Ultrafast Dynamical Behavior of Optical Response of Materials

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General behavior of the transient response of materials excited by a stepwise optical field has been studied by means of numerical analysis based on a model of the inhomogeneously broadened two-level atomic system with relaxation obeying the quantum mechanical equation of motion. The time dependences of the polarization and the excited state probability of atoms are investigated in detail under a wide variety of conditions including both the resonant and far off-resonant excitations. The behaviors are found to be quite different depending on the relative magnitudes of the light frequency, the center frequency and the bandwidth of transition, the Rabi frequency, the longitudinal and transverse relaxation rates. Two kinds of response times are defined to describe the rapidity of the response, and the physical parameters governing them are determined for a variety of cases. Another kind of response time originated from the statistical behavior of atoms is further considered and discussed. Based on these results, the range of the values of the response times are estimated in general. The results for both cases with and without the rotating wave approximation are also calculated and compared.

1. Introduction

Recent progress in the field of ultrashort light pulses and ultrafast spectroscopy revealed many aspects of ultrafast processes extending into the femtosecond region in a wide field of physics, chemistry, biology and engineering. Among them, various microscopic dynamical processes in materials after optical excitation, such as relaxation, energy transfer, molecular vibration and rotation, and so on, have been the subjects of extensive study, and their enormous information has been accumulated.

The optical excitation process itself is also a fundamental ultrafast process, which describes the time evolution of how excited atoms and atomic polarization are created, grow, and approach to steady states. This is of fundamental importance from the viewpoints of both the physics of extremely short time region and the basis for ultrafast opto-electronic devices. Nevertheless, this problem has hitherto been not the subject of thorough investigation, and has been left in a blackbox in most textbooks and articles of related fields.

It is sometimes mentioned that the absorption of light occurs in an extremely short time of the order of or less than 1 femtosecond, but its basis is not entirely clear. In some cases, the use of uncertainty principle is of help to understand the problem to some extent. However, this type of discussion will not be satisfactory because of the complexity of the problem. In order to get the correct results of the problem, careful analysis of the fundamental equation is indispensable.

The purpose of the present paper is to provide a solution of the above problem by the following approach. First, a simple but general model of materials and light is assumed. Then, basic quantum mechanical equations representing their interaction are solved as rigorously as possible without using weak
field and rotating wave approximations, and the transient responses of materials to the applied field are obtained under a wide variety of conditions. Special attentions are payed on the rapidity of the material response. So, several kinds of response times are defined, and their dependencies on physical parameters governing the optical process are investigated. The analysis is mainly made numerically by means of computer simulation with plenty of graphical results.

2. Model of the Optical Process

In order to make the problem in a concrete form, we must first consider the model or approximations for both the material and the light field contributing to the optical excitation process.

As a general model of materials we adopt the two-level atomic system with inhomogeneous broadening and relaxation, which is simple but sufficient in the first step because it includes all the effects essential to the problem. Here, the word “atom” is used to represent all kinds of microscopic particles including atoms, molecules, ions, electrons, and so on.

The inhomogeneous broadening means in general the distribution of transition frequencies and can manifest to some extent the features of continuously distributed multi-energy-level structures. The relaxation effects are represented here in terms of two kinds of constant, the longitudinal and transverse relaxation rates. This approximation will become invalid in the extremely short time scale of the order of optical period due to the appearance of non-Markovian effect. Nevertheless, this simple relaxation model will serve to understand the relaxation effects in our problem in a conceptual way.

A classical light field with a single frequency $\nu$ is considered here. The quantum effect of light appears generally only for very weak field of one-photon level or in the fluctuation properties of light. In order to obtain the exact transient response of materials, the optical electric field with a step function envelope of the form

$$E(t) = \begin{cases} E_0 \cos (2\pi \nu t + \phi) & (t \geq 0) \\ 0 & (t < 0) \end{cases}$$

is assumed. Only the time dependence of the field has been incorporated, because the wave propagation effect is not considered here. This optical field interacts with the above-described two-level atomic system through the electric dipole interaction. We take the macroscopic polarization $P$ and the excited state population (or probability $\rho_e$) as physical quantities representing the material response. The problem to be solved is to find the time dependences of $P$ and $\rho_e$ for the initial condition that at the time $t = 0$ all atoms are in the ground state, and to examine their behaviors as functions of the light frequency, the transition frequency, the inhomogeneous width, the Rabi frequency, and the two kinds of relaxation rates.

