²⁾ as in the interpretation of Ben-Reuven^[17]. And only an equilibrium ensemble of rotators rotating equally in both directions ($\omega_0 \gtrsim 0$) absorbs either of the two circularly polarized components of light both in a resonant and a nonresonant manner, and both together with twice the intensity (Fig. 2b).

These explanations are needed for a correct interpretation of the result of nonadiabatic collisions which together with the usual frequency exchange ($\omega_j l \leftrightarrow \omega_{j'} l'$, $j > l$, $j' > l'$) give rise to an exchange between transitions which differ only by the sign of the frequency ($\omega_j l \leftrightarrow \omega_l j$) as a result of which absorption alternates with emission. In order to identify this latter process with its classical analogue discussed in the preceding section it remains for us to convince ourselves that together with a reversal of the sign of absorption the polarization of the resonantly interacting component of the light wave is also reversed.

With this in mind we consider the transition $j = 0 \leftrightarrow j = 1$ (Fig. 3), which is at the same time the simplest and the essentially quantum transition (classical theory is

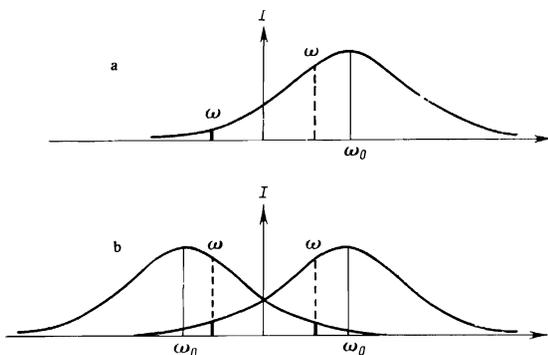


FIG. 2. The resonance (dotted line) and the nonresonance (solid curve) absorption of light by a two-level system (a) and by a rotator (b).

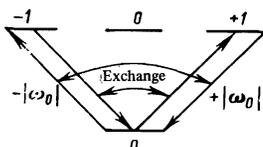


FIG. 3. The transition $j = 0 \leftrightarrow j = 1$.

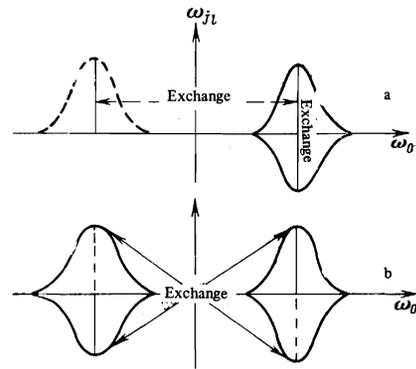


FIG. 4. Spectral exchange of nonadiabatic origin: a) in a two-level system, b) in a rotator.

valid only for $j, j' \gg 1$). The block of the fundamental matrix relating to it has the form

$$G = \begin{pmatrix} \langle 10 | G | 10 \rangle & \langle 10 | G | 01 \rangle \\ \langle 01 | G | 10 \rangle & \langle 01 | G | 01 \rangle \end{pmatrix} = \begin{pmatrix} i(\omega - \omega_0) + \Gamma & -\beta \\ -\beta^* & i(\omega + \omega_0) + \Gamma \end{pmatrix}; \quad (2.16)$$

$$\Gamma = \Gamma' + i\Gamma'' = \langle 10 | \mathbf{p} | 1 \rangle = \left\langle 1 - \frac{1}{3} \tilde{S}_{00} \sum_m \tilde{S}_{mm} \right\rangle, \quad (2.17a)$$

$$\beta = \beta' + i\beta'' = -\langle 10 | \mathbf{p} | 1 \rangle = \frac{1}{3} \langle (-1)^m \langle 1m | \tilde{S} | 00 \rangle \langle 00 | \tilde{S} | 1, -m \rangle \rangle. \quad (2.17b)$$

