Theory of resonance multiphoton transitions in a three-level system under the influence of a strong electromagnetic field

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The resonance multiphoton transition between two levels due to the influence of a strong, low-frequency electromagnetic field is investigated in the adiabatic approximation. The case when a third level, intermediate between the two given ones, is also resonant, is investigated. The applicability of time-dependent perturbation theory to this problem is discussed. Results are presented for the transition probabilities as a function of the resonance multiplicities, the multiphoton matrix elements, and the resonance detunings. It is shown how the present theory can be applied to resonance transitions in real atoms, which are irradiated by a strong electromagnetic wave.

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1. INTRODUCTION

The theoretical analysis of experiments on multiphoton excitation of atoms by an electromagnetic field becomes considerably complicated when the energy of some intermediate discrete atomic level turns out to be close to an integer number of the absorbed quanta. The basic difficulty in the solution of the problem lies in the fact that standard time-dependent perturbation theory is not valid near a resonance. On the other hand, the development of a resonance approximation is hampered by the "double resonance nature" of the system.

The basic method, used in the present work for determination of the multiphoton transition probabilities, is the adiabatic approximation.[1] It is mathematically equivalent to the WKB approximation for the problem of above-barrier reflection. The adiabatic approximation is applicable when the frequency of the external electromagnetic field is small in comparison with the separations between the atomic levels. In actual fact the present restriction is not very stringent due to the same numerical reason, according to which the WKB approximation usually works well even for not too large quantum numbers. This was demonstrated by Zaretskiĭ and Kraĭnov[2] in application to a calculation of the transition probabilities in a two-level system.

The problem of resonance excitation for a real atom is very complicated. The basic qualitative aspects of this physical process can be seen from an idealized problem, whose solution is also presented in the present article. The idealization consists of the replacement of a real atom by a system consisting of three nondegenerate levels having energies ε_1, ε_2, and ε_3. Thus, all nonresonant discrete states of the atom and the states of the continuous spectrum are discarded. The problem consists in the determination of the probability for the multiphoton transition 1 → 3, and also the determination of the populations of the levels 1, 2, and 3. For example, the solution of the present problem describes the case when a three-level system is artificially created from a degenerate level by some kind of constant field.

In Sec. 2 the simpler problem of a multiphoton transition in a two-level system is considered first. The special case when the transition probability is proportional to the time (the so-called linear regime) was investigated by Zaretskiĭ and Kraĭnov.[2] The calculational method is borrowed from the work of Bychkov and Dykhne,[3] which is devoted to the breakdown of semiconductors by a low-frequency electromagnetic field. The population of the states in a three-level system, when level 2 is resonant, is calculated in Sec. 3 by that same method. In Sec. 4 different limiting cases of the obtained general expression are considered, for which the results have a simple form and meaning. Finally, in Sec. 5 the competition of the resonance transition 1 → 2 → 3 with the direct transition 1 → 3, which arises upon moving away from resonance, is investigated. Applications of the present theory are discussed in the Conclusion. The question of justification of the method is examined in the Appendix.

2. A TWO-LEVEL SYSTEM IN A LOW-FREQUENCY FIELD

In the adiabatic approximation the variation of the initial (lower) state of a two-level system due to the influence of an external field $V = d\mathscr{E}\sin\omega t$ during a period of time $T = \pi/\omega$ is determined by the unitary matrix

$$A = \begin{pmatrix} De^{iS_1} & -R^* e^{iS_1} \\ Re^{iS_2} & De^{iS_2} \end{pmatrix} \tag{1}$$

(see the article by Bychkov and Dykhne[3]). Here S_1 and S_2 are defined by

$$S_1 = \int_0^{\pi/\omega} E_1(t)\,dt - \frac{\pi}{2}, \qquad S_2 = \int_0^{\pi/\omega} E_2(t)\,dt + \frac{\pi}{2}, \tag{2}$$

where the quantity

$$E_{1,2}(t) = \mp {}^1/_2 (\varepsilon^2 + 4V_{12}^2)^{1/2} \tag{3}$$

denotes the system's energy in the adiabatic field,[2] d_{12} is the dipole matrix element connecting the given levels, and $\mp(1/2)\,\varepsilon$ are the unperturbed energies of these levels. The correction terms $\pm\pi/2$ in Eqs. (2) arise upon allowance for the next order (i.e., the next after the lowest order) WKB approximation.[2] The condition for the adiabatic method has the form $\varepsilon \gg \omega$.

