Equations for nonlinear spectroscopy of solids

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A system of equations for the total density matrix of a solid solution is used in the dynamic approach framework to derive approximate equations, which are generalizations of the optical Bloch equations. In contrast to the latter, the new equations contain functions of real absorption bands I^g and real fluorescence bands I^e of impurity centers. Therefore, as the intensity of the exciting light approaches zero the new equations yield all the results of linear spectroscopy of impurity centers, including those that do not follow from the optical Bloch equations. The approximations under which the new equations reduce to the optical Bloch equations are found. The new equations can be applied also to amorphous media where additional tunnel degrees of freedom are important.

1. INTRODUCTION

It is known that the total density matrix of a system can provide a comprehensive description even of such a complex entity as a solid solution. However, we then have to deal with an infinite series of coupled equations for the elements of the total density matrix, which cannot be solved without simplifications. The optical Bloch equations, used widely in discussing various effects in nonlinear optics and spectroscopy of solids,[1-3] are such simplified equations.

However, in the spectroscopy of solid solutions one meets also situations where not everything can be explained on the basis of the optical Bloch equations. For example, it follows from the Bloch equations that a dip in the population of the ground state of atoms exposed to illumination has the Lorentzian profile. This result reflects the circumstance that in the derivation of the Bloch equations it is assumed that the profile of a homogeneous line representing the absorption of light by a two-level atom is Lorentzian. However, we know from experiments that the profile of a real band of an impurity center is much more complex: it consists of a zero-phonon line (ZPL) and an associated phonon wing, which is reflected also in the dip profile. The phonon wing can have a complex structure with very sharp peaks. Even the ZPL, which has the Lorentzian profile near the resonance frequency ω_{10}, exhibits non-Lorentzian wings[4] already at two or three homogeneous half-widths from ω_{10}. When the temperature is increased, the intensity is transferred from the ZPL to the phonon wing. The absorption (I^g) and fluorescence (I^e) bands of an impurity center are nonresonant and can have any profile.

All these observations can be described satisfactorily by a theory of optical band profiles put forward in Refs. 5 and 6. However, these linear-spectroscopy phenomena do not follow from the optical Bloch equations. The equations for nonlinear spectroscopy do not reduce to the results of linear spectroscopy. This conflict can be removed only on the basis of equations more general than the optical Bloch equations. When deriving the new equations from an infinitely dimensional system for elements of the total density matrix we must bear in mind the functions representing real absorption (I^g) and fluorescence (I^e) bands of solid solutions. Such equations are derived for the first time in the present paper.

The central problem in the derivation of the required equations is a selection of the approach needed to allow for the electron–phonon interaction. This interaction can be included either stochastically or dynamically. In the stochastic approach the optical line profile is governed by various "jumps" of the resonance frequency. This approach is unacceptable in tackling the problem formulated above, because it cannot account for any of the above-mentioned observations from linear spectroscopy of solids. Clearly, this serious shortcoming of the classic approach is not fully understood because it has so far been used widely in calculations of phase relaxations in solids, as is done—for example—in Ref. 7 and in the papers cited there. In the dynamic approach a resonance frequency is modulated by harmonic vibrations of an impurity and of its immediate environment, i.e., it is governed by the local dynamics of an impurity center. This is exactly the approach that has been used earlier to obtain all the above-mentioned results of linear spectroscopy. Therefore, we shall begin with the dynamic approach in the present paper.

Our aim will be to find for nonlinear spectroscopy equations which would contain functions of the real absorption I^g, and fluorescence I^e bands of an impurity center. In Secs. 2 and 3 such a system is derived from the system of equations for the total density matrix. In Sec. 4 the new equations are used to consider the profile of the dips. It is shown that these new equations yield a dip with a complex profile consisting of a zero-phonon part and a phonon wing, in agreement with the experimental results. The approximation which reduces the new equations to the optical Bloch equations is identified in Sec. 5.

