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Transition Cross Sections in Two-Photon Process

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Abstract The concept of transition cross section is re-examined in two-photon process. The rate equations and the relevant transition cross sections are good approximation in the region where the diagonal elements of the density matrix change slowly with time. The rate coefficients are derived explicitly: those describing formally the single photon process will be subject to a significant modification for strong light field compared with that of the weak laser field and those describing formally the multi-photon process can also be constructed from the parameters relevant to the real single photon process. The optimization of power distribution of laser fields changes dramatically from weak to strong total laser intensity available. To describe the interference effect originated either from the multi-mode laser field or from a group of energy levels located closely needs more complicated computation of the transition cross sections than using the Bloch equations directly.

Key words two-photon process, rate equations, Bloch equations.

1 Introduction

Multi-Photon process is important in excitation and ionization of materials with lasers. There are two kinds of multi-photon process: one is with near resonance intermediate levels, such as atomic vapor laser isotope separation (AVLIS); the other is with far off-resonance intermediate levels, such as Raman spectroscopy, single-color multi-photon ionization, and some strong excitation in solids. Normally, rate equations and relevant transition cross sections are used to address these processes[1]. For example, it is very important to know the transition cross sections at every step of the ionization ladder in AVLIS[2]. However, the plausibility of using rate equations and transition cross sections in multi-photon process was inspected and discussed by several authors. Wilcox and Lamb discussed the general relationship between the rate equations and the density matrix for a multi-level system and derived the expression of the transition cross section for microwave-optical excitation[3]. Ackarhalt

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and Shore derived the rate equations of two-level atom from the Bloch equations with considering spontaneous emission and collision and discussed briefly the case of multi-level atom[4]. Paisner and Solarz also derived a general formation connecting the rate coefficients with the Rabi frequency between separate transitions[5]. In the last literature, the authors pointed out that the saturation effect of one transition would change the "heuristic" rate equations in which only the transitions between the adjacent levels were considered.

In this paper, we shall use the simplest multiphoton process, i.e. two-photon process, to examine the conditions leading the simplification from Bloch equation to the rate equations. We find that the rate equations hold only in the "long pulse" situation where the laser pulse duration should be much longer than any relaxation process of the material system. We also find that the saturation effect leads the "transition cross section" for adjacent transitons approaching to each other when the relevant transition dipole moments exhibit large difference and hence the laser utilization rate which is important in AVLIS will be improved. As an example of single color two-photon process, we derive the rate coefficient and its lineshape. The rate equations can also demonstrate the interference effect of multi-mode laser or of closely spacing energy level group. In this case, the rate equations show no advantage over the Bloch equations.

2 Conditions for the Simplification from Bloch Equations to Rate Equations

Our simplest model is shown in Fig. 1. The three-level atom is with a bound state 1 and two excited states 2 and 3 whcih decay to the states outside these three states with a rate R_2 and R_3 respectively. Two laser light fields with frequencies ω_{12}^{L} and ω_{23}^{L} match the atomic transition ω_{12}^{a} and ω_{23}^{a} respectively. The technique to obtain suitable Bloch equations for such a system is to choose a convenient interaction representation, and the transformation of the density matrix elements ρ_{ij} and the interaction Hamiltonian V between the interaction representation and the Schrödinger one are

$$\rho_{ij} = \rho_{ij}^{Sch}\exp(i\omega_{ij}^{a}t), \qquad V_{ij} = V_{ij}^{Sch}\exp(i\omega_{ij}^{a}t)$$

