Excitation of atoms by off-resonance light pulses

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The excitation of a two-level and of certain three-level systems by light pulses that vary weakly during times of the order of the reciprocal frequency detunings is analyzed. Expressions are obtained with which to estimate the selectivities attained in various schemes for the detection of rare isotopes by the method of laser multistep ionization of atoms.

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1. INTRODUCTION

One might think that the subject of the present article has been fully covered. A large number of monographs (e.g., Refs. 1–4) and original articles have been devoted to the interaction between atoms and light fields. I know, however, of no papers containing, in particular, the answer to the following simple question: Assume that a quasimonochromatic light pulse $E(t)\cos\Omega t$ of frequency located far on a radiation-broadened line acts on a two level atom, and let the characteristic time of variation of the envelope $E(t)$, which is of the order of the pulse duration τ_p, satisfy the intermediate relations

$$\tau_p \ll \Gamma^{-1}, \tag{1}$$

$$\tau_p \gg |\Omega-\omega_{10}|^{-1}, \tag{2}$$

where Γ^{-1} is the time of spontaneous decay of the upper level and ω_{10} is the transition frequency. Assume next that the amplitude E satisfies the condition

$$(d_{01}E/2\hbar)\,\tau_p \sim 1, \tag{3}$$

where d_{01} is the dipole moment of the transition. The question is: what is the probability of finding the atom on the upper level after the pulse has practically terminated?

This question arises inevitably, for example, in the problem of detecting rare isotopes by the method of multistep laser photoionization of atoms.[5,6] Indeed, let the pulse of the first step be at resonance with a transition in the rare-isotope atom and let it excite this atom with a probability of the order of unity [condition (3)]; let furthermore the detuning due to the isotopic shift in the atom of the background isotope satisfy the condition (2). The answer to the question posed yields then in fact the lower bound of the selectivity of the method, although the isotopic shift in the subsequent steps can of course increase the selectivity.[7]

It may seem at first glance that the answer can be given directly in terms of the transition rate expressed via the cross section on the wing of a homogeneously broadened profile of width Γ:

$$W \approx \frac{d_{01}^2\overline{E^2}}{4\hbar^2(\Omega-\omega_{10})^2}\,\Gamma\tau_p. \tag{4}$$

In itself, however, this formula, which describes the probability of departure of a photon from the incident wave, does not distinguish between real excitation of the upper level and elastic scattering of a photon, and it turns out that this formula, when conditions (1)–(3) are satisfied, describes just the scattering process.

Another approach to the problem is possible. We forget for the time being the spontaneous decay and assume the pulse to be turned on and off adiabatically slowly. It is then known[8] that the atoms can be at each instant of time on a quasienergy level that is adiabatically coupled to the ground state. This means that after the pulse is turned off the atom has unity probability of remaining in the ground state. We arrive thus at the assumption that the source of the population of the upper level can be only the nonadiabaticity and the spontaneous transitions from a lower quasilevel to an upper quasilevel that is adiabatically coupled with the excited state of the atom.

We shall hardly ever deal in this paper with the nonadiabatic part of the atom excitation. It is well known (see, e.g., Ref. 1) that this effect is exponentially small in the parameter $(\Omega-\omega_{10})\tau_p$, and we shall assume that it can be neglected.

In our investigation of the atom excitation on account of spontaneous transitions between quasilevels we confine ourselves to a phenomenological description of the spontaneous relaxation, within the framework of the density-matrix formalism. The simplest variant of such a description is quite sufficient not only for a two-level atom 1,2 but also for a multilevel one, if there are no identical frequencies in the system.[9] In addition, we use a resonance approximation, i.e., despite the relatively large detuning from resonance we shall assume that the detuning is substantially smaller than the transition frequency.

The excitation of a two-level system is considered in Sec. 2. In Sec. 3 we explain the physical meaning of the result. In the sections that follow we analyze the excitations of certain three-level systems that are of interest from the viewpoint of previously proposed schemes for the detection of rare isotopes.

2. TWO-LEVEL SYSTEM

The equations for the density-matrix elements of a two-level system in a light-pulse field will be written in the form

$$\begin{aligned} d\rho_{00}/dt &= -iFu+\Gamma\rho_{11},\\ d\rho_{11}/dt &= iFu-(\Gamma+\tilde{\Gamma})\rho_{11},\\ du/dt &= -i\delta v-2iF(\rho_{00}-\rho_{11})-{}^1/_2(\Gamma+\tilde{\Gamma})u,\\ dv/dt &= -i\delta u-{}^1/_2(\Gamma+\tilde{\Gamma})v. \end{aligned} \tag{5}$$

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Here u and v are antisymmetric and symmetric linear combinations of off-diagonal elements of the density matrix:

$$u=\rho_{01}e^{-i\delta t}-\rho_{10}e^{i\delta t}, \quad v=\rho_{01}e^{-i\delta t}+\rho_{10}e^{i\delta t}.$$

We have also introduced the following notation: $\delta=\Omega-\omega_{10}$; $F=d_{01}E/2\hbar$ is the matrix element of the interaction operator of the atom with the field and is assumed for simplicity to be real; Γ is the rate of the spontaneous $1\to0$ transition; $\tilde{\Gamma}$ is the rate of the spontaneous decay of the excited level via other possible channels. (The indices labeling these quantities have been omitted for brevity.) In accordance with the statements made in the Introduction, it is assumed also that F depends on the time, changes very little over a time of the order of δ^{-1}, and vanishes as $t\to\pm\infty$.

