Alteration of atomic multiplet in an intense varying field

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An analytic solution is obtained for the problem of alteration of a multiplet in a varying external field when the interaction between the atom and field is comparable in magnitude with the multiplet splitting and the usual perturbation theory is invalid. The cases of one-photon resonance, two-photon resonance, and an external field of nonresonant frequency are considered. The spontaneous emission spectrum is discussed for transitions between multiplet levels of atoms in a field. Some features of the probabilities for 3- and 4-photon ionization in the presence of intermediate multiplet resonances are also discussed.

1. INTRODUCTION

The change in the atomic spectrum in an external electric field, i.e., the Stark effect, plays an important role in the interpretation of nonlinear optical phenomena in atomic gases. Studies of this phenomenon can also be used to obtain valuable information on the atomic parameters and the statistical properties of radiation.

The Stark effect has now been adequately investigated both theoretically and experimentally for isolated atomic levels in nonresonant-frequency external fields, and for a pair of isolated levels in a resonant field.[1] These isolated levels can be degenerate, i.e., they can be the levels of a hydrogen-like atom,[2] or the magnetic sublevels in the field of partially polarized radiation.[3,4]

However, it is frequently necessary to deal with a group of closely spaced levels and, in particular, multiplets which, on the one hand, cannot be regarded as degenerate and, on the other, the Stark interaction between them cannot be taken into account via perturbation theory because the interaction matrix element turns out to be of the order of the separation between the levels of the multiplet of the unperturbed atom in the case of strong fields. The solution of the problem of the transformation of a multiplet in a strong constant field has been reported in the literature.[5,6] In this paper we show that similar results can be obtained for a varying field. Three classes of problems arise, depending on the field frequency: 1) two multiplets in a field of frequency ω which is roughly equal to the separation between the multiplets; 2) two multiplets separated by $\sim 2\omega$; two-photon resonance; 3) multiplet in nonresonant field (in this case, resonances at frequencies 3ω, 4ω ... are possible). This classification is connected with the first nonvanishing order of Feynman graphs which give the corrections. In the case of single-photon resonance, the energy corrections arise even for graphs with a single vertex in the external field. In the case of two-photon resonance and a nonresonant field, the energy corrections arise in the second order.

The above problems can be solved in closed form within the framework of the following approximations: 1) the external-field frequency ω is much greater than Δ, where Δ is the splitting of the multiplet in the absence of the field; 2) the multiplet is localized in the atomic spectrum: if D is the distance between the multiplet and the level nearest to it, which is not a member of the multiplet and is optically connected with it, then $D \gg \Delta$; 3) if the multiplet does not resonate

at ω and 2ω with other atomic levels, the external field does not mix the multiplet with the level nearest to it; $V \ll D$. If, on the other hand, there is a resonance, the field mixes only the resonating multiplets which are assumed localized in the atomic spectrum. The first condition is satisfied at optical and infrared frequencies but at lower frequencies this condition may be violated. Therefore, there is no continuous transition from the formulas obtained in the present work to the case of constant fields.

We shall confine our attention to linearly polarized fields. The case of arbitrary polarization can be analyzed in a similar way but the resulting formulas are much more unwieldy and obscure the basic point, i.e., the role of level multiplicity. The role of the polarization is considered for isolated levels in[3,4].

2. NONRESONATING FIELD

The wave function $\psi_{AM}(t)$ for an atom in a field will be sought in the form of an expansion in terms of the eigenfunctions of the atom in the absence of the field, i.e., $|\lambda jM\rangle$:[1)]

$$\psi_{AM}(t) = \sum_J a_J(t) \exp(-iE_{AJ}t) |\Lambda JM\rangle$$
$$+ \sum_{\lambda j} b_{\lambda j}(t) \exp(-iE_{\lambda j}t) |\lambda jM\rangle. \tag{1}$$

In this expression j is the total angular momentum of the atom, M is its component along the field, and λ are the remaining quantum numbers. Terms corresponding to the $\{\Lambda J\}$ multiplet are separated out in Eq. (1).

The coefficients a and b satisfy the following equations:

$$i\dot{a}_J = \sum_{J'} \langle \Lambda JM | V(t) | \Lambda J'M \rangle \exp[i(E_{\Lambda J} - E_{\Lambda J'})t] a_{J'}(t)$$
$$+ \sum_{\lambda j} \langle \Lambda JM | V(t) | \lambda jM \rangle \exp[i(E_{\Lambda J} - E_{\lambda j})t] b_{\lambda j}(t),$$

$$i\dot{b}_{\lambda j} = \sum_J \langle \lambda jM | V(t) | \Lambda JM \rangle \exp[i(E_{\lambda j} - E_{\Lambda J})t] a_J(t)$$

$$+ \sum_{\lambda' j'} \langle \lambda jM | V(t) | \lambda' j'M \rangle \exp[i(E_{\lambda j} - E_{\lambda' j'})t] b_{\lambda' j'}(t), \tag{2}$$

where $V(t) = -d_z F \cos \omega t$ is the Hamiltonian for the interaction between the atom and the electric field of the wave, F is the amplitude of this field, and d is the dipole-moment operator.

