# Two–photon absorption

I. Pérez-Arjona, G.J. de Valcárcel, and Eugenio Roldán
*Departament d'Òptica, Universitat de València*
*Dr. Moliner 50, 46100–Burjassot, Spain*

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Two–photon absorption is theoretically analyzed within the semiclassical formalism of radiation–matter interaction. We consider an ensemble of inhomogeneously broadened three–level atoms subjected to the action of two counterpropagating fields of the same frequency. By concentrating in the limit of large detuning in one–photon transitions, we solve perturbatively the Bloch equations in a non-usual way. In this way we derive an analytical expression for the width of the two–photon resonance that makes evident sub-Doppler two–photon spectroscopy. We also derive an analytical expression for the Stark shift of the two–photon resonance.

*Keywords:* Spectroscopy; quantum optics; two–photon precesses.

Se analiza teóricamente la absorción de dos fotones dentro del formalismo semiclásico de la interacción entre la radiación y la materia. Consideramos un conjunto, con ensanchamiento inhomogéneo, de átomos de tres niveles sometido a la acción de dos campos contrapropagantes de igual frequencia. Resolvemos perturbativamente las ecuaciones de Bloch del sistema de una forma no usual concentrándonos en el límite de alta desintonía de las transiciones a un fotón. De esta forma obtenemos una expresión analítica para la anchura de la resonancia a dos fotones en la que se pone de manifiesto la posibilidad de espectroscopía sub–Doppler a dos fotones. También obtenemos una expresión analítica para el desplazamiento Stark de la resonancia a dos fotones.

*Descriptores:* Espectroscopia; óptic cuántica; precesos a dos fotones

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## 1. Introduction

Two–photon absorption (TPA) is one of the most basic radiation–matter interaction mechanisms. It consists in the excitation of an atom or molecule from a lower quantum state $|1\rangle$ to an excited state $|2\rangle$ of the same parity as $|1\rangle$ in a single step. In this case the initial and final states cannot be connected through an electric-dipole transition. Thus parity conservation implies that two light quanta must be absorbed simultaneously. The theory of TPA was first developed by Maria Göppert–Mayer in 1931 in her Ph.D. Thesis [1].

As a multiphoton process, TPA is closely related to Raman scattering. In the latter process, one photon is absorbed while the other is simultaneously emitted, the energy difference being retained by the molecule. While spontaneous Raman scattering was observed as early as 1928 [2], TPA was not observed until 1961 [3] after the advent of the laser (in fact TPA is one of the first nonlinear optical phenomena demonstrated with the aid of laser radiation). The reason for that delay in the observation of the two multiphoton processes lies in the fact that while in spontaneous Raman scattering the scattered light intensity is proportional to the intensity of the incoming radiation, in TPA the power absorbed is proportional to the square of the intensity of the incoming field and thus higher excitation energy is required for TPA.

TPA is a very important tool in laser spectroscopy as it makes possible the transition between two states that cannot be connected by electric–dipole interaction. Of course these transitions can also be investigated by making use of resonant one–photon processes through an intermediate level, but in this case the measured linewidth of the process is increased by the linewidths of the two successive one–photon absorptions. TPA also allows the coherent excitation of molecules to states whose energies fall in the far ultraviolet, by making use of visible radiation, for which coherent sources are easily available.

One of the most outstanding features of TPA is that it allows sub–Doppler precision measurements [Raman scattering also allows the investigation of transitions in which the initial and final states are of the same parity. With respect to Doppler compensation, in Raman scattering it is only partial and the degree of compensation depends on the energy difference between the initial and final molecular states]. This last fact was first analyzed by Vasilenko *et al.* [4] in 1970 and observed in 1974 [5, 6]. Doppler broadening comes from the fact that atoms moving with different velocities "see" the field with different frequencies because of the Doppler effect. This is a source of inhomogeneity that increases the measured absorption linewidth. In one–photon transitions this limitation cannot be easily overcome unless subtle phenomena such as the Lamb-dip produced by spectral hole burning are exploited. In TPA, however, there is a simple way of (almost) getting rid of Doppler broadening. This occurs when the two photons inducing the transition come from two counterpropagating beams of equal frequency. In this case all atoms are in resonance with the two–photon process since the Doppler frequency shifts of the two photons "seen" by the atom are opposite among them, independent of the atom's velocity. Hence the sum of the energies of the two photons, as "seen" by any atom, is twice the energy of a single photon in the laboratory frame, and the inhomogeneity almost disappears.

In quantum optics textbooks, TPA is often introduced after field quantization [7]. Nevertheless TPA does not need the existence of photons to be understood and some textbooks analyze the phenomenon from a semiclassical point of view [8] that is, by treating matter quantum–mechanically and radiation classically (in this semiclassical approach one must understand that the word photon refers to the amount of energy absorbed by the atom, not to any quantum already existent in the free electromagnetic field). There are several ways of studying TPA in this semiclassical approach: derivation of nonlinear susceptibilities, application of standard perturbation theory, even derivation of exact analytical results. Nevertheless to our knowledge no standard textbook derives the main characteristics of TPA (such as Doppler compensation and the Stark shift of the resonance) within the semiclassical frame. In this article we give a compact and clear presentation of TPA from a semiclassical point of view, by solving perturbatively the equations of motion for the density matrix elements.

## 2. Semiclassical density matrix equations

Let us consider a classical monochromatic electromagnetic field of the form

$$\mathbf{E}(z,t) = \mathbf{e}\left[E_1 \cos(\omega t + kz) - E_2 \cos(\omega t - kz)\right], \quad (1)$$

where $\mathbf{e}$ is the unit polarization vector (linear polarization is considered) and $E_1$ and $E_2$ are the constant real amplitudes of two counterpropagating plane waves of angular frequency $\omega$ and wavenumber $k$, which travel along the $z$ axis. Note that this form of writing the total field is completely general for the superposition of two counterpropagating monochromatic linearly polarized waves of equal polarization, since any dephasing between them can be removed by suitable choice of time and space origins. This field represents a standing wave when $E_1 = E_2$ and a traveling wave if either $E_1$ or $E_2$ is taken to be zero.

This classical field interacts with a medium composed of three–level atoms (Fig. 1): levels $|1\rangle$ and $|2\rangle$ of the same parity, and contrary to that of the intermediate level $|0\rangle$. This is the simplest level scheme that allows the description of TPA in terms of the usual electric–dipole Hamiltonian. In this way, the transition $|1\rangle \longleftrightarrow |2\rangle$ is produced via the virtual transitions $|1\rangle \longleftrightarrow |0\rangle$ and $|0\rangle \longleftrightarrow |2\rangle$ (state $|0\rangle$ is kept far from resonance). The existence of an intermediate level enhances the excitation probability between states $|1\rangle$ and $|2\rangle$ as will be shown.