It is not difficult to develop a procedure for finding the successive terms of the asymptotic expansion of the solution of the equations in (5) in powers of the shortest time $1/\delta$ in the system. Since $\rho_{00}=1$ and $\rho_{11}=u=v=0$, as $t\to-\infty$, we can write formally

$$u(t)=-2i\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\int_{-\infty}^{t}F(\tau)\left[\rho_{00}(\tau)-\rho_{11}(\tau)\right]\times\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}\tau\right)\cos\delta(t-\tau)\,d\tau, \tag{6}$$

$$\rho_{11}(t)=i\exp\left[-(\Gamma+\tilde{\Gamma})t\right]\int_{-\infty}^{t}F(\tau)u(\tau)\exp\left[(\Gamma+\tilde{\Gamma})\tau\right]d\tau, \tag{7}$$

$$\rho_{00}(t)=1-i\int_{-\infty}^{t}F(\tau)u(\tau)\,d\tau+\Gamma\int_{-\infty}^{t}\rho_{11}(\tau)\,d\tau. \tag{8}$$

Next (see, e.g., Ref. 10), integrating (6) by parts, we obtain the following asymptotic expansion:

$$u(t)=-\frac{2i}{\delta^2}\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d}{dt}\left[(\rho_{00}-\rho_{11})F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]+\frac{2i}{\delta^4}\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d^3}{dt^3}\left[(\rho_{00}-\rho_{11})F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]-\ldots \tag{9}$$

and we apply to Eqs. (7)–(9) the usual procedure of successive approximations in powers of $1/\delta^2$. In first order, substituting $\rho_{00}=1$ and $\rho_{11}=0$ in (9) and integrating, we find

$$u=-\frac{2i}{\delta^2}\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d}{dt}\left[F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right], \tag{10}$$

$$\rho_{11}=F^2/\delta^2, \tag{11}$$

$$\rho_{00}=1-\frac{F^2}{\delta^2}-\frac{\tilde{\Gamma}}{\delta^2}\int_{-\infty}^{t}F^2(\tau)\,d\tau. \tag{12}$$

So far, no terms that vanish as the field amplitude (or F) tends to zero have appeared in the expression for ρ_{11}. Equation (11) describes the usual coherent admixture, in a light field, of the wave function of the excited state to the wave function of the ground state. The first principal nonvanishing term appears in the next approximation. Omitting the intermediate steps, we write down for ρ_{11} an expression that is accurate to terms $\sim1/\delta^4$:

$$\rho_{11}(t)=\frac{F^2}{\delta^2}-\frac{3F^4}{\delta^4}-\frac{2F}{\delta^4}\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d^2}{dt^2}\left[F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]+\frac{1}{\delta^4}\exp\left[-(\Gamma+\tilde{\Gamma})t\right]\left\{\frac{d}{dt}\left[F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]\right\}^2-\frac{\Gamma F^2}{\delta^4}\int_{-\infty}^{t}F^2(\tau)\,d\tau+\frac{\Gamma}{\delta^4}\exp\left[-(\Gamma+\tilde{\Gamma})t\right]\int_{-\infty}^{t}F^4(\tau)\exp\left[(\Gamma+\tilde{\Gamma})\tau\right]d\tau. \tag{13}$$

The last term in (13) describes the "incoherent" part of the population of the excited state and is precisely the one of principal interest to us. If condition (1) is satisfied we can single out the times when it can actually be assumed that the pulse was terminated, but the spontaneous decay did not manage to occur. For these times there remains precisely the last term. It yields

$$\rho_{11}\approx(\overline{F^4}/\delta^4)\Gamma\tau_p, \tag{14}$$

where the bar denotes time averaging. The remaining terms in (13) describe the coherent part of the population,[1] which follows the instantaneous values of the field amplitude and its derivatives. Of somewhat different form is the last term—it describes the quasistationary correction to (11) for the irreversible departure of atoms via other spontaneous-decay channels.

3. INTERPRETATION OF THE LAST TERM OF (13)

The physical meaning of the result of Sec. (2) is contained in fact in the paper by Zel'dovich.[8] This result can be obtained without resorting to calculation, and using only the well known structure of the quasienergy states (QES) of the two-level system. Denoting by φ_0 and φ_1 the quasienergy wave eigenfunctions, and by ψ_0 and ψ_1 the wave functions of the stationary states, we have

$$\varphi_0=\theta_{00}\psi_0+\theta_{01}\psi_1, \quad \varphi_1=\theta_{10}\psi_0+\theta_{11}\psi_1,$$

where $|\theta_{00}|=|\theta_{11}|\approx1$, $|\theta_{01}|=|\theta_{10}|\approx|F/\delta|$ at $|F/\delta|\ll1$. As noted in the Introduction, when conditions (1)–(3) are satisfied the presence of population on the upper level after the termination of the pulse is due to spontaneous transitions from the lower QES to the upper QES in the course of the pulse. In this process,[8,13] two photons of frequency Ω are absorbed from the field and the atom emits simultaneously one photon of frequency $2\Omega-\omega_{10}$; the rate of the process is $\omega_{01}=|\theta_{01}\theta_{10}|^2\Gamma\approx(F/\delta)^4\Gamma$. This leads directly to Eq. (14).