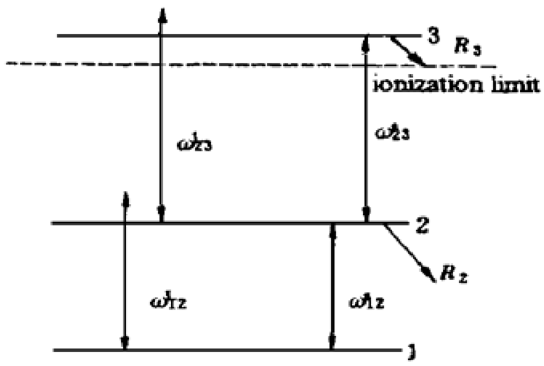

Fig. 1 A three-level atom and two-photon process

The difference between our interaction representation and the normal one is that we use the atomic resonant frequency ω_{ij}^{a} in the transformation instead of the laser frequencies which have several values in the few-mode case. In this new representation, the Bloch equations are:

$$d\rho_{nm}/dt = -\rho_{nm}R_{nm} - (2\pi i/h)\sum_k(V_{nk}\rho_{km} - \rho_{nk}V_{km}) \tag{1}$$

where

$$V_{nk} = \langle n|(-e\mathbf{r}\cdot\mathbf{E}\exp(i\delta_{nk}t)|k\rangle = -\mu_{nk}\cdot\mathbf{E}\exp(i\delta_{nk}t) = -(\hbar\Omega_{nk}/2)\exp(i\delta_{nk}t) \tag{2}$$

$$\mu_{nk} = \langle n|e\mathbf{r}|k\rangle \tag{3}$$

$$\Omega_{nk} = 2\mu_{nk}\cdot\mathbf{E}/\hbar, \qquad \delta_{nk} = \omega_{nk}^{L} - \omega_{nk}^{a} \tag{4}$$

For our three-level atom, the motion equations of the density matrix elements are

$$d\rho_{11}/dt = (i/2)[\Omega_{12}\rho_{21}\exp(i\delta_{12}t) - \Omega_{12}^{*}\rho_{12}\exp(-i\delta_{12}t)] \quad (5)$$

$$d\rho_{22}/dt = -(i/2)[\Omega_{12}\rho_{21}\exp(i\delta_{12}t) - \Omega_{12}^{*}\rho_{12}\exp(-i\delta_{12}t)] + (i/2)[\Omega_{23}\rho_{32}\exp(i\delta_{23}t) - \Omega_{23}^{*}\rho_{23}\exp(-i\delta_{23}t)] - \rho_{22}R_2 \quad (6)$$

$$\delta\rho_{33}/dt = -(i/2)[\Omega_{23}\rho_{32}\exp(i\delta_{23}t) - \Omega_{23}^{*}\rho_{23}\exp(-i\delta_{23}t)] - \rho_{33}R_3 \quad (7)$$

$$d\rho_{12}/dt = (i/2)[(\rho_{22} - \rho_{11})\Omega_{12}\exp(i\delta_{12}t) - \rho_{13}\Omega_{23}^{*}\exp(-i\delta_{23}t)] - \rho_{12}R_2/2 \quad (8)$$

$$d\rho_{23}/dt = (i/2)[(\rho_{33} - \rho_{22})\Omega_{23}\exp(i\delta_{23}t) + \rho_{13}\Omega_{12}^{*}\exp(-i\delta_{12}t)] - \rho_{23}(R_2 + R_3)/2 \quad (9)$$

$$d\rho_{13}/dt = (i/2)[\rho_{23}\Omega_{12}\exp(i\delta_{12}t) - \rho_{12}\Omega_{23}\exp(i\delta_{23}t)] - \rho_{13}R_3/2 \quad (10)$$

Now we try to find an approximation solution of the Bloch equations. If ρ_{11}, ρ_{22} and ρ_{33} change slowly with time, then

$$\rho_{12} = a_{12}\exp(i\delta_{12}t) \quad (11)$$

$$\rho_{23} = a_{23}\exp(i\delta_{23}t) \quad (12)$$

$$\rho_{13} = a_{13}\exp[i(\delta_{23} + \delta_{12})t] = a_{13}\exp(i\delta_{13}t) \quad (13)$$

will be a possible solution. On the other hand, the dampling mechanism will smooth the Rabi oscillation of the diagonal elements at the time scale $t \gg 1/R_2$, $1/R_3$. Let us take an example to confirm this conclusion: $R_2 = 1$, $R_3 = 5$, $\Omega_{12} = 5$, $\Omega_{23} = 6$, $\delta_{12} = 3$, $\delta_{23} = 4$, and $\delta_{13} = 7$. Fig. 2 shows the Fourier transform of some elements of the density matrix. For the total interaction time (we take $t = 0 \sim 10$), they exhibit quite complicated spectral behaviour. When we take the transform after $t = 2$, the diagonal element ρ_{11} decays to a zero frequency component and the non-diagonal elements approach the frequency components described by equations (11) ~ (13).

