Quasiresonant spectral line broadening in the impact approximation

M. L. Strekalov and A. I. Burshteĭn

Institute of Chemical Kinetics and Combustion, Siberian Department, USSR Academy of Sciences

(Submitted August 10, 1975)
Zh. Eksp. Teor. Fiz. **70**, 862–871 (March 1976)

Isotopic and hyperfine structure collapse of the atomic-spectrum structure resulting from resonant interaction between colliding particles is calculated. The relaxation matrices of both processes are determined and a qualitative difference is found between them. After averaging the spectrum structure over the pressure, this difference leads in one case to a broadening and in the other to a narrowing of the spectrum with increasing pressure.

PACS numbers: 32.10.Nw

INTRODUCTION

The isotopic and hyperfine structure of atomic absorption spectra broadened by resonance collisions is calculated in the present paper within the framework of the impact theory of the broadening of overlapping lines.

In resonance interaction, the broadening is always accompanied by the transfer of excitations, which leads to the result that both colliding particles take part in the light absorption, and the role of one of them does not reduce at all to the occasional interruption of the absorption process for its partner in the collision. Account of the change in the internal state of the perturbing particle in the collision process is always necessary in the broadening by its own gas and, as is well known,[1–2] manifests itself in a specific broadening and line shift.

If the gas is a mixture of isotopes, the lines of which are spectrally resolved, then the resonance interaction between them leads not only to a broadening, but also to the exchange of positions in the spectrum (spectral exchange), which appears, with increase in pressure, as a distinct transformation of the isotopically mixed components and can serve as a means of measurement of the cross sections of resonance transfer with a small energy deficit. It turns out that the "pseudocollapse," which is due to the resonance interaction, by averaging the frequencies of the isotopic components, shifts the mean frequency of the line remaining in the spectrum but, in contrast to the previously considered cases of field[4,5] and rotational[6] structures, leaves the width of the "collapsing" spectrum without change. The latter continues to increase linearly with increase in pressure.

Besides the resonance interaction, exchange interaction, which is responsible for broadening of the hyperfine components of the spectrum of magnetic resonance of the ground state, has also been considered. It was shown that exchange of electron spins in collisions broadens the hyperfine components at the same rate as it exchanges them. The equality of the secular and nonsecular elements of the relaxation operator gives rise to an extremal course of the collapse, which is manifest in the fact that the lines merge at the center of the spectrum upon increase in the pressure, and subsequently the spectrum narrows with increase in the frequency of the collisions. This is the only explanation of the EPR-spectrum exchange narrowing inherent in gases to the same extent as in condensed media,[7,8] when the exchange mechanism of broadening predominates.

1. GENERAL FORMALISM

We consider a gas consisting of a mixture of isotopes with partial densities n_i ($i=1, 2$) at thermal equilibrium with a temperature T, and denote the total gas density by $n=n_1+n_2$. If the Doppler broadening is small in comparison with the impact broadening, then all the atoms are subjected to the action of a uniform field $\mathscr{E}_x(t)=\mathscr{E}_0\cos\omega t$. In this case, as is well known,[9] the linearly absorbed intensity

$$I(\omega)=\frac{\omega}{\hbar}n\mathscr{E}_0^2\,\mathrm{th}\left(\frac{\hbar\omega}{2kT}\right)\mathrm{Re}\int_0^\infty dt\,e^{i\omega t}K(t)\tag{1.1}$$

is determined by the Fourier transform of the dipole-moment correlation function

$$K(t)=\frac{n_1}{n_1+n_2}K_1(t)+\frac{n_2}{n_1+n_2}K_2(t),\tag{1.2}$$

where

$$K_i(t)=\frac{1}{2}\mathrm{Tr}\,\rho(i)\left[d_i^{(x)}(t)d_i^{(x)}(0)+d_i^{(x)}(0)d_i^{(x)}(t)\right]\quad(i=1,2).\tag{1.3}$$

Here $\rho(i)$ is the equilibrium density matrix and $\mathbf{d}_i(t)$ is the dipole moment operator of the i-th atom.

The time evolution of $\mathbf{d}_i(t)$ in the impact approximation is determined by two essentially different components. The first determines the time development of the dipole moment over its free path, the second describes its change as a result of pair collisions. The effect of interaction with the perturbing molecules is represented by the impact operator, the method of derivation of which can be found in many places.[10,11] Therefore, without going into detail, we write down the set of equations which describe the time evolution of the dipole moment of each of the two interacting isotopes, in a form that is most suitable for further applications:

$$\dot{\mathbf{d}}_i(t)=\frac{i}{\hbar}[H_0(i),\mathbf{d}_i(t)]-\Big\langle n\mathbf{d}_i(t)-\sum_{k=1,2}n_k\,\mathrm{Tr}_k\,\rho(k)\times S^+(i,k)[\mathbf{d}_i(t)+\mathbf{d}_k(t)]S(i,k)\Big\rangle. \tag{1.4}$$

$H_0(i)$ is the Hamiltonian of the i-th atom on its free path, $S(i, k)$ is the two-particle scattering matrix; the angle brackets denote averaging over the impact parameter $\mathbf{b}$ and the relative velocity of the colliding particles $\mathbf{v}$.