Furthermore, the notation

$$R=i\exp\left\{i\int_0^{t_{12}}[E_2(t)-E_1(t)]dt\right\}, \tag{4}$$

is introduced, where t_{12} is the turning point in the complex time plane, determined by the condition $E_1(t_{12})=E_2(t_{12})$. In the article by Zaretskiĭ and Kraĭnov[2] it was shown that the quantity $R\sim\mathscr{E}^K$ as $\mathscr{E}\to 0$, where K denotes the (odd integer) number of quanta absorbed. From the quasiclassical point of view, the quantity R denotes the coefficient of above-barrier reflection. Finally, $D=(1-|R|^2)^{1/2}$ denotes the transmission coefficient. In perturbation theory the quantity R is of the order of the multiphoton matrix element. The quantities $S_{1,2}$ have the meaning of the change in the classical action of the states 1 and 2 during the period π/ω.

The variation of the system after N periods, i.e., during the time $t=\pi N/\omega$, has the form A^N. In order to evaluate A^N it is first necessary to reduce the matrix A to diagonal form. In this connection the problem simplifies if it is taken into consideration that, to within terms of lowest order in R, expression (1) can be written in the form

$$A=e^{iS_1}\begin{pmatrix}1 & -R\\ R & 1+i\gamma\end{pmatrix}. \tag{5}$$

Here the quantity $\gamma\equiv\pi(\varepsilon-K\omega+\Delta\varepsilon)/\omega$ characterizes the detuning of the multiphoton resonance; $\Delta\varepsilon$ is the dynamical Stark effect, $\Delta\varepsilon\approx d_{12}^2\mathscr{E}^2/4\varepsilon$.

Carrying out the indicated procedure, let us determine the probability for occupation of the upper level 2:

$$w_2(t)=\frac{R^2}{R^2+(\gamma/2)^2}\sin^2\left[\sqrt{R^2+(\gamma/2)^2}\frac{\omega t}{\pi}\right]. \tag{6}$$

In analogy to the case of exact resonance for $K=1$,[4] in the exact K-photon resonance ($\gamma=0$) the upper and lower levels are identically populated, i.e., population inversion is impossible in a two-level system. Formula (6) was derived by Manykin[5] in the regime of perturbation theory for the multiphoton matrix element ($R\sim\mathscr{E}^K$) and for the limiting case of an exact resonance ($\gamma=0$).

Expression (6) becomes invalid when the resonance detuning γ is so large that the usual nonresonant population of the upper level, determined by first order perturbation theory, begins to dominate. The corresponding condition has the form $(d_{12}\mathscr{E}/\varepsilon)>R/\gamma$. In the linear regime in time ($d_{12}\mathscr{E}/\varepsilon\ll R/\gamma\ll 1$, $t\ll 1/\gamma\omega$), from formula (6) we obtain the probability per unit time of the transition 1 → 2 found by Zaretskiĭ and Kraĭnov.[2] The corresponding law of energy conservation has the form $\varepsilon-K\omega+\Delta\varepsilon=0$.

The results stated here are generalized below to the case of a three-level system.