The unperturbed hamiltonian $\widehat{H}_0$ of the three–level atoms is given by (see level diagram in Fig.1)

$$\widehat{H}_0 = \hbar\left(\omega_{20}|2\rangle\langle 2| - \omega_{01}|1\rangle\langle 1|\right), \quad (2)$$

and the origin of energies has been taken at the intermediate state $|0\rangle$. Since levels $|2\rangle$ and $|1\rangle$ have the same parity, and contrary to that of state $|0\rangle$, the allowed electric–dipole

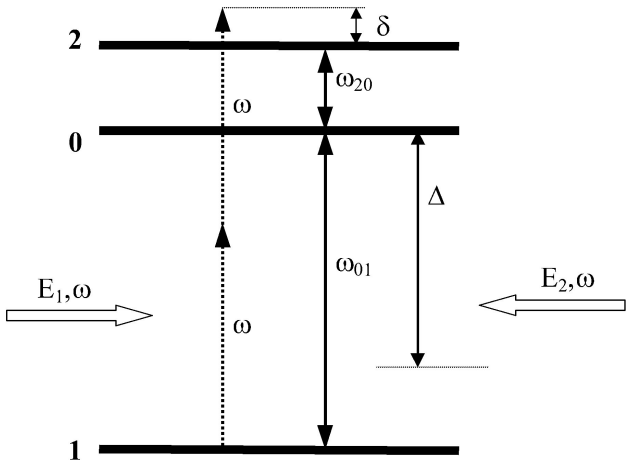


FIGURE 1. Energy level diagram of the three–level atoms considered in the model. See text.

transitions are $|1\rangle \longleftrightarrow |0\rangle$ and $|0\rangle \longleftrightarrow |2\rangle$. Thus the dipole–moment operator is written as

$$\widehat{\boldsymbol{\mu}} = \boldsymbol{\mu}_{20}|2\rangle\langle 0| + \boldsymbol{\mu}_{02}|0\rangle\langle 2| + \boldsymbol{\mu}_{10}|1\rangle\langle 0| + \boldsymbol{\mu}_{01}|0\rangle\langle 1|, \quad (3)$$

where $\boldsymbol{\mu}_{ij} = \langle i|\widehat{\boldsymbol{\mu}}|j\rangle$, that can be taken to be real without loss of generality through proper choice of the basis states phases ($\boldsymbol{\mu}_{ij} = \boldsymbol{\mu}_{ji}$). The interaction hamiltonian of an atom located at $z$ reads $\widehat{H}_1(z,t) = -\widehat{\boldsymbol{\mu}} \cdot \mathbf{E}(z,t)$ and the total hamiltonian that governs the coherent evolution of the atoms is then $\widehat{H}_S = \widehat{H}_0 + \widehat{H}_1$, where the subscript $S$ is used to denote the Schrödinger picture implicitly adopted. Before solving the Schrödinger equation, it is convenient to remove fast oscillations at optical frequencies appearing in the hamiltonian. This is accomplished by transforming from the Schrödinger picture to the field–interaction picture. The appropriate unitary operator for making such transformation is

$$\widehat{U}(t) = e^{i\omega t}|2\rangle\langle 2| + |0\rangle\langle 0| + e^{-i\omega t}|1\rangle\langle 1|. \quad (4)$$

Note that this operator is similar to that defining the Dirac picture but, instead of removing the fast free atomic evolution (which would be accomplished with the operator $\widehat{U}_D(t) = e^{i\omega_{20}t}|2\rangle\langle 2| + |0\rangle\langle 0| + e^{-i\omega_{01}t}|1\rangle\langle 1|$), we remove the fast dynamics originating from the optical frequency of the field. In the new picture, the state vector $|\psi\rangle$ of the system $\left(|\psi\rangle = \widehat{U}\ |\psi_S\rangle\right)$ obeys the following Schrödinger equation:

$$i\hbar\frac{d}{dt}|\psi\rangle = \widehat{H}\ |\psi\rangle,$$

where the hamiltonian $\widehat{H}$ in the new picture is calculated [10] through

$$\widehat{H} = \widehat{U}\,\widehat{H}_S\widehat{U}^{-1} + i\hbar\frac{\partial\widehat{U}}{\partial t}\widehat{U}^{-1}. \quad (5)$$

After performing the rotating wave approximation [7, 8] (that consists in removing fast oscillating terms) the hamil-

tonian reads

$$\widehat{H}(z) = \hbar\left(-\delta_2 |2\rangle\langle 2| + \delta_1 |1\rangle\langle 1| - \mu E |2\rangle\langle 0| - E |0\rangle\langle 1| + h.c.\right), \quad (6)$$

where

$$E = \phi_1 e^{ikz} - \phi_2 e^{-ikz}, \quad (7)$$

$$\phi_{1(2)} = \frac{\boldsymbol{\mu}_{10}\cdot\mathbf{e}}{2\hbar} E_{1(2)}, \qquad \mu = \frac{\boldsymbol{\mu}_{20}\cdot\mathbf{e}}{\boldsymbol{\mu}_{10}\cdot\mathbf{e}}, \quad (8)$$

$$\delta_{1(2)} = \omega - \omega_{01(20)}, \quad (9)$$

and $h.c.$ stands for hermitian–conjugate [Under a unitary transformation, any operator $\widehat{O}_S$ (in the Schrödinger picture) transforms according to the rule $\widehat{O} = \widehat{U}\widehat{O}_S\widehat{U}^{-1}$. Notice that $\widehat{H}$ is not transformed in the same way]. Note that the new picture, in combination with the rotating wave approximation, yields a hamiltonian independent of time. $E$ ($\mu E$) is half the complex Rabi frequency of the field associated with the lower (upper) transition of an atom located at position $z$.

Now we determine the evolution equation of the density matrix (more properly: the population matrix, see below). We choose to work with the density matrix instead of the state vector since in this way relaxation and pumping processes can be (phenomenologically) incorporated into the model in a simple way. As we are considering not a single molecule but a large number of molecules which are moving at different velocities, an ensemble average must be performed. The ensemble averaged density matrix is usually called population matrix [11]. This ensemble must be defined for each velocity and, since the interaction depends on space, the population matrix must also be defined as a function of the position $z$:

$$\widehat{\rho}(v;z,t) = \mathcal{N}(v)^{-1}\sum_a \widehat{\rho}_a(v;z,t). \quad (10)$$

Here $\widehat{\rho}$ is the population matrix, $\widehat{\rho}_a$ is the density matrix for an atom labeled by $a$, and $a$ runs along all molecules with velocity $v$ that, at time $t$, are within $z$ and $z+dz$ . $\mathcal{N}(v)$ is the number of such molecules, which is assumed to be independent of $z$ and $t$ (homogeneity and stationarity of the velocity distribution is assumed). The equation of evolution of the population matrix is formally like the Schrödinger–von Neumann equation governing the evolution of the density matrix of a single atom, plus an additional term [11]:

$$(\partial_t + v\partial_z)\rho_{ij} = (i\hbar)^{-1}\left[\widehat{H},\widehat{\rho}\right]_{ij} + \left(\hat{\Gamma}\widehat{\rho}\right)_{ij}, \quad (11)$$

$(i,j=0,1,2)$. $\hat{\Gamma}\widehat{\rho}$ describes irreversible processes (relaxations and pumping) and $\hat{\Gamma}$ is a generalized Liouvillian. In this article we shall consider the simple expression

$$\left(\hat{\Gamma}\widehat{\rho}\right)_{ij} = -\gamma\rho_{ij} + \gamma\,\delta_{i,1}\delta_{j,1}, \quad (12)$$

with $\delta$ the Kronecker delta. The first contribution describes relaxations in a situation in which all density matrix elements decay with the same constant $\gamma$ (absence of dephasing collisions [11]). The second contribution (pump) guarantees that the ground state $|1\rangle$ is asymptotically filled in the absence of interaction. With this choice for $\hat{\Gamma}\widehat{\rho}$, $Tr(\hat{\rho}) = 1$ always. We adopt this simple limit because the expressions are much clearer and the details of the relaxation processes do not modify the essential physics of TPA.

By substituting Eqs.(6) and (12) into Eq.(11), the final equations of evolution of the population matrix elements run

$$(\partial_t + v\partial_z)\rho_{22} = -\gamma\rho_{22} + i\mu\left(E\rho_{02} - E^*\rho_{20}\right), \quad (13)$$

$$(\partial_t + v\partial_z)\rho_{00} = -\gamma\rho_{00} + i\left(E\rho_{10} - E^*\rho_{01}\right) - i\mu\left(E\rho_{02} - E^*\rho_{20}\right), \quad (14)$$

$$(\partial_t + v\partial_z)\rho_{11} = \gamma(1-\rho_{11}) + i\left(E^*\rho_{01} - E\rho_{10}\right), \quad (15)$$

$$(\partial_t + v\partial_z)\rho_{21} = -(\gamma - i\delta)\rho_{21} + iE\left(\mu\rho_{01} - \rho_{20}\right), \quad (16)$$

$$(\partial_t + v\partial_z)\rho_{20} = -\left(\gamma - i\frac{\delta-\Delta}{2}\right)\rho_{20} + i\mu E\left(\rho_{00} - \rho_{22}\right) - iE^*\rho_{21}, \quad (17)$$

$$(\partial_t + v\partial_z)\rho_{01} = -\left(\gamma - i\frac{\delta+\Delta}{2}\right)\rho_{01} + iE\left(\rho_{11} - \rho_{00}\right) + i\mu E^*\rho_{21}, \quad (18)$$

where

$$\delta = \delta_1 + \delta_2 = 2\omega - \omega_{21}, \quad (19)$$

$$\Delta = \delta_1 - \delta_2 = \omega_{20} - \omega_{01}, \quad (20)$$

have the meaning of two–photon detuning and intermediate level detuning, respectively (see Fig.1). The above equations should be complemented with the evolution equation of the electromagnetic field. Nevertheless we shall consider $E$ as a parameter. This corresponds to a physical situation in which the gas of molecules is confined within a small region of the space which is large compared with the radiation wavelength but small enough for neglecting field depletion (thin film approximation).

Note that $\Delta$ is a structural parameter of the atoms, and we shall consider only the case in which $\Delta$ is a very large quantity as compared with the rest of frequencies $(\gamma,\delta,E)$ appearing in the problem. This limit guarantees that one–photon processes (*i.e.* the electric–dipole transitions $|1\rangle \longleftrightarrow |0\rangle$ and $|0\rangle \longleftrightarrow |2\rangle$) are severely punished since the one-photon detunings $\delta_1\,(\approx\Delta)$ and $\delta_2\,(\approx -\Delta)$ are much larger than the widths of the one-photon resonances. For example, consider the states $|2\rangle = 8S_{1/2}$, $|0\rangle = 7P$ and $|1\rangle = 6S_{1/2}$ of Cs. In this case [12] $\omega_{01} = 4.098\cdot 10^{18}s^{-1}$ and $\omega_{20} = 0.489\cdot 10^{18}s^{-1}$ and thus $\Delta = -3.609\cdot 10^{18}s^{-1}$. Cs is a gas and the one–photon transitions width can be estimated to be given by their Doppler width which, at room temperature are (see Sec. 4) $2.6\cdot 10^8 s^{-1}$ and $2.21\cdot 10^9 s^{-1}$ for the upper and lower transitions, respectively: in this case

there are nine orders of magnitude between $\Delta$ and the width of the one–photon resonances.

Equations (13)-(18) do not admit a simple analytical solution in the general case but can be solved perturbatively in the case of very large $\Delta$. This is done in the next section.

## 3. Perturbative solution of the steady state

In this section we solve perturbatively the equations of evolution of the density matrix in steady state ($\partial_t \to 0$). Note that this is the state asymptotically reached by the system due to the presence of relaxations. Here we present the main results and leave the details to Appendix A. As commented, we shall consider the limit $\Delta \gg \gamma, \delta, E$. We also consider that the inhomogeneous width $\gamma_v$ (see Sec. 4) is small as compared with $\Delta$, that is, we assume that $\Delta \gg kv$ with $k$ the field wavenumber. This can be made formally explicit by writing $\Delta = \varepsilon^{-1}\Delta_1$ with $\Delta_1$ a quantity of the same order of magnitude as the rest of the frequencies present in the problem and $0 < \varepsilon \ll 1$ (smallness parameter). We also make a series expansion of the density matrix elements of the form

$$\rho_{ij}(z) = \sum_{n=0}^{\infty} \varepsilon^n \rho_{ij}^{(n)}(z). \tag{21}$$

Substituting this expansion in the population matrix equations and identifying terms of equal powers in $\varepsilon$, one gets

$$0 = (v\partial_z + \gamma)\,\rho_{22}^{(n)} + -i\mu\left(E\rho_{02}^{(n)} - E^*\rho_{20}^{(n)}\right), \tag{22}$$

$$0 = (v\partial_z + \gamma)\,\rho_{00}^{(n)} - i\left(E\rho_{10}^{(n)} - E^*\rho_{01}^{(n)}\right) + i\mu\left(E\rho_{02}^{(n)} - E^*\rho_{20}^{(n)}\right), \tag{23}$$

$$0 = -\gamma + (v\partial_z + \gamma)\,\rho_{11}^{(n)} + i\left(E\rho_{02}^{(n)} - E^*\rho_{20}^{(n)}\right), \tag{24}$$

$$0 = (v\partial_z + \gamma - i\delta)\,\rho_{21}^{(n)} - iE\left(\mu\rho_{01}^{(n)} - \rho_{20}^{(n)}\right), \tag{25}$$

$$-i\tfrac{1}{2}\Delta_1\rho_{20}^{(n+1)} = \left(v\partial_z + \gamma - i\tfrac{1}{2}\delta\right)\rho_{20}^{(n)} - i\mu E\left(\rho_{00}^{(n)} - \rho_{22}^{(n)}\right) + iE^*\rho_{21}^{(n)}, \tag{26}$$

$$i\tfrac{1}{2}\Delta_1\rho_{01}^{(n+1)} = \left(v\partial_z + \gamma - i\tfrac{1}{2}\delta\right)\rho_{01}^{(n)} - iE\left(\rho_{11}^{(n)} - \rho_{00}^{(n)}\right) - i\mu E^*\rho_{21}^{(n)}, \tag{27}$$

where $n$ runs from $-1$ to $\infty$. Note that these equations refer to an ensemble of atoms moving with velocity $v$ located at $z$. These equations can be solved at each order $n$ of $\varepsilon$. We can integrate the first four equations to obtain the populations $\rho_{ii}^{(n)}$ and the two–photon coherence $\rho_{21}^{(n)}$ if we know the value of the one photon coherences at this order ($\rho_{01}^{(n)}$ and $\rho_{20}^{(n)}$). These quantities are obtained from the two last equations. Note that the form of these last two equations (which relate two consecutive orders) allow the values of the one-photon coherences at a given order $n+1$ to be algebraically determined in terms of the previous order $n$. In particular, for $n = -1$ we obtain $\rho_{01}^{(0)} = \rho_{20}^{(0)} = 0$, since $\rho_{ij}^{(-1)} = 0$. These values allow to solve, from the first four equations, for the rest of matrix elements at order $n = 0$. Next, $\rho_{01}^{(1)}$ and $\rho_{20}^{(1)}$ are determined from the last two equations and so on. There is just a single point that deserves some explanation and concerns the integration in $z$ of the first four equations. Notice that although we do not know any boundary conditions (in terms of $z$) for the variables, we can make use of the knowledge that, when the field is off ($E = 0$), all variables must vanish at any order but $\rho_{11}^{(0)}$, which must be equal to unity since $Tr(\hat{\rho}) = 1$. In Appendix A the equations are solved systematically. In the following we make use of the result of the integration.

## 4. Velocity and space averages

We must concentrate on the calculation of a quantity directly related with measurement. We shall consider the fluorescence intensity from the system, which is directly proportional to the amount of population excited to the upper level. The fluorescence signal collected by a detector will come from all atoms (all velocities) existing within a finite region (of length $L$) of the system. Thus it is necessary to perform both spatial and velocity averages. The spatial average reads

$$\left\langle \rho_{22}^{(n)}(v) \right\rangle_z = \frac{1}{L}\int_0^L dz\, \rho_{22}^{(n)}(v,z), \tag{28}$$

where we shall take, as already commented, $L \gg \lambda$ (with $\lambda$ the light wavelength) since typically the detector will collect the fluorescence from a "macroscopic" region of the system. It is evident that only the spatial dc component of $\rho_{22}^{(n)}(v,z)$ will contribute to the spatial average (28) since $L \gg \lambda$, as stated. Consequently it will suffice to calculate only those terms.

With respect to the velocity average a few words are in order. In a gas, inhomogeneous broadening is due to the Doppler effect which is different for each atomic velocity. The atomic velocities of a gas obey the Maxwell–Boltzmann distribution

$$\mathcal{G}(v) = \frac{1}{u\sqrt{\pi}}\exp\left[-\left(\frac{v}{u}\right)^2\right] = \frac{2k}{\gamma_v}\sqrt{\frac{\ln 2}{\pi}}\exp\left[-\left(\frac{2kv}{\gamma_v/\sqrt{\ln 2}}\right)^2\right], \tag{29}$$

with $u$ the most probable velocity given by $u = \sqrt{2k_BT/m}$ ($k_B$ is Boltzmann's constant, $T$ is the absolute temperature,

and $m$ is the molecular mass). $\gamma_v = 2\sqrt{\ln 2}ku$ is the inhomogeneous HWHM (half–width at half maximum) in terms of the frequency $\Omega = 2kv$ (the factor 2 is added for later convenience, since in TPA it is not the radiation frequency -or its wavenumber- that is the important parameter but twice its value). The problem with the Gaussian distribution is that some integrals appearing in the final expressions cannot be evaluated analytically. In order to obtain analytic expressions as simple as possible, we shall consider a Lorentzian distribution for the atomic velocities

$$\mathcal{L}(v) = \frac{1}{\pi}\frac{u}{u^2+v^2} = \frac{2k}{\pi}\frac{\gamma_v}{\gamma_v^2+(2kv)^2}, \qquad (30)$$

where $\gamma_v = 2ku$ is the inhomogeneous HWHM (half–width at half maximum) in terms of the frequency $\Omega = 2kv$. The results obtained with this distribution will differ quantitatively but not qualitatively from the Gaussian distribution, as will be shown.

The averaged population of the excited level is then calculated through

$$\left\langle \rho_{22}^{(n)} \right\rangle = \int_{-\infty}^{+\infty} dv \left\langle \rho_{ij}^{(n)}(v) \right\rangle_z \mathcal{L}(v). \qquad (31)$$

Clearly the averaging order is unimportant. We could first perform the velocity average and then the spatial average, obtaining the same result. From the computational viewpoint however it is more convenient to perform first the spatial average since in this way the ac-components (in terms of $z$) of $\rho_{22}^{(n)}$ are removed from the calculations from the beginning.

From Eqs.(84) and (86) of Appendix B, the fully averaged population of the upper level reads, up to order $\varepsilon^3$,

$$\langle \rho_{22} \rangle = \varepsilon^2 \left\langle \rho_{22}^{(2)} \right\rangle + \varepsilon^3 \left\langle \rho_{22}^{(3)} \right\rangle \equiv N_2 + N_3$$

where

$$N_2 = 8\mu^2 \left(\frac{\phi^2}{\gamma\Delta}\right)^2 \left[\frac{(1+\tilde{\gamma}_v)(1+A^4)}{(1+\tilde{\gamma}_v)^2+\tilde{\delta}^2} + \frac{4A^2}{1+\tilde{\delta}^2}\right], \qquad (32)$$

and

$$N_3 = 16\mu^2\left(\mu^2-1\right)\left(1+A^2\right)\tilde{\delta}\left(\frac{\phi^2}{\gamma\Delta}\right)^3 (\mathcal{B}_1+\mathcal{B}_2), \qquad (33)$$

$$\mathcal{B}_1 = A^2\left[\frac{2}{\left(1+\tilde{\delta}^2\right)^2} + \frac{1}{\tilde{\gamma}_v}\left(\frac{1}{1+\tilde{\delta}^2} - \frac{1}{(1+\tilde{\gamma}_v)^2+\tilde{\delta}^2}\right)\right],$$

$$\mathcal{B}_2 = 2\left(1+A^4\right)\frac{(1+\tilde{\gamma}_v)}{\left[(1+\tilde{\gamma}_v)^2+\tilde{\delta}^2\right]^2}.$$

In writing Eqs.(32) and (33) we have introduced the notation

$$\phi_1 \equiv \phi, \qquad \phi_2 \equiv A\phi, \qquad (34)$$

and the normalized frequencies

$$\tilde{\gamma}_v \equiv \frac{\gamma_v}{\gamma}, \qquad \tilde{\delta} \equiv \frac{\delta}{\gamma}. \qquad (35)$$

Note that $\varepsilon^n$ combines with $\Delta_1^{-n}$ in both orders $n = 2$ and $n = 3$ to yield $\Delta^{-n}$, leading to a final expression independent of $\varepsilon$. Next we analyze these expressions.

## 5. Analysis of the results

### 5.1. Strength and width of the resonance

In order to analyze the strength and width of the resonance it suffices to consider the dominant term $N_2$. General results are: (i) TPA is proportional to the squared field intensity $\left(\phi^2\right)^2$, (ii) The existence of an intermediate level with a finite detuning $\Delta$ enhances the probability of the process (the smaller $\Delta$ the larger amount of excited population), and (iii) The maximum transfer of population is produced at $\tilde{\delta} = 0$ (this result will be corrected at the next order; see next subsection). Let us consider some special cases.

In the case of homogeneous broadening ($\tilde{\gamma}_v = 0$),

$$N_2^{\rm hom} = 8\mu^2\left(\frac{\phi^2}{\gamma\Delta}\right)^2 \frac{A^4+4A^2+1}{1+\tilde{\delta}^2}. \qquad (36)$$

Note that $N_2^{\rm hom}$ is proportional to $(A^4+4A^2+1)$, which in its turn is proportional to the mean value of the squared field intensity -a signature of two–photon absorption. This factor is six times larger for standing waves than for traveling waves. Note that this (important) numerical factor is the single difference between standing and traveling wave configurations in this homogeneous broadening limit. We conclude that, from an experimental point of view, it is most convenient to illuminate the cell with a traveling wave and make it reflect on a mirror located after the cell in order to produce a standing wave. This represents no extra energetic cost and the fluorescence signal collected in this way is 6 times larger than without the mirror.

With a non-null inhomogeneous broadening two limits of interest are: a) excitation with a traveling wave ($A = 0$)

$$N_2^{TW} = 8\mu^2\left(\frac{\phi^2}{\gamma\Delta}\right)^2 \frac{(1+\tilde{\gamma}_v)}{(1+\tilde{\gamma}_v)^2+\tilde{\delta}^2}, \qquad (37)$$

and b) excitation with a standing wave ($A = 1$)

$$N_2^{SW} = 8\mu^2\left(\frac{\phi^2}{\gamma\Delta}\right)^2 \left[\frac{4}{\left(1+\tilde{\delta}^2\right)} + \frac{2(1+\tilde{\gamma}_v)}{(1+\tilde{\gamma}_v)^2+\tilde{\delta}^2}\right]. \qquad (38)$$

Note that the effect of the inhomogeneous broadening is dramatically different for traveling wave or for standing wave cases: if $\tilde{\gamma}_v \gg 1$ (*i.e.* $\gamma_v \gg \gamma$, inhomogeneous limit) $N_2^{TW} \to 0$, whereas in the same limit $N_2^{SW} \to (2/3)N_2^{\rm hom,SW}$, where $N_2^{\rm hom,SW}$ is obtained from $N_2^{\rm hom}$ by putting $A = 1$.

In order to make clearer comparisons among different cases we next analyze the maximum of $N_2$ (that occurs at $\tilde{\delta}=0$ as stated) and its width in terms of $\tilde{\delta}$.

The maximum of $N_2$ reads

$$N_2^{\max}=8\mu^2\left(\frac{\phi^2}{\gamma\Delta}\right)^2\left[\frac{(A^4+4A^2+1)+4\tilde{\gamma}_v A^2}{(1+\tilde{\gamma}_v)}\right]. \quad (39)$$

In Fig. 2, $N_2^{\max}$ (normalized to its maximum value, for $A=1$ and $\tilde{\gamma}_v=0$) is plotted as a function of the inhomogeneous-to-homogeneous widths ratio $\tilde{\gamma}_v$ for different values of $A$. Clearly, for $A=1$ (standing wave) TPA is almost insensitive to the amount of inhomogeneous broadening, whereas for $A=0$ (travelling wave) the decrease in TPA is dramatic for ratios as moderate as $\tilde{\gamma}_v=1$ or larger.

As a function of the normalized detuning $\tilde{\delta}$, $N_2$ has a bell shape whose FWHM $\Gamma$ is easily calculated from Eq.(32), and reads

$$\Gamma^2=4\left[\sqrt{w+(w-1)^2 f^2}+(w-1)f\right], \quad (40)$$

$$w=(1+\tilde{\gamma}_v)^2, \quad (41)$$

$$f=\frac{1}{2}\frac{1+A^4-4(1+\tilde{\gamma}_v)A^2}{1+A^4+4(1+\tilde{\gamma}_v)A^2}. \quad (42)$$

For a homogeneously broadened line ($\tilde{\gamma}_v=0:w=1$) the width reads $\Gamma_{\rm hom}=2$ (*i.e.* in terms of the detuning $\delta$ the width reads $2\gamma$). In the special case of a traveling wave ($A=0:f=1/2$) the width reads $\Gamma^{TW}=2(1+\tilde{\gamma}_v)$, *i.e.*, the width is the sum of the homogeneous and inhomogeneous widths. For a standing wave ($A=1$) no simple expression is obtained; nevertheless in the special case of large inhomogeneous broadening ($\tilde{\gamma}_v\gg 1: f\to -1/2, w\to\infty$) the width reads $\Gamma^{SW}(\tilde{\gamma}_v\to\infty)=2(1+1/2\tilde{\gamma}_v)$ which tends to the homogeneous width 2 for sufficiently large inhomogeneous broadening. This last result is a fundamental property of TPA: sub–Doppler spectroscopy can be performed in TPA experiments by using a standing wave [1, 3–6, 9].

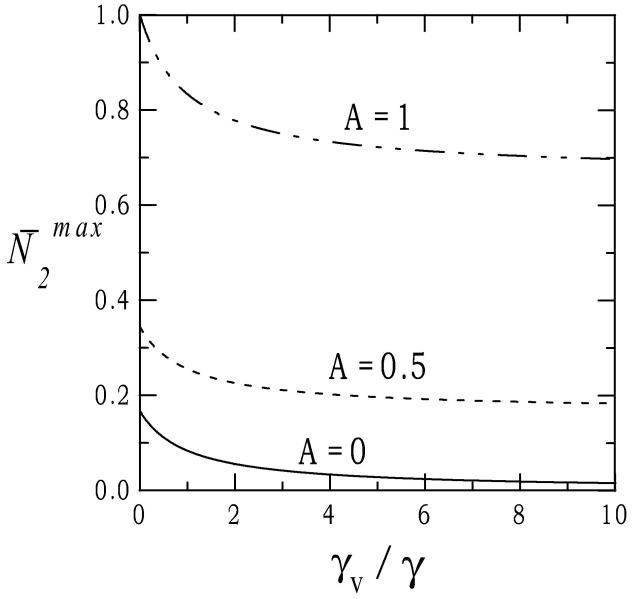


FIGURE 2. Maximum value of the population excited to the upper atomic level as a function of the inhomogeneous to homogeneous width ratio $\gamma_v/\gamma$ for several values of $A$. $\bar{N}_2^{\max}$ is $N_2^{\max}$ normalized to its maximum value (that corresponds to a homogeneously broadened medium ($\gamma_v=0$) pumped by a standing wave ($A=1$)).

In Fig. 3 we plot $\Gamma/_{\rm hom}$, as given by Eq.(40), as a function of the normalized inhomogeneous width $\tilde{\gamma}_v$ for $A=1$ and $A=0.5$. Clearly, for any value of $A$ different from zero, $\Gamma/_{\rm hom}$ first grows until it reaches a maximum and finally decreases tending to unity for large enough $\tilde{\gamma}_v$. Of course the optimum situation corresponds to $A=1$ [$A\neq 1$ can be understood as the sum of a traveling wave and a standing wave. Thus the result in that case is the sum of the two contributions. As the $TW$ contribution is less important the larger is $\gamma_v$ and the contribution of the $SW$ is basically independent of $\gamma_v$ this explains the above result. The main difference between $A=1$ and $A\neq 1$ lies in the strength of the resonance as shown in Fig. 2]. Thus for large enough $\tilde{\gamma}_v$ the inhomogeneous broadening does not contribute at all to the width of the resonance.

In Fig. 4 we show the same representation for $A=1$ (full line) together with the numerical integration assuming a Gaussian velocity distribution. It can be seen that the dependence is qualitatively the same and that only relatively small numerical deviations are appreciated between both cases. This confirms that the exact form of the velocity distribution is not very important, whenever it is bell shaped.

### 5.2. Shift of the resonance

As we have seen, at order $\varepsilon^2$ the maximum of the resonance is located at $\tilde{\delta}=0$. Nevertheless, two–photon processes induce a shift of the resonance, the so called Stark shift. This shift is only captured at third order of the perturbative expansion. Making use of Eqs. (32) and (33), we compute $\partial(N_2+N_3)/\partial\tilde{\delta}=0$ and obtain

$$\tilde{\delta}_{\rm Stark}=2\left(1+A^2\right)\left(\mu^2-1\right)\left(\frac{\phi^2}{\gamma\Delta}\right)\times\frac{(1+A^4)+A^2(1+\tilde{\gamma}_v)\left(2+5\tilde{\gamma}_v/2+\tilde{\gamma}_v^2\right)}{(1+A^4)+4A^2(1+\tilde{\gamma}_v)^3}, \quad (43)$$

which is the Stark shift. Note that this shift is proportional to $\left(\phi^2/\gamma\Delta\right)$, and is thus of order $\varepsilon$. Note also that whenever $\mu=1$ [*i.e.* when both one-photon transitions have equal electric dipole matrix elements, see Eq.(8)] the shift vanishes. We see that the sign of the shift depends both on the sign of the intermediate level detuning $\Delta$ and on the asymmetry between both one–photon transitions through the quantity $\left(\mu^2-1\right)$.

Particular cases of interest are: a) excitation with a traveling wave ($A=0$)

$$\tilde{\delta}_{Stark}^{TW}=2\left(\mu^2-1\right)\left(\frac{\phi^2}{\gamma\Delta}\right), \quad (44)$$

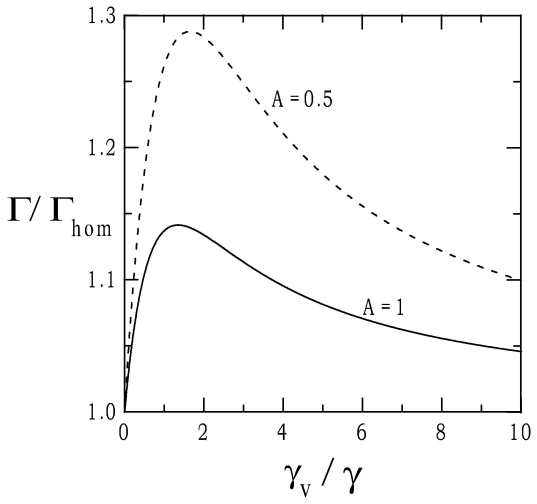


FIGURE 3. Width of the two photon resonance normalized to the homogeneous width as a function of $\gamma_v/\gamma$ for two values of $A$. (Notice that for a traveling wave, $A = 0$, the width grows linearly with the inhomogeneous width as $2\gamma_v/\gamma$.

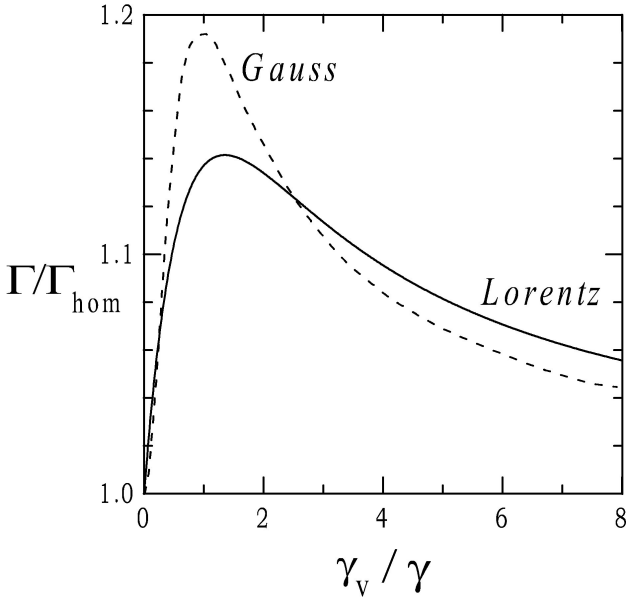


FIGURE 4. As in Fig.3 for a standing wave ($A = 1$) for both Lorentzian (full line) and Gaussian (dashed line) velocity distributions.

which is independent of the inhomogeneous broadening, and b) excitation with a standing wave ($A = 1$)

$$\tilde{\delta}^{SW}_{Stark} = \left(\mu^2 - 1\right)\left(\frac{\phi^2}{\gamma\Delta}\right)\left[1 + \frac{5 + 3\tilde{\gamma}_v + \tilde{\gamma}_v^2}{1 + 2\left(1 + \tilde{\gamma}_v\right)^3}\right], \quad (45)$$

which tends to $\tilde{\delta}^{TW}_{Stark}/2$ for $\tilde{\gamma}_v \to \infty$. In Fig. 5 $\tilde{\delta}^{SW}_{Stark}/\tilde{\delta}^{TW}_{Stark}$ is represented as a function of the inhomogeneous width for both Lorentzian broadening (Eq.(43)) and Gaussian broadening. Again it can be appreciated that the results are very similar for both types of inhomogeneous broadening.

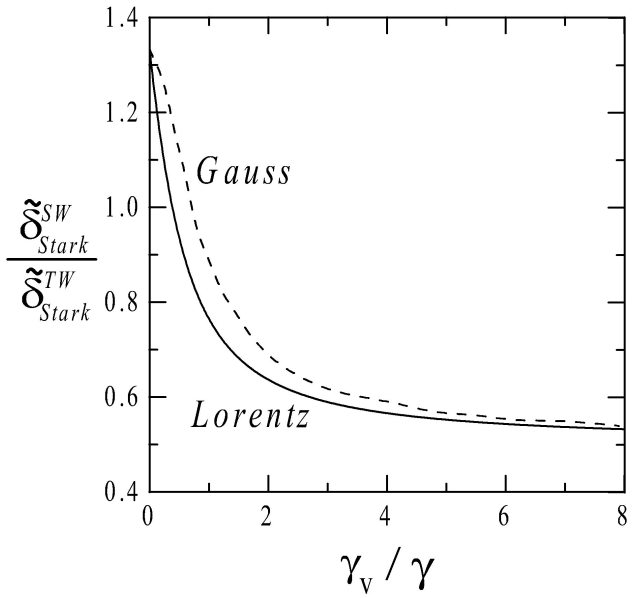


FIGURE 5. Dependence of the Stark shift on $\gamma_v/\gamma$ for a standing wave ($A = 1$) for both Lorentzian (full line) and Gaussian (dashed line) velocity distributions.

## 6. Conclusion

In this article we have analytically studied two–photon absorption (TPA) in an inhomogeneously broadened medium pumped by two counterpropagating light beams of equal frequency. By making use of perturbative techniques, we have derived explicit analytical expressions for the strength and width of the resonance as well as for the Stark shift in the case of Lorentzian broadening. Comparison with Gaussian broadening (numerically computed) has shown that the qualitative features of TPA are quite independent of the specific type of inhomogeneous broadening.

## Appendix A

At order $\varepsilon^{-1}$ one trivially gets

$$\rho^{(0)}_{01} = \rho^{(0)}_{20} = 0. \quad (46)$$

At order $\varepsilon^0$ the equations are

$$v\partial_z\rho^{(0)}_{22} = -\gamma\rho^{(0)}_{22}, \quad (47)$$

$$v\partial_z\rho^{(0)}_{00} = -\gamma\rho^{(0)}_{00}, \quad (48)$$

$$v\partial_z\rho^{(0)}_{11} = 1 - \gamma\rho^{(0)}_{11}, \quad (49)$$

$$v\partial_z\rho^{(0)}_{21} = -\left(\gamma - i\delta\right)\rho^{(0)}_{21}, \quad (50)$$

$$v\partial_z\rho^{(0)}_{20} = -\frac{i}{2}\Delta\rho^{(1)}_{20} + iE\mu\left(\rho^{(0)}_{00} - \rho^{(0)}_{22}\right) - iE^*\rho^{(0)}_{21}, \quad (51)$$

$$v\partial_z\rho_{01}^{(0)} = +\frac{i}{2}\Delta\rho_{01}^{(1)} + iE\left(\rho_{11}^{(0)} - \rho_{00}^{(0)}\right) - iE^*\mu\rho_{21}^{(0)}, \quad (52)$$

whose solution is

$$\rho_{11}^{(0)}(v,z) = 1, \quad (53)$$

$$\rho_{22}^{(0)}(v,z) = \rho_{00}^{(0)}(v,z) = \rho_{21}^{(0)}(v,z) = 0, \quad (54)$$

and

$$\rho_{01}^{(1)}(v,z) = -\frac{2}{\Delta}\left(\phi_1 e^{ikz} - \phi_2 e^{-ikz}\right), \quad (55)$$