As noted in the introduction, we assume that $V \ll D \equiv \min\{|E_{\Lambda J} - E_{\lambda j}|\}$ and, therefore, we can take into account the contribution of the coefficients b to the

coefficients a in accordance with perturbation theory. We do this by omitting the second term in the second equation in (2) and integrating the resulting equation with respect to time. Since it will become evident that coefficients a are slow functions of time (frequency $\sim\Delta$), they can be taken outside the integral sign.

Substituting the result into the first equation in Eq. (2), and retaining only the slowly varying terms in this equation, we obtain (see[7]):

$$i\dot{a}_J = \sum_{J'} G_{JJ'}^{\Lambda\Lambda'M} \exp[i(E_{\Lambda J} - E_{\Lambda'J'})t]a_{J'},$$

$$G_{JJ'}^{\Lambda\Lambda'M} = G_{JJ'}^{\Lambda\Lambda'M(+)} + G_{JJ'}^{\Lambda\Lambda'M(-)},$$ (3)

$$G_{JJ'}^{\Lambda\Lambda'M(\pm)} = -\frac{F^2}{4}\sum_{\lambda j}\frac{\langle\Lambda JM|d_z|\lambda jM\rangle\langle\lambda jM|d_z|\Lambda'J'M\rangle}{E_{\lambda j} - (E_{\Lambda J} \pm \omega + i\varepsilon)}$$

The choice of the retarded Green function for the unperturbed atom in Eq. (3) is dictated, among other things, by the need to ensure that the resulting quasistationary states be of the decay type. If the $|\Lambda JM\rangle$ level also has the decay width γ_J, which is not connected with the effect of the field $F\cos\omega t$ on the atom, the right-hand side of Eq. (3) must be augmented by the term $-i\gamma_J a_J a_J$.

The set of equations in (3) can be reduced to a set of equations with constant coefficients by substituting

$$a_J(t) = a_{J'}(t)\exp(iE_{\Lambda J}t).$$ (4)

For the column of coefficients a' we have

$$i\dot{a}' = Qa',$$
$$Q_{JJ'} = (E_{\Lambda J} - i\gamma_J)\delta_{JJ'} + G_{JJ'}^{\Lambda\Lambda M}.$$ (5)

This is a Schrödinger type equation with a time-independent Hamiltonian in a finite-dimensional space. However, the effective Hamiltonian Q in Eq. (5) is, in general, non-self-adjoint even when $\gamma_J = 0$, and the multiplet splitting of the levels in the energy denominators in the parameters $G(E_{\Lambda J} \approx E_{\Lambda J'},$ for $J \neq J')$ is neglected. In fact, if for the levels of the $\{\Lambda J\}$ multiplet we have an open single-photon ionization channel, the quantity $i\varepsilon$ in the denominator of $G^{(+)}$ cannot be omitted, and this means that Q is not self-adjoint.

One of the consequences of this fact is that the eigenvectors corresponding to different eigenvalues of the matrix Q are nonorthogonal. Physically, the nonorthogonality of the quasistationary states corresponds to the possibility of the decay of these states into the same channel, and this is precisely what happens when the levels of the multiplet are mixed by the external field. The theory of nonorthogonal quasistationary states and of the scattering by these states has recently been developed (see, for example,[8]). From the mathematical standpoint it is very convenient that the matrix Q becomes symmetric when the multiplet splitting is neglected in the denominators of the parameters G. Since we have assumed that $\Delta \ll D$ in the derivation of Eq. (3), this does not lead to a deterioration in the accuracy of the results.

We shall now confine our attention to LS coupling. Let L and S be the orbital and spin angular momenta of the $\{\Lambda J\}$ multiplet, and l the orbital angular momentum of the intermediate states

$$|\lambda jM\rangle = \sum_{m\mu} C_{lmS\mu}^{JM}\varphi_{\lambda lm}\chi_{S\mu},$$

where φ and χ are the orbital and spin parts of the wave function. We assume that $E_{\Lambda J} = E_{\Lambda L}$, $E_{\lambda j} = E_{\lambda L}$

for all J, j, and standard calculations then yield

$$Q_{JJ'} = (E_{\Lambda J} - i\gamma_J)\delta_{JJ'} - \frac{F^2}{4}\sum_{m\mu}\alpha_{Lm}C_{LmS\mu}^{JM}C_{LmS\mu}^{J'M},$$

$$\alpha_{Lm} = -\frac{(L+1)^2 - m^2}{L+1}\frac{D_{L+1}}{[(2L+1)(2L+3)]^{1/2}} + \frac{m^2}{L(L+1)}D_L$$
$$- \frac{(L^2 - m^2)D_{L-1}}{L[(2L-1)(2L+1)]^{1/2}}$$ (6)

$$D_l = \sum_\lambda \langle\varphi_{\lambda L}\|d\|\varphi_{\lambda l}\rangle\langle\varphi_{\lambda l}\|d\|\varphi_{\Lambda L}\rangle$$
$$\times\left[\frac{1}{E_{\lambda l} - (E_{\Lambda L} + \omega + i\varepsilon)} + \frac{1}{E_{\lambda l} - (E_{\Lambda L} - \omega + i\varepsilon)}\right],$$

$$\langle\varphi_{\Lambda Lm}|d_z|\varphi_{\lambda lm}\rangle = C_{lm10}^{Lm}\langle\varphi_{\Lambda L}\|d\|\varphi_{\lambda l}\rangle.$$

