MULTIPHOTON EXCITATION OF ATOMS

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A general equation is derived for the probability of multiphoton excitation of atoms as a function of the incident radiation intensity. It is shown that transparency of a resonantly absorbing medium may occur which is not due to saturation of the transition but to resonance detuning induced by the radiation. The atomic parameters for two-, three-, and four-photon excitation of alkali metals and helium are evaluated by the quantum defect method.

1. INTRODUCTION

IN investigations of interactions between strong electromagnetic fields and atoms the possibility of multiphoton resonance at isolated intermediate atomic levels often plays an important role. Examples are resonant Raman scattering, harmonic generation with the possibility of resonance, multiphoton resonance in multiphoton ionization etc. It is important to understand how the probabilities of these processes depend on detuning, the widths of the resonance level and the laser line, and the radiation intensity.

When fields act upon atoms, shifts and broadening of the resonance levels can significantly affect the way in which the probability of a particular process depends on the external field intensity. This is easily seen from the following simple considerations. In the general case resonance detuning Δ is a function of both the frequency and intensity of the external field. By varying the frequency at a fixed intensity we obtain the well-known dependence of the probability of the process on the external field frequency. However, at a fixed frequency an increase of intensity is accompanied by a shift of the atomic level; this in turn changes the detuning and consequently makes the probability dependent on the field intensity. It is easily seen that

$$\Delta E(I) \sim \max(\Gamma, \Gamma_f), \tag{1}$$

is a necessary condition of this dependence; here $\Delta E(I)$ is the level shift as a function of the intensity, Γ and Γ_f are the widths of the laser line and atomic level, respectively. The possible "transparency" of the absorbing medium is thus not associated with saturation of the resonant transition but with resonance detuning induced by the field. We shall now proceed with a more detailed study of this process in the multiphoton excitation of atoms.

2. FUNDAMENTAL EQUATIONS

From general quantum mechanical considerations we obtain the following equation for the probability that an atom will be excited from level i to level f with the absorption of N quanta having the frequencies k_1, $k_2, \ldots, k_N$ and polarizations $\epsilon_{\lambda_1}, \epsilon_{\lambda_2}, \ldots, \epsilon_{\lambda_N}$[1]:

$$W_{i\to f}^{(N)} = 2\pi(2\pi\alpha)^N \sum_{\lambda} \int\ldots\int \frac{(k_1 \ldots k_{if})^3}{(2\pi)^{3N}} \eta_{\lambda}^{(N)}(k) \mathcal{G}^{(N)}(\mathbf{k}, \lambda) g(k) d^N k d^N \Omega_{\mathbf{k}},$$

where $\alpha = 1/137$,

$$\eta_{\lambda}^{(N)}(k) = \Big| \sum_{\Pi(1\ldots N)} \Big\langle f | (\mathbf{r}_1 \mathbf{e}_{\lambda_1}) G_{E_i + k_2 + \ldots + k_N}(\mathbf{r}_1, \mathbf{r}_2) \ldots \cdot G_{E_i + k_N}(\mathbf{r}_{N-1}, \mathbf{r}_N)(\mathbf{r}_N \mathbf{e}_{\lambda_N}) | i \Big\rangle \Big|^2, \tag{3}$$

$\sum$ denotes summation over all permutations of the numbers (1, 2, ...),

$$\mathcal{G}^{(N)}(\mathbf{k}, \lambda) = \mathrm{Sp}\{\rho(0) a_{\mathbf{k}_1\lambda_1}^{\pm} \ldots a_{\mathbf{k}_N\lambda_N}^{\pm} a_{\mathbf{k}_1\lambda_1} \ldots a_{\mathbf{k}_N\lambda_N}\}$$

is the N-th order correlation function of the field, $\rho(0)$ is the field density matrix at the initial moment, $a_{\mathbf{k}\lambda}^{+}$ and $a_{\mathbf{k}\lambda}$ are the creation and annihilation operators of photons in a given mode, $g(k)$ is the shape of the final atomic level (assuming that the initial level is much narrower than the final level), and G_E is the Green's function for an electron undergoing the transition (see below).