We are thus attempting in fact to identify the last term of Eq. (13) for ρ_{11} with the population of the upper QES of the atom. We should like to show here that the remaining terms of (13) have no connection with the population of the upper QES. This, however is impossible in the framework of the QES concept, since we are considering a situation in which

the amplitude of the external field changes with time.[2)] We proceed therefore differently, using the test-field method (seem e.g., Ref. 2) but in not quite the usual modification. The take a test pulse of duration τ_t and satisfying the following conditions:

$$\tau_t \ll \tau_p, \quad \tau_t \gg |\delta|^{-1}. \tag{15}$$

The first of these conditions permits, as it were, to probe the "instantaneous" resonances of the atom, while the second ensures a sufficient resolution of the transition from the upper level (or quasilevel) into a certain third state and of a two-photon transition from the lower level into the same state, with participation of one photon of the effective field and one photon of the test wave.

It will be shown in Sec. A of the Appendix that in such a probing system the absorption of the system at a frequency at resonance with the upper level is proportional to the combination

$$R=\rho_{11}-{}^1/_2(\mathrm{Re}\,\eta)v-{}^1/_2 i(\mathrm{Im}\,\eta)u, \tag{16}$$

where the function η satisfies the equation

$$\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d}{dt}\left[\eta\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]-i\delta\eta+iF\eta^2=iF \tag{17}$$

with an initial condition corresponding to vanishing of η as $F\to 0$, i.e., in the absence of the effective field. Solving Eq. (17) by successive approximations we arrive, accurate to terms $\sim 1/\delta^3$, at the expressions

$$\mathrm{Re}\,\eta = -\frac{F}{\delta}+\frac{1}{\delta^3}\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d^2}{dt^2}\left[F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]+\frac{F^3}{\delta^3},$$
$$\mathrm{Im}\,\eta=\frac{1}{\delta^2}\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d}{dt}\left[F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]. \tag{18}$$

Equations for u and ρ_{11} were already written above [see (9) and (13)]. For v we have, accurate to terms $\sim 1/\delta^3$,

$$v=-2\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\int_{-\infty}^{t}F(\tau)\,[\rho_{00}(\tau)-\rho_{11}(\tau)]\,+\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}\tau\right)\sin\delta(t-\tau)\,d\tau$$
$$=-\frac{2F}{\delta}+\frac{4F^3}{\delta^3}+\frac{2\tilde{\Gamma}F}{\delta^3}\int_{-\infty}^{t}F^2(\tau)\,d\tau$$
$$+\frac{2}{\delta^3}\exp\left(-\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\frac{d^2}{dt^2}\left[F\exp\left(\frac{\Gamma+\tilde{\Gamma}}{2}t\right)\right]. \tag{19}$$

Substituting (9), (13), (18), and (19) in (16) we obtain accurate to terms $\sim 1/\delta^4$,

$$R=\frac{\tilde{\Gamma}}{\delta^4}\exp[-(\Gamma+\tilde{\Gamma})t]\int_{-\infty}^{t}F^4(\tau)\exp[(\Gamma+\tilde{\Gamma})\tau]\,d\tau,$$

i.e., as expected, R is exactly equal to the last term of (13).

Although we are interested in this article in the action of pulsed fields on an atom, we note nevertheless that the result is meaningful also for the stationary case (of course, when there are no extraneous channels for the decay of the upper level, i.e, $\tilde{\Gamma}=0$). In this case the last term of (13) reduces simply to $(F/\delta)^4$. From the result of this section it is clear it is precisely to this quantity (and not to ρ_{11}) that the resonant response of the atom is proportional near the frequency of the transition from the upper level to some third state.

Thus, in the stationary case the population of the upper QES should be $(F/\delta)^4$. This can in fact be demonstrated by different methods (e.g., by rewriting Eqs. (5) in the quasienergy representation and simply finding the stationary solution).

4. THREE LEVEL SCHEME USED IN THE METHOD OF ENRICHING THE INITIAL STATE

Let us consider the system shown in Fig. 1. We assume that the atom whose excitation probability is of interest to us is in the state $|0\rangle$, whereas the frequency of the light pulse is much closer to the frequency ω_{12} of the $|1\rangle\to|2\rangle$ transition than to the frequency ω_{10} of $|1\rangle\to|0\rangle$. This situation is typical of a previously proposed[14,15] method of detecting rare isotopes, which can be called enrichment of the initial state. In this method the atoms of all the isotopes are initially predominant in the state $|2\rangle$, and then the atoms of the background isotopes are pumped by a cw laser into the state $|0\rangle$. In this process, at sufficient spacing between the levels $|0\rangle$ and $|2\rangle$ and at typical values of the isotopic shift, one can obtain very high rare-isotope enrichment of the level $|2\rangle$ (see Ref. 14). We next apply a pulse at the frequency of the $|2\rangle\to|1\rangle$ transition in the rare-isotope atom, and the estimate of the selectivity will be primarily connected with the probability of exciting the background isotope from the $|0\rangle$ states, i.e., we arrive precisely at our three-level scheme shown in Fig. 1, in which δ_{12} is the isotopic shift.