In the external field formalism,[11b,12] the scattering matrix is characterized by the quantum degrees of freedom of only one of the particles participating in the collision; the second is regarded as the source of the external field. This limiting case is easily discerned from (1.4): if, for example, we make the substitution $S(1, 2)\to S(1)$, and assume that $n_2 \gg n_1$, then the well known kinetic equation of impact theory is obtained[11b]:

$$\dot{\mathbf{d}}_1(t)=\frac{i}{\hbar}[H_0(1),\mathbf{d}_1(t)]-n_2\langle\mathbf{d}_1(t)-S^+(1)\mathbf{d}_1(t)S(1)\rangle. \tag{1.5}$$

If the gas of interest to us is dissolved in the mass of another, but spectral exchange between the perturbed and perturbing particles (nonresonant collisions) is absent, then the internal structure of the latter can be accounted for by a natural extension of (1.5) (see also Refs. 11, 12):

$$\dot{\mathbf{d}}_1(t)=\frac{i}{\hbar}[H_0(1),\mathbf{d}_1(t)]-n_2\langle\mathbf{d}_1(t)-\mathrm{Tr}_2\,\rho(2)S^+(1,2)\mathbf{d}_1(t)S(1,2)\rangle. \tag{1.6}$$

However, in the presence of resonances, the set of equations (14) generally does not reduce to (1.6) and certainly not to (1.5). Criteria for the applicability of Eq. (1.6) in the resonance situation will be discussed later.

The Hamiltonian H_0 is spherically symmetric in the absence of a constant external field; therefore, it is natural to seek a solution of Eqs. (1.4), (1.5), and (1.6) likewise in a spherically symmetric form:

$$\langle jm|d_q(t)|j'm'\rangle=(-1)^{j-m}\langle j\|d(t)\|j'\rangle\begin{pmatrix} j & 1 & j' \\ -m & q & m' \end{pmatrix}, \tag{1.7}$$

assuming that only the reduced matrix elements of the dipole moment change with time. The expression in the large parentheses is the $3j$-symbol, j is the total electron angular momentum of the atom. For simplicity, the remaining quantum numbers are omitted. Convoluting (1.4) with the help of (1.7), we get a set of equations for the reduced matrix elements of the dipole moments:

$$\begin{gathered}\Big[\Big(\frac{\partial}{\partial t}-i\omega_{j_1j_1'}\Big)\delta_{j_1l_1}\delta_{j_1'l_1'}+n_1\Gamma_{11}(j_1j_1'l_1l_1')+n_2\Gamma_{12}(j_1j_1'l_1l_1')\Big]\langle l_1\|d(1)\|l_1'\rangle\\ -n_2\Gamma_{12}(j_1j_1'l_2l_2')\langle l_2\|d(2)\|l_2'\rangle=0,\\ \Big[\Big(\frac{\partial}{\partial t}-i\omega_{j_2j_2'}\Big)\delta_{j_2l_2}\delta_{j_2'l_2'}+n_2\Gamma_{22}(j_2j_2'l_2l_2')+n_1\Gamma_{21}(j_2j_2'l_2l_2')\Big]\langle l_2\|d(2)\|l_2'\rangle\\ -n_1\Gamma_{21}(j_2j_2'l_1l_1')\langle l_1\|d(1)\|l_1'\rangle=0.\end{gathered} \tag{1.8}$$

Summation is carried out in (1.8) over the dummy indices. We label the multiplet structure of the ground-state term by j_1, and l_1, and that of the excited state by j_1' and l_1'; we use the same notation for atom 2.

In Eqs. (1.8),

$$\begin{aligned}\Gamma_{11}(j_1j_1'l_1l_1')=\Big\langle&\delta_{j_1l_1}\delta_{j_1'l_1'}-\sum_{\substack{mnq\\jj'}}(-1)^{m_1-j_1+l_1-n_1}\begin{pmatrix} j_1 & 1 & j_1' \\ -m_1 & q & m_1' \end{pmatrix}\begin{pmatrix} l_1 & 1 & l_1' \\ -n_1 & q & n_1' \end{pmatrix}\\ &\times\rho_{jj}(1)\Big[\Big\langle\begin{matrix} j_1m_1\\ jm\end{matrix}\Big|S^+(1,1)\Big|\begin{matrix} l_1n_1\\ j'm'\end{matrix}\Big\rangle\Big\langle\begin{matrix} l_1'n_1'\\ j'm'\end{matrix}\Big|S(1,1)\Big|\begin{matrix} j_1'm_1'\\ jm\end{matrix}\Big\rangle\\ &-\Big\langle\begin{matrix} j_1m_1\\ jm\end{matrix}\Big|S^+(1,1)\Big|\begin{matrix} j'm'\\ l_1n_1\end{matrix}\Big\rangle\Big\langle\begin{matrix} j'm'\\ l_1'n_1'\end{matrix}\Big|S(1,1)\Big|\begin{matrix} j_1'm_1'\\ jm\end{matrix}\Big\rangle\Big]\Big\rangle\end{aligned} \tag{1.9}$$