2. EQUATIONS FOR ELEMENTS OF THE DENSITY MATRIX

Electronically excited states of impurity centers exhibit relaxation of two types, phase and energy, with times T_2 and T_1. Phase relaxation is the result of the electron–phonon interaction, whereas energy relaxation of fluorescing centers is due to spontaneous radiative transitions. The total Hamiltonian of the system should be selected so that both relaxation mechanisms are manifested in the system in question. This condition is satisfied by the following Hamiltonian of the system:

$$H=H_0+\hat{\Lambda}=[E+V(\mathbf{R})]B^+B+H^g(\mathbf{R})+H_\perp+\hat{\Lambda}. \qquad (1)$$

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Here, B^+ and B are the creation and annihilation operators of an electron excitation of energy E in an impurity center; $H^g(\mathbf{R})$ and $H^e(\mathbf{R}) = H^g(\mathbf{R}) + V(\mathbf{R})$ are the phonon Hamiltonians in the ground (g) and excited (e) electron states; $H_\perp$ is the Hamiltonian of the transverse electromagnetic field; $\hat{\Lambda}$ is the operator representing the interaction of electrons with photons. The electron–phonon interaction $V(\mathbf{R})$ is the difference between multidimensional Franck–Condon potential surfaces:

$$V(\mathbf{R})=(\mathbf{R}+\mathbf{a})\frac{U^e}{2}(\mathbf{R}+\mathbf{a})-\mathbf{R}\frac{U^g}{2}\mathbf{R}=\mathbf{a}\frac{U^e}{2}\mathbf{a}+\mathbf{a}U^e\mathbf{R}+\mathbf{R}\frac{W}{2}\mathbf{R}. \tag{2}$$

In the harmonic approximation this interaction is a quadratic form of the phonon coordinates $\mathbf{R}$. It is characterized by parameters of two types: $\mathbf{a}$ is a multidimensional vector representing displacements of equilibrium positions and $W = U^e - U^g$ is the difference between the force matrices of a crystal containing excited and unexcited impurities.

The eigenfunctions of the individual terms in Eq. (1) are found from the following equations:

$$B^+B|0\rangle=0,\quad B^+B|1\rangle=|1\rangle,\quad H_\perp|\mathbf{v}\rangle=\boldsymbol{\omega}\mathbf{v}|\mathbf{v}\rangle,$$
$$H^g(\mathbf{R})|\boldsymbol{\alpha}\rangle=\mathbf{v}^g\boldsymbol{\alpha}|\boldsymbol{\alpha}\rangle,\quad H^e(\mathbf{R})|\boldsymbol{\beta}\rangle=\mathbf{v}^e\boldsymbol{\beta}|\boldsymbol{\beta}\rangle. \tag{3}$$

Here, $|\mathbf{v}\rangle$, $|\boldsymbol{\alpha}\rangle$ and $|\boldsymbol{\beta}\rangle$ are products of oscillator functions. The components of multidimensional vectors $\boldsymbol{\omega}$, $\mathbf{v}^g$, $\mathbf{v}^e$ and $\mathbf{v}$, $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ are the frequencies and quantum numbers of normal oscillator modes. Since harmonic vibrations of the crystal lattice in different electron states are not orthogonal to one another, it follows that the multidimensional Franck–Condon integrals are nonorthogonal:

$$\langle\alpha|\beta\rangle=\langle\beta|\alpha\rangle\neq\delta_{\alpha\beta}.$$

In order to simplify the problem for the reader we shall "exclude" spontaneous radiative transitions from consideration in the present section and we shall assume that $H_\perp$ contains only one laser mode of frequency ω_b with the number of photons v_b. The eigenfunctions of the Hamiltonian H_0 in Eq. (1) are then

$$|\alpha\rangle\rangle=|0\rangle|v_b\rangle\boldsymbol{\alpha}\rangle,\quad |\beta\rangle\rangle=|1\rangle v_b'\rangle|\beta\rangle.$$