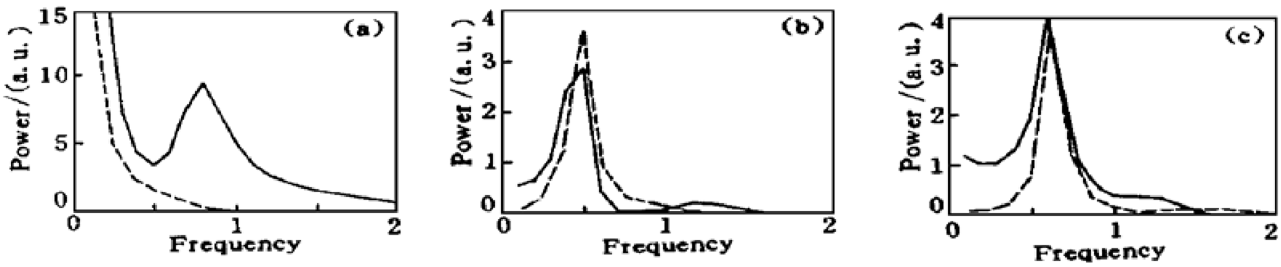

Fig. 2 Fourier transform spectra of some elements of the density matrix. (a) ρ_{11}, (b) ρ_{12}, (c) ρ_{23}, and (d) ρ_{13}. Solid lines represent $t = 0 \sim 10$, dash lines represent $t = 2 \sim 10$. The parameters chosen are: $R_2 = 1$, $R_3 = 5$, $\Omega_{12} = 5$, $\Omega_{23} = 6$, $\delta_{12} = 3$, $\delta_{12} = 3$, $\delta_{12} = 4$, and $\delta_{13} = 7$

Substituting equations (11) ~ (13) into (8) ~ (10) and after solving the coefficients, the equations (5) ~ (7) can be written as:

$$d\rho_{11}/dt = W_{12}(\rho_{22} - \rho_{11}) + W_{13}(\rho_{33} - \rho_{11}) \quad (14)$$

$$d\rho_{22}/dt = W_{12}(\rho_{11} - \rho_{22}) + W_{23}(\rho_{33} - \rho_{22}) - R_2\rho_{22} \quad (15)$$

$$d\rho_{33}/dt = W_{23}(\rho_{23} - \rho_{33}) + W_{13}(\rho_{11} - \rho_{33}) - R_3\rho_{33} \quad (16)$$

where

$$W_{12} = W_{21} = |\Omega_{12}|^2\,\mathrm{Im}\{[(\delta_{23} - i(R_2 + R_3)/2)(\delta_{13} - iR_3/2) - |\Omega_{12}|^2/4 + |\Omega_{23}|^2/4]/2D\} \quad (17)$$

$$W_{23} = W_{32} = |\Omega_{23}|^2\,\mathrm{Im}\{[(\delta_{12} - iR_2/2)(\delta_{13} - iR_3/2) + |\Omega_{12}|^2/4 - |\Omega_{23}|^2/4]/2D\} \quad (18)$$

$$W_{13} = W_{31} = -|\Omega_{12}|^2|\Omega_{23}|^2\,\mathrm{Im}\{1/8D\} \quad (19)$$

$$D = (\delta_{12} - iR_2/2)[\delta_{23} - i(R_2 + R_2)/2](\delta_{13} - iR_3/2) - (\delta_{12} - iR_2/2)|\Omega_{12}|^2/4 -$$

$$[\delta_{23} - i(R_2 + R_3)/2]|\Omega_{23}|^2/4 \tag{20}$$

Equation (14) ~ (20) are the rate equations and rate coefficients of two-photon process. The relevant transition cross section is defined as

$$\sigma_{ij} = W_{ij}/I_{ij} \tag{21}$$

where I_{ij} is the power density of the laser.