The nondiagonal element of this matrix is a measure of the "phase memory" of the system^[18], i.e., of the degree of coherence of the j -terms arising in collisions and remaining in spite of averaging over all the impact parameters^[19]. Its structure enables us to see which particular transitions exchange among themselves: in the given specific case ($11 | d_1 | 00$) with $\langle 00 | d_{-1} | 1, -1 \rangle$ and $\langle 1, -1 | d_{-1} | 00 \rangle$ with $\langle 00 | d_{-1} | 11 \rangle$ (Fig. 3). The sign of the quantum $\hbar \omega_j l \lesssim 0$ which determines the direction of the transition (absorption or emission) changes together with the sign of its polarization (identical with the m -component of the upper level) which labels the classical resonance frequency ω_0 . In this the rotator essentially differs from the two-level system^[17,18] in the case of which the nonadiabatic collisions exchange only absorption with emission, and this in classical language is equivalent to inverting the phase of the harmonic oscillator while retaining the same frequency^[17]:

$$x = x_0 \cos(\omega_0 t + \varphi) \rightarrow x_0 \cos(\omega_0 t - \varphi).$$

However, formally, an inversion of the frequency while retaining the same phase transforms $x(t)$ in exactly the same manner. Therefore the spectroscopic manifestation of exchange in a two-level and a three-level system, the latter of which in this case is a rotator, has many aspects in common. Only in the former case the exchange occurs with a fictitious (forbidden) line, while in the latter case both transitions are allowed (Fig. 4).

Indeed, the spectrum corresponding to the fundamental matrix (2.16),

$$I(\omega) \sim d^2 (\rho_0 + \rho_1) \text{Re} \left[\frac{-i - \beta' / \Omega}{\omega - \Omega - i\Gamma'} + \frac{-i + \beta' / \Omega}{\omega + \Omega - i\Gamma''} \right], \quad (2.18)$$

$$\Omega = [(\omega_0 - \Gamma'')^2 - |\beta|^2]^{1/2}$$

can be obtained from the solution of a more general problem^[19] by the following redefinition of its parameters: $d_a = -d_b = d$ ($\omega = 0$, $\Delta/2 = \omega_0$, $\Gamma_a = \Gamma_b^* = \Gamma$), while the spectrum of a two-level system is obtained if one of the lines is assumed to be forbidden: $d_b = 0$ (the rest remains the same). If we are dealing with a vibrational-rotational spectrum ω should be measured not from

zero, but from the vibrational frequency. On being added to it a positive quantum shifts the resonance to the right, while a negative quantum shifts it to the left thereby forming the P- and the R-components represented by corresponding terms in (2.18). Whether Ω is real or purely imaginary, i.e., whether we are dealing with a spectrum before collapse or after, depends on the rate ($|\beta|$) at which exchange between them occurs.

The present treatment differs from the solution of the classical problem discussed in the preceding section only by the fact that the possibility is taken into account of phase disruption occurring in addition to exchange. In the case $\Gamma'' = \beta'' = 0$, $\Gamma' = \beta' = W$ they are phenomenologically identical. Thus, taking into account the nonadiabatic nature of collisions leads to a qualitatively different broadening of the low frequency components of the spectrum (and at high pressures of the spectrum as a whole) than in the original theory of Anderson^[4].

Switching on an external field introduces a still more essential correction making an adiabatic spectral exchange possible which is not observable in an isotropic space and which does not have a classical analogue. Even if the effect of the field on the result of a collision is not significant and the P-operator remains the same, the appearance in the Hamiltonian of a field term alters the symmetry of H and makes it impossible to reduce the basic kinetic equation (2.4) to its reduced variant (2.11). The complex structure arising in the case of the field from each rotational line can be calculated only by a direct solution of the corresponding secular problem. In an adiabatic theory its rank does not exceed the number of similarly polarized components (depolarization by collisions is not possible), but it must be greater than unity in order that exchange between them should take place. It is evident that degeneracy of both j-terms which guarantees the existence of the same polarization in a multiple number of components remains as before a necessary condition for the existence of adiabatic exchange^[20]. It is satisfied for all rotational transitions except for the lowest one ($j=0 \rightarrow j=1$).