We shall need to specify the form of the correlation function $\mathcal{G}^{(N)}$. For simplicity we assume that we have independent field modes, so that the density matrix can be factored[1]:

$$\rho(0) = \prod_i \rho_{\mathbf{k}_i\lambda_i}(0), \tag{4}$$

where $\rho_{\mathbf{k}_i\lambda_i}$ is the density matrix of the i-th mode. Equation (4) applies to thermal radiation, for example.

When (4) is fulfilled the correlation function can be put into the form

$$\mathcal{G}^{(N)}(\mathbf{k}, \lambda) = \langle m(\mathbf{k}_1\lambda_1)\rangle \cdot \ldots \cdot \langle m(\mathbf{k}_N\lambda_N)\rangle,$$

where $\langle m(\mathbf{k}, \lambda)\rangle$ is the average number of photons having momentum $\mathbf{k}$ and polarization ϵ_λ.

When, furthermore, the spectral intensities are represented by

$$I_{k\lambda} = \frac{k^3}{(2\pi)^3} \int d\Omega_{\mathbf{k}} \langle m(\mathbf{k}, \lambda)\rangle, \tag{5}$$

Eq. (2) becomes

$$W_{i\to f}^{(N)} = 2\pi(2\pi\alpha)^N \sum_{\lambda} \int d^N k I_{k_1\lambda_1} \ldots I_{k_{N_\lambda}N} \eta_{\lambda}^{(N)}(k) g(k). \tag{6}$$

We shall assume hereinafter that all photons are polarized in the z direction; therefore the λ index will be omitted.

For a qualitative analysis of (6) it will be assumed

[1] Atomic units are used in the present work.

that the spectral intensities I_k and the final state g(k) have Gaussian shapes with the half-widths Γ and Γ_f:

$$I = \frac{I}{\sqrt{\pi}\Gamma}\exp\left\{-\frac{(k-k_0)^2}{\Gamma^2}\right\},$$
$$g(k) = \frac{1}{\sqrt{\pi}\Gamma_f}\exp\left\{-\frac{(\omega_{fi}^0 + \Delta E - k_1 - k_2 - \ldots - k_N)^2}{\Gamma_f^2}\right\}. \quad (7)$$

Here ω_{fi}^0 is the energy difference between the atomic levels in the absence of an external field and $\Delta E \equiv \omega_{fi} - \omega_{fi}^0$. In addition, Γ_f depends on the external field intensity.

Direct numerical calculations show that $\eta^{(N)}$ is a slowly varying function of k within the limits of Γ and Γ_f, and can therefore be taken outside the integrals. As a result we obtain

$$W_{i\to f}^{(N)} = 2\sqrt{\pi}\left(\frac{I}{I_0}\right)^N \frac{1}{\Gamma_{\text{eff}}}\exp\left\{-\frac{\Delta^2}{\Gamma_{\text{eff}}^2}\right\}\eta^{(N)}(k_0), \quad (8)$$

where

$$\Gamma_{\text{eff}} = \sqrt{\Gamma_f^2 + N\Gamma^2}, \quad \Delta \equiv \Delta^0 + \Delta E, \quad \Delta^0 = \omega_{fi}^0 - Nk_0,$$

$I_0 = 14.038 \times 10^{16}\,\text{W/cm}^2$; $\eta^{(N)}$, Δ, and Γ_{eff} are reckoned in atomic units.

From (8) we see that when (1) is not fulfilled (for example, when the radiation linewidth greatly exceeds the level shifts, or when the external field is of low intensity) we obtain the familiar intensity dependence $W_{i\to f}^{(N)} \sim I^N$. On the other hand, we can easily imagine a situation where for sufficiently large values of ΔE and $N\Gamma^2 \gg \Gamma_f^2$ the probability $W_{i\to f}^{(N)}$ becomes a decreasing function of the intensity; this can be interpreted as resonance detuning by the external field (see the numerical example below).