3 Saturation Effect of the Transition Cross Section

When there is only one laser light field in the interaction, $\Omega_{23} = 0$, for example, then

$$W_{12} = W_{21} = \Omega_{12}^2 R_2/(4\delta_{12}^2 + R_2^2) \tag{22}$$

$$W_{23} = W_{32} = W_{13} = W_{31} = 0 \tag{23}$$

This is the same result of the literature[4]. On the other hand, if $\Omega_{12} = 0$, then

$$W_{23} = W_{32} = \Omega_{23}^2 R_3/[4\delta_{23}^2 + (R_2 + R_3)^2] \tag{24}$$

$$W_{12} = W_{21} = W_{13} = W_{31} = 0 \tag{25}$$

These expressions show no saturation effect in the single photon process. It is interesting to point out that the rate coefficients of two-photon process in weak signal approximation from (17) ~ (19) are just the same expressions (22) and (24), with the two-photon transition rate $W_{13} = W_{31} = 0$. Such equations considered only the transition between adjacent levels and used the rate coefficients obtained from single photon process. Normally, such equations are called "heuristic" rate equation limit[5] in the strong signal region.

In the strong signal region, the heuristic rate equations are not adequate. Suppose $\delta_{12} = \delta_{12} = 0$ (double resonance), $R_2 = 1$, $R_3 = 5$, $\Omega_{12} = 1$, and $\Omega_{23} = 4$. The rate coefficients calculated in single photon and two-photon process are shown in table 1:

Table 1. Rate coefficients in single and two-photon process

	W_{12}	W_{23}	W_{13}
single photon	1	2.6667	/
two-photon	0.1181	2.5197	0.1260

The populations calculated by using Bloch equations, heuristic rate equations, and two-photon rate equations are shown in Fig. 3. We see that in this slight saturation situation ($\Omega_{ij} \sim R_j$), the results from two-photon rate equations (dashed lines) approach those from the Bloch equations (solid lines), much better than those from the heuristic rate equations (dotted lines).

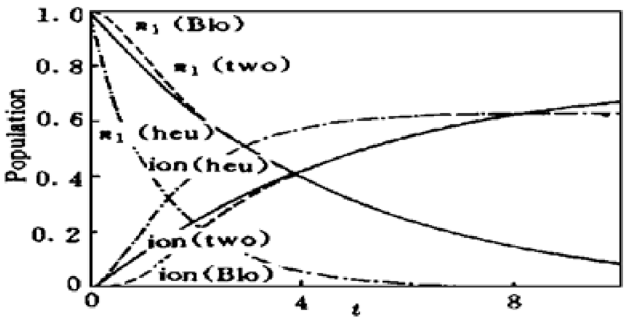

Fig. 3 Populations calculated by Bloch (Blo), heuristic rate equations (heu), and two-photon rate equations (two). The ionization process is from the autoionization state level 3. The parameters are $\delta_{12} = 0$, $\delta_{23} = 0$ (double resonance), $R_2 = 1$, $R_3 = 5$, $\Omega_{12} = 1$, and $\Omega_{23} = 4$

For the double resonance case, the rate coefficients reduce to

$$W_{12} = W_{21} = \Omega_{12}^2[\Omega_{12}^2 - \Omega_{23}^2 + R_3(R_2 + R_3)]/C \tag{26}$$

$$W_{23} = W_{32} = \Omega_{23}^2(-\Omega_{12}^2 + \Omega_{23}^2 + R_2 R_3)/C \tag{27}$$

$$W_{13} = W_{31} = \Omega_{12}^2\Omega_{23}^2/C \tag{28}$$

$$C = R_2R_3(R_2 + R_3) + R_2\Omega_{12}^2 + (R_2 + R_3)\Omega_{23}^2 \tag{29}$$

In comparsion with the single photon process (22) and (24), the saturation effect in two-photon process will reduce the values of W_{12} and W_{23}. On the other hand, the two-photon transition coefficient W_{13} incresses with strong laser fields. Fig. 4 shows this situation.