We shall assume, naturally, that the frequency detunings and the rates of the spontaneous decay satisfy the conditions (1) and (2). We estimate the population of the upper level $|1\rangle$ at the end of the pulse, using the concepts of spontaneous transitions between the QES. For our case we have for the quasienergy wave eigenfunctions

$$\varphi_i=\sum_{k=1}^{3}\theta_{ik}\psi_k, \tag{20}$$

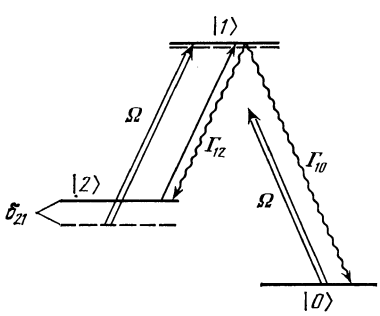

FIG. 1. Three-level system used in the method of enriching the initial state. The dashed lines give the level positions in the rare-isotope atom. A single arrow denotes the continuous radiation that enriches the level $|2\rangle$ relative to the rare-isotope atom. The double arrows denote the pulsed field, in which the probability of exciting the background-isotope atom from the state $|0\rangle$ is of interest to us.

$$|\theta_{ii}|\approx 1, \quad |\theta_{01}|\approx|\theta_{10}|\approx|F_{01}/\delta_{10}|,$$
$$|\theta_{12}|\approx|\theta_{21}|\approx|F_{12}/\delta_{21}|. \tag{21}$$

The rate of the spontaneous transition to a QES that is adiabatically coupled to the upper level is

$$w_{01}=|\theta_{01}\theta_{10}|^2\Gamma_{10}+|\theta_{01}\theta_{12}|^2\Gamma_{12}, \tag{22}$$

and since $|\delta_{10}|\gg|\delta_{21}|$, we arrive at the expression

$$\rho_{11}\approx(\overline{F_{01}^2}/\delta_{10}^2)\,(\overline{F_{12}^2}/\delta_{21}^2)\,\Gamma_{12}\tau_p. \tag{23}$$

Section B of the Appendix contains an equation (A.5) for ρ_{11}, obtained accurate to terms $\sim 1/\delta^4$ from the equations for the density-matrix elements. The incoherent term, as expected, is completely described by the rate (22).

5. TWO-STEP EXCITATION IN A THREE-LEVEL SYSTEM

Let the atom be acted on by two pulses with frequencies Ω_1 and Ω_2 close respectively to the frequencies ω_{10} and ω_{21}, but not at resonance in the sense of conditions (2) and (3). Two cases must be distinguished here. In the first the pulses do not overlap substantially in time, and in the second the pulses act on the atom simultaneously.

It is implied in the first case, of course, that the total time of the action on the atom is shorter than the spontaneous decay times of both excited states. The calculation of the population ρ_{22} of the upper level then reduces simply to multiplying the excitation probabilities of two two-level systems. We have

$$\rho_{22}\approx((\overline{F_{01}^4}/\delta_{10}^4)\,\Gamma_{10}\tau_p^{(1)}]\,[(\overline{F_{12}^4}/\delta_{21}^4)\,\Gamma_{21}\tau_p^{(2)}]. \tag{24}$$

This procedure is easily generalized to include also excitation with a larger number of steps.

The second case is more subtle. The main contribution to the population of the upper level (after the termination of the pulse) is made here by spontaneous transitions (during the pulse) from the lower QES to the upper. Assuming that the detuning from the two-photon resonance is large enough, so that the condition

$$|(\Omega_1-\omega_{10})+(\Omega_2-\omega_{21})|^{-1}=|\delta_{10}+\delta_{21}|^{-1}\ll\tau_p$$

is satisfied, we supplement the coefficients (21) in the expansion (20) by the following two:

$$|\theta_{02}|\approx\left|\frac{F_{01}F_{12}}{\delta_{10}(\delta_{10}+\delta_{21})}\right|, \quad |\theta_{20}|\approx\left|\frac{F_{01}F_{12}}{\delta_{21}(\delta_{10}+\delta_{21})}\right|. \tag{25}$$

The rate of the spontaneous transition of interest to us is

$$w_{02}=|\theta_{01}\theta_{20}|^2\Gamma_{10}+|\theta_{02}\theta_{21}|^2\Gamma_{21}. \tag{26}$$