3. A THREE-LEVEL SYSTEM IN A LOW-FREQUENCY FIELD

In the case of a three-level system placed in a low-frequency field, 3×3 matrices appear instead of 2×2 matrices. The time evolution of the system, consisting of levels with energies ε_1, ε_2, and ε_3, during the period π/ω is now determined in the resonance case by a product of 3×3 matrices, one of which contains the block matrix for the transition 1 → 2 and the second contains the block matrix for the transition 2 → 3. Substituting the matrix (5) into the expression for each partial matrix and multiplying, we find the matrix $A(1\to 2\to 3)$ of the resonance transition[1)]:

$$A(1\to2\to3)=e^{i(S_1+S_3)}\begin{pmatrix}1-i\beta & -R & 0\\ R & 1+i(2\gamma-\beta) & -R'\\ 0 & R' & 1+i\beta\end{pmatrix}. \tag{7}$$

Just as for the two-level system, only the main terms are retained in Eq. (7) The quantities

$$\beta\equiv\frac{\pi(\varepsilon_3-\varepsilon_1-K\omega+\Delta\varepsilon_{31})}{\omega},\quad \gamma\equiv\frac{\pi(\varepsilon_2-\varepsilon_1-n\omega+\Delta\varepsilon_{21})}{\omega},$$

appearing in Eq. (7), characterize the detunings of the resonance 1 → 3 and 1 → 2, respectively. The quantity R' is defined in analogy to (4) with the replacement of 1 → 2 by 2 → 3; $\Delta\varepsilon_{31}$ and $\Delta\varepsilon_{21}$ denote the dynamic Stark effects for the corresponding detunings.

The energies $E_{1,2,3}(t)$ are found from the solution of the cubic equation for the adiabatic approximation. The turning points ($E_i(t)=E_j(t)$) are radical singular points in the complex time plane. We note that, as proved in general form by Zaretskiĭ and Kraĭnov,[6] the quantities R and R' are proportional to $\mathscr{E}^n$ and $\mathscr{E}^{K-n}$, respectively, in the range of validity of perturbation theory in $\mathscr{E}$.

The eigenvalues $1+ix$ ($x\ll 1$) of the matrix $A(1\to 2\to 3)$ (formula (7)) are determined by the solution of the cubic equation

$$(x^2-\beta^2)(x+\beta-2\gamma)-R^2(x-\beta)-R'^2(x+\beta)=0. \tag{8}$$

All three roots $x_{1,2,3}$ of this equation are real; this is obvious from the conservation of total probability in the system.

Over N periods ($t=\pi N/\omega$) the state vector is determined by the expression A^N. Diagonalizing A and raising the diagonal matrix of the N-th power, we obtain the amplitudes of states 1 and 3:

$$A_1(t)=[\beta(x_1-x_3)(x_2-x_1)(x_3-x_2)]^{-1}[x_2x_3(x_1-\beta)(x_3-x_2)\exp(ix_1\omega t/\pi)$$
$$+\text{ two cyclic permutations}$$
$$A_3(t)=RR'[(x_1-x_3)(x_2-x_1)(x_3-x_2)]^{-1}[(x_3-x_2)\exp(ix_1\omega t/\pi)$$
$$+\text{ two cyclic permutations} \tag{9}$$

An expression for $A_2(t)$ is not given since we shall determine the population of the second level from the law of conservation of the number of particles.

We see that in an external field each of the three levels ε_1, ε_2, and ε_3 is split into three quasilevels. The separation between these quasilevels is equal to

$$\omega\pi^{-1}|x_2-x_1|,\quad \omega\pi^{-1}|x_3-x_2|,\quad \omega\pi^{-1}|x_1-x_3|.$$

respectively. If the values of β and γ are increased (departure from the resonance approximation), an infinite number of additional quasilevels appears whose energies differ, according to Floquet's theorem, from the energies of any three basis levels by $n\omega$, where n is an arbitrary integer.

Expressions (9) are definitive when $\beta \sim \gamma \sim R, R'$. In such form they are not very clear due to the cumbersome Cardano formulas for the roots of Eq. (8). Different limiting situations will be considered in the next section, enabling us to describe the population of the levels by simpler analytic expressions.

4. SATURATION IN A THREE-LEVEL SYSTEM

We note that the results derived above are valid for times $t \ll RR'/\omega$. In the opposite case saturation associated with the nonresonance transition described by the two-level matrix $A(1 \to 3)$ will play an essential role.