3. NUMERICAL RESULTS AND DISCUSSION

In the calculations of specific atomic transitions the most complex task is the computation of the atomic parameters $\eta^{(N)}(k)$, which in the general case are expressed by the sum of an (N − 1)-fold infinite series. In calculating $\eta^{(N)}(k)$ we use the Green's function for an optical electron in an atom, formulated in the approximation called the quantum defect method.[2] It is shown in[2] that the optical electron Green's function

$$G_E(\mathbf{r},\mathbf{r}') = \sum_{n=1}\frac{\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')}{E_n - E} + \int dE'\frac{\psi_{E'}^*(\mathbf{r})\psi_{E'}(\mathbf{r}')}{E' - E}$$

can be represented by

$$G_E(\mathbf{r},\mathbf{r}') = \sum_{l,m} g_l(E;r,r')Y_{lm}^*(\mathbf{r}')Y_{lm}(\mathbf{r}),$$

$$g_l(E;r,r') = -\frac{\nu}{rr'}\frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)}M_{\nu,l+\frac12}\left(\frac{2r_<}{\nu}\right)W_{\nu,l+\frac12}\left(\frac{2r_>}{\nu}\right)$$
$$-\frac{\nu}{rr'}\frac{\Gamma(l+1-\nu)}{\Gamma(l+1+\nu)}\frac{\sin\pi(\mu_l(\nu)+l)}{\sin\pi(\mu_l(\nu)+\nu)}W_{\nu,l+\frac12}\left(\frac{2r}{\nu}\right)W_{\nu,l+\frac12}\left(\frac{2r'}{\nu}\right). \quad (9)$$

Here $\nu = 1/\sqrt{-2E}$; $r_>(r_<)$ is the larger (smaller) of the two quantities r and r'; $\mu_l(\nu)$ is the quantum defect interpolated in accordance with the experiment atomic spectrum: $E_{nl} = -Z^2/2[n - \mu_l(E_{nl})]^2$; M and W are Whittaker functions.

Utilizing (9) and integrating over the angle variables in (3), we represent the expression for $\eta^{(N)}(k)$ by radial integrals of the Whittaker functions:

$$\int_{r_0}^{\infty} r_1\,dr_1\,W_{\nu_f,l_f+\frac12}\left(\frac{2r_1}{\nu_f}\right)M_{\nu_1,l_1+\frac12}\left(\frac{2r_1}{\nu_1}\right)\int_{r_1}^{\infty} r_2\,dr_2$$
$$\times W_{\nu_1 l_1+\frac12}\left(\frac{2r_2}{\nu_1}\right)M_{\nu_2,l_2+\frac12}\left(\frac{2r_2}{\nu_2}\right)\ldots\int_{r_{N-1}}^{\infty} r_N\,dr_N\,W_{\nu_{N-1},l_{N-1}+\frac12}\left(\frac{2r_N}{\nu_{N-1}}\right)$$
$$\times W_{\nu_i,l_i+\frac12}\left(\frac{2r_N}{\nu_i}\right). \quad (10)$$

The lower integration limit r_0 removes the unphysical divergence of the W functions at r = 0 and can be set equal to the radius of the atomic residue. Since each inner integral in (10) has a single variable limit, integration with a constant interval makes (10) actually equivalent to a simple integral. This fact greatly reduces the calculating time, which also becomes somewhat dependent on the number of photons participating in the transition. The Whittaker functions are easily calculated by means of expansions into convergent power series.[3]

Table I. The parameter $\eta^{(2)}(k_1, k_2)$ for two-photon excitation $2^1S \to 6^1S$ in a He atom

k_1/ω_{fi}^0	$\eta^{(2)}(k_1,k_2)$ 10^2 at. units	k_1/ω_{fi}^0	$\eta^{(2)}(k_1,k_2)$ 10^2 at. units	k_1/ω_{fi}^0	$\eta^{(2)}(k_1,k_2)$ 10^2 at. units
0.15	7.381	0.275	0.2823	0.4	0.07253
0.175	0.3740	0.3	—	0.425	0.04600
0.2	0.05740	0.325	5.093	0.475	0.003246
0.225	0.003484	0.35	0.4282	0.475	0.002731
0.25	0.05186	0.375	0.1501	0.5	0.002522

Table II. The parameter $\eta^{(2)}(k_1, k_2)$ for two-photon excition 6s → 9d in a Cs atom

k_1/ω_{fi}^0	$\eta^{(2)}(k_1,k_2)$ 10^5 at. units	k_1/ω_{fi}^0	$\eta^{(2)}(k_1,k_2)$ 10^5 at. units	k_1/ω_{fi}^0	$\eta^{(2)}(k_1,k_2)$ 10^5 at. units
0.1	39.11	0.275	0.6412	0.4	1.653
0.125	355.55	0.3	0.05298	0.425	1.308
0.15	10097.6	0.325	9.813	0.45	1.152
0.175	35.55	0.35	6.613	0.475	1.056
0.2	8.142	0.375	2.471	0.5	1.038
0.225	3.360				
0.25	1.582				