Hence

$$\rho_{22}\approx\frac{1}{\delta_{10}^2\delta_{21}^2(\delta_{10}+\delta_{21})^2}(\overline{F_{01}^4F_{12}^2}\Gamma_{10}\tilde{\tau}_p+\overline{F_{01}^2F_{12}^4}\Gamma_{21}\tilde{\tau}_p), \tag{27}$$

where $\tilde{\tau}_p$ should be taken to mean the characteristic time of overlap of the two pulses. The first term of (26) describes a process in which two photons of frequency Ω_1 and one photon of frequency Ω_2 are absorbed from the field and the atom emits simultaneously a photon of frequency $2\Omega_1+\Omega_2-\omega_{10}-\omega_{21}$, while the second term describes a process with absorption of one Ω_1 photon and two Ω_2 photons and emission of a photon of frequency $\Omega_1+2\Omega_2-\omega_{10}-\omega_{21}$. From a comparison of (27) and (24) it can be seen that, other conditions being equal, the atom is more strongly excited when the two pulses are superimposed in time. Both terms of (27) correspond exactly to the two incoherent terms of ρ_{22} in the complete equation (A.6) given in Sec. C of the Appendix accurate to terms $\sim 1/\delta^6$.

It should be noted that Eq. (27) is valid also in the particular case when one of the fields is stationary. In this case $\tilde{\tau}_p$ should be taken to mean simply the duration of the pulse of the second field.

6. CONCLUSION

Returning to the problem of detecting rare isotopes by the method of multistep laser photoionization of atoms, we present some simple estimates. We consider first the selectivity of the one-step excitation, assuming that the pulse inverts the population in the atom of the rare isotope ($\pi/2$ pulse), and taking for the sake of argument the pulse duration to be an order of magnitude shorter than the time of the spontaneous decay ($\Gamma\tau_p=0.1$). Then, using (14), we arrive at the estimate

$$S_1\approx\rho_{11}^{-1}\approx 10^{-3}(\delta_{sh}/\Gamma)^4C, \tag{28}$$

where δ_{sh} is the isotopic shift of the transition frequency, and C is a numerical factor of the order of unity and depends on the shape of the pulse. [For example, $C=2$ for the Gaussian pulse $F(t)=F_0\exp(-t^2/\tau_p^2)$.] Typical ratios of the natural isotopic shift and the radiative width of the level are 10^2–10^3 (or even more), so that $S_1=10^5-10^9$. In addition, for those cases when the isotopic natural shift is small, it is possible[16] to have a rather large isotope Doppler shift in the collinear direction when working with an accelerated atomic beam.

When isotopic shift is present for several transitions, excitation by successive pulses leads to multiplication of the single-step selectivities [see, in particular, Eq. (24)]. (The use of accelerated beams makes this possibility universal.[16]) We, however, discuss also another situation, when the isotopic shift is relatively large only for the first transition $|0\rangle\to|1\rangle$, and compare the selectivity $S_2^{(0)}$ of a successive two-step resonant excitation with the selectivity $S_2^{(\Delta)}$ of a two-photon res-

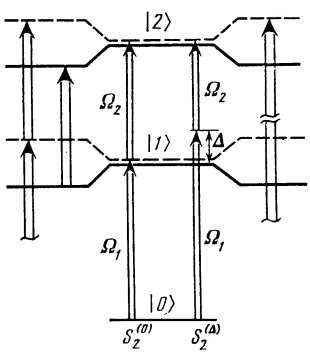

FIG. 2. Illustrating the comparison of two possible schemes of detecting a rare-isotope ion at a small isotopic shift in the transition $|1\rangle\to|2\rangle$. The dashed lines show the positions of the rare-isotope atom levels. $S_2^{(0)}$ and $S_2^{(\Delta)}$ are respectively the selectivities of the two-step and two-photon excitation (see the text).

onant excitation with detuning Δ at the intermediate level (see Fig. 2 and Ref. 17). The value of $S_2^{(0)}$ is given in fact by the estimate (28). In two-photon excitation of a rare isotope, the population is inverted at

$$|\overline{F_{01}F_{12}}/\Delta|\tau_p \approx \pi/2.$$

Interest attaches to the realistic case when $\Gamma_{21} < \Gamma_{10}$. Putting $F_{01} = F_{12}$ and $\Gamma_{21}\tau_p = 0.1$ we obtain from (27) the estimate

$$S_2^{(\Delta)} \approx 10^{-2}\frac{\delta_{sh}^2|\Delta|}{\Gamma_{10}\Gamma_{21}^2},$$

$$\frac{S_2^{(\Delta)}}{S_2^{(0)}} \approx 10\left(\frac{\Gamma_{10}}{\Gamma_{21}}\right)^2\frac{\Gamma_{10}|\Delta|}{\delta_{sh}^2}, \tag{29}$$

i.e., for example at $\Gamma_{10}/\Gamma_{21} \sim 10$ and $\Gamma_{10}/|\delta_{sh}| \sim 10^{-3}$, one can expect in two-photon excitation with intermediate detuning an gain in an approximate ratio $|\Delta/\delta_{sh}|$. Of course, the larger the detuning Δ, the higher the required radiation intensities.