are the reduced matrix elements of the impact operator, and are responsible for the self-broadening. The broadening by the extraneous gas is represented in (1.8) by the matrix elements of the impact operator, which has the same structure as in the formalism of the external field (1.6):

$$\begin{aligned}\Gamma_{12}(j_1j_1'l_1l_1')=\Big\langle&\delta_{j_1l_1}\delta_{j_1'l_1'}-\sum_{\substack{mnq\\jj'}}(-1)^{m_1-j_1+l_1-n_1}\begin{pmatrix} j_1 & 1 & j_1' \\ -m_1 & q & m_1' \end{pmatrix}\begin{pmatrix} l_1 & 1 & l_1' \\ -n_1 & q & n_1' \end{pmatrix}\\ &\times\rho_{jj}(2)\Big\langle\begin{matrix} j_1m_1\\ jm\end{matrix}\Big|S^+(1,2)\Big|\begin{matrix} l_1n_1\\ j'm'\end{matrix}\Big\rangle\Big\langle\begin{matrix} l_1'n_1'\\ j'm'\end{matrix}\Big|S(1,2)\Big|\begin{matrix} j_1'm_1'\\ jm\end{matrix}\Big\rangle\Big\rangle.\end{aligned} \tag{1.10}$$

The appearance in Eqs. (1.8) of additional elements of the impact operator

$$\begin{aligned}\Gamma_{12}(j_1j_1'l_2l_2')=\Big\langle&\sum_{\substack{mnq\\jj'}}(-1)^{m_1-j_1+l_2-n_2}\begin{pmatrix} j_1 & 1 & j_1' \\ -m_1 & q & m_1' \end{pmatrix}\begin{pmatrix} l_2 & 1 & l_2' \\ -n_2 & q & n_2' \end{pmatrix}\rho_{jj}(2)\\ &\times\Big\langle\begin{matrix} j_1m_1\\ jm\end{matrix}\Big|S^+(1,2)\Big|\begin{matrix} j'm'\\ l_2n_2\end{matrix}\Big\rangle\Big\langle\begin{matrix} j'm'\\ l_2'n_2'\end{matrix}\Big|S(1,2)\Big|\begin{matrix} j_1'm_1'\\ jm\end{matrix}\Big\rangle\Big\rangle,\end{aligned} \tag{1.11}$$

is, in principle, a new feature that distinguishes the kinetic equation (1.8) from (1.6), and even more, from (1.5). These elements are responsible for the recoil experienced by the perturbing particle in the collision process. Exchange of excitation is taken into account in the self-broadening by the last term on the right side of (1.9). The notation used for the elements of the S matrix has a simple meaning: the upper indices refer to the first particle, and the lower, to the second. The elements of the impact operator for the second particle are obtained from (1.9)–(1.11) by the corresponding substitution $1\to 2$.

In the case in which the particles collide with an energy deficit $\Delta\omega=\omega_{j_1'j_1}-\omega_{j_2'j_2}$ such that $\Delta\omega\tau_c \gg 1$ (τ_c is the mean time of the collision), the matrix elements (1.11) are exponentially small (like $\exp(-\Delta\omega\tau_c)$) and the set of equations (1.8) reduces to the kinetic equation (1.6), which is written down for each of the particles separately. But in the reverse situation, $\Delta\omega\tau_c \ll 1$, the complete system of equations is necessary only if the detuning $\Delta\omega$ is small or comparable with the value of the matrix elements of the impact operator (1.11). In the opposite case (large $\Delta\omega$) we can always carry out a secular simplification of the Γ operator and reduce the situation to the solution of Eq. (1.6).

2. ABSORPTION SPECTRUM IN A GAS OF RESONANTLY INTERACTING ISOTOPES

The resonance broadening of a spectral line is determined by the interaction of the excited atom with the other atoms surrounding it. We shall assume that the population of the excited level is small, so that the principal contribution is made by collisions of the excited atom with unexcited ones. We denote by j the total electron angular momentum of the excited atom, and by j_0 that of the unexcited one. We assume that the isotopes have different frequencies of the ground-state transition $\omega_i = \omega_{jj_0}(i)$, and the detuning is such that the condition of nonadiabaticity $\Delta\omega\tau_c \ll 1$ is satisfied, but $\omega_i\tau_c \gg 1$, which enables us to neglect the nonresonance transitions. In what follows, we shall assume that the isotopes are equivalent in the sense of their electric interaction with each other; therefore all the constants are the same for the two isotopes (see, however, Ref. 13).