Table III

$\mathcal{E}$, 10^6 V/cm	0.8	0.9	1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8
ΔE, cm^{-1}	1.50	1.90	2.34	2.83	3.37	3.95	4.59	5.27	5.99	6.76	7.58
K	2.84	2.74	2.60	2.40	2.16	1.84	1.44	0.94	0.34	−0.38	−1.26

We computed the $\eta^{(N)}$ parameters for transitions that are observable at available laser frequencies. These were the two-photon excitations $2'S \to 6'S$ in He and $6s \to 9d$ in Cs at the ruby laser frequency $\omega = 14\,402\ cm^{-1}$:

$$\eta^{(2)}_{He} = 4.66 \cdot 10^3 \text{ at. units}, \quad \eta^{(2)}_{Cs} = 1.034 \cdot 10^5 \text{ at. units},$$

the three-photon excitations $4s \to 4f$ in K and $6s \to 6f$ in Cs at the neodymium laser frequency $\omega = 9433\ cm^{-1}$:

$$\eta^{(3)}_{K} = 1.76 \cdot 10^{12} \text{ at. units}, \quad \eta^{(3)}_{Cs} = 1.535 \cdot 10^{11} \text{ at. units},$$

and the four-photon excitation $3s \to 7s$ in Na at the neodymium laser frequency:

$$\eta^{(4)}_{Na} = 7.4 \cdot 10^{15} \text{ at. units}.$$

It is of interest that from the standpoint of the hydrogen-like model the result $\eta^{(3)}_{Cs} < \eta^{(3)}_{K}$ is unexpected and indicates that the real atomic structure plays an important role in multiphoton excitation.

In connection with the development of two-photon spectroscopy it is of interest to calculate $\eta^{(2)}$ for different frequencies of the absorbed photons. Tables I and II give values of $\eta^{(2)}(k_1, k_2)$ for He and Cs depending on the frequency of one of the photons. The energy unit is here the energy of the transition between the given levels: $E_f - E_i = \omega^0_{fi}$.

We shall now consider how the shifting of atomic levels in an external field affects multiphoton absorption in the case of three-photon excitation of the 4f level in K. The characteristic resonance pattern for this transition was observed in[4], where four-photon ionization of potassium was investigated with a tunable laser. It was found that the probability of four-photon ionization obeys the I^4 law only when the three-photon resonance is considerably detuned; when the detuning is diminished the probability becomes proportional to I^K with $K < 4$.

We calculate the possible values of K on the basis of (8) and the assumption that the atomic level shift is determined by the quadratic Stark effect. For the dynamic polarizability of the 4s and 4f levels of potassium at the ruby laser frequency, calculated by the procedure described in[5], we have $\alpha_{4S} = 640$ at. units and $\alpha_{4f} = (-490 + 55i)$ at. units. We then obtain

$$K(I) = \ln\left(\frac{W(I+\delta I)}{W(I)}\right) \Big/ \ln\left(\frac{I+\delta I}{I}\right).$$

In the case of zero detuning ($\omega^0_{fl} = Nk_0$) we obtain

$$K(I) = N - 2\left(\frac{\Delta E}{\Gamma_{eff}}\right)^2\left(1 - \frac{\Gamma_f^2}{\Gamma_{eff}^2}\right) - \frac{\Gamma_f^2}{\Gamma_{eff}^2}.$$

Here we assume that Γ_i is determined by ionization broadening; this corresponds to the experimental conditions in[4]. Assuming $\Gamma = 3\ cm$[4] for the laser width, we obtain the values of K(I) given in Table III.

Our results show that atomic level shifts induced by an external field can strongly change the dependence of multiphoton excitation probability on the field intensity. Specifically, Table III shows that in sufficiently high fields K(I) becomes negative, i.e., the excitation probability falls off with increasing intensity (the medium becomes transparent). As already mentioned in our Introduction, this behavior of W(I) results from the detuning of three-photon resonance induced by a strong Stark shift, i.e., the Stark shift displaces the atomic line into a wing of the laser emission line. The behavior of the curve in the region where the laser and atomic lines overlap slightly depends on the line shapes; it is clear, however, that W(I) remains qualitatively unchanged.

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