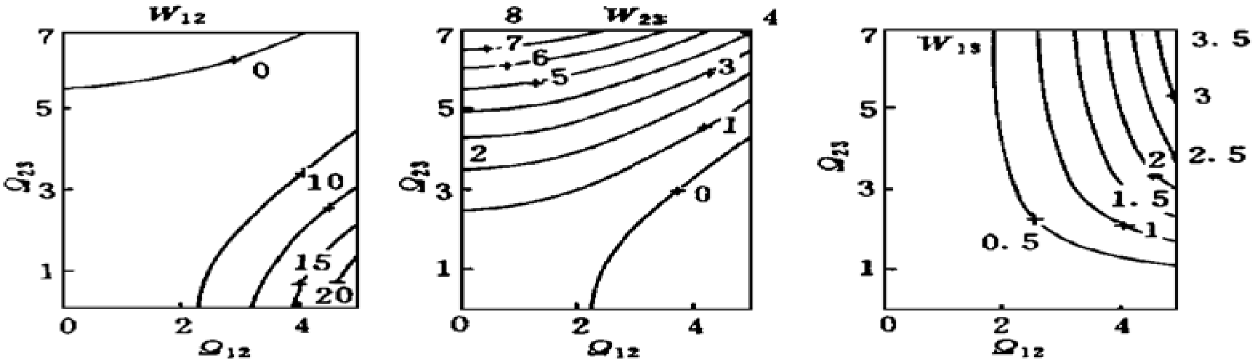

Fig. 4 W_{12}, W_{23} and W_{13} versus Ω_{12} and Ω_{23}. Parameters: $\delta_{12} = \delta_{23} = 0$, $R_2 = 1$, $R_3 = 5$

4 Improvement of the Ultilization Efficiency of Laser Energy Due to the Saturation Effect

In the case of multi-color photoionization, one needs optimizing the distribution of laser power for different laser frequencies with constant total laser power available. For our simplest two-photon model, suppose that $|\mu_{12}|^2/R_2 \gg |\mu_{23}|^2/(R_2 + R_3)$. According to the heuristic rate equations, the laser power density should satisfy $I_{23} \gg I_{12}$ to guarantee $W_{12} \sim W_{23}$ and then no transition bottle-neck exits. On the other hand, the photon number absorbed in each transition is about the same, so most power at frequency ω_{23} will not be absorbed and causes the photon utilization efficiency very low. Fortunately this picture is not true due to the saturation effect. Strong laser fields decrease W_{12} and W_{23} which decrease the role of single transition between adjacent levels whereas increase W_{13} presenting the role of "direct" two-photon transition. We can distribute both laser powers to approach to each other with closer portion to be absorbed. The total result will improve the utilization efficiency of laser power.

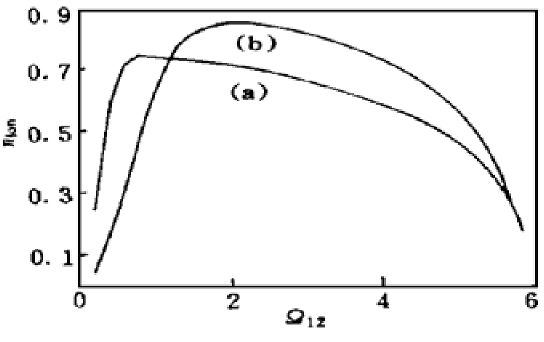

Fig. 5 Ion yield versus the distribution of laser powers. The parameters are: $R_2 = 1$, $R_3 = 5$, interaction time $t = 10$, double resonance. Suppose $|\mu_{12}| = |\mu_{23}|$, the available laser power $\Omega_{12}^2 + \Omega_{23}^2 = 36$

We take an example to illustrate such an improvement. Suppose that $|\mu_{12}| = |\mu_{23}|$, then the optical energy at these two frequencies obeys

$$E_{12}/E_{23} = \Omega_{12}^2/\Omega_{23}^2$$

We try to find the Ω_{12} for maximum ion yield at the a total optical energy

$$\Omega_{12}^2 + \Omega_{23}^2 = 36$$

and $R_2 = 1$, $R_3 = 5$ as in above example. The result from Bloch equations and the rate equations with the two-photon transition is exactly the same [Fig. 5(b)] which is quite different from the heuristic equations without the saturation effect and direct two-photon transition

[Fig. 5(a)]. The maximum ion yield improved in the two-photon process compared to the single photon process. For these maximum ion yield, the two-photon equations demand $E_{12}/E_{23} \sim 1/8$ instead of 1/36 in the heuristic rate equations.