We shall retain in the operator $\hat{\Lambda}$ only the terms conserving the total number of excitations. Then the product of the functions $|0\rangle|\nu_b\rangle|\alpha\rangle$ may go over only to a similar product under the action of the operator $\hat{\Lambda}$: $|1\rangle|v_b - 1|\rangle|\beta\rangle$. Bearing this point in mind, we find that the system of equations for the density matrix considered in the basis of the functions $|\alpha\gg$ and $|\beta\gg$ is

$$\begin{aligned}
\dot{\rho}_{\alpha\alpha}&=-i\sum_{\beta}(\Lambda_{\alpha\beta}\rho_{\beta\alpha}-\rho_{\alpha\beta}\Lambda_{\beta\alpha}),\\
\dot{\rho}_{\beta\alpha}&=-i\omega_{\beta\alpha}\rho_{\beta\alpha}-i\Lambda_{\beta\alpha}(\rho_{\alpha\alpha}-\rho_{\beta\beta})+\ldots,\\
\dot{\rho}_{\alpha\beta}&=-i\omega_{\alpha\beta}\rho_{\alpha\beta}-i\Lambda_{\alpha\beta}(\rho_{\beta\beta}-\rho_{\alpha\alpha})+\ldots,\\
\dot{\rho}_{\beta\beta}&=-i\sum_{\alpha}(\Lambda_{\beta\alpha}\rho_{\alpha\beta}-\rho_{\beta\alpha}\Lambda_{\alpha\beta}),
\end{aligned} \tag{5}$$

where

$$\omega_{\beta\alpha}=\omega_{10}+\mathbf{v}^e\boldsymbol{\beta}-\omega_b-\mathbf{v}^g\boldsymbol{\alpha}=-\omega_{\alpha\beta},\quad \Lambda_{\alpha\beta}=-i\Lambda\langle\alpha|\beta\rangle=\Lambda_{\beta\alpha}^*,$$
$$\Lambda=\omega_{10}(4\pi/\hbar\omega_bV)^{1/2}v_b^{1/2}\mathbf{de}_b. \tag{6}$$

Here, $\omega_{10} = E/\hbar$ and $\mathbf{d}$ are the frequency and dipole moment of an electron transition; $\boldsymbol{\omega}_b$, v_b, and $\mathbf{e}_b$ are the frequency of laser functions, their number, and polarization vector; V is the volume occupied by the radiation.

In the system of equations (5) the elements $\rho_{\alpha\alpha'}$ and $\rho_{\beta\beta'}$ do not appear explicitly nor do the equations for these elements. These elements are diagonal in the electron indices, but nondiagonal in the phonon indices. Obviously, relaxation of such elements with time is governed by the anharmonicity. It is responsible not only for energy relaxation in the phonon subsystem, but also for phase relaxation in the same subsystem. Bearing in mind that phase relaxation in the phonon subsystem is faster than in the electron subsystem, we can assume in Eq. (5) that

$$\rho_{\alpha\alpha'}=\rho_{\beta\beta'}=0. \tag{7}$$

In this approximation, which underlies also the Bloch equations, we can ignore all the terms not shown explicitly in Eq. (5).

3. ALLOWANCE FOR SPONTANEOUS RADIATIVE TRANSITIONS

We shall now allow for the fact that $H_\perp$ contains an infinite sum of modes of the transverse electromagnetic field. Then, in the functions $|\alpha\gg$ and $|\beta\gg$ we must show additionally how many phonons of a nonlaser mode with a wave vector $\mathbf{k}$ is contained in each state. We shall introduce the following brief notation for the eigenfunctions of the Hamiltonian H_0:

$$\begin{aligned}
&|0\rangle|v_b\rangle|\alpha\rangle=\left|\begin{matrix}0\\ \alpha\end{matrix}\right\rangle,\qquad |1\rangle|v_b-1\rangle|\beta\rangle=\left|\begin{matrix}0\\ \beta\end{matrix}\right\rangle,\\
&|0\rangle|v_b-1\rangle|1_{\mathbf{k}}\rangle|\alpha\rangle=\left|\begin{matrix}\mathbf{k}\\ \alpha\end{matrix}\right\rangle,\qquad |1\rangle|v_b-2\rangle|1_{\mathbf{k}}\rangle|\beta\rangle=\left|\begin{matrix}\mathbf{k}\\ \beta\end{matrix}\right\rangle,\\
&|0\rangle|v_b-2\rangle|1_{\mathbf{k}}1_{\mathbf{k}'}\rangle|\alpha\rangle\left|\begin{matrix}\mathbf{kk}'\\ \alpha\end{matrix}\right\rangle,\\
&|1\rangle|v_b-3\rangle|1_{\mathbf{k}}1_{\mathbf{k}'}\rangle|\beta\rangle=\left|\begin{matrix}\mathbf{kk}'\\ \beta\end{matrix}\right\rangle,
\end{aligned} \tag{8}$$

We shall be interested only in elements of the total density matrix reduced in respect of the indices of the spontaneously emitted photons:

$$\begin{aligned}
\rho_{\alpha\alpha}&=\rho_{\alpha\alpha}^{00}+\sum_{\mathbf{k}}\rho_{\alpha\alpha}^{\mathbf{kk}}+\frac{1}{2!}\sum_{\mathbf{kk}'}\rho^{\mathbf{kk}'}_{\alpha}{}^{\mathbf{kk}'}_{\alpha}+\ldots,\\
\rho_{\beta\beta}&=\rho_{\beta\beta}^{00}+\sum_{\mathbf{k}}\rho_{\beta\beta}^{\mathbf{kk}}+\frac{1}{2!}\sum_{\mathbf{kk}'}\rho^{\mathbf{kk}'}_{\beta}{}^{\mathbf{kk}'}_{\beta}+\ldots,\\
\rho_{\beta\alpha}&=\rho_{\beta\alpha}^{00}+\sum_{\mathbf{k}}\rho_{\beta\alpha}^{\mathbf{kk}}+\frac{1}{2!}\sum_{\mathbf{kk}'}\rho^{\mathbf{kk}'}_{\beta}{}^{\mathbf{kk}'}_{\alpha}+\ldots,\\
\rho_{\alpha\beta}&=\rho_{\alpha\beta}^{00}+\sum_{\mathbf{k}}\rho_{\alpha\beta}^{\mathbf{kk}}+\frac{1}{2!}\sum_{\mathbf{kk}'}\rho^{\mathbf{kk}'}_{\alpha}{}^{\mathbf{kk}'}_{\beta}+\ldots
\end{aligned} \tag{9}$$

For each element of the matrix that occurs in the infinite sums of Eq. (9) we can obtain its own equation. For example,

$$\dot{\rho}_{\alpha\alpha}^{00}=-i\sum_{\beta}(\Lambda_{\alpha\beta}\rho_{\beta\alpha}^{00}-\rho_{\alpha\beta}^{00}\Lambda_{\beta\alpha}),$$

$$\dot{\rho}_{\alpha\alpha}^{\mathbf{kk}}=-i\sum_{\beta}(\Lambda_{\alpha\beta}\rho_{\beta\alpha}^{\mathbf{kk}}-\rho_{\alpha\beta}^{\mathbf{kk}}\Lambda_{\beta\alpha})-i\sum_{\beta}(\lambda_{\alpha\beta}^{\mathbf{k}}\rho_{\beta\alpha}^{0\mathbf{k}}-\rho_{\alpha\beta}^{\mathbf{k}0}\lambda_{\beta\alpha}^{\mathbf{k}}),\tag{10}$$

In the above equations there is a matrix element $\lambda_{\alpha\beta}^{\mathbf{k}}=-i\lambda_{\mathbf{k}}\langle\alpha|\beta\rangle$ in which $\lambda_{\mathbf{k}}$ is defined by the expression for Λ subject to the substitutions $\omega_b\to\omega_{\mathbf{k}}$, $v_b\to 1$ and $\mathbf{e}_b\to\mathbf{e}_{\mathbf{k}}$. Infinite chains of coupled equations of the type given by Eq. (10) can be split only approximately. These approximations undoubtedly underlie the optical Bloch equations which allow phenomenologically for the T_1 processes.