We shall assume that the system $1 \to 3$ is tuned to exact resonance, i.e., $\beta = 0$. The solution of Eq. (8) has the form $x_1 = 0$, $x_{2,3} = \gamma \pm (\gamma^2 + R^2 + R'^2)^{1/2}$. Substituting this solution into Eqs. (9), we obtain explicit expressions for the amplitudes of the states. We present only the average values of the level populations for $\gamma = 0$ (just like the upper level, the intermediate level is tuned to exact resonance):

$$n_1 = \overline{|A_1(t)|}^2 = (R'^4 + {}^1/_2 R^4)(R^2 + R'^2)^{-2},$$
$$n_2 = R^2/2(R^2 + R'^2), \quad n_3 = {}^3/_2 R^2 R'^2 (R^2 + R'^2)^{-2}. \tag{10}$$

The maximum population of level 3 is equal to $n_3 = 3/8$. In this connection $n_2 = 2/8$ and $n_1 = 3/8$. We see that here there is no inversion of the average population with respect to the lower state 1. However, one can easily verify that for $R'^2 < R^2 < 2R'^2$ we have $n_3 > n_2$ and $n_3 > n_1$, i.e., inversion of the average population with respect to both the intermediate level and the lower level. In order to realize such conditions it is necessary, in particular, to have the same multiplicity for the transitions $1 \to 2$ and $2 \to 3$, that is, $K = 2_n$. Maximum inversion is achieved for $R = R'\sqrt{2}$, when $n_3 = 0.37$, $n_2 = 0.29$, and $n_1 = 0.34$. By the same token a three-level system differs substantially from a two-level system, since in the latter case there is no inversion of the average population.

Let us mention a clear limiting case of formula (10). If $R \gg R'$, then $n_1 \approx 1/2$, $n_2 \approx 1/2$, and $n_3 \approx 0$. The case $R \ll R'$ is also qualitatively understandable:

$$n_1 \approx 1 - 2R^2/R'^2, \quad n_2 = R^2/2R'^2, \quad n_3 = 3R^2/2R'^2.$$

The last case corresponds to a multiquantum first transition and a second transition involving few quanta ($K < 2n$).

5. INTERFERENCE BETWEEN DIRECT AND RESONANCE TRANSITIONS

In this section we shall investigate the interference between the direct transition $1 \to 3$ and the resonance transition $1 \to 2 \to 3$ (see Sec. 3) which appears upon moving away from the intermediate resonance. In this article the problem will be considered only in the linear regime with respect to the time (between states 1 and 3). The total amplitude $A(1 \to 3)$ of the direct transition $1 \to 3$ during time t is obtained from the results of Sec. 2. We obtain

$$A(1 \to 3) = R'' \frac{\exp(i(S_3 - S_1)N - 1)}{\exp(i(S_3 - S_1)) - 1}.$$

The quantity R'' is defined in analogy to expression (4) with the replacement of the indices $1 \to 2$ by $1 \to 3$. The amplitude $A(1 \to 2 \to 3)$ of the resonance transition is found from Eq. (9). The expressions for x_1, x_2, and x_3 are determined by means of the appropriate limiting transition to the linear regime ($\gamma \gg \beta \gg R, R'$) in Eq. (8). Adding the direct and resonance amplitudes together, raising the modulus of the sum to the second power, and changing to the linear regime in time, we obtain the transition probability per unit time

$$w_{13} = \frac{2\omega^2}{\pi} \left| R'' + \frac{\omega R R'}{2\pi(\varepsilon_2 - \varepsilon_1 - n\omega + \Delta\varepsilon_{21})\sqrt{2}} \right|^2 \delta(\varepsilon_3 - \varepsilon_1 - K\omega + \Delta\varepsilon_{31}). \tag{11}$$

Formula (11) determines the interference between direct and resonance transitions as a function of the detuning.