5 Line Shape of Two-Photon Process

It is interesting to study the case of detuning. Fig. 6 shows the case of near-resonance intermediate level. The parameters are $R_2 = 1$, $R_3 = 5$, $\Omega_{12} = 1$, and $\Omega_{23} = 4$. In Fig. 6(a), the peaks of W_{12} correspond to the dressed states of levels 2 and 3 via Ω_{23} (Autler-Townes effect). This effect plays a minor role in Fig. 6(b) for W_{23} because Ω_{12} is small in our parameters chosen. Fig. 6(c) and Fig. 6(d) show the two-photon rate coefficient W_{13} and its contour

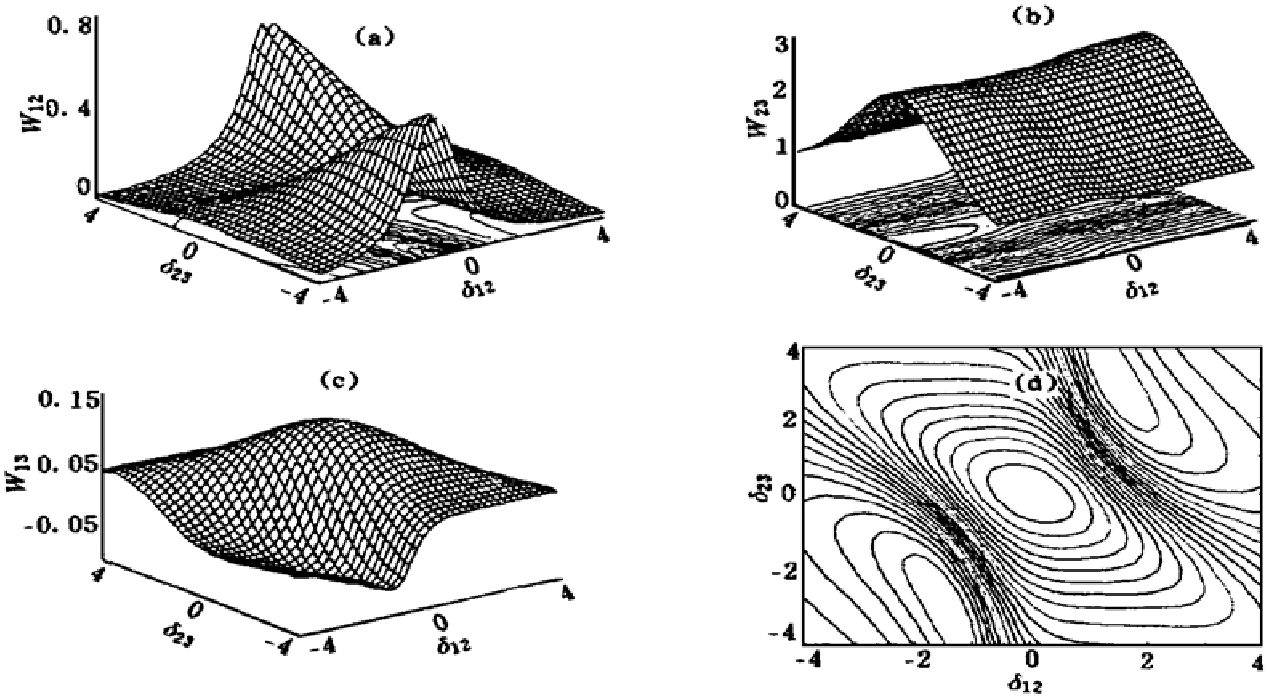

Fig. 6 Line shapes and their contours of two-photon rate coefficients. (a) W_{12}, (b) W_{23}, (c) W_{13}, and (d) contour of W_3. The parameters are $R_2 = 1$, $R_3 = 5$, $\Omega_{12} = 1$, and $\Omega_{23} = 4$

