
ON TWO PHOTON ABSORPTION PROCESS AND ANGULAR MOMENTUM FORMALISM

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Abstract:

Non-linear optical properties in recent times has attracted a number of research workers as it developed new techniques novel methods to provide information's about electronic properties of atoms/molecules. New semiconducting properties are being explored. One of the observed non-linear processes of matter in interaction with radiation is two-photon absorption process. The superposition principle in quantum mechanics admits of a rotation of the Hilbert space for the system. Making use of this fact a geometrical representation of the Schrodinger equation for two photon absorption process is by treating the Hamiltonian and the Density matrix of the system as vectors in a space spanned by angular momentum matrices for $J=1$ as basis vectors. This description specializes the general three level problem into a problem of equi spaced levels with proper matrix elements between the two pairs of levels.

Key words: Two-photon absorption, superposition principle, rotation of Hilbert space, density matrix, angular momentum as basis vectors.

INTRODUCTION :

The TWO PHOTON ABSORPTION (TPA) process, coined first of all by Maria Goeppert-Mayer in 1931 in her doctoral dissertation [1], was detected thirty years later in Fluorescence effect in Europium doped crystal [2,3]. A Two Photon Absorption process is defined as simultaneous absorption of two photons of identical or different frequencies by material. The atom/molecule excite from their normal state to a higher energy state. The energy difference between the two states being equal to the sum of energies of two photons.

Unlike One Photon Absorption (OPA) process, which is a linear process as atomic transition rate shows linear relation with light intensity and is observable for weak intensities, the two photon absorption process is a non-linear optical process in which the atomic transition rate is proportional to square of the intensity of light [4]. Hence the selection rule for TPA is different from OPA and arises due to conservation of angular momentum.

In TPA, two photons add up to bridge the energy gap between the two energy levels which is large compared to energy of an individual photon. If the energy gap has an intermediate state, not necessarily mid way, the TPA process is possible by absorbing two separate photons of different frequencies or energies which are in resonance with the two energy gaps. The process is called Resonant TPA process or 1+1 absorption process. In other type of the observed process, of the Two photons absorption, the absorption takes place without any intermediate state and is called Non-resonant TPA process. The process is explained as by formation of a virtual state between the atomic levels. The virtual state with respect to lower and upper levels being equal to the photon energy of each of two photons absorbed. The formation of virtual state are supposed to be due to interaction of photons with atom /molecule.

The TPA being is a nonlinear process and nonlinearity of a process demands the interaction strength to increase faster than that for linear process, these are best observed and studied with pulsed laser sources.

There are several reasons for studying non-linear processes in quantized media. Multiple -photon effects give information regarding material properties such as the parity of states or the oscillator strengths of the transitions[5]. For example, if the eigen states have a definite parity, then two-photon absorption occurs between states of same parity. This non-linear effect may therefore be used to study the coupling between the states, whereas the electric dipole transition can not be used for the purpose because it is between states of opposite parity. One of the motivations for studying these non-linear processes is that much of the macroscopic behavior of materials results from the multiple photon effects between energy levels or energy bands. Non-linear elements have extensive applications as harmonic generators, modulators, detectors and parametric oscillators. Another important point to note is that the study of multiple photon phenomena have provided an interesting example for the illustration of the perturbative procedures as applied to quantized media. The usual procedure that appears in the literature to deal with the non-linear processes has been the evaluation of the elements of the density operator describing the state of the interacting system in different orders of perturbation.

Non-linear optical properties, in general, developed new techniques and spectroscopic methods to collect a lot of information's about molecular electronic structures. In semiconductor physics [13] one can determine the microscopic

properties like Band gap, Carrier life time etc. Nowadays the TPA phenomenon is being used for optical logic gate [6], 3D Optical data storage [7-8] 3D Micro fabrication [9], Organic chromophores [10,14] etc.

If we examine the equations of motion for the density operator or if we consider the semiclassical equations involving interaction between radiation and matter [Pantel & Puthoff] we see that these equations are non-linear. Product of variables are involved in the equation and so in addition to single-photon effects or the linear effects, various non-linear processes also occur. For example it has been observed [11-12] that for certain materials there is a resonant absorption of electromagnetic radiation at one-half the transition frequency. This interaction is termed two-photon absorption, because in terms of the photon energy of the radiation it is necessary for two photons to be absorbed for the transition to occur in the medium.

Other two-photon processes include the absorption of radiation at the two different frequencies so that the sum of the frequencies equals the transition frequency and Raman oscillation which is the absorption of radiation at a frequency greater than the transition frequency and the emission of radiation at the difference frequency.

Attempts have been made for a qualitative understanding of two-photon absorption phenomena by obtaining the Hamiltonian operator and density operator of the system as vectors in a space spanned by the components of angular momentum matrices for $J=1$ as basis vectors.

TWO PHOTON ABSORPTION PROCESS AT SAME FREQUENCY

GEOMETRICAL PICTURE FOR TWO – PHOTON ABSORPTION PROCESS :

For our purpose we consider a single atom having three isolated energy levels, energy eigenvalues being E_a , E_b , and E_c ($E_a > E_b > E_c$) and the corresponding eigenkets being respectively $|a\rangle$, $|b\rangle$ and $|c\rangle$.

In a representation in which the unperturbed Hamiltonian of the atom is the diagonal matrix.

$$H_0 = \begin{pmatrix} E_a & 0 & 0 \\ 0 & E_b & 0 \\ 0 & 0 & E_c \end{pmatrix} \quad (1)$$

The eigenkets are the column matrices

$$\begin{aligned} |a\rangle &= \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ |b\rangle &= \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \\ |c\rangle &= \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \end{aligned} \quad (2)$$

The three components of angular momentum operator for $J=1$ are the matrices

$$M_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad (3)$$

$$M_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad (4)$$

$$M_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (5)$$

The square of the total angular momentum operator is

$$M^2 = M_x^2 + M_y^2 + M_z^2 \quad (6)$$

using eq. (3), (4) and (5) we obtain M^2 to be the unit matrix

$$M^2 = 2 \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In terms of the matrix M_z given by eq. (5) and M^2 given by eq. (7), the unperturbed Hamiltonian given by eq. (1) can be rewritten as

$$H_0 = \frac{1}{2} (\omega_z M_z + \omega_0 M^2) \quad (8)$$

where

$$\omega_z = \frac{E_a - E_c}{2\hbar} \quad (9)$$

and

$$\omega_0 = \frac{E_a + E_c}{2\hbar^2} \quad (10)$$

Let us now consider the interaction of the atom with an external electromagnetic field without referring to the type of interaction for generality. The interaction Hamiltonian V is the non - diagonal matrix.

$$V = \begin{pmatrix} 0 & V_{ab} & V_{ac} \\ V_{ba} & 0 & V_{bc} \\ V_{ca} & V_{cb} & 0 \end{pmatrix} \quad (11)$$

Using the non - diagonal angular momentum matrices M_x and M_y given respectively by eqs. (3) and (4), eq. (11) can be expressed in the form-

$$V = \frac{1}{2} (\omega_x M_x + \omega_y M_y) \quad (12)$$

where

$$\omega_x = \frac{1}{\sqrt{2\hbar}} (V_{ab} + V_{ba}) \quad (13)$$

and

$$\omega_y = \frac{i}{\sqrt{2\hbar}} (V_{ab} - V_{ba}) \quad (14)$$

We further observe the following :

$$V_{ac} = 0 = V_{ca} \quad (15)$$

$$V_{ab} = V_{bc} \quad (16)$$

The total Hamiltonian for the interacting system is thus given using eqs. (8) and (12) by

$$\begin{aligned} H &= H_0 + V \\ &= \frac{1}{2} (\omega_x M_x + \omega_y M_y + \omega_z M_z) + \frac{1}{2} \omega_0 M^2 \end{aligned} \quad (17)$$

THE DENSITY MATRIX OF THE SYSTEM

The density matrix representing the state of the interacting system is the 3 x 3 matrix

$$\rho = \begin{pmatrix} \rho_{aa} & \rho_{ab} & \rho_{ac} \\ \rho_{ba} & \rho_{bb} & \rho_{bc} \\ \rho_{ca} & \rho_{cb} & \rho_{cc} \end{pmatrix} \quad (18)$$

Like the total Hamiltonian, the density matrix ' ρ ' given by (18) can be expressed in terms of the angular momentum matrices M_x, M_y, M_z & M^2 as

$$\rho = \frac{1}{2} (\gamma_x M_x + \gamma_y M_y + \gamma_z M_z) + \frac{1}{2} \gamma_0 M^2 \quad (19)$$

where

$$\gamma_x = \frac{\sqrt{2}}{\hbar} (\rho_{ab} + \rho_{ba}) \quad (20)$$

$$\gamma_y = i \frac{\sqrt{2}}{\hbar} (\rho_{ab} - \rho_{ba}) \quad (21)$$

$$\gamma_z = \frac{1}{\hbar} (\rho_{aa} - \rho_{cc}) \quad (22)$$

And

$$\gamma_0 = \frac{1}{2\hbar^2} (\rho_{aa} + \rho_{cc}) = \frac{\rho_{bb}}{\hbar^2} \quad (23)$$

We also observe that

$$\rho_{ac} = 0 = \rho_{ca} \quad (24)$$

$$\rho_{bb} = \frac{1}{2} (\rho_{aa} + \rho_{cc}) \quad (25)$$

$$\rho_{ab} = \rho_{bc} \quad (26)$$

GEOMETRICAL PICTURE OF THE INTERACTING SYSTEM.