Let us turn our attention to the absence of width in the resonance denominator of expression (11). If γ, by decreasing, approaches the value RR', the concept of probability per unit time loses its meaning. This confirms the results of Kazakov, Makarov, and Fedorov.[7] Further, in the case $\beta = 0$ the population of the upper level 3 is given by

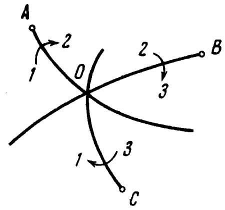
$$\frac{4R^2 R'^2}{\gamma^2 + R^2 + R'^2} \sin^4 \left[\frac{\omega t}{\pi} (\gamma^2 + R^2 + R'^2)^{1/2} \right].$$

If we set $t \to 0$ in this formula, the transition probability per unit time increases like t^3. This is also in agreement with the results of article[7].

6. CONCLUSION

In conclusion let us investigate how the proposed theory might be applied in order to describe various experiments. The simplest case is a two-photon resonance transition associated with the presence of an additional intermediate resonance. One of the effects which can be observed in this connection is resonance fluorescence. In the radiation spectrum around the frequency ω of the external field, there will be two satellites on each side; at exact resonance their distances to the center of the line are equal to R and $2R$. This generalizes the well known phenomenon of the appearance of satellites for a two-level system.[8] In the case of a two-level system there is, as is well known, one satellite on each side (one can easily see that there will also be one satellite in the case of a multiphoton resonance in a two-level system).

Now let us consider the case of resonance multiphoton transitions. In the experimental formulation of the problem, usually only the first transition $1 \to 2$ is a multiphoton transition. As a rrule the second transition $2 \to 3$ takes place with the absorption of one or two photons. In the resonance denominator (10) the quantity R^2 can always be neglected in comparison with R'^2 due to the multiquantum nature of the first transition ($R \sim \mathscr{E}^n$, $R' \sim \mathscr{E}^{K-n}$). This means that saturation with respect to the transition $1 \to 2$ does not occur in resonance multiphoton excitation. In particular, the present result confirms the well known formula derived by Keldysh[9] for the



probability of resonance multiphoton ionization.

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APPENDIX

Let us discuss the question of the validity of the method presented in this article. Let us consider the complex time plane (see the figure). Let us denote the point

$$s_i = \mathrm{Im}\int^{t} E_i dt,$$

where $t = t_{12}$ by A, the corresponding point where $t = t_{23}$ by B, and the point where $t = t_{13}$ by C. The notation 1 → 2 on the figure means that in the region where the numeral 2 is placed we have $s_2 > s_1$, but in the region where the numeral 1 is placed, we have $s_1 > s_2$. These regions are separated by the Stokes line AO on which $s_1 = s_2$. The notation 2 → 3 and 3 → 1 is defined in analogous fashion.

Multiplication of two matrices was utilized for the determination of the resonance transition matrices (7). In this connection, in the time plane one should move from the point A along the curve AO.[3] At the point O, where $s_1 = s_2 = s_3$, the direction of motion should change to OB, where $s_2 = s_3$. It is necessary for the validity of the method that one should have $s_3 < s_1 = s_2$ on the Stokes line AO, and $s_1 < s_2 = s_3$ on the Stokes line OB. This will be true in the case when the numerals 1, 2, and 3 are arranged in cyclic fashion. Precisely such a case is shown in the figure. In the case of an anticyclic arrangement of the indices, the method becomes incorrect. The question of what numerical values of the problem's parameters will cause the arrangement of indices to be cyclic or anticyclic is solved separately in each specific case by numerical methods, and this question is not investigated in the present article.

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An approximate method for calculating intermolecular interaction

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A method is discussed which allows the determination for arbitrary molecules of the angular dependence of the intermolecular potential from the experimentally-determined averaged (over the angles) potential. The method is based on the effective pair interaction approximation. As an illustration, the potential curves for different relative orientations of the molecules H_2-H_2 are computed. The curves are found to be in good agreement with the results obtained by other methods.

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1. INTRODUCTION

To solve a number of concrete problems (thermal diffusion, the cooling of interstellar gas, relaxation in a shock wave, line broadening, etc.), it is necessary to know the total and the differential cross sections for elastic and inelastic interactions of molecules.[1] However, partial transition cross sections and angular distributions have been measured directly in experiments only for a very limited number of molecular pairs: