ROLE OF SATURATION IN THE MULTIPHOTON TRANSITIONS

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The effects of a medium (of collisions) on the probability for two-photon absorption in a three-level system are analyzed. It is shown qualitatively that saturation can occur, under conditions more stringent than for one-photon saturation. A possible mechanism for lowering the population state of the radiation flux during multiphoton ionization is discussed.

1. Saturation occurs in one-photon transitions because of an effect of the medium on an absorbing system (at atom or molecule) in an electromagnetic field; this saturation can be observed in the case of sufficiently long relaxation times [1, 2]. In this paper we will qualitatively analyze the effects of a medium (i.e., of collisions) on the probability for two-photon absorption in order to determine whether saturation can occur during multiphoton transitions and to determine the form in which it is displayed.

We consider the system described by the Hamiltonian

\[ H = H_1 + H_R + H_{1R} = H_0 + H_{1R}, \]  

(1)

where \( H_1 \) is the Hamiltonian of the absorbing molecule, \( H_R \) is that of the external monochromatic radiation field (of frequency \( \omega \)), and \( H_{1R} \) describes the intersection of the \( H_1 \) and \( H_R \) subsystems. We assume collisions between molecules to be elastic, so the Hamiltonian describing the interaction due to collisions does not appear in Eq. (1) [1].

We assume that the last collision occurs at \( t = 0 \) and that no collisions occur between 0 and \( t \). Then to determine the probability for a transition \( A \rightarrow B \) (\( A = a, n \), where \( n \) is the state of the field in terms of population numbers, and \( a \) is the initial state of the molecule; and \( B = b, m \) in the interval \( (0, t) \) we can use the unitary operator \( S(t) \):

\[ P_{BA}(t) = |S(t)_{ba,an}|^2, \]

(2)

where \( S(t)_{an}(0) = \psi(t) \) is the function of the system at time \( t \), which satisfies the Schrödinger equation with Hamiltonian (1). Operator \( S \) satisfies

\[ HS = i\hbar \dot{S}, \quad S(0) = 1. \]

(3)

In the interaction picture, the transition probability is

\[ P_{BA}(t) = |V(t)_{ba,an}|^2. \]

(4)

Retaining the term in \( H_{1R} \) which is linear in the field, we can write the operator \( V(t) \) in the long-wave approximation as

\[ V = 1 + \sum_{i=1}^{\infty} V_i; \]

(5)

\[ V_s = \left( \frac{1}{i\hbar} \right)^s \int_0^t \int_0^{t_1} \int_0^{t_2} \ldots \int_0^{t_{s-1}} dt_s B(t_s) \ldots B(t_1), \]

where \( B = \gamma g(t)(ae^{-i\omega t} + a^+e^{i\omega t}), g(t) = S_1^{-1}p_2S_1, \) \( a^+ \) and \( a \) are the creation and annihilation operators,

\[ \gamma = -\frac{e}{\nu} (2\hbar \nu)^{1/2}, \quad \text{and} \quad S_1 = \exp(-i\hbar H_1/\hbar). \]
To take the effects of the medium into account, we must average (4) over the time \(t\) during which no collisions occur (i.e., over the mean free time of the absorbing molecule). The distribution of free times \(t\) is [3]

\[
P(t) = \sigma \exp(-\sigma t), \quad \sigma = \tau^{-1},
\]

where \(\tau\) is the mean free time (the relaxation time). The transition probability per unit time averaged in this manner is

\[
p = \sigma^2 \int_0^\infty dt \exp(-\sigma t) |V(t)|^2;
\]

where it is assumed that the relaxation time is much greater than the period of the radiation field.

Since \(t = 0\) is the time in which the last collision occurs, and a thermal equilibrium is reestablished after each collision, we can use a Boltzmann density matrix \(\rho_0\) for the equilibrium state to average (7) over initial states \((a, b)\) of the molecule. In this manner we can find the total probability of a transition involving the absorption of \(N\) photons from the field.