3. Basic Equations

The dynamical behavior of the two-level atomic system interacting with the light field is described by the density matrix equation of motion of the form

$$\frac{\partial \rho_{D}}{\partial t} = -\frac{4\pi i}{\hbar} (H_{ab}\rho_{ab} - \rho_{ab}H_{ab}) - \gamma_l (\rho_D - \rho_{D}^0)$$

$$\frac{\partial \rho_{bb}}{\partial t} = -\frac{2\pi i}{\hbar} H_{bb}\rho_{bb} - (\gamma_l + 2\pi i \nu_b)\rho_{bb},$$

where the suffices $a$ and $b$ denote the lower and upper levels, $\nu_b$ is the transition frequency, $\rho_D = \rho_{aa} - \rho_{bb}$, $\rho_D^0$ is the equilibrium value of $\rho_D$, and $\gamma_l$ and $\gamma_l$ are the longitudinal and transverse relaxation rates, respectively. The matrix elements of the interaction Hamiltonian are given by

$$H_{ab} = H_{ab}^* = -\mu E(t)$$

where $E(t)$ is given by Eq. (1), $\mu = \mu_{ba} = \mu_{bb}^*$ is the electric dipole matrix element, and we assumed $\mu_{aa} = \mu_{bb} = 0$.

Now, we transform the density matrix $\rho$ to the Bloch vector $(u, v, w)$ defined by the relation

$$\rho_{ab} = \frac{1}{2} (u + iv) \exp [-i(2\pi \nu t + \phi)]$$

$$\rho_{bb} = w$$

Then, the density matrix equations of motion are transformed to the equations

$$\frac{du}{dt} = -2\pi \nu_b w \sin (4\pi \nu t + 2\phi) + 2\pi (\nu_b - \nu) v - \gamma_l u$$

$$\frac{dv}{dt} = 2\pi \nu_b w [1 + \cos (4\pi \nu t + 2\phi)] - 2\pi (\nu_b - \nu) u - \gamma_l v$$
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\[ \frac{dw}{dt} = 2\pi \nu_k \left[ u \sin(4\pi \nu t + 2\phi) - v \left[ 1 + \cos(4\pi \nu t + 2\phi) \right] \right] - \gamma \left( w - w_0 \right), \tag{9} \]

where \( \nu_k = \mu E_0 / h \) is the Rabi frequency (not angular), and \( w_0 = \rho_{bb}^{(0)} \). In the rotating wave approximation, the sin and cos terms in Eqs. (7)-(9) are dropped, but here we retain them to investigate their effect.

In terms of \( u, v, w \), the atomic polarization \( p \) and the upper level probability \( \rho_{bb} \) are given by

\[ p(t, \nu_0) = \mu \left\{ u \cos(2\pi \nu t + \phi) + v \sin(2\pi \nu t + \phi) \right\}, \tag{10} \]

\[ \rho_{bb}(t, \nu_0) = \frac{1}{2} \left( 1 - w \right). \tag{11} \]

The macroscopic polarization \( P \) and the upper level population \( N_b \) are derived from Eqs. (10) and (11) incorporating the inhomogeneous broadening as

\[ P(t) = N \int_0^\infty p(t, \nu_0) g(\nu_0) d\nu_0, \tag{12} \]

\[ N_b(t) = N \int_0^\infty \rho_{bb}(t, \nu_0) g(\nu_0) d\nu_0, \tag{13} \]

where \( N \) is the atomic number density, and \( g(\nu_0) \) is the distribution function characterizing the inhomogeneous broadening with the normalization condition

\[ \int_0^\infty g(\nu_0) d\nu_0 = 1. \tag{14} \]

In the later calculation a Gaussian distribution function with the center frequency \( \nu_c \) and the band width \( \nu_b \) of the form

\[ g(\nu_0) = \frac{1}{\nu_b \sqrt{4\ln 2}} \exp \left\{ -4\ln 2 \left( \frac{\nu_0 - \nu_c}{\nu_b} \right)^2 \right\} \tag{15} \]

will be used. The probability of finding a specific atom in any of the distributed upper levels is given by the quantity

\[ \rho_s = N_b(t) / N, \tag{16} \]

which we call here the excited state probability.

Analytical solutions of Eqs. (7)-(9) could be obtained under some limited conditions such as rotating wave or weak field approximation with homogeneous or extremely inhomogeneous broadening\(^7,8\). Most of the solutions are, however, obtained here by a numerical analysis in order to examine more general cases. The graphical representation directly given from the numerical analysis is quite useful for understanding the problem even when analytical solutions are possible. The numerical analysis can be carried out conveniently by introducing the dimensionless variables and parameters as

\[ T = \nu t, C = \nu_c / \nu, B = \nu_b / \nu, R = \nu_k / \nu, \]

\[ G_L = \gamma_L / \nu, G_T = \gamma_T / \nu, \tag{17} \]

In terms of these quantities, all the basic equations are easily transformed to dimensionless forms.

4. Results of Calculation

The results of numerical calculations are categorized into three groups, and are shown respectively in Fig. 1, Fig. 2 and Fig. 3. In each figure the time evolutions of both the polarization \( P \) and the excited state probability \( \rho_s \) are simultaneously shown for several typical cases. The ordinate of each figure has been normalized to its maximum value in the displayed range, and so the absolute values of \( P \) and \( \rho_s \) are not explicitly indicated. It is seen in all figures that both \( P \) and \( \rho_s \) approach to some steady states after their transient variations. Each figure involves in general two kinds of time variations, i.e., oscillatory behavior and monotonic rise or decay.

Fig. 1 shows the results when the light frequency is exactly resonant to the central frequency of a homogeneously broadened transition. It should be noted that both \( P \) and \( \rho_s \) exhibit entirely different features depending on the relative magnitudes of \( \nu_k \), \( \gamma_L \) and \( \gamma_T \). In the case (a) the periods of oscillation are \((2\nu_b)^{-1} \) and \( \nu_c^{-1} \) for \( P \) and \( \rho_s \), respectively, in the transient regime, while their decay times are governed by \( \gamma_T^{-1} \). In the case (b) the period of oscillation in \( P \) is \( \nu_c^{-1} \), and its rise and decay times are governed by \( \gamma_T^{-1} \) and \( \nu_b^{-1} \), respectively, and the rise time in \( \rho_s \) by \( \nu_c^{-1} \). In the case (c) the periods of oscillation in \( P \) and \( \rho_s \) are \( \nu_c^{-1} \) and \( (2\nu)^{-1} \), and their rise times are governed by \( \gamma_T^{-1} \) and \( \gamma_L^{-1} \), respectively.

Fig. 2 shows the results when the light frequency is far off-resonant to a homogeneously broadened transition. In this situation the period of the oscillatory variation is the inverse off-resonance frequency \( \Delta^{-1} \) \((\Delta = \nu_c - \nu)\) in the transient regime for both \( P \) and

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Fig. 1  Time dependences of the polarization $P$ and the excited state probability, $\rho_e$ when the light frequency is resonant to a homogeneously broadened transition ($\nu_R = 0$, $\Delta = \nu_c - \nu = 0$, $\phi = 0$)

(a) $v_R \gg \gamma_T, \gamma_L$  
\[ \gamma_L / \nu = 0.2, \quad \gamma_T / \nu = 0.03 \]

(b) $\gamma_T \gg v_R \gg \gamma_L$  
\[ \gamma_R / \nu = 0.01, \quad \gamma_L / \nu = 0, \quad \gamma_T / \nu = 0.2 \]

(c) $\gamma_T, \gamma_L \gg v_R$  
\[ \gamma_R / \nu = 0.005, \quad \gamma_L / \nu = \gamma_T / \nu = 0.2 \]
FIG. 2 Time dependences of the polarization $P$ and the excited state probability $\rho_e$ when the light frequency is far off-resonant to a homogeneously broadened transition ($v_0 = 0$, $\Delta \gg \gamma_k, \gamma_L, \gamma_T$, $\phi = 0$)

(a) $\gamma_k \gg \gamma_T \approx \gamma_L$ ($v_k / \nu = 0.2$, $\gamma_L / \nu = \gamma_T / \nu = 0.05$, $\Delta / \nu = 0.5$)

(b) $\gamma_T \approx \gamma_L \gg \gamma_k$ ($v_k / \nu = 0.03$, $\gamma_L / \nu = \gamma_T / \nu = 0.1$, $\Delta / \nu = 0.5$)

(c) $\gamma_T \gg \gamma_L \gg \gamma_k$ ($v_k / \nu = 0.002$, $\gamma_L / \nu = 0.02$, $\gamma_T / \nu = 0.1$, $\Delta / \nu = 0.5$)
Fig. 3 Time dependences of the polarization $P$ and the excited state probability $P_e$ for an inhomogeneously broadened transition

(a) $\Delta = 0, \gamma_k \gg \gamma_T, \gamma_L$  
($\nu_k / \nu = 0.05, \gamma_L / \nu = \gamma_T / \nu = 0, \nu_b / \nu = 0.3$)

(b) $\Delta = 0, \gamma_T \approx \gamma_L \gg \nu_k$  
($\nu_k / \nu = 0.001, \gamma_L / \nu = \gamma_T / \nu = 0.03, \nu_b / \nu = 0.2$)

(c) $\Delta / \nu = 0.5$  
($\nu_k / \nu = 0.001, \gamma_L / \nu = \gamma_T / \nu = 0, \nu_b / \nu = 0.1$)
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(I)

\[ P \text{ (polarization)} \]

(II)

\[ \rho_e \text{ (excited state probability)} \]

Fig. 4 Comparison of the solutions with (I) and without (II) the rotating wave approximation for a homogeneously broadened transition.