The required approximations are easiest to find by an analysis not of the system of equations for the density matrix, but of the system of equations for the amplitudes of the probability of a transition from a state m_0 to a state m:

$$G_m(t)=-i\langle m|\exp(-itH/\hbar)|m_0\rangle,\tag{11}$$

which satisfy the following system of equations

$$\dot{G}_m(t)=-i\omega_m G_m(t)-i\sum_{l}\frac{\Lambda_{ml}}{\hbar}G_l(t).\tag{12}$$

Here, $|m\rangle$ and $\hbar\omega_m$ are the eigenfunctions and the eigenvalues of the operator H_0 in Eq. (1). Since the sums of Eq. (19) and the equations of Eq. (10) contain elements of the total (unreduced) density matrix of a system with a Hamiltonian H, it follows that each element of such a matrix can be represented by a product of amplitudes. For example, we find that

$$\rho_{\beta\ \alpha}^{\mathbf{k}\ \mathbf{kk}'}(t)=G_{\beta}^{\mathbf{k}}(t)\,(\dot{G}^{*})_{\alpha}^{\mathbf{kk}'}(t).\tag{13}$$

The method of allowing for the T_1 processes which creates new equations and these in turn yield the optical Bloch equations can be based on the following four approximations.

a. The statistical weight of the states containing two or more photons in each nonlaser mode, is ignored, i.e., among—for example—two-photon states **k** and **k**′ no allowance is made for the states **k** = **k**′, etc.

b. It is assumed that the number v_b of photons in a laser mode is large and therefore the loss of photons from a laser mode can be ignored by assuming that

$$\Lambda:\Lambda':\Lambda'':\ldots=v_b^{1/2}:(v_b-1)^{1/2}:(v_b-2)^{1/2}:\ldots\approx 1:1:1:\ldots.\tag{14}$$

c. It is assumed that the divergences which appear in quantum electrodynamics in the ultraviolet range of wavelengths can be eliminated by renormalization of the charge and mass of an electron. Then the divergence can be ignored. We thus obtain the following equations

$$\sum_{\mathbf{k}}\lambda_{\beta\alpha}{}^{\mathbf{k}}G_{\alpha}{}^{\mathbf{k}}=-\frac{i}{2T_1}\langle\beta|\alpha\rangle\sum_{\beta'}\langle\alpha|\beta'\rangle G_{\beta'}{}^{0},$$

$$\sum_{\mathbf{k}}\lambda_{\beta\alpha}{}^{\mathbf{k}}G_{\alpha}^{\mathbf{kk}'}=-\frac{i}{2T_1}\langle\beta|\alpha\rangle\sum_{\beta'}\langle\alpha|\beta'\rangle G_{\beta'}{}^{\mathbf{k}'},\tag{15}$$

where

$$\frac{1}{T_1}=2\pi\sum_{\mathbf{k}}\lambda_{\mathbf{k}}{}^{2}\delta(\omega_{10}-\omega_{\mathbf{k}})=\frac{4}{3}\left(\frac{2\pi}{\lambda}\right)^{3}\frac{d^2}{\hbar}\tag{16}$$

is the probability of spontaneous emission of light by an excited electron level. Here, λ is the wavelength of light with the resonance frequency ω_{10}.

d. Since the ratio Λ/E, where $E=\hbar\omega_{10}$, is very small it follows that we can ignore also the sums

$$\sum_{\mathbf{k}}\lambda_{\beta\alpha}^{k}G_{\beta}{}^{\mathbf{k}}\approx-\frac{i}{2T_1}G_{\beta}{}^{0}\frac{\Lambda}{E},$$

$$\sum_{\mathbf{k}}\lambda_{\beta\alpha}^{\mathbf{k}}G_{\beta}^{\mathbf{kk}'}\approx-\frac{i}{2T_1}G_{\beta}{}^{\mathbf{k}'}\frac{\Lambda}{E},\ldots\tag{17}$$

The conditions (17) allow us to drop a number of elements from the density matrix, whereas the condition (15) and the approximation given by Eq. (7) permit replacement of some matrix elements with others. For example, we find that

$$\sum_{\mathbf{k}}\lambda_{\beta\alpha}^{\mathbf{k}}\rho_{\alpha\beta}^{\mathbf{k}0}=-i\langle\alpha|\beta\rangle\frac{\rho_{\beta\beta}^{00}}{2T_1}\langle\beta|\alpha\rangle.\tag{18}$$

The approximations **a–d** and Eq. (7) undoubtedly form the basis of the optical Bloch equations. Each of the approximations is well justified. This makes the optical Bloch equations very effective.

The approximations **c** and **d** make it possible to split a chain of equations for elements of the total matrix. If we then add up the split equations to form infinite sums of Eq. (9), we find that in the case of the sums $\rho_{\alpha\alpha}$, $\rho_{\beta\beta}$, $\rho_{\alpha\beta}$, $\rho_{\beta\alpha}$, which are elements of the reduced matrix, we obtain the following system of equations:

$$\begin{aligned}\dot{\rho}_{\alpha\alpha}&=-i\sum_{\beta}(\Lambda_{\alpha\beta}\rho_{\beta\alpha}-\rho_{\alpha\beta}\Lambda_{\beta\alpha})+\frac{1}{T_1}\sum_{\beta}\langle\alpha|\beta\rangle\rho_{\beta\beta}\langle\beta|\alpha\rangle,\\ \dot{\rho}_{\beta\alpha}&=-i(\omega_{\beta\alpha}-i/2T_1)\rho_{\beta\alpha}-i\Lambda_{\beta\alpha}(\rho_{\alpha\alpha}-\rho_{\beta\beta}),\\ \dot{\rho}_{\alpha\beta}&=i(\omega_{\beta\alpha}+i/2T_1)\rho_{\alpha\beta}+i\Lambda_{\alpha\beta}(\rho_{\alpha\alpha}-\rho_{\beta\beta}),\\ \dot{\rho}_{\beta\beta}&=-i\sum_{\alpha}(\Lambda_{\beta\alpha}\rho_{\alpha\beta}-\rho_{\beta\alpha}\Lambda_{\alpha\beta})-\frac{1}{T_1}\rho_{\beta\beta}.\end{aligned}\tag{19}$$

If $1/T_1\to 0$ the above system reduces to the system of equations (5). The system (19) allows us to consider nonlinear optical processes in solids allowing for the actual profiles of the optical absorption and fluorescence bands. This can be demonstrated by considering partially reduced "spectral" nondiagonal elements

$$\begin{aligned}\rho_{10}(\Omega,t)&=\pi\sum_{\alpha\beta}\langle\alpha|\beta\rangle\rho_{\beta\alpha}(t)\,\delta(\Omega-\omega_{\beta\alpha}),\\ \rho_{01}(\Omega,t)&=\pi\sum_{\alpha\beta}\langle\beta|\alpha\rangle\rho_{\alpha\beta}(t)\,\delta(\Omega-\omega_{\beta\alpha})\end{aligned}\tag{20}$$

and the completely reduced diagonal elements

$$\rho_{00}=\sum_{\alpha}\rho_{\alpha\alpha},\qquad \rho_{11}=\sum_{\beta}\rho_{\beta\beta}.\tag{21}$$

It follows from Eq. (21) that

$$\rho_{\alpha\alpha}=p_{\alpha}\rho_{00},\qquad \rho_{\beta\beta}=p_{\beta}\rho_{11}\qquad