Our concluding remark concerns the influence of nonmonochromaticity of the radiation on the obtained estimate (28), in the sense that the width $\Delta\nu_{las}$ of the laser-pulse spectrum can be larger than the width set by the pulse duration. In this case the estimate of the selectivity is changed, for now the intensity needed to saturate the transition in the rare-isotope atom is larger by the factor by which $\Delta\nu_{las}$ exceeds τ_p^{-1}. Since the probability of exciting the upper level in a two-level system with detuning is proportional to the square of the intensity [see Eq. (14)], the decrease of the selectivity on one step is $[\Delta\nu_{las}\tau_p]^2$. (Of course, we assume here that the spectral intensity of the laser pulse at the frequency of the transition in the background-isotope atom is small enough for Eq. (14) to be meaningful at all.) Since cw lasers have better spectral characteristics than pulsed lasers, it is possible that a realistic scheme will be one in which the atom is acted upon in one of the steps by a stationary field. Everything necessary for estimates of the selectivities for this case is contained in the results above (see the remarks at the ends of Secs. 3 and 5).

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APPENDIX

The Appendix employs a common system, written in the resonance approximation, of equations for the density-matrix elements of a three-level system in a two-frequency field. It is assumed that the level $|1\rangle$ lies above the level $|0\rangle$, but the level $|2\rangle$ can be either above (Secs. A and C) or below (Sec. B) level $|1\rangle$. The last two cases differ in the sign of the detuning $\delta_{21} = \pm(\Omega_2 - |\omega_{21}|)$ of the field frequency from the transition frequency (positive at $\omega_{21} > 0$ and vice versa). Spontaneous decays from levels $|1\rangle$ and $|2\rangle$ through other channels ($\tilde{\Gamma}_1$ and $\tilde{\Gamma}_2$) and introduced in the common equations. For the sake of brevity, the off-diagonal elements of the density matrix are explicity designated $\tilde{\rho}_{jk} = \rho_{jk}\exp(-i\delta_{jk}t)$ in place of their linear combinations u and v in (5). In this notation, the equations take the form

$$\begin{aligned}
d\rho_{00}/dt &= -iF_{01}(\tilde{\rho}_{01}-\tilde{\rho}_{10}) + \Gamma_{10}\rho_{11},\\
d\rho_{11}/dt &= iF_{01}(\tilde{\rho}_{01}-\tilde{\rho}_{10}) - iF_{12}(\tilde{\rho}_{12}-\tilde{\rho}_{21})\\
&\quad -(\Gamma_{10}+\Gamma_{12}+\tilde{\Gamma}_1)\rho_{11} + \Gamma_{21}\rho_{22},\\
d\rho_{22}/dt &= iF_{12}(\tilde{\rho}_{12}-\tilde{\rho}_{21}) - (\Gamma_{21}+\tilde{\Gamma}_2)\rho_{22} + \Gamma_{12}\rho_{11},\\
d\tilde{\rho}_{01}/dt &= -i\delta_{10}\tilde{\rho}_{01} - {}^1/_2(\Gamma_{10}+\Gamma_{12}+\tilde{\Gamma}_1)\tilde{\rho}_{01} - iF_{01}(\rho_{00}-\rho_{11})\\
&\quad -iF_{12}\tilde{\rho}_{02},\\
d\tilde{\rho}_{12}/dt &= -i\delta_{21}\tilde{\rho}_{12} - {}^1/_2(\Gamma_{10}+\Gamma_{12}+\tilde{\Gamma}_1+\Gamma_{21}+\tilde{\Gamma}_2)\tilde{\rho}_{12}\\
&\quad -iF_{12}(\rho_{11}-\rho_{22}) + iF_{01}\tilde{\rho}_{02},\\
d\tilde{\rho}_{02}/dt &= -i(\delta_{10}+\delta_{21})\tilde{\rho}_{02} - {}^1/_2(\Gamma_{21}+\tilde{\Gamma}_2)\tilde{\rho}_{02} + iF_{01}\tilde{\rho}_{12} - iF_{12}\tilde{\rho}_{01},\\
\tilde{\rho}_{10} &= \tilde{\rho}_{01}^*, \quad \tilde{\rho}_{21} = \tilde{\rho}_{12}^*, \quad \tilde{\rho}_{20} = \tilde{\rho}_{02}^*.
\end{aligned} \tag{A.1}$$

Of course, in these equations either $\Gamma_{12} \equiv 0$ or $\Gamma_{21} \equiv 0$. In addition, the quantities F_{01} and F_{12} are assumed to tend smoothly enough to zero as $t \to \pm\infty$ (see the formulation of the problem in the Introduction).

A. *Regarding the test-field method (Sec. 3).* We assume in Eqs. (A.1) that $\Gamma_2 = \Gamma_{12} = \Gamma_{21} = 0$ and neglect the quantity ρ_{22} in the equation for $\tilde{\rho}_{12}$. In addition, we assume ρ_{11}, $\tilde{\rho}_{01}$, and $\tilde{\rho}_{10}$ to be given functions of the time and determined by the solution of Eqs. (5) for a two-level system. As a result we arrive at the following abbreviated inhomogeneous system of equations:

$$\begin{aligned}
d\tilde{\rho}_{12}/dt &= iF_{01}\tilde{\rho}_{02} - i\delta_{21}\tilde{\rho}_{12} - {}^1/_2(\Gamma_{10}+\tilde{\Gamma}_1)\tilde{\rho}_{12} - iF_{12}\rho_{11}(t),\\
d\tilde{\rho}_{02}/dt &= -i(\delta_{10}+\delta_{21})\tilde{\rho}_{02} + iF_{01}\tilde{\rho}_{12} - iF_{12}\tilde{\rho}_{01}(t).
\end{aligned} \tag{A.2}$$