(a) far off-resonant ($\Delta / \nu = 0.5$),
(b) resonant ($\Delta = 0$),

\[ \gamma_r / \nu = 0.03, \quad \gamma_i / \nu = \gamma_r / \nu = 0.1 \]
\[ \gamma_r / \nu = 0.005, \quad \gamma_i / \nu = \gamma_r / \nu = 0.2 \]
$\rho_s$, but in the steady state regime it becomes $v^{-1}$
for $P$ and $(2v)^{-1}$ for $\rho_s$. The decay time of
their envelope in the cases (a) and (b) is governed by
$\gamma_T^{-1}$
and in the case (c) the decay time of $P$ and
and the rise time of $\rho_s$ are governed by $\gamma_T^{-1}$ and $\gamma_L^{-1}$,
respectively. It is to be noted that even under
the conditions of far off-resonant excitation, the relaxation
processes affect remarkably the transient material
response.

Fig. 3 shows the results for more complicated
situations where both the wide inhomogeneous broadenings and
the relaxation effects are involved. There the results for both the resonant
((a) and (b))
and far off-resonant ((c)) excitations have been shown.
In the case (a), the periodic variations of $\rho_s$ and the
envelope of $P$ and their decay times are all governed
by $v_R^{-1}$ irrespective of $v_b$. In the case (b) the rise
time of $P$ is governed by $v_B^{-1}$, while that of $\rho_s$ by
$\gamma_L^{-1} \approx \gamma_T^{-1}$. The behavior of the case (c) is similar to
Fig. 2 (b) except that the transient decay times are
governed by $v_B^{-1}$ rather than by $\gamma_T^{-1} \approx \gamma_L^{-1}$.

In Fig. 4 two kinds of results of calculation with
and without the rotating wave approximation are
compared for typical cases of resonant and far off-
resonant excitation. It is seen that the differences
between the two solutions are little (too small to be
indicated graphically) in the polarization $P$, while
appreciable differences appear in the excited state
probability $\rho_s$ for both the resonant and far off-resonant
conditions and for both the transient and steady state
regimes.

5. Consideration on Response Times

The individual transient behavior presented in
Sec. 4 cannot be described in terms of a few
physical parameters due to its complexity. However,
from the inspection of the results, one would find that
in general two kinds of response times can be defined
in each case and that they can be a measure to
represent the rapidity of the material response. These
are : (1) $\tau_w$ = the elapse time when the material response
reaches the maximum or its specific fractional value,
and (2) $\tau_r$ = the time constant with which the material
response approaches to some steady state.

For both the polarization and the excited state
probability, $\tau_w$ and $\tau_r$ can be determined individually,
and therefore, we find generally four kinds of response
times denoted by $\tau_{wp}$, $\tau_{wr}$, $\tau_{qs}$, $\tau_{qs}$, where the suffices
$p$ and $q$ correspond to the polarization and the excited
state probability, respectively.

From the results of Sec. 4, the response times thus
defined are found to be strongly dependent on the
relative magnitudes of the Rabi frequency $v_R$, the

| Table 1 Physical parameters governing the four kinds of response times |

<table>
<thead>
<tr>
<th>Material response</th>
<th>Polarization</th>
<th>Excited state probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response times</td>
<td>$\tau_{wm}$</td>
<td>$\tau_{wp}$</td>
</tr>
<tr>
<td>(i) $v_R \gg \gamma_T, \gamma_L$</td>
<td>$(4v_R)^{-1}$</td>
<td>$\sim \gamma_T^{-1}$</td>
</tr>
<tr>
<td>(ii) $\gamma_T \gg v_R \gg \gamma_L$</td>
<td>$\sim \gamma_T^{-1}$</td>
<td>$\sim v_R^{-1}$</td>
</tr>
<tr>
<td>(iii) $\gamma_T \gg v_R \gg \gamma_L$</td>
<td>$\sim \gamma_T^{-1}$</td>
<td>$\sim v_R^{-1}$</td>
</tr>
<tr>
<td>(iv) $\gamma_T \gg \gamma_L$</td>
<td>$(2\Delta)^{-1}$</td>
<td>$\gamma_T^{-1}$</td>
</tr>
</tbody>
</table>

$\Delta = 0$, homogeneous broadening ($v_R = 0$)
resonant ($\Delta = 0$), inhomogeneous broadening ($v_R \gg v_R, \gamma_T, \gamma_L$)
far off-resonant, homogeneous broadening ($v_R = 0$)
far off-resonant, inhomogeneous broadening ($v_R \gg v_R, \gamma_T, \gamma_L$)
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off-resonance frequency $\Delta$, the bandwidth $\nu_b$, the longitudinal and transverse relaxation rates $\gamma_L$ and $\gamma_T$, and to be respectively governed by one of these parameters. The results for a number of typical cases covering wide conditions are summarized in Table I.