For simplicity, Let us consider the zero of energy to correspond to the intermediate energy level, that is, let us consider $E_b = 0$. We can then write.

$$E_a = \frac{1}{2} \hbar \omega \quad (27)$$

$$E_b = -\frac{1}{2} \hbar \omega \quad (28)$$

Where ' ω ' is the transition frequency between the lowest and highest energy level.

Under such a consideration ω_0 given by eq (10) becomes zero. and the total Hamiltonian given by eq. (17) takes the form

$$H = \frac{1}{2} (\omega_x M_x + \omega_y M_y + \omega_z M_z) \quad (29)$$

we may rewrite eq. (29) as

$$H = \frac{1}{2} \vec{\omega} \cdot \vec{M} = \vec{W} \cdot \vec{M} \quad (30)$$

and interpret the Hamiltonian of the interacting system to be represented by a vector \vec{W} in a space spanned by M_x, M_y, M_z as the basis vectors $\frac{1}{2} \omega_x, \frac{1}{2} \omega_y$ and $\frac{1}{2} \omega_z$ being the components of \vec{W} along the three axes represented by M_x, M_y and M_z respectively.

Further let us consider γ_0 given by (23) to be zero. This essentially means $\rho_{bb} = 0$ i.e. the probability of finding the atom in the middle state to be zero. Under such a consideration the density matrix given by eq. (19) assumes the form

$$\rho = \frac{1}{2} (\gamma_x M_x + \gamma_y M_y + \gamma_z M_z) \quad (31)$$

we may rewrite eq. (31) as,

$$\rho = \frac{1}{2} \vec{Y} \cdot \vec{M} = \vec{R} \cdot \vec{M} \quad (32)$$

and interpret the density matrix of the interacting system to be represented by a vector \vec{R} in the space spanned by M_x, M_y & M_z as the basis vectors, $\frac{1}{2} \gamma_x, \frac{1}{2} \gamma_y$ and $\frac{1}{2} \gamma_z$ being the components of \vec{R} along the three axes represented by M_x, M_y & M_z respectively.

The density matrix ρ satisfies the equation

$$i\hbar \frac{d\rho}{dt} = [H, \rho] \quad (33)$$

using ρ given by eq. (32) and H given eq. (30) in eq. (33) we obtain

$$\frac{i\hbar}{2} [\dot{r}_x M_x + \dot{r}_y M_y + \dot{r}_z M_z] = \left[\frac{1}{2} (\omega_x M_x + \omega_y M_y + \omega_z M_z), \frac{1}{2} (r_x M_x + r_y M_y + r_z M_z) \right]$$

Carrying out the commutator on the right hand side and using the well known commutation relation between the operators M_x, M_y, M_z & M^2 given below

$$[M_i, M_j] = i\hbar M_k \quad (i, j, k \text{ form an even permutation of } x, y, z)$$

and

$$[M^2, M_i] = 0$$

and then comparing the coefficients of M_x , M_y & M_z on the two sides of the above equation we obtain

$$\begin{aligned} \dot{r}_x &= \frac{1}{2}(\omega_y r_z - \omega_z r_y) \\ \dot{r}_y &= \frac{1}{2}(\omega_z r_x - \omega_x r_z) \\ \dot{r}_z &= \frac{1}{2}(\omega_x r_y - \omega_y r_x) \end{aligned} \quad (34)$$

The above equations can be combined in the form

$$\dot{\vec{R}} = \vec{W} \times \vec{R} \quad (35)$$

Eq. (35) represents a precessional motion of the vector \vec{R} about the vector \vec{W} in the space defined by angular momentum as basis vectors.

Conclusion :

Form the above simple mathematical approach it is seen that a general three level problem specializes to a problem of three equi-spaced energy levels in the angular momentum formalism. It is further seen from equations (15) and (16) that while the matrix elements of the interaction Hamiltonian connecting the lowest and highest state are zero, those connecting the lowest and the middle and the middle and the highest state are equal. These results and the results expressed by equations (24) to (26) suggest that the atom initially in the lowest energy state can make transitions to the highest state by absorbing two photons simultaneously at the frequency $\frac{1}{2} \omega$ without making any actual transition to the middle state because $\rho_{bb} = 0$ means that the probability of finding the atom in the middle state is zero for all times.

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