We introduce the notation $d_i = \langle j_0|d(t)|j\rangle_i$. Then the set of equations (1.8) will be written in the following fashion:

$$\frac{d}{dt}\begin{pmatrix} d_1 \\ d_2 \end{pmatrix} = \begin{pmatrix} -i(\omega_1 - n_1\beta) - n\Gamma & in_2\beta \\ in_1\beta & -i(\omega_2 - n_2\beta) - n\Gamma \end{pmatrix}\begin{pmatrix} d_1 \\ d_2 \end{pmatrix}, \qquad (2.1)$$

where the matrix element of the impact parameter, which is responsible for transfer of the excitation,

$$i\beta = \frac{i}{2j_0+1}\sum_{JM}\begin{Bmatrix} j & J & j_0 \\ j & 1 & j_0 \end{Bmatrix}\langle \mathrm{Im}\, S_{MM}{}^{J}\rangle \qquad (2.2)$$

is pure imaginary, and the matrix element of the impact operator characterizing the collision without excitation transfer,

$$\Gamma = \left\langle 1 - \frac{1}{(2j_0+1)(2j+1)}\sum_{JM}\mathrm{Re}\, S_{MM}{}^{J}\right\rangle \qquad (2.3)$$

is always real. The expression in the curly brackets is the $6j$-symbol, S^J_{MM} are the elements of the scattering matrix in the basis

$$|JM\rangle_\pm = (2J+1)^{1/2}(-1)^{j-j_0+M}\sum_{mm_0}\begin{pmatrix} j & j_0 & J \\ m & m_0 & -M \end{pmatrix}\frac{1}{\sqrt{2}}\left(\left|\begin{matrix} jm \\ j_0m_0 \end{matrix}\right\rangle \pm \left|\begin{matrix} j_0m_0 \\ jm \end{matrix}\right\rangle\right). \qquad (2.4)$$

In the derivation of (2.1)–(2.3), we have shown that the ground state $|j_0m_0\rangle$ is not excited by the collisions, and we have further set $\rho_{jj} = 0$ and $\rho_{j_0j_0} = (2j_0+1)^{-1}$.

The solution of the set of equations with constant coefficients (2.1) is trivial, and we shall not describe it, but only give the final results—the loss spectrum (1.1):

$$I(\omega) = \frac{\omega}{3\hbar}n\mathscr{E}_0{}^2\frac{(2j+1)}{(2j_0+1)}\frac{g^2}{4}\left[\frac{n\Gamma A_+}{(\omega-\bar{\omega}+\Delta_+)^2+(n\Gamma)^2} + \frac{n\Gamma A_-}{(\omega-\bar{\omega}-\Delta_-)^2+(n\Gamma)^2}\right] \qquad (2.5)$$

The nonresonance components in (2.5) are omitted. The intensities are given by the formula

$$A_\pm = 1 \mp \frac{\Delta n}{n}\frac{\Delta\omega}{2\Omega} \pm \frac{n\beta}{2\Omega}, \qquad (2.6)$$

where

$$\bar{\omega} = \frac{\omega_1+\omega_2}{2}, \quad \Delta\omega = \omega_1 - \omega_2, \quad \Delta n = n_1 - n_2, \quad g^2 = \frac{\langle j_0|d|j\rangle^2}{2j+1},$$

and the shifts by the expressions

$$\Delta_\pm = \pm{}^1/_2 n\beta + \Omega, \quad \Omega = {}^1/_2[(\Delta\omega - \Delta n\beta)^2 + 4n_1n_2\beta^2]^{1/2}. \qquad (2.7)$$

The coefficient $\frac{1}{3}$ in Eq. (2.5) appears because of the fact that in reality, instead of the correlation function (1.3), it is better to calculate the correlation function $\langle \mathbf{d}(t)\mathbf{d}(0)\rangle$, which is equal to $3\langle d_x(t)d_x(0)\rangle$ in isotropic space. Moreover, we have taken it into account that $\tanh(\hbar\omega/2kT) \approx 1$ since $\hbar\omega \gg 2kT$ at optical frequencies.

The loss spectrum in a gas that is homogeneous in isotopic composition is obtained from Eq. (2.5) for $\Delta\omega = 0$:

$$\varepsilon''(\omega) = \frac{8\pi}{\omega}\mathscr{E}_0{}^{-2}I(\omega) = \frac{4\pi}{3\hbar}ng^2\frac{2j+1}{2j_0+1}\frac{n\Gamma}{(\omega-\bar{\omega}+n\beta)^2+(n\Gamma)^2}. \qquad (2.8)$$

The presence of a line shift $n\beta$, in addition to its broadening, is a consequence of the correct account of the recoil in the collision of the particles. In the external-field formalism the shift is determined by the imaginary part of the diagonal element of the impact parameter (1.10) and should inevitably be absent in the resonance interaction ($\mathrm{Im}\Gamma = 0$, as is clear from (2.3)). The parameter β is negative as a rule. It was shown in Ref. 2a that, because of the nonanalytic character of the real part of the scattering amplitude as a function of the scattering angle, there is an additional component in the line shift (in addition to (2.2)):

$$\frac{4\pi}{9\hbar}ng^2\frac{2j+1}{2j_0+1}.$$

Actually, the effect of the far quasistatic wing of the line on the position of its center is accounted for by this term. This takes the calculation outside the framework of the impact approximation.