Next, we estimate the numerical values of the response times, whose distribution is determined by that of the parameters, $T_1 = \nu_L^{-1}$ and $T_2 = \nu_T^{-1}$ (longitudinal and transverse relaxation times), $\nu_R^{-1}$ (Rabi flopping period), $\nu_B^{-1}$ and $\nu_f^{-1}$.

The values of $T_1$ and $T_2$ are known to distribute over a wide range from a few femtosecond to above milliseconds depending on materials and transitions. The value of $\nu_L^{-1}$ is governed by the light intensity $I$ and the dipole matrix element $\mu$. With typical values of $\mu = 1$ Debye and $I = 10^{-6} - 10^{12}$ W/cm$^2$, $\nu_R^{-1}$ amounts to $7 \times 10^{-5} - 10^{-14}$ s, which roughly overlaps to the range of the relaxation times. The values of $\Delta^{-1}$ and $\nu_B^{-1}$ can easily be found to be $t_o/F$, where $t_o = \nu_f^{-1}$ is the optical period, and $F$ is the ratio of $\Delta$ (or $\nu_B$) to $\nu$. They can have short values comparable to $t_o$ ($2 \text{ fs for } 0.6 \mu\text{m wavelength}$).

A conclusion of the above consideration is that the response times of materials cover a quite wide range, and not limited to a specific time region.

It is also possible to consider another kind of response time defined from entirely different point of view. Now, we define a response time $\tau_q$, during which at least one excited atom is created after the onset of optical excitation. The value of $\tau_q$ is determined from the relation $V N_0(\tau_q) = 1$ or $P_e(\tau_q) = (NV)^{-1}$, where $V$ is the volume of the material subject to the optical field, and is found to be much less than the values of $\tau_v$ and $\tau_{\nu}$ by several orders of magnitudes. For typical values of $NV = 10^9$, $\nu_L^{-1} = 10^{-9}$ s, $\nu_B^{-1} = 10^{-14}$ s, $\tau_q$ amounts to the order of $10^{-18} - 10^{-22}$ s. The extremely short nature of this kind of response time is, however, not peculiar to optical excitation processes, but can be found to be common in general physical processes consisting of statistical events. The same consideration and results, therefore, apply also to pure relaxation processes.

6. Summary and Conclusion

Ultrafast transient responses of materials to a stepwise optical field are analyzed in detail under a wide range of conditions by using the model of the inhomogeneously broadened two-level atomic system with relaxation. Apart from the details, the essential points of the results are summarized as follows.

1. The transient response shows a wide variety of dynamical behaviors both qualitatively and quantitatively, which are strongly dependent on the relative magnitudes of the light frequency, the center frequency and the bandwidth of material transition, the longitudinal and transverse relaxation rates, and the Rabi frequency. The description of the process in terms of response times requires their clear definitions of several kinds.

2. The material response times cover a wide range of value extending from femtosecond to above millisecond depending on various conditions. It is therefore not always true that optical absorption process is extremely fast being in the range of or below femtosecond. Some definition of response time leads to a value several orders below femtosecond, but this kind of result is not peculiar to optical excitation processes, but rather common to statistical processes.

3. Even under the far off-resonant condition, relaxation processes make an important contribution to the transient behavior. This result will also call a revision of the common sense or generally accepted idea in this field. This is regarded as one of the manifestations of an important fact that the real excitation is always present even for the applied optical field with any degree of off-resonant frequencies.

4. The difference between the two kinds of calculated results with and without the rotating wave approximation is little in the polarization, but is prominent in the excited state probability for both resonant and non-resonant conditions.

The present paper offered the results for an idealized situation to clarify the basic concept. Further problems are left to be studied for the application to more realistic or extended situations. Among these are: (1) extension to more complicated energy level structures, (2) non–Markovian relaxation effect, (3) effects of coherence properties and quantum nature of light, (4) extension to multi-photon and multi-wave optical processes, and so on. These problems are to be investigated individually in detail.
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