For the sake of definiteness we consider the simplest of them ($j=1 \rightarrow j=2$). In an electric field \mathcal{E} directed along the propagation vector of the light wave ($\mathbf{H} = \mathbf{H}_0 - d_0 \mathcal{E}$) the degeneracy of the multiplet 1-2 is partially removed and a stark structure^[21] consisting of three lines arises (Fig. 5)

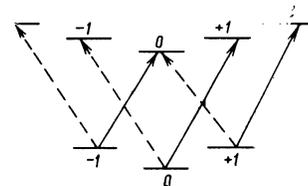
$$\omega_{2m,1n} = \omega_{21} - \frac{I}{210\hbar} \left(\frac{d\mathcal{E}}{\hbar} \right)^2 (32 + 5m^2 - 63n^2), \quad (2.19)$$

which are allowed by the selection rules: $m = n \pm 1$. Each of them consists of two components of opposite polarization. Examination of the explicit form of the operator (2.7) enables one to verify easily that adiabatic collisions ($\langle j\alpha | \tilde{S} | j'\alpha' \rangle = \delta_{jj'} \langle \tilde{S}_{\alpha\alpha'} \rangle$) broaden and mutually exchange all lines of the same polarization. For example,

$$P = \begin{pmatrix} \frac{3}{5}\gamma_1 + \frac{1}{3}\gamma_2 + \frac{1}{15}\gamma_3 & \frac{3\sqrt{2}}{10}\gamma_1 - \frac{\sqrt{2}}{6}\gamma_2 - \frac{2\sqrt{2}}{15}\gamma_3 & \frac{\sqrt{6}}{10}\gamma_1 - \frac{\sqrt{6}}{6}\gamma_2 + \frac{\sqrt{6}}{15}\gamma_3 \\ \frac{3\sqrt{2}}{10}\gamma_1 - \frac{\sqrt{2}}{6}\gamma_2 - \frac{2\sqrt{2}}{15}\gamma_3 & \frac{3}{10}\gamma_1 + \frac{1}{6}\gamma_2 + \frac{8}{15}\gamma_3 & \frac{\sqrt{3}}{10}\gamma_1 + \frac{\sqrt{3}}{6}\gamma_2 - \frac{4\sqrt{3}}{15}\gamma_3 \\ \frac{\sqrt{6}}{10}\gamma_1 - \frac{\sqrt{6}}{6}\gamma_2 + \frac{\sqrt{6}}{15}\gamma_3 & \frac{\sqrt{3}}{10}\gamma_1 + \frac{\sqrt{3}}{6}\gamma_2 - \frac{4\sqrt{3}}{15}\gamma_3 & \frac{1}{10}\gamma_1 + \frac{1}{2}\gamma_2 + \frac{2}{5}\gamma_3 \end{pmatrix}. \quad (2.20)$$

As is evident from the definition itself of $\gamma_K = \langle 21 | p(\kappa) | 21 \rangle$, these constants are the rates of relaxation of dipole ($\kappa=1$), quadrupole ($\kappa=2$) and octopole ($\kappa=3$) moments for the transition. In the case of weak collisions:

FIG. 5. Stark components of opposite polarization; the dotted lines correspond to $\omega_0 < 0$, the solid lines correspond to $\omega_0 > 0$.



$\gamma_3 < \gamma_2 < \gamma_1$, the rate of exchange has the same scale as the individual broadening of components determined by the diagonal elements of P. But if the collisions are so strong that the rate of relaxation does not depend on the multipolarity: $\gamma_1 = \gamma_2 = \gamma_3$, then exchange is absent entirely, since all the nondiagonal elements in (2.20) vanish. Thus, the existence or the absence of exchange can serve as a criterion of whether the collisions are "weak" or "strong."

But the actual manifestation of exchange is the same as usual^[19,20]. As long as the splitting of the Stark components is considerably greater than their width, the latter is fundamentally determined by the diagonal elements of (2.20). But when as the pressure is increased the exchange between the components leads to a collapse of the structure, then a single line arises shifted in frequency but of width γ_1 which is the same as in the absence of the field. If γ_2 and γ_3 are negligibly small compared to γ_1 , then all the components of the allowed structure have a different width and the smallest of them increases with pressure by an order of magnitude more slowly than after collapse. In accordance with this the determination from the Stark structure of all three relaxation constants, if they are comparable in magnitude, is not only possible in principle, but is practically realizable.

¹A summation is carried out over dummy indices.

²The origin of this interpretation is, apparently, associated with the incorrect definition of the correlation function which was utilized by Ben-Reuven^[17] in the unsymmetrized form (with respect to an interchange of d(t) and d). As a result of this the resonant and the non-resonant components of the spectrum appeared in it with the weights respectively of the upper and lower states, whereas in actual fact they are of equal magnitude.

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Translated by G. Volkoff

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