It is clear from this that Q is symmetric. The diagonal matrix elements Q_{JJ} determine the level positions in a weak field when the interaction between neighboring levels of the multiplet can be taken into account through perturbation theory. The quantity

$$\alpha_{JM} = \sum_{m\mu}\alpha_{Lm}(C_{LmS\mu}^{JM})^2$$ (7)

is then the polarizability of the level JM. It is readily seen that α_{Lm} are the polarizabilities of the m-sublevels of states with orbital angular momentum L when the spin-orbit interaction can be neglected, and determine the spectrum in the strong field (see below).

Let us introduce the eigenvectors $f^{(k)}$ and matrices Q as follows:

$$Qf^{(k)} = q_k f^{(k)}, \qquad (f^{(k)T}f^{(k')}) = \delta_{kk'},$$ (8)

where T represents transposition. The orthonormalization condition given by Eq. (8) is a consequence of the symmetry of Q. If $\gamma_J = 0$ and the field frequency is less than the multiplet ionization potential, the matrix Q can be regarded as real and hence Hermitian, without loss of generality. In this case, $f^{(k)}$ can be taken to be a real vector, and transposition is equivalent to Hermitian conjugation.

Consider the expansion

$$a'(t) = \sum_k g_k(t)f^{(k)}; \qquad g_k(t) = C_k\exp(-iq_k t),$$ (9)

where C_k are arbitrary constants. Substituting Eqs. (9) and (4) into the first term in Eq. (1), we obtain the general solution of the time-dependent Schrödinger equation

$$\psi_{\Lambda LSM}(t) = \sum_k C_k\Phi_{\Lambda LSM}^{(k)}\exp(-iq_k t),$$ (10)

$$\Phi_{\Lambda LSM}^{(k)} = \sum_J f_J^{(k)}|\Lambda LSJM\rangle.$$

For example, for a wave function which at $t = 0$ has a definite total angular momentum J_0, the constants C_k can be found from the completeness condition for $f^{(k)}$: $C_k = f_{J_0}^{(K)}$.

It is clear from Eq. (10) that in an arbitrary field the spectrum of the multiplet is determined by the eigenvalues q_k of the matrix Q, and the corresponding quasistationary states are the functions $\Phi^{(k)}$. As already noted, if the ionization potential is less than the radiation frequency, the functions $\Phi^{(k)}$ are not orthogonal or normalized. The normalization of $\Phi^{(k)}$ can be performed, but there is not much point in this because the functions are not orthogonal.

For the doublet level the eigenvalues of Q can readily be found in the general form, as follows:

$$q_{1,2} = \frac{1}{2}[E_{L+\frac{1}{2}} + E_{L-\frac{1}{2}} - i(\gamma_{L+\frac{1}{2}} + \gamma_{L-\frac{1}{2}})]$$

$$-\frac{1}{8}F^2(\alpha_{LM+\frac{1}{2}} + \alpha_{LM-\frac{1}{2}}) \pm \frac{1}{2}\left[\Delta^2 + \Delta F^2 \frac{M^2}{2L+1}(\alpha_{LM+\frac{1}{2}} - \alpha_{LM-\frac{1}{2}})\right.$$

$$\left. + \frac{1}{16}F^4(\alpha_{LM+\frac{1}{2}} - \alpha_{LM-\frac{1}{2}})^2\right]^{\frac{1}{2}}, \quad (11)$$

where $\Delta \equiv E_{L+1/2} - E_{L=1/2} - i(\gamma_{L+1/2} - \gamma_{L=1/2})$ and the α_{Lm} are defined by Eq. (6).

In the case of a weak field $\alpha_{Lm}F^2 \ll |\Delta|$ and we have from Eq. (11)

$$q_{1,2} = E_{L\pm\frac{1}{2}} - i\gamma_{L\pm\frac{1}{2}} - \frac{1}{4}\alpha_{L\pm\frac{1}{2}, M}F^2;$$

where

$$\alpha_{L\pm\frac{1}{2},M} = \frac{L+\frac{1}{2}\pm M}{2L+1}\alpha_{LM-\frac{1}{2}} + \frac{L+\frac{1}{2}\mp M}{2L+1}\alpha_{LM-\frac{1}{2}}$$

is the polarizability of the level JM. For a strong field $\alpha_{LM}F^2 \gg |\Delta|$ and we have

$$q_{1,2} = \frac{1}{2}[E_{L+\frac{1}{2}} + E_{L-\frac{1}{2}} - i(\gamma_{L+\frac{1}{2}} + \gamma_{L-\frac{1}{2}})] - \frac{1}{4}\alpha_{LM\pm\frac{1}{2}}F^2.$$

It is clear from the above formulas that in a weak field the quasistationary states are those with a definite total angular momentum and a definite component of this momentum in the direction of the field. In a strong field, on the other hand, the total angular momentum is not conserved and the components of the orbital angular momentum and of the spin in the direction of the field are good quantum numbers.