Analysis of the general formulas (2.5)–(2.7) shows that as long as $\Delta\omega \gg n\beta$, the broadening of the components of the spectrum (2.5) takes place independently. The doublet consists of two isotopic components, each of which is centered at the frequency $\omega_i - n_i\beta$ ($i = 1, 2$) with the intensity ratio n_1/n_2. When $\Delta\omega \ll n\beta$, one of the components (with A_-), decreasing in intensity, vanishes completely and the spectrum becomes such as it should be in the case of a homogeneous gas (with $\Delta\omega = 0$) with the only difference that its center is shifted to the frequency $\langle\omega\rangle - n\beta$, where

$$\langle\omega\rangle = \frac{n_1}{n_1+n_2}\omega_1 + \frac{n_2}{n_1+n_2}\omega_2.$$

It is appropriate to call this phenomenon "pseudocollapse," to distinguish it from the previously studied collapse of the field[4,5] and rotational[6] structures which arose when the expression under the square root in Ω (2.7) represented the difference, and not the sum, of the squares. In the case of pseudocollapse, only the location and line intensity transform nonlinearly with increase in pressure; their widths do not. This unique transformation of the shifts and intensities of the isotopically mixed components of the spectrum can be of great help in the spectroscopic estimate of the cross sections of resonance collisions of atoms taking place with a small energy deficit.

In conclusion, we note that for the values of j and j_0 that are most interesting from the spectroscopic point of view, the numerical estimate of the parameters Γ and β can be found in[14] (Table 7.6). For example, for $j = 1$ and $j_0 = 0$, we have

$$\Gamma = 2.41\pi g^2/\hbar, \quad \beta = 1.11\pi g^2/\hbar.$$

3. ACCOUNT OF THE HYPERFINE STRUCTURE

The results of the previous section are easily generalized to the case in which the hyperfine structure of the lines of the resonance transition are taken into account. The basic assumption which we make use of here is that during the time of the collision, the state of the nucleus does not change. This is justified by the fact that, as a rule, $\Delta\omega_F\tau_c \ll 1$, where $\Delta\omega_F$ is the characteristic hyperfine splitting; therefore the nuclear spin cannot flip during the time τ_c. Since the interaction does not depend on the nuclear spins, the reduced matrix elements of the dipole moment $\langle j_0F|d(t)|jF'\rangle$ differ from $\langle j_0|d(t)|j\rangle$ in (1.7) only by a constant.[15] Therefore, the set of equations describing the evolution of $\langle j_0F_i|d(t)|jF_i'\rangle$ has the same form as (1.8) with the same matrix elements of the impact operator (1.9)–(1.11), in which we mean by j and l the total angular momentum of the atom F. Generally speaking, this was obvious earlier, since the property of j as the total electron angular momentum in (1.7) has been used nowhere.

The further courses of the discussion is as follows: the vectors $|{}^{F_1M_1}_{F_2M_2}\rangle$, which enters as the bracketing operators of the S matrix in (1.9)–(1.11), resolve into the total basis set of vectors of the system $|F_1F_2FM\rangle$; these in turn are expressed in terms of the vectors $|JIFM\rangle$ and the elements of the impact operator are calculated simply in this basis. Here J and I are the total electron and nuclear angular momenta, respectively, of the system. The connection between representations which differ by the scheme of addition of the angular momenta is universally known.[15] In order to take into account the possibility of resonance transfer of the excitation in the collisions of the isotopes, it is necessary to introduce an even set and an odd set of vectors of the system $|JIFM\rangle_\pm$ (see (2.4)). Calculation of the elements of the impact operator give the same results in this representation as in (2.2) and (2.3), since the nuclear variables have no effect on it. Omitting the intermediate calculations, we give the final result: the nonzero reduced matrix elements of the impact operator, which characterize the collision without excitation transfer, are

$$\Gamma_{12}(F_1F_1'F_1F_1')=\Gamma_{21}(F_2F_2'F_2F_2')=\Gamma, \tag{3.1}$$

while the matrix elements responsible for the transfer of the excitation are given by the relation

$$\Gamma_{12}(F_1F_1'F_2F_2')=i\left[\frac{(2F_1+1)(2F_1'+1)(2F_2'+1)}{2F_2+1}\right]^{1/2}\sum_{FIJM}(2F+1)(2I+1) \times\begin{Bmatrix}F_1' & F & F_2\\ F_2' & 1 & F_1\end{Bmatrix}\begin{Bmatrix}j & j_0 & J\\ I_1 & I_2 & I\\ F_1' & F_2 & F\end{Bmatrix}\begin{Bmatrix}j_0 & j & J\\ I_1 & I_2 & I\\ F_1 & F_2' & F\end{Bmatrix}\langle \mathrm{Im}\, S^J_{MM}\rangle \tag{3.2}$$

and reduce to a single parameter β, excluding the trivial case $I_1=I_2=0$, only for $j_0=0$ (or $j=0$). The matrix elements Γ_{21} are obtained from (3.2) by interchanging the indices 1 by 2. The impact-operator elements responsible for the self-broadening consist of two terms: the first is, naturally, (3.1), and the second is (3.2), in which we must set $I_1=I_2$. The expression in the curly brackets is the $9j$ symbol. In the derivation of (3.1) and (3.2), we made essential use of the circumstance that the lower level is not perturbed by the collisions ($S^+=1$).