respectively. There is a peak at double resonance and two negative minimal located at $\delta_{12} = \pm 1.4$, $\delta_{23} = \pm 3.1$. The relevant rate coefficients are $W_{12} = 0.4040$, $W_{23} = 1.3688$, and $W_{13} = -0.0651$. In some cases, W_{12}, W_{23} or W_{13} takes negative value when there is Rabi flip-flop for the population. As we pointed out at the beginning, the rate equations approximation is not adequate for such cases and one cannot expect to infer more physical meaning from the rate coefficients.

Another important case is single-color two-photon process with off-resonance intermediate levels. We can simplify the expression (19) by setting

$$|\delta_{12}| \sim |\delta_{23}| \gg \delta_{13},\ \Omega_{12},\ \Omega_{23}.$$

and obtain

$$W_{13} = |\Omega_{12}|^2 |\Omega_{23}|^2 R_3 / 4\delta_{12}^2 (4\delta_{13}^2 + R_3^2) \tag{30}$$

6 Interference Effect in Two-Photon Process

The interference effect will appear when several transition channels from the ground state to the final excited state exist. There are two important kinds of interference effect in two-photon process. The first kind of interference is due to the fact that more than one intermediate level located closely together which respond simultaneously to both laser fields. A famous example is two-photon transition $3S - 3P - 4D$ in sodium[6]. We modify this example in a simplified way as shown in Fig. 7(a). For a symmetrical system with $d = 2$, $\Omega_{12} = \Omega_{13} = 1$, $\Omega_{24} = \Omega_{34} = 3$, $R_2 = R_3 = 1$, and $R_4 = 5$, the ion yield from level 4 at $t = 10$ versus the detuning from the middle point calculated by using Bloch equations is shown in Fig. 7 (b). As a comparison, we also show the situation where only one intermediate state (2 or 3) exists. It is clear that the destructive interference from these two intermediate states has a significant contribution. The second kind of interference is due to a multi-mode laser field. A simplest example is shown in Fig. 8 (a) where the first laser field contains two modes separated each other by d. The detuning δ of the middle frequency to the state 2 is used as a tunable parameter and the second laser is exactly resonant to the transition between states 2 and 3. Fig. 8 (b) shows the ion yield from level 3 calculated by using Bloch equations and with the parameters: $\Omega_{12}^1 = \Omega_{12}^2 = 1$, $\Omega_{13} = 3$, $d = 2$, $R_2 = 1$, $R_3 = 5$, and $t = 10$. As a comparison we also show the result in Fig. 8 (b) when the first laser field contains one mode only. It is interesting to point out that the maximum ion yield for one mode is larger than that for two-mode even the total laser power is larger for the latter case.