3. SINGLE-PHOTON RESONANCE

Let us now consider the case illustrated in Fig. 1 when the field frequency ω lies in the region of anomalous dispersion of the atom, which corresponds to transitions between the sublevels of the multiplets $\{\Lambda J\}$ and $\{\Lambda'J\}$. The atomic wave function will be sought in the form of an expansion in terms of the function $|\Lambda JM\rangle$ and $|\Lambda'IM\rangle$. The expansion coefficients a_J and a_I satisfy a set of equations similar to Eq. (2) which in the resonance approximation assumes the form

$$i\dot{a}_J = -i\gamma_J a_J - \frac{1}{2}F\sum_I \langle\Lambda JM|d_z|\Lambda'IM\rangle\exp[i(E_{\Lambda J} + \omega - E_{\Lambda'I})t]a_I,$$

$$(12)$$

$$i\dot{a}_I = -i\gamma_I a_I - \frac{1}{2}F\sum_J \langle\Lambda'IM|d_z|\Lambda JM\rangle\exp[i(E_{\Lambda'I} - \omega - E_{\Lambda J})t]a_J$$

The coefficients of this set become constants after the substitution

$$a_J(t) = a_J'(t)\exp(iE_{\Lambda J}t), \quad a_I(t) = a_I'(t)$$
$$\times \exp(i(E_{\Lambda'I} - \omega)t).$$

The column $a' = (a_{J1}\ldots a_{I1}\ldots)^T$ of the unknowns satisfies the equation

$$i\dot{a}' = Qa', \quad Q_{JI} = Q_{IJ} = -\frac{1}{2}F\langle\Lambda JM|d_z|\Lambda'IM\rangle,$$

$$(13)$$

$$Q_{JJ} = E_{\Lambda J} - i\gamma_J, \quad Q_{II} = E_{\Lambda'I} - \omega - i\gamma_I.$$

The matrix Q is symmetric since the matrix elements d are real. Proceeding as in the case of a nonresonant field, we obtain the following general expression for the atomic wave function:

$$\psi(t) = \sum_k C_k[\Phi_{\Lambda M}^{(k)}\exp(-iq_kt)$$

$$+ \Phi_{\Lambda'M}^{(k)}\exp(-i(q_k+\omega)t)], \quad (14)$$

$$\Phi_{\Lambda M}^{(k)} = \sum_J f_J^{(k)}|\Lambda JM\rangle, \quad \Phi_{\Lambda'M}^{(k)} = \sum_I f_I^{(k)}|\Lambda'IM\rangle.$$
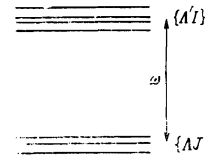
FIG. 1

It is clear from Eq. (14) that an atom placed in the resonance field has a larger number of observable spectral lines: if N is the total number of levels in both multiplets of the unperturbed atom,[2] the total number of energy levels of the atom in the field is 2N, and in each multiplet level there are N such levels. For example, the spontaneous emission spectrum of the atom in the region near ω should contain for each value of $|M|$ a total of $N(N-1)$ spectral lines with $\Delta M = 0$ which differ in frequency from ω. On the other hand, the number of linearly independent solutions of the time-dependent Schrödinger equation is, as in the absence of the field, equal to N in accordance with the number of arbitrary constants C_k in Eq. (14).

Consider a simple case: the resonance interaction between the singlet level $S_{1/2}$ (this lower multiplet will be denoted by S) and the doublet $P_{1/2}$, $P_{3/2}$ (the upper-multiplet components will be denoted by P and P'). We shall substitute

$$(E_{P,P'} - i\gamma_{P,P'}) - (E_S - i\gamma_S) \equiv \delta_{1,2}, \quad \delta \equiv \frac{1}{2}(\delta_1 + \delta_2),$$

$$\Delta \equiv \delta_2 - \delta_1, \quad \varepsilon \equiv \frac{1}{6}\delta_1 + \frac{1}{12}\delta_2.$$

The matrix Q then takes the form

$$
\begin{array}{ccc}
S & P & P' \\
\end{array}
$$
$$
\begin{array}{c}
S \\ P \\ P'
\end{array}
\left(
\begin{array}{ccc}
E_S - i\gamma_S & FMd/\sqrt{3} & -Fd/\sqrt{6} \\
FMd/\sqrt{3} & E_P - i\gamma_P - \omega & 0 \\
-Fd/\sqrt{6} & 0 & E_{P'} - i\gamma_{P'} - \omega
\end{array}
\right), \quad
\begin{array}{l}
d \equiv \langle\varphi_{S0}|d_z|\varphi_{P0}\rangle, \\
M = \pm\frac{1}{2}.
\end{array}
$$

The eigenvalues of Q can be found from the Cardano formula

$$q_k = E_S - i\gamma_S + \frac{2}{3}\delta - x_k, \quad x_1 = r_1 + r_2, \quad x_{2,3} = -\frac{r_1 + r_2}{2} \pm \frac{\sqrt{3}}{2}i(r_1 - r_2),$$

$$r_{1,2} = (u \pm \sqrt{v})^{\frac{1}{3}}, \quad u = \frac{\delta}{27}(\delta_1\delta_2 - 2\Delta^2) + \frac{1}{2}\left(\varepsilon - \frac{1}{6}\delta\right)F^2d^2, \quad (15)$$

$$v = u^2 - \frac{1}{27}[\frac{1}{3}\delta^2 - \delta_1\delta_2 + \frac{1}{4}F^2d^2].$$