2. We first consider one-photon absorption. Since with \(n - m = 1\) the even terms in sum (5) vanish because of the orthogonality of the field states, we have

\[|V_{BA}|^2 = U_a^*U_1 + 2\text{Re}(U_a^*U_2) + U_2^*U_3 + 2\text{Re}(U_2^*U_4) + \ldots,
\]

where \(U_a \equiv (V_{ab})_{a,b-1,0}a, b\). For simplicity we assume a two-level system \((a, b)\) retaining only the resonant terms in calculating \(U_a\). Then we have

\[
U_a^*U_1 = F |v_{ab}|^2 \frac{8}{\hbar^2} (1 - \cos \delta t),
\]

\[
2\text{Re}(U_a^*U_2) = -F |v_{ab}|^2 \frac{8}{\hbar^2} \left(1 - \cos \delta t - \frac{\delta t}{2} \sin \delta t\right),
\]

\[
U_2^*U_3 + 2\text{Re}(U_2^*U_4) = F |v_{ab}|^2 \frac{4}{\hbar^2} \left[8 (1 - \cos \delta t) + \delta t \cos \delta t - \delta t \sin \delta t\right],
\]

where \(F = n(\gamma' \mu_{BA}/\hbar)^2, \delta = \omega - \omega_{BA}, \mu_{ab}\) is the matrix element of the \(z\) component of the dipole moment, \(\mu\) is the mass, \(\gamma' = \gamma/e\), and \(e\) is the charge. Substituting (8) into (7), we find

\[
p = \frac{4\pi}{\hbar} n w |v_{ab}|^2 \frac{2}{\hbar^2 + \sigma^2} \left[1 - \frac{8\pi}{\hbar} \frac{\omega n |v_{ab}|^2}{\sigma^2 + \sigma^2} + \left(\frac{8\pi}{\hbar} \frac{\omega n |v_{ab}|^2}{\sigma^2 + \sigma^2}\right)^2 + \ldots\right]
\]

\[
= \frac{4\pi n \omega}{\hbar} |v_{ab}|^2 \left(\frac{2}{\hbar^2 + \sigma^2} + \frac{8\pi}{\hbar} \omega n |v_{ab}|^2\right).
\]

3. Using the same approach as that which led to (9) in the case of one-photon absorption, we will now analyze the absorption of two photons in a three-level system \((a, d, b) = (1, 2, 3)\), where \(d(2)\) is the intermediate level. In this case we have

\[|V_{BA}|^2 = U_a^*U_2 + 2\text{Re}(U_a^*U_4) + U_2^*U_3 + 2\text{Re}(U_3^*U_4) + \ldots
\]

Retaining only the first two terms in (10) (which are proportional to \(n^2\) and \(n^3\), respectively), we have, in the resonance approximation,

\[|V_{BA}|^2 = \left(\frac{2\pi n}{\hbar \omega}\right)^2 \omega_2^2 \omega_3^2 |v_{12}|^4 |v_{21}|^4 \left(I_2 + \left(\frac{2\pi n}{\hbar \omega}\right)^2 \omega_2^2 |v_{12}|^2 |v_{21}|^2 2\text{Re}(I_2' I_2') + \omega_3^2 |v_{21}|^2 2\text{Re}(I_3' I_3') + \ldots\right).
\]

Here

\[
I_2 = \int_0^t dt_1 \int_0^{t_1} dt_2 \exp - i(\delta_{12} t_1 + \delta_{21} t_2);
\]

\[
I_2' = \int_0^t \int_0^{t_1} dt_2 \exp - i(\delta_{12} (t_1 - t_2) + \delta_{21} t_2);
\]

\[
I_3' = \int_0^t \int_0^{t_1} dt_2 \exp - i(\delta_{12} t_1 + \delta_{21} (t_2 - t_1 + t_2)).
\]