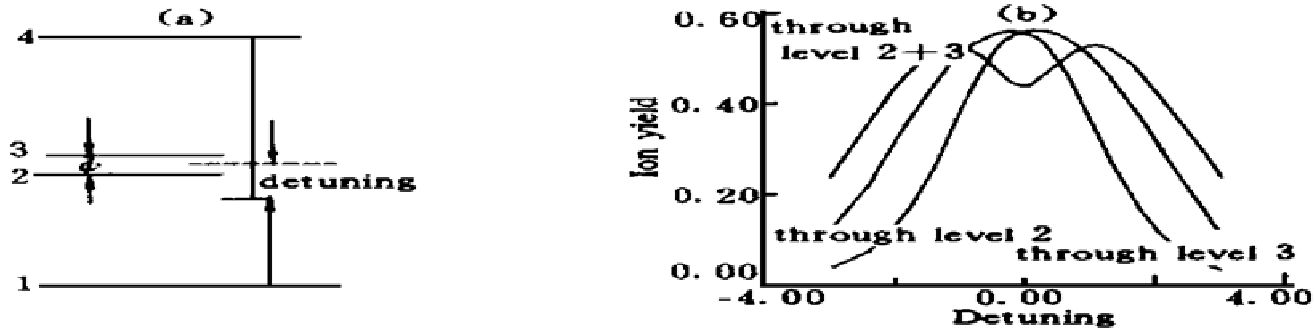

Fig. 7 (a) A simplest interfernce example from two intermediate states 2 and 3 separated each other by d. Exact two-photon resonance excitation with a detuning to the middle position of the intermediate levels. (b) Ion yield calculated by using Bloch equations. The parameters are given in the text

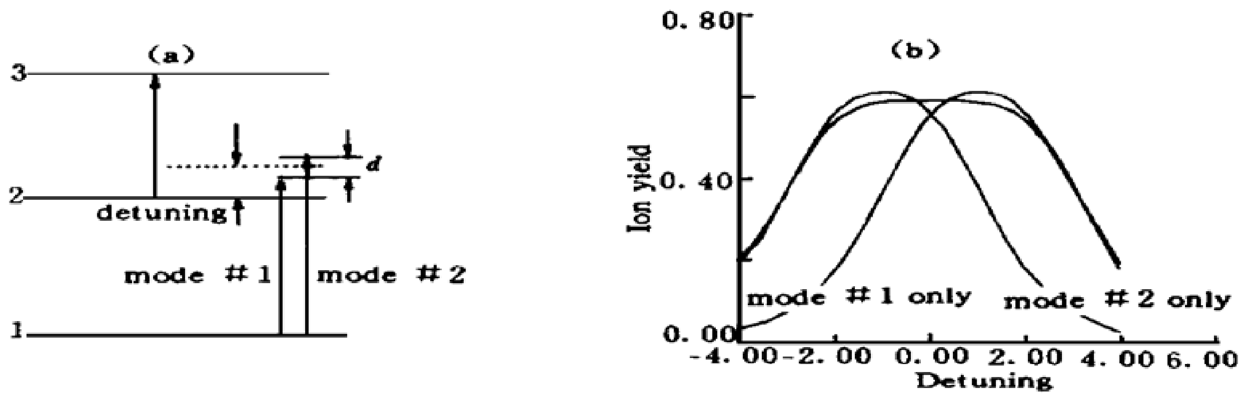

Fig. 8 (a) A simplest interference example from a two-mode laser field for the first transition. (b) Ion yield calculated by using Bloch equations. The parameters are given on the paper

It is possible to obtain proper rate equations and their rate coefficients for the interference cases mentioned above. Taking the first case as an example, we need solving the linear equations containing 5 complex variables ρ_{12}, ρ_{13}, ρ_{24}, ρ_{34}, and ρ_{14}. Substituting them into the Bloch equations containing the diagonal elements then we have 6 rate coefficients W_{12}, W_{13}, W_{23}, W_{24}, W_{34}, and W_{14}. Such a calculation is more cumbersome compared to solve Bloch equations directly, without any advantages, and will not be performed here.

7 Conclusion

Rate equations and their coefficients for two-photon process are derived for the simplest case. Rate equations are a good approximation only after a time scale which is longer than the decay constant. The rate coefficients are functions of detunings, light intensities, and material constants. For the more complicated situation, such as multi-channel ionization, Bloch equations are more convenient than rate equations.

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双光子过程中的跃迁截面

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摘 要 重新检验了双光子过程中跃迁截面的概念: 当密度矩阵中对角元随时间的变化缓慢时, 速率方程和相关的跃迁截面是很好的近似。导出速率系数的表达式: 在强光场中描述单光子过程中的系数要作很大的修改, 而描述双光子过程的系数可从单光子过程的系数导出。激光场的功率分配的最佳化随总功率的强度而激烈变化。当有多个能级或多个激光模式的干涉效应时, 利用跃迁截面的计算比直接利用布洛赫方程的计算还要复杂。

关键词 双光子过程, 速率方程, 布洛赫方程。