The limiting case of two interacting levels is obtained from the above formulas if one of the frequency differences, say, δ_2 is much greater than δ_1 and Fd. If we restrict ourselves to terms $\sim(\delta_1/\delta_2)^2$ and $\sim(Fd/\delta_2)^2$, we obtain

$$q_1 = E_S - i\gamma_S + \delta_2, \quad q_{2,3} = E_S - i\gamma_S + \frac{\delta_1}{2} \pm \left(\frac{\delta_1^2}{4} + \frac{F^2d^2}{12}\right)^{\frac{1}{2}}.$$

The eigenvalue q_1 corresponds to the time-independent coefficient $a_{P'}$ and zero values of a_P and a_S. In other words, in this particular limiting case, the field does not affect the energy of the $P_{3/2}$ level and does not mix this level with other states. For the $S_{1/2}$ and $P_{1/2}$ levels we have the results of the usual two-level approximation.

Now consider the case of a strong field: $f^2d^2 \gg |\Delta|^2$. We are assuming that $\delta_1 \approx \delta_2 \approx \delta$ but we are not assuming that δ_1 and δ_2 are small in comparison with Fd. In this limit (and in the general case) there are three eigenvalues

$$q_1 = E_S - i\gamma_S + \delta, \quad q_{2,3} = E_S - i\gamma_S + \frac{\delta}{2} \pm \left(\frac{\delta^2}{4} + \frac{F^2d^2}{4}\right)^{\frac{1}{2}}.$$

However, the function $\Phi^{(1)}$ given by Eq. (14), which corresponds to q_1, can be readily verified to be identically equal to zero. The level S and the spin-degenerate level P therefore do split into only two sublevels. This limiting case corresponds to complete neglect of the spin-orbit interaction right from the outset.

4. TWO-PHOTON RESONANCE

Let us again consider the case illustrated in Fig. 1, but let us now suppose that the distance between the multiplets is approximately 2ω. If we combine the methods described in Sec. 2 and 3, we obtain the equations for the slowly varying coefficients

$$i\dot{a}_J = -i\gamma_J a_J + \sum_{J'} G_{JJ'}^{\Lambda\Lambda M} \exp\{i(E_{\Lambda J} - E_{\Lambda J'})t\}a_{J'}$$
$$+ \sum_I G_{JI}^{\Lambda\Lambda'M(+)} \exp\{i(E_{\Lambda J} - E_{\Lambda'I} + 2\omega)t\}a_I,$$

(16)

$$i\dot{a}_I = -i\gamma_I a_I + \sum_{I'} G_{II'}^{\Lambda'\Lambda'M} \exp\{i(E_{\Lambda'I} - E_{\Lambda'I'})t\}a_{I'}$$
$$+ \sum_J G_{IJ}^{\Lambda'\Lambda M(-)} \exp\{i(E_{\Lambda'I} - E_{\Lambda J} - 2\omega)t\}a_J.$$

In contrast to Eqs. (2) and (16), we now have mixing of the coefficients for both multiplets, and in contrast to Eqs. (12) and (16) there are terms connected with the ordinary quadratic Stark effect.

Equation (16) reduces to a set with constant coefficients through the substitution

$$a_J(t) = a_J'(t)\exp\{iE_{\Lambda J}t\}, \quad a_I(t) = a_I'(t)\exp\{i(E_{\Lambda'I} - 2\omega)t\}.$$

The resulting matrix of coefficients will be written straight away for the case of LS coupling, neglecting multiplet splitting in the nonresonance denominators of G:

$$i\dot{a}' = Qa', \quad Q_{JJ'} = (E_{\Lambda J} - i\gamma_J)\delta_{JJ'} - \tfrac{1}{4}F^2 \sum_{m\mu} \alpha_{\Lambda Lm} C_{LmS\mu}^{JM} C_{LmS\mu}^{J'M},$$

$$Q_{II'} = (E_{\Lambda'I} - 2\omega - i\gamma_I)\delta_{II'} - \tfrac{1}{4}F^2 \sum_{m\mu} \alpha_{\Lambda'L'm} C_{L'mS\mu}^{IM} C_{L'mS\mu}^{I'M},$$ (17)

$$Q_{IJ} = Q_{JI}^* = -\frac{F^2}{4}\sum_{\lambda'm\mu} C_{LmS\mu}^{JM} C_{L'mS\mu}^{IM} \frac{\langle\varphi_{\Lambda'L'm}|d_z|\varphi_{\lambda lm}\rangle\langle\varphi_{\lambda lm}|d_z|\varphi_{\Lambda Lm}\rangle}{E_{\lambda l} - E_{\Lambda L} - \omega}.$$

The quantities α_{Lm} are given by Eqs. (6) and (7), and in the matrix elements Q_{JI} we have used the resonance condition $E_{\Lambda L} + \omega \approx E_{\Lambda'L'}$. Since we are assuming in this paper that the interaction between the atom and the field is of the electric dipole type, the spin functions of the multiplets $\{\Lambda J\}$ and $\{\Lambda'I\}$ should be the same in order that $Q_{IJ} \neq 0$. We note that the generalization of these results to nondipole interaction is a trivial exercise.