We are interested in its solution that goes to zero as $t \to -\infty$. We introduce formally the solutions of the corresponding homogeneous system in the form

$$\{\tilde{\rho}_{12} = P(t),\ \tilde{\rho}_{02} = \chi(t)P(t)\}, \qquad \{\tilde{\rho}_{12} = \eta(t)Q(t),\ \tilde{\rho}_{02} = Q(t)\}, \tag{A.3}$$

which satisfy the condition $P(-\infty) = Q(-\infty) = 1$ and $\chi(-\infty) = \eta(-\infty) = 0$. Solving after this substitution the inhomogeneous system by a method similar to the WKB approximation we find that at a small value of δ_{21}, which cancels out the Stark shift of level $|1\rangle$, the first of the solutions in (A.3) is nonoscillating, whereas the second is rapidly oscillating. The solution, of interest to us, of the inhomogeneous system (for $\tilde{\rho}_{12}$) is written in the form

$$\begin{aligned}
\tilde{\rho}_{12}(t) &= -iP\int_{-\infty}^{t}\frac{F_{12}}{P(1-\chi\eta)}(\rho_{11}-\eta\tilde{\rho}_{01})\,d\tau\\
&\quad + i\eta Q\int_{-\infty}^{t}\frac{F_{12}}{Q(1-\chi\eta)}(\chi\rho_{11}-\tilde{\rho}_{01})\,d\tau.
\end{aligned} \tag{A.4}$$

Retaining in (A.4) only the nonoscillating first term and substituting it is Eq. (A.1) for ρ_{22}, we find that at $F_{01} \neq 0$ the role of ρ_{11} is played by a combination of the quantities ρ_{11}, $\tilde{\rho}_{01}$, and $\tilde{\rho}_{10}$. The function $\eta(t)$ in (16) and (17) corresponds to that introduced by definition in (A.3).

B. *Regarding Sec. 4.* We put $\Gamma_{21} = \Gamma_2 = 0$ in Eqs. (A.1) and use the same procedure of finding an asymptotic expansion of the solution as in Sec. 2 for a two-level system. Accurate to terms $\sim 1/\delta_{10}^2$, the matrix elements $\tilde{\rho}_{01}$, $\tilde{\rho}_{10}$, ρ_{00} and ρ_{11} correspond to expressions (10)–(12) and to the first term

in (19). To the same order, we have

$$\rho_{22}=\frac{\Gamma_{12}}{\delta_{10}^{2}}\int_{-\infty}^{t}F_{01}^{2}(\tau)\,d\tau,\quad \tilde{\rho}_{02}=\frac{F_{01}F_{12}}{\delta_{10}(\delta_{10}+\delta_{21})}\quad \tilde{\rho}_{12}=0.$$

Continuing the successive approximation procedure, we obtain for ρ_{11} the following expression, which is accurate to terms $\sim 1/\delta^4$:

$$\rho_{11}(t)=\left\{\frac{F_{01}^{2}}{\delta_{10}^{2}}-\frac{3F_{01}^{4}}{\delta_{10}^{4}}-\frac{2F_{01}}{\delta_{10}^{4}}\exp\left(-\frac{\Gamma_1}{2}t\right)\frac{d^2}{dt^2}\left[F_{01}\exp\left(\frac{\Gamma_1}{2}t\right)\right]+\frac{1}{\delta_{10}^{4}}\exp(-\Gamma_1 t)\left[\frac{d}{dt}\left(F_{01}\exp\left(\frac{\Gamma_1}{2}t\right)\right)\right]^2\right.$$

$$\left.-\frac{\Gamma_{12}+\tilde{\Gamma}_1}{\delta_{10}^{4}}F_{01}^{2}\int_{-\infty}^{t}F_{01}^{2}(\tau)\,d\tau+\frac{\Gamma_{10}}{\delta_{10}^{4}}\exp(-\Gamma_1 t)\int_{-\infty}^{t}F_{01}^{4}(\tau)\exp(\Gamma_1\tau)\,d\tau\right\}$$

$$+\frac{2F_{01}^{2}F_{12}^{2}}{\delta_{10}^{3}(\delta_{10}+\delta_{21})}+\frac{\Gamma_{12}F_{12}^{2}}{\delta_{10}^{2}\delta_{21}^{2}}\int_{-\infty}^{t}F_{01}^{2}(\tau)\,d\tau+\frac{\Gamma_{12}}{\delta_{10}^{2}\delta_{21}^{2}}\exp(-\Gamma_1 t)\int_{-\infty}^{t}F_{01}^{2}(\tau)F_{12}^{2}(\tau)\exp(\Gamma_1\tau)\,d\tau,\qquad (A.5)$$

where $\Gamma_1=\Gamma_{10}+\Gamma_{12}+\tilde{\Gamma}_1$ is the total rate of spontaneous decay of the level $|1\rangle$. The terms in the curly brackets in (A.5) duplicate, with slight modification, expression (13) for ρ_{11} in the case of a two-level system. From among the new terms, only the last one does not vanish as the field amplitude tends to zero. Its meaning was explained in Sec. 4. If the pulse duration is shorter than the time of spontaneous decay of the upper level, we arrive at expression (23), where it is also taken into account that the quantities F_{01} and F_{12} are proportional to each other, since the field in the scheme of Sec. 4 has only one frequency.

C. *Regarding Sec. 5.* We put $\Gamma_{12}=0$ in Eqs. (A.1) and use the same procedure of finding the asymptotic expansion of the solution as before. Here we are interested in an expression for ρ_{22} accurate to terms $\sim 1/\delta^6$. The intermediate calculations are quite lengthly, and we write therefore only the final result:

$$\rho_{22}(t)=\frac{F_{01}^{2}F_{12}^{2}}{\delta_{10}^{2}(\delta_{10}+\delta_{21})^{2}}+\frac{2(F_{01}^{2}F_{12}^{4}-F_{01}^{4}F_{12}^{2})}{\delta_{10}^{3}(\delta_{10}+\delta_{21})^{3}}-\frac{3F_{01}^{4}F_{12}^{2}}{\delta_{10}^{4}(\delta_{10}+\delta_{21})^{2}}-\frac{1}{\delta_{10}^{2}(\delta_{10}+\delta_{21})^{4}}$$

$$\times\left\{2\exp\left(-\frac{\Gamma_2}{2}t\right)F_{01}F_{12}\frac{d^2}{dt^2}\left[F_{01}F_{12}\exp\left(\frac{\Gamma_2}{2}t\right)\right]-\exp(-\Gamma_2 t)\left[\frac{d}{dt}\left(F_{01}F_{12}\exp\left(\frac{\Gamma_2}{2}t\right)\right)\right]^2\right\}$$

$$+2\left[\frac{1}{\delta_{10}^{2}\delta_{21}(\delta_{10}+\delta_{21})^{3}}-\frac{1}{\delta_{10}^{4}\delta_{21}(\delta_{10}+\delta_{21})}\right]F_{01}F_{12}^{2}\exp\left(-\frac{\Gamma_1}{2}t\right)\frac{d^2}{dt^2}\left[F_{01}\exp\left(\frac{\Gamma_1}{2}t\right)\right]$$

$$+\left[\frac{2}{\delta_{10}^{3}(\delta_{10}+\delta_{21})^{3}}+\frac{1}{\delta_{10}^{4}(\delta_{10}+\delta_{21})^{2}}\right]F_{12}^{2}\exp(-\Gamma_1 t)\left\{\frac{d}{dt}\left[F_{01}\times\exp\left(\frac{\Gamma_1}{2}t\right)\right]\right\}^2$$

$$-\frac{\Gamma_1 F_{01}^{2}F_{12}^{2}}{\delta_{10}^{4}(\delta_{10}+\delta_{21})^{2}}\int_{-\infty}^{t}F_{01}^{2}(\tau)\,d\tau+\frac{\Gamma_{10}F_{12}^{2}}{\delta_{10}^{4}\delta_{21}^{2}}\exp(-\Gamma_1 t)\int_{-\infty}^{t}F_{01}^{4}(\tau)\times\exp(\Gamma_1\tau)\,d\tau+\frac{\Gamma_{21}F_{12}^{2}}{\delta_{10}^{2}\delta_{21}^{2}(\delta_{10}+\delta_{21})^{2}}$$

$$\times\exp(-\Gamma_1 t)\int_{-\infty}^{t}F_{01}^{2}(\tau)F_{12}^{2}(\tau)\exp(\Gamma_1\tau)\,d\tau+\frac{1}{\delta_{10}^{2}\delta_{21}^{2}(\delta_{10}+\delta_{21})^{2}}\exp(-\Gamma_2 t)\left\{\Gamma_{10}\int_{-\infty}^{t}F_{01}^{4}(\tau)F_{12}^{2}(\tau)\exp(\Gamma_2\tau)\,d\tau\right.$$

$$\left.+\Gamma_{21}\int_{-\infty}^{t}F_{01}^{2}(\tau)F_{12}^{4}(\tau)\exp(\Gamma_2\tau)\,d\tau\right\},\qquad (A.6)$$

where Γ_1 and Γ_2 are the total velocities of the spontaneous decays of the levels $|1\rangle$ and $|2\rangle$. When the field amplitudes tend to zero, only the last term does not vanish. It describes the incoherent part of the population of the level $|2\rangle$ by spontaneous transitions from a lower QES to the very uppermost. If the duration of at least one of the pulses is shorter than the time of spontaneous decay of level $|2\rangle$, we arrive at expression (27).

[1)]The division of the population of the excited level into coherent and incoherent parts is the usual terminology applicable to the situation when it is necessary, for example, to distinguish between elastic scattering and fluorescence (see, e.g., Refs. 11 and 12).

[2)]One could, for example, rewrite (5) in the quasienergy representation, but in this case it is impossible to be completely rid of the coherent admixture of the upper QES in the lower one—terms that contain derivatives of the field amplitude remain.

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