4. MAGNETIC RESONANCE OF THE GROUND STATE

In this section we investigate the absorption of microwave power by a gas of identical atoms in the ground state, in the presence of a constant magnetic field B oriented along the z axis. The magnetic field will be assumed to be sufficiently strong so that the coupling of the electron angular momentum J with the nuclear angular momentum I can be regarded as broken. In such a case, the unperturbed Hamiltonian is

$$H_0=\mu gBJ_z+\hbar AJ_zI_z, \tag{4.1}$$

where μ is the Bohr magneton, g the Landé gyromagnetic ratio, and A the constant of hyperfine interaction. Collision of the atom turns on the exchange interaction

$$V(t)=-\hbar\Delta(t)\mathbf{J}_1\mathbf{J}_2, \tag{4.2}$$

in which $\Delta(t)$ is the exchange integral and is a functional of the classical trajectory of the colliding particles $\mathbf{R}(t)$.

In the representation of the total electron angular momentum of the pair of colliding particles

$$|JM\rangle=(2J+1)^{1/2}(-1)^M\sum_{m_1m_2}\begin{pmatrix}j_0 & j_0 & J\\ m & m & -M\end{pmatrix}\left|\begin{matrix}m_1\\ m\end{matrix}\right\rangle \tag{4.3}$$

the scattering matrix is diagonal and does not depend on M:

$$S_J=e^{i\delta_J},\quad \delta_J=\left[\frac{J(J+1)}{2}-j_0(j_0+1)\right]\int_{-\infty}^{+\infty}\Delta(t)\,dt. \tag{4.4}$$

Substituting the S-matrix elements calculated in the basis (4.3) in (1.9)–(1.11), we obtain the impact-operator matrix element responsible for the broadening, and the impact-parameter matrix element that determines the frequency of the spin exchange:

$$\gamma=\left\langle 1-\sum_{JJ'}\frac{(2J+1)(2J'+1)}{(2j_0+1)}\begin{Bmatrix}J & 1 & J'\\ j_0 & j_0 & j_0\end{Bmatrix}^2 S_J^*S_{J'}\right\rangle, \tag{4.5}$$

$$\beta=\left\langle\sum_{JJ'}(-1)^{J+J'}\frac{(2J+1)(2J'+1)}{(2j_0+1)}\begin{Bmatrix}J & 1 & J'\\ j_0 & j_0 & j_0\end{Bmatrix}^2 S_J^*S_{J'}\right\rangle. \tag{4.6}$$

Since the expression under summation in (4.6) is symmetric in J, J', it is easy to prove that the parameter β is real, in correspondence with its definition. We can show by direct calculation that the rate of spin relaxation β is identical with the frequency of spin exchange for all j_0 except $j_0=0$. For $j_0=0$, the interaction (4.2), broadening this state, is absent.

In a homogeneous external magnetic field, the dipole moment matrix elements $\mu_x(t)=-\mu gJ_x(t)$ cannot be written down in the form (1.7), since the symmetry of the Hamiltonian H_0 is reduced from spherical to axial. Therefore, we expand the operator of the angular momentum $J_x(t)$ in terms of the irreducible tensor operators $\hat{T}_q^{\varkappa}$[15]; only operators with $\varkappa=1$ enter into the expansion in the case of a homogeneous field[16]:

$$J_x(t)=\sum_q(-1)^q J_{-q}(t)T_q^1, \qquad (4.7)$$

where $J_{-q}(t)$ are already c numbers (not operators!), equal to

$$J_{-q}(t)=\sqrt{3}\sum_{mm'}(-1)^{m-j_0-q}\begin{pmatrix} j_0 & 1 & j_0 \\ -m & q & m' \end{pmatrix}\langle m|J_x(t)|m'\rangle, \qquad (4.8)$$

and

$$J_0(0)=0, \quad J_{\pm1}(0)=\mp[j_0(j_0+1)(2j_0+1)/6]^{1/2}. \qquad (4.9)$$

By virtue of our assumptions, the z projection of the nuclear spin does not change in the collision process; therefore, relaxation transitions are possible only between states with identical values of M. Here the spin exchange is accompanied by frequency exchange if the colliding atoms belong to different components of the hyperfine structure (HFS). The set of equations for $J_q(t)$ which describes the spin exchange between components of the HFS has a form similar to (1.8):

$$\begin{aligned} \dot J_q(M_1)&=[-iq(\omega_0+AM_1)-n\gamma]J_q(M_1)+\frac{n\gamma}{2I+1}\sum_{M_2'}J_q(M_2'),\\ \dot J_q(M_2)&=[-iq(\omega_0+AM_2)-n\gamma]J_q(M_2)+\frac{n\gamma}{2I+1}\sum_{M_1'}J_q(M_1'), \end{aligned} \qquad (4.10)$$