$$\rho_{20}^{(1)}(v,z) = 0. \quad (56)$$

At order $\varepsilon^1$ the equations are

$$v\partial_z\rho_{22}^{(1)} = -\gamma\rho_{22}^{(1)} + i\mu\left(E\rho_{02}^{(1)} - E^*\rho_{20}^{(1)}\right), \quad (57)$$

$$v\partial_z\rho_{00}^{(1)} = -\gamma\rho_{00}^{(1)} + i\left(E\rho_{10}^{(1)} - E^*\rho_{01}^{(1)}\right) - i\mu\left(E\mu\rho_{02}^{(1)} - E^*\rho_{20}^{(1)}\right), \quad (58)$$

$$v\partial_z\rho_{11}^{(1)} = -\gamma\rho_{11}^{(1)} + i\left(E^*\rho_{01}^{(1)} - E\rho_{10}^{(1)}\right), \quad (59)$$

$$v\partial_z\rho_{21}^{(1)} = -(\gamma - i\delta)\rho_{21}^{(1)} + iE\left(\mu\rho_{01}^{(1)} - \rho_{20}^{(1)}\right), \quad (60)$$

$$v\partial_z\rho_{20}^{(1)} = -\left(\gamma - \frac{i}{2}\delta\right)\rho_{20}^{(1)} - \frac{i}{2}\Delta_1\rho_{20}^{(2)} + iE\mu\left(\rho_{00}^{(1)} - \rho_{22}^{(1)}\right) - iE^*\rho_{21}^{(1)}, \quad (61)$$

$$v\partial_z\rho_{01}^{(1)} = -\left(\gamma - \frac{i}{2}\delta\right)\rho_{01}^{(1)} + \frac{i}{2}\Delta_1\rho_{01}^{(2)} + iE\left(\rho_{11}^{(1)} - \rho_{00}^{(1)}\right) - iE^*\mu\rho_{21}^{(1)}, \quad (62)$$

and integration along $z$ has to be carried out. By using Eqs. (55), it is straightforward to obtain that

$$\rho_{ii}^{(1)}(v,z) = 0, \qquad i = 0,1,2 \quad (63)$$

$$\rho_{21}^{(1)}(v,z) = -\frac{2i\mu}{\Delta_1}\left[\frac{\phi_1^2}{D_+}e^{2ikz} - \frac{2\phi_1\phi_2}{D_0} + \frac{\phi_2^2}{D_-}e^{-2ikz}\right], \quad (64)$$

and

$$\rho_{20}^{(2)}(v,z) = \frac{4i\mu}{\Delta_1^2}\left[-\frac{\phi_1^2\phi_2}{D_+}e^{3ikz} + \left(\frac{\phi_1^3}{D_+} + \frac{2\phi_1\phi_2^2}{D_0}\right)e^{ikz} - \left(\frac{\phi_2^3}{D_-} + \frac{2\phi_1^2\phi_2}{D_0}\right)e^{-ikz} + \frac{\phi_1\phi_2^2}{D_-}e^{-3ikz}\right], \quad (65)$$

$$\rho_{01}^{(2)}(v,z) = \frac{4i\mu^2}{\Delta_1^2}\left\{-\frac{\phi_1^2\phi_2}{D_+}e^{3ikz} + \left[\frac{(\gamma + D_+)\phi_1}{2\mu^2} + \left(\frac{\phi_1^3}{D_+} + \frac{2\phi_1\phi_2^2}{D_0}\right)\right]e^{ikz} - \left[\frac{(\gamma + D_-)\phi_2}{2\mu^2} + \left(\frac{\phi_2^3}{D_-} + \frac{2\phi_1^2\phi_2}{D_0}\right)\right]e^{-ikz} + \frac{\phi_1\phi_2^2}{D_-}e^{-3i\,k\,z}\right\}, \quad (66)$$

with

$$D_\pm = \gamma - i(\delta \mp 2kv), \quad (67)$$

$$D_0 = \gamma - i\delta. \quad (68)$$

At order $\varepsilon^2$ it is not necessary to compute all the terms since we are only interested in $\rho_{22}^{(2)}$ and $\rho_{20}^{(3)}$ (the latter is necessary for calculating $\rho_{22}^{(3)}$ at order $\varepsilon^3$) [Notice that if one is interested only in the analysis of the strength and width of the resonance (and not of the Stark shift), it is enough to calculate the non-oscillating term in Eq.(73) by direct substitution of (65) in Eq.(69), quite a simple task. The rest of the terms are necessary for obtaning of $\rho_{22}^{(3)}$ which becomes a simple but tedious task]. The necessary equations are

$$v\partial_z\rho_{22}^{(2)} = -\gamma\rho_{22}^{(2)} + i\,\mu\left(E\rho_{02}^{(2)} - E^*\rho_{20}^{(2)}\right), \quad (69)$$

$$v\partial_z\rho_{00}^{(2)} = -\gamma\rho_{00}^{(2)} + i\left(E\rho_{10}^{(2)} - E^*\rho_{01}^{(2)}\right) - i\mu\left(E\rho_{02}^{(2)} - E^*\rho_{20}^{(2)}\right), \quad (70)$$

$$v\partial_z\rho_{21}^{(2)} = -(\gamma - i\delta)\rho_{21}^{(2)} + iE\left(\mu\rho_{01}^{(2)} - \rho_{20}^{(2)}\right), \quad (71)$$

$$v\partial_z\rho_{20}^{(2)} = -\left(\gamma - i\frac{\delta}{2}\right)\rho_{20}^{(2)} - i\frac{\Delta_1}{2}\rho_{20}^{(3)} + i\mu E\left(\rho_{00}^{(2)} - \rho_{22}^{(2)}\right) - iE^*\rho_{21}^{(2)}, \quad (72)$$

and the searched quantities are given by

$$\rho_{22}^{(2)}(v,z) = \frac{4\mu^2}{\gamma\Delta_1^2}\left[\frac{\phi_1^4}{D_+} + \frac{\phi_2^4}{D_-} + \frac{4\phi_1^2\phi_2^2}{D_0}\right] + c.c. + -\frac{16\mu^2\phi_1\phi_2}{\Delta_1^2}\left(\frac{\gamma + ikv}{\gamma - 2ikv}\right)\left[\frac{\phi_1^2}{D_0^* D_+} + \frac{\phi_2^2}{D_0 D_-^*}\right]e^{i2kz} + c.c. + \text{terms with } e^{\pm i4kz}, \quad (73)$$

$$\rho_{00}^{(2)}(v,z)=\frac{8}{\Delta_1^2}\left[\phi_1^2+\phi_2^2-\frac{\gamma+ikv}{\gamma+2ikv}\phi_1\phi_2e^{i2kz}-c.c.\right]+\text{terms with } e^{inkz}\quad(n\neq 0,\pm 2)\,, \tag{74}$$

$$\begin{aligned}\rho_{21}^{(2)}(v,z)=&\frac{4\mu\phi_1\phi_2}{\Delta_1^2D_0}\left[\gamma+D_0+\left(\mu^2-1\right)\left(2\frac{\phi_1^2+\phi_2^2}{D_0}+\frac{\phi_1^2}{D_+}+\frac{\phi_2^2}{D_-}\right)\right]\\&-\frac{2\mu\phi_1^2}{\Delta_1^2D_0}\left[\gamma+D_++2\left(\mu^2-1\right)\left(2\frac{\phi_2^2}{D_0}+\frac{\phi_1^2+\phi_2^2}{D_-}\right)\right]e^{i2kz}\\&-\frac{2\mu\phi_2^2}{\Delta_1^2D_0}\left[\gamma+D_-+2\left(\mu^2-1\right)\left(2\frac{\phi_1^2}{D_0}+\frac{\phi_1^2+\phi_2^2}{D_+}\right)\right]e^{-i2kz}\\&+\text{terms with } e^{inkz}\quad(n\neq 0,\pm 2)\end{aligned} \tag{75}$$

from the three first equations and, from the last equation,

$$\rho_{20}^{(3)}(v,z)=\rho_{20}^{(3,+)}e^{ikz}+\rho_{20}^{(3,-)}e^{-ikz}+terms\ with\ e^{inkz},\ n\neq\pm 1 \tag{76}$$

where

$$\begin{aligned}\rho_{20}^{(3,+)}=\frac{8\mu\phi_1}{\Delta_1^3}\Bigg\{&\left[\frac{\left(\mu^2-1\right)}{D_+^2}-\frac{4\mu^2}{\left|D_+\right|^2}\right]\phi_1^4+2\phi_1^2+\left[\frac{\left(\mu^2-1\right)}{D_0}\left(\frac{2}{D_0}+\frac{3}{D_+}+\frac{D_0}{D_+^2}\right)\right.\\&\left.-\frac{4\mu^2}{D_0^*}\left(\frac{4}{D_0}-\frac{(\gamma+ikv)}{D_+(\gamma-2ikv)}\right)\right]\phi_1^2\phi_2^2+\left[4-\frac{D_+}{D_0}+\frac{\gamma}{\gamma+2ikv}\right]\phi_2^2\\&+\left[\frac{\left(\mu^2-1\right)}{D_0}\left(\frac{1}{D_-}+\frac{2}{D_0}\right)-\frac{4\mu^2}{D_-^*}\left(\frac{1}{D_-}+\frac{(\gamma+ikv)}{D_0(\gamma-2ikv)}\right)\right]\phi_2^4\Bigg\},\end{aligned} \tag{77}$$

and

$$\begin{aligned}\rho_{20}^{(3,-)}=-\frac{8\mu\phi_2}{\Delta_1^3}\Bigg\{&\left[\frac{\left(\mu^2-1\right)}{D_-^2}-\frac{4\mu^2}{\left|D_-\right|^2}\right]\phi_2^4+2\phi_2^2+\left[\frac{\left(\mu^2-1\right)}{D_0}\left(\frac{2}{D_0}+\frac{3}{D_-}+\frac{D_0}{D_-^2}\right)\right.\\&\left.-\frac{4\mu^2}{D_0^*}\left(\frac{4}{D_0}+\frac{(\gamma-ikv)}{D_-(\gamma+2ikv)}\right)\right]\phi_2^2\phi_1^2+\left[4-\frac{D_-}{D_0}+\frac{\gamma}{\gamma-2ikv}\right]\phi_1^2\\&+\left[\frac{\left(\mu^2-1\right)}{D_0}\left(\frac{1}{D_+}+\frac{2}{D_0}\right)-\frac{4\mu^2}{D_+^*}\left(\frac{1}{D_+}-\frac{(\gamma-ikv)}{D_0(\gamma+2ikv)}\right)\right]\phi_1^4\Bigg\}.\end{aligned} \tag{78}$$

Finally, at order $\varepsilon^3$ we are only interested in obtaining the value of the population of the excited level. Thus we only need

$$v\partial_z\rho_{22}^{(3)}=\gamma\rho_{22}^{(3)}+i\mu(E\rho_{02}^{(3)}-E^*\rho_{20}^{(3)}). \tag{79}$$

The spatial dc-component of $\rho_{22}^{(3)}$ finally reads

$$\begin{aligned}\rho_{22,dc}^{(3)}=&\frac{32\mu^2\left(\mu^2-1\right)}{\Delta^3}\left[\left(\frac{\delta-2kv}{\left|D_+\right|^4}\right)\left(\phi_1^2+\phi_2^2\right)\phi_1^4\right.\\&+\left(\frac{\delta-kv}{\left|D_+\right|^2}\phi_1^2+\frac{\delta+kv}{\left|D_-\right|^2}\phi_2^2+\frac{\delta}{\left|D_0\right|^2}\left(\phi_1^2+\phi_2^2\right)\right)\\&\left.\times\frac{\phi_1^2\phi_2^2}{\left|D_0\right|^2}+\left(\frac{\delta+2kv}{\left|D_-\right|^4}\right)\left(\phi_1^2+\phi_2^2\right)\phi_2^4\right].\end{aligned} \tag{80}$$

## Appendix B

At order $\varepsilon^2$ the spatially–averaged population of the excited level, Eq.(73), is

$$\left\langle\rho_{22}^{(2)}(v)\right\rangle_z=\frac{4\mu^2}{\gamma\Delta_1^2}\left[\frac{\phi_1^4}{D_+}+\frac{\phi_2^4}{D_-}+\frac{4\phi_1^2\phi_2^2}{D_0}\right]+c.c. \tag{81}$$

Now the averaging over velocities has to be carried out. As $v$ only appears in $\rho_{22}^{(2)}(v)$ through $D_\pm(v)$ the only integrals to be done are of the type

$$int_1=\frac{1}{\pi}\int_{-\infty}^{+\infty}d(2kv)\,\frac{\gamma_v}{\gamma_v^2+(2kv)^2}\frac{\gamma}{\gamma^2+(\delta\pm 2kv)^2}, \tag{82}$$

whose result is

$$int = \frac{\gamma + \gamma_v}{(\gamma + \gamma_v)^2 + \delta^2}, \tag{83}$$

and thus the averaged upper level population results to be

$$\left\langle \rho_{22}^{(2)} \right\rangle = \frac{8\mu^2}{\gamma \Delta_1^2} \left[ \frac{\gamma + \gamma_v}{(\gamma + \gamma_v)^2 + \delta^2} \left( \phi_1^4 + \phi_2^4 \right) + 4\phi_1^2 \phi_2^2 \frac{\gamma}{\gamma^2 + \delta^2} \right]. \tag{84}$$

At order $\varepsilon^3$ the situation is similar. Now the integrals that appear when making the velocity averaging of Eq.(80) are of the type $int_1$ and also of the type

$$int_2(n) = \frac{1}{\pi} \int_{-\infty}^{+\infty} d(2kv) \frac{\gamma_v}{\gamma_v^2 + (2kv)^2} \times \frac{(2kv)}{\left[ \gamma^2 + (\delta \pm 2kv)^2 \right]^n}, \tag{85}$$

$(n = 1, 2)$ whose result is

$$int_2(1) = \frac{\gamma_v \delta}{(\gamma + \gamma_v)^2 + \delta^2},$$

$$int_2(2) = \frac{\gamma_v \delta}{(\gamma + \gamma_v)^2 + \delta^2} \frac{(\gamma + \gamma_v)(3\gamma + \gamma_v) + \delta^2}{2\gamma^2}.$$

The final result reads

$$\rho_{22}^{(3)} = 16\mu^2 \left(1 + A^2\right) \left(\mu^2 - 1\right) \delta \left( \frac{\phi^2}{\gamma \Delta_1} \right)^3 \times \left[ \gamma^2 A^2 \left( \frac{1}{\gamma_v |D_0|^2} - \frac{1}{\gamma_v \left[ (\gamma + \gamma_v)^2 + \delta^2 \right]} + \frac{2\gamma^2}{|D_0|^4} \right) + \frac{2\gamma^2 \left(1 + A^4\right)(\gamma + \gamma_v)}{\left[ (\gamma + \gamma_v)^2 + \delta^2 \right]^2} \right]. \tag{86}$$


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