The general properties of the solution given by Eq. (17) are the same as in the case of the single-photon resonance. In particular, the upper and lower multiplets have N energy levels each, but the resolved spectral lines can be observed only during transitions to the levels of a third multiplet which enters into a combination with one of the multiplets or with both at once.

The simplest example of the situation considered above occurs in the case of the two-photon resonance of the singlet state $S_{1/2}$ (which will be denoted by S below) and the doublet $D_{3/2}$, $D_{5/2}$ (denoted by D and D', respectively). Let us substitute

$$\beta_{IM, JM} \equiv \sum_{\lambda lm\mu} C_{LmS\mu}^{JM} C_{L'mS\mu}^{IM} \frac{\langle\varphi_{\Lambda'L'm}|d_z|\varphi_{\lambda lm}\rangle\langle\varphi_{\lambda lm}|d_z|\varphi_{\Lambda Lm}\rangle}{E_{\lambda l} - E_{\Lambda L} - \omega},$$

$$\alpha_{JJ'M} \equiv \sum_{m\mu} \alpha_{\Lambda Lm} C_{LmS\mu}^{JM} C_{LmS\mu}^{J'M},$$

$$\delta_{1,2} \equiv (E_{D, D'} - i\gamma_{D, D'}) - (E_S - i\gamma_S) - 2\omega.$$

The eigenvalues of Q which, in this case, can again be found from the Cardano formula, will not be written out here because of lack of space.

The limiting case of the two-level system in a field of frequency ω which is close to half the level separation is considered in[9] and is obtained if one of the frequency differences, for example, δ_2, is much greater than δ_1 and αF^2. In this case,

$$q_1 = E_S - i\gamma_S + \delta_2 - \frac{F^2}{4}\alpha_{D'M},$$

$$q_{2,3} = E_S - i\gamma_S - \frac{F^2}{8}(\alpha_D + \alpha_S) + \frac{\delta_1}{2} \pm \left\{\left[\frac{\delta_1}{2} - \frac{F^2}{8}(\alpha_D + \alpha_S)^2\right]^2 - \frac{F^4}{16}|\beta_{SD}|^2\right\}^{1/2}.$$

The D' level does not mix with the others and exhibits only the quadratic Stark shift. For the S and D levels we have the same result as in[9], namely, the difference from the single-photon resonance is that the simple matrix element $F \cdot d$ is replaced by a composite element, and the quadratic Stark shift of the S and D levels is taken into account.

The case considered in Sec. 2, i.e., that of a doublet in a nonresonance field, occurs when δ_1 and δ_2 are much greater than Δ and βF^2. In this case, the S level does not mix with the others, and the behavior of the D and D' levels in the field is determined by Eq. (11). The strong-field limit $F^2d^2 \gg |\Delta|^2$ is obtained if we set $\Delta = 0$. It is readily verified that the eigenvalue

$$q_1 = E_D - i\gamma_D - 2\omega - \frac{F^2}{4}\left(\alpha_D - \frac{\beta_{SD}}{\beta_{SD'}}\alpha_{DD'}\right)$$

corresponds to a wave function which is identically zero [eigenvector $f^{(1)T} = (0, 1, -\beta_{SD}/\beta_{SD'})$], i.e., as in Sec. 3 we have the two-level system in the case of a completely degenerate multiplet.

We shall now consider some applications of the above results.

5. TIME DEPENDENCE OF THE PROBABILITY OF THREE-PHOTON IONIZATION IN THE PRESENCE OF TWO-PHOTON RESONANCE

Suppose that at time t = 0 the atom is in the ground state which, for the sake of simplicity, will be regarded as a singlet state. For t > 0, the atomic wave function will then be

$$\psi(t) = \sum_k f_1^{(k)}[\Phi_\Lambda^{(k)} e^{-iq_k t} + \Phi_{\Lambda'}^{(k)} e^{-i(q_k + 2\omega)t}],$$

(18)

$$\Phi_\Lambda^{(k)} = f_1^{(k)}|0\rangle, \quad \Phi_{\Lambda'}^{(k)} = \sum_I f_I^{(k)}|\Lambda'I\rangle,$$

in accordance with Sec. 4, where $|0\rangle$, $|\Lambda'I\rangle$ are the wave functions for the ground state and the intermediate resonance of the unperturbed atom (the index M is omitted).

We shall suppose that single-photon ionization is possible from the states $|\Lambda'I\rangle$, and the probability of radiative deactivation of these levels to lower lying states is small. The reduction in time of the norm of the function given by Eq. (18) then describes the three-photon ionization of the atom. The probability that at time t the atom will not be ionized is of the form

$$W(t) = |\langle\psi(t)|\psi(t)\rangle|^2 = \sum_{k,k'} f_1^{(k)*} f_1^{(k')} (\hat{f}^{(k)T}, \hat{f}^{(k')})\exp\{i(q_k^* - q_{k'})t\}. \quad (19)$$

B. A. Zon and B. G. Katsnel'son

It is readily seen that this formula contains terms which oscillate in time and the amplitude of the oscillations falls exponentially due to the presence of imaginary parts in the eigenvalues q_k. Such interference phenomena are a consequence of the nonorthogonality of quasi-stationary states of the atom in the field: $(\hat{f}^{(k)T}, \hat{f}^{(k')}) \neq \delta_{kk'}$.

Another possible interpretation can be given in terms more usual for quantum electronics and nonlinear optics. It is well known that if the n-level system is placed in an alternating field, the probability of observing the system in one of the states is an oscillating function of time.[10] In this case, the probability of finding an atom in any of the states $|\Lambda'I\rangle$ is

$$W_{\Lambda'}(t) = \sum_{k,k'} f_1^{(k)*} f_1^{(k')} \left(\sum_l f_l^{(k)*} f_l^{(k')} \right) \exp\{i(q_k^* - q_{k'})t\}. \quad (20)$$

This quantity contains oscillating factors. Since single-photon ionization is possible from the states $|\Lambda'I\rangle$, the consequence of the oscillations in $W_{\Lambda'}(t)$ is an oscillation in the ionization probability. However, in contrast to Eq. (20), the quantity given by Eq. (19) contains not the factors $\sum_I f_I^{(k)*} f_I^{(k')}$ but the factors $(\hat{f}^{(k)T}, \hat{f}^{(k')})$ which contains additional terms of the form $\sum_J f_J^{(k)*} f_J^{(k')}$ (in the present case, the quantity J has a unique value). This result indicates the presence of an ionization width in the $|0\rangle$ level which is mixed strongly with the levels $|\Lambda'I\rangle$ by the field. As a result, the quantity given by Eq. (19) oscillates because the probabilities of ionization from the states $|0\rangle$ and $|\Lambda'J\rangle$ are different.

For numerical estimates we note that the characteristic energy splitting of the atomic levels in the field are of the order of 1 cm^{-1}. The corresponding oscillation periods are $\sim 10^{-10}$ sec. It is important to note that this type of time dependence of the ionization probability is also found to occur for the resonance between isolated levels. However, for the single-photon resonance, the presence of noncoherent processes in a strong electro-magnetic field probably leads to the suppression of the effect.[11]

6. MULTIPHOTON RESONANCE

The properties of the three-photon ionization probability discussed in the preceding section appear under the conditions of saturation of the two-photon transition. If more than two photons are necessary for resonance to occur, then for fields well away from saturation the population of the resonance levels modified by the field can be described in terms of perturbation theory.[3] However, existing perturbation theory formulas must be used with caution because, in the general case, the effective Hamiltonian for the quasistationary states is not self-adjoint and the Schrödinger and Dirac representations are connected by a nonunitary transformation.

Let us now formulate the perturbation theory. It is assumed that the atom does not resonate at the frequencies ω and 2ω. The quasistationary states developed in Sec. 2 are eigenfunctions of the Hamiltonian

$$H_0 + h = \sum_{\Lambda M} (H_0 + h)_{\Lambda M},$$
$$(H_0 + h)_{\Lambda M} = \sum |\Lambda JM\rangle Q_{JJ'}\langle \Lambda J'M|, \quad (21)$$

where H_0 is the Hamiltonian for the atom in the absence of the field, and the matrix Q for the ΛJ shell is defined by Eq. (5). The Schrödinger equation for the wave function of the atom in the field is

$$i \partial\psi/\partial t = [H_0 + h + (V(t) - h)]\psi, \quad (22)$$

and its solution will be sought in the form of an expansion in terms of the eigenfunctions given by Eq. (10) of the operator of Eq. (21):

$$\psi_M(t) = \sum_{\Lambda k} A_{\Lambda k}(t) e^{-iq_{\Lambda k}t} \Phi_{\Lambda M}^{(k)}.$$

We shall take $\tilde{V}(t) = V(t) - h$ as the perturbation determining the coefficients $A_{\Lambda k}$. However, the operator h is time-independent, and its application does not lead to the appearance of atomic transitions between the shells. Therefore, in the lower orders of perturbation theory we substitute $\tilde{V}(t) = V(t)$.

Let us now introduce the eigenfunctions of the operator $(H_0 + h)^+$:

$$\tilde{\Phi}_{\Lambda M}^{(k)} = \sum_J f_J^{(k)*} |\Lambda JM\rangle.$$

It is readily seen that Eq. (8) leads to the mutual orthogonality of the functions $\tilde{\Phi}_{\Lambda M}^{(k)}$ and $\Phi_{\Lambda M}^{(k)}$:

$$\langle \tilde{\Phi}_{\Lambda M}^{(k)} | \Phi_{\Lambda M}^{(k')} \rangle = \delta_{kk'}. \quad (23)$$

Using Eqs. (22) and (23), we obtain the following equation for the coefficients $A_{\Lambda k}$:

$$\dot{A}_{\Lambda k} = -i \sum_{\Lambda'k'} \langle \tilde{\Phi}_{\Lambda M}^{(k)} | V(t) | \Phi_{\Lambda'M}^{(k')} \rangle \exp\{i(q_{\Lambda k} - q_{\Lambda'k'})t\} A_{\Lambda'k'}. \quad (24)$$

Solving the integral equation corresponding to Eq. (24) by the method of successive approximations, we obtain the perturbation theory series.

Consider as an example the four-photon ionization of an atom from the singlet state in the presence of three-photon resonance. In third-order perturbation theory, and assuming adiabatic switching-on of the field, we obtain the following values for the coefficients $A_{\Lambda k}$ for the resonance levels:

$$A_{\Lambda k}^{(3)}(t) = -\frac{F^3}{8} \sum_{\Lambda_1 k_1 \Lambda_2 k_2} \exp\{i(q_{\Lambda k} - q_0 - 3\omega)t\}$$
$$\times \frac{\langle \tilde{\Phi}_{\Lambda M}^{(k)} | d_z | \Phi_{\Lambda_2 M}^{(k_2)} \rangle \langle \tilde{\Phi}_{\Lambda_2 M}^{(k_2)} | d_z | \Phi_{\Lambda_1 M}^{(k_1)} \rangle \langle \tilde{\Phi}_{\Lambda_1 M}^{(k_1)} | d_z | \Phi_0 \rangle}{(q_{\Lambda k} - q_0 - 3\omega)(q_{\Lambda_2 k_2} - q_0 - 2\omega)(q_{\Lambda_1 k_1} - q_0 - \omega)}. \quad (25)$$

In the nonresonant denominators of Eq. (25) we can neglect multiplet and Stark splitting of the levels. Using the orthogonalization condition (8), we obtain

$$A_{\Lambda k}^{(3)}(t) = -\frac{F^3}{8} \frac{U_{\Lambda k,0}}{q_{\Lambda k} - q_0 - 3\omega} \exp\{i(q_{\Lambda k} - q_0 - 3\omega)t\},$$
$$U_{\Lambda k,0} = \sum_{\Lambda_1 J_1 \Lambda_2 J_2} \frac{\langle \tilde{\Phi}_{\Lambda M}^{(k)} | d_z | \Lambda_2 J_2 M \rangle \langle M \Lambda_2 J_2 | d_z | \Lambda_1 J_1 M \rangle \langle \Lambda_1 J_1 M | d_z | \Phi_0 \rangle}{(E_{\Lambda_2} - E_0 - 2\omega)(E_{\Lambda_1} - E_0 - \omega)}. \quad (26)$$

The quantities given by Eq. (26) can now be used to find the probability of four-photon ionization. Neglecting the effect of the external field on the wave functions in the continuous spectrum, we obtain the following expression for the ionization probability per unit time:

$$dW = \left(\frac{F}{2}\right)^8 \left| \sum_k \frac{U_{f,\Lambda k} U_{\Lambda k,0}}{q_{\Lambda k} - q_0 - 3\omega} \right|^2 \frac{mp\, d\Omega_p}{(2\pi)^2},$$
$$U_{f,\Lambda k} = \langle p | d_z | \Phi_{\Lambda M}^{(k)} \rangle.$$

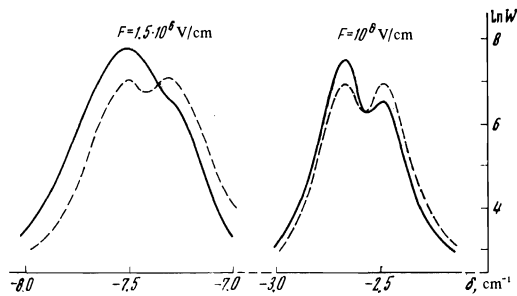In this expression p is the momentum of the ejected electron.

FIG. 2. Dependence of the probability of four-photon ionization of cesium (in relative units) on the departure from the three-photon resonance frequency $\delta = E_{5/2} - E_S - 3\omega$. The solid line shows the ionization probability with allowance for the doublet level mixing; the broken line shows the result without mixing.

Figure 2 shows the probability of four-photon ionization of the cesium atom as a function of the laser beam frequency (neodymium laser) with and without the correction for the doublet level mixing. The necessary atomic parameters were calculated within the framework of the quantum-defect method.[13] It is clear from the figure that in a strong field the frequency dependence of the ionization probability has one maximum, but in a weak field there are two maxima. This difference is due to the fact that in the strong field the spin-orbital coupling is broken and new selection rules are introduced, namely, the component of the orbital angular momentum of the electron is conserved. As a result, multiphoton transitions are associated with the population of only the level with $l_z = 0$, and the spin-orbital coupling cannot mix the splitting of the $l_z = 0$ and $|l_z| = 1$ levels by the field.

The results of the present paper have also been used to calculate the probability of stimulated absorption (emission) for transitions between multiplet states. The results for the singlet-doublet transition are given in[14]. It is noted that saturation is reached in the usual fashion[10] only when the departure from resonance is much greater than the multiplet splitting. However, if the two are of the same order, the stimulated absorption probability has a maximum at first and reaches its asymptotic level from above.

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98