but, in contrast with the case of spherical symmetry, the Hamiltonian H_0 in (4.10) is diagonal in q only because the quantization axis coincides with the direction of the field B. Here $\omega_0=\mu gB/\hbar$ is the Larmor precession frequency. The impact operator in (4.10) is also diagonal in q. This fact is not accidental, and follows directly from the theorem proved by D'yakonov and Perel',[17] according to which the impact parameter in an isotropic space reduces to diagonal form in the $\varkappa q$ representation. Solution of Eqs. (4.10) is easily found by transforming to the Fourier expansion of the components

$$J_q(t)=\frac{1}{2}\sum_{M_1=-I}^{I}J_q(M_1)+\frac{1}{2}\sum_{M_2=-I}^{I}J_q(M_2),$$

i.e.,

$$J_q(\omega)=\int_0^\infty dt\, e^{i\omega t}J_q(t). \qquad (4.11)$$

Simple algebraic transformations lead to the result

$$J_q(\omega)=J_q(0)\frac{f_q(\omega)}{1-n\gamma f_q(\omega)} \qquad (4.12)$$

where

$$f_q(\omega)=\frac{1}{2I+1}\sum_{M=-I}^{I}\frac{1}{-i[\omega-q(\omega_0+AM)]+n\gamma}. \qquad (4.13)$$

With account of the initial condition (4.9) and also with use of the expansion $\tanh(\hbar\omega/2kT)\approx\hbar\omega/2kT$ for $\hbar\omega\ll 2kT$, we get the final expression for the absorbed intensity (1.1):

$$I(\omega)=\frac{\omega}{2}B_0^2\chi_{xx}''(\omega)=\frac{\omega^2}{2}B_0^2\frac{\chi_0}{2}\operatorname{Re}\sum_{q=\pm1}\frac{f_q(\omega)}{1-n\gamma f_q(\omega)}. \qquad (4.14)$$

Here χ_0 is the statistical magnetic susceptibility of the system:

$$\chi_0=n\frac{j_0(j_0+1)}{3kT}(\mu g)^2.$$

The nonresonance component with $q=-1$ in (4.14) can be omitted.

In the region of slow exchange $A\gg n\gamma$, all the components of the HFS are resolved and have a Lorentzian shape with halfwidth $n\gamma$. In the region of rapid exchange, $A\ll n\gamma$, the spectrum collapses: all the lines join (at the Larmor precession frequency ω_0) in a single line, the halfwidth of which

$$\Delta\omega_{1/2}=\frac{I(I+1)}{3}\frac{A^2}{n\gamma} \qquad (4.15)$$

decreases with increase in the collision frequency, assuring the narrowing of the HFS spectrum with pressure.

A phenomenon of this type has already been observed in the molecular spectroscopy of gases after pressure averaging of the hyperfine structure of the electron paramagnetic resonance spectrum.[18]

We estimate the possibility of observation of this effect in atomic spectroscopy. For example, for the important case $j_0=\frac{1}{2}$, we have from Eq. (4.5) (or (4.6)),

$$\gamma=\langle v\sigma_{\text{exch}}\rangle, \quad \sigma_{\text{exch}}=\int_0^\infty 2\pi b\,db\,\sin^2\int_{-\infty}^{+\infty}\frac{\Delta(t)}{2}dt. \qquad (4.16)$$

The numerical estimate of the cross section of spin exchange in collisions of alkali metals is given in Ref. 14 (Table 7.2). The characteristic scale of the quantities $\langle v\sigma\rangle/\langle v\rangle\sim10^{-14}$ cm^2; therefore, we can expect that the HFS spectrum of the alkali metals collapses completely even at pressures of the order of several atmospheres. For ^{39}K, we have $n\gamma\gg A$ even at 2 atm ($T=500\,^\circ$K).

[1] A. P. Kazantsev, Zh. Eksp. Teor. Fiz. 51, 1751 (1966) [Soviet Phys. JETP 24, 1183 (1967)].

[2] a) Yu. A. Vdovin and V. M. Galitskiĭ, Zh. Eksp. Teor. Fiz. 52, 1345 (1967) [Soviet Phys. JETP 25, 894 (1967)]; b) Yu. A. Vdovin and N. A. Dobrodeev, Zh. Eksp. Teor. Fiz. 55, 1047 (1968) [Soviet Phys. JETP 28, 544 (1969)] c) Yu. A. Vdovin, V. M. Galitskiĭ and V. V. Yakimets, in: Voprosy teorii atomnykh stolknovenii (Problems of atomic collision theory) Atomizdat, 1970.

[3] A. Ben-Reuven, Phys. Rev. 4A, 2115 (1971).

[4] M. L. Sterkalov and A. I. Burshteĭn, Zh. Eksp. Teor. Fiz. 61, 101 (1971). [Soviet Phys. JETP 34, 53 (1972)].

[5] A. I. Burshteĭn and G. I. Smirnov, Zh. Eksp. Teor. Fiz. 65, 2174 (1973) [Soviet Phys. JETP 38, 1085 (1974)].

[6] A. I. Burshteĭn, M. L. Strekalov and S. I. Temkin, Zh. Eksp. Teor. Fiz. 66, 894 (1974) [Soviet Phys. JETP 39, 433 (1974)].

[7] K. M. Salikhov, A. B. Doctorov, Yu. M. Molin and K. I. Zamarev, J. Magn. Reson. 5, 189 (1971).

[8] D. Kivelson, J. Chem. Phys. 33, 1094 (1960).

[9] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[10] E. G. Pestov and S. G. Rautian, Zh. Eksp. Teor. Fiz. 56, 902 (1969); 64, 2032 (1973) [Soviet Phys. JETP 29, 488 (1969); 37, 1025 (1973)].

[11] A. I. Burshteĭn, a) Dokl. Akad. Nauk 166, 577 (1966) [Soviet

Phys. Doklady 11, 65 (1966)] b) Kvantovaya kinetika (Quantum Kinetics) Pt. II, Novosibirsk Univ. Press, 1968.
[12] P. W. Anderson, Phys. Rev. 76, 647 (1949).
[13] Yu. A. Vvodin and V. M. Galitskiĭ, Zh. Eksp. Teor. Fiz. 69, 103 (1975) [Soviet Phys. JETP 42, 51].
[14] B. M. Smirnov, Asimptoticheskie metody v teorii atomnykh stolknoveniĭ (Asymptotic methods in the theory of atomic collisions) Ch. 7, Atomizdat, 1973.
[15] A. Edmonds, Angular Momenta in quantum mechanics, Princeton, 1957.
[16] M. P. D'yakonov, Zh. Eksp. Teor. Fiz. 47, 2213 (1964) [Soviet Phys. JETP 20, 1484 (1965)].
[17] M. I. D'yakonov and V. I. Perel', Zh. Eksp. Teor. Fiz. 48, 345 (1965) [Soviet Phys. JETP 22, 227 (1965)].
[18] T. J. Schaafsma and D. Kivelson, J. Chem. Phys. 49, 5235 (1968).

Translated by R. T. Beyer

Transitions from a discrete level to the continuous spectrum upon adiabatic variation of the potential

E. A. Solov'ev

Leningrad State University

(Submitted August 27, 1975)
Zh. Eksp. Teor. Fiz. 70, 872–882 (March 1976)

An adiabatic approximation describing transitions between a molecular term and the continuous spectrum is developed. The motion of the nuclei is assumed to be classical. The developed approximation is utilized for an investigation of the processes which take place during the collision of a negative ion with a neutral atom. A universal distribution with respect to the momenta of the emitted electrons is obtained for this case, this distribution being valid for all momenta. The effect of the formation of a quasistationary *s*-term on the low-energy part of the spectrum of the emitted electrons is considered. The probability of populating the discrete levels of the system via the continuous spectrum is calculated. Possible applications of the approximation developed in this work to other problems in the theory of atomic collisions are discussed.

PACS numbers: 34.10.+x

1. INTRODUCTION

One of the important problems in the theory of atomic collisions is the problem of the interaction of a molecular term with the continuous spectrum when, on the one hand, the motion of the nuclei can be regarded as classical and, on the other hand, as sufficiently slow. The goal of the theory is a calculation of the populations of the discrete terms and the momentum distribution of the electrons which are emitted into the continuous spectrum. The results obtained in this field are basically connected with either the exactly soluble model of Demkov–Osherov[1] or else with an assumption concerning the smallness of the interaction between the term and the continuous spectrum.[2] The interaction of a term with the continuous spectrum is not small in the majority of experimentally important cases. At the same time the models describe only the low-energy part of the spectrum of the emitted electrons, where one can abstract from the specific features of the utilized models, and do not permit one to investigate certain effects connected with reverse motion of the system with respect to the term. Thus, the existing theory does not give a complete description of the cited processes. In this connection an approach which does not contain any restrictions on the form of the Hamiltonian and the behavior of the terms, but only utilizes the smallness of the colliding particles' velocity, is of interest. Such a problem is solved in the present article.

The approximation developed in Sec. 2 is not related to either model representations or to an assumption concerning the smallness of the interaction of a term with the continuous spectrum. It is asymptotically exact with respect to the small parameter v which characterizes the time rate of change of the electronic Hamiltonian. The electron wave function is sought in the form of an integral over the energy E of the adiabatic wave functions, in the same way as this is done in the Demkov–Osherov model. Such an approach differs from that adopted in the theory of nonadiabatic transitions between discrete terms[3] by the fact that the expansion in terms of states of the instantaneous Hamiltonian is still integrated over E. This difference has a simple physical meaning. The integration over the energy allows one to uniquely take into consideration the retardation, which is unimportant for transitions between discrete levels due to the localized nature of the wave functions.

In Secs. 3 and 4 the approximation is utilized in order to investigate the processes which take place during the collision of a negative ion with a neutral atom. In spite of the fact that the theory is most highly developed for this case, the approximation developed in this article enables us to obtain a number of new results. The momentum distribution is calculated for the reaction involving the detachment of an electron, the result being valid for all momenta of the emitted electrons (the previously obtained results only pertain to the low-energy part of the spectrum of the emitted electrons). The influence of the turning point of the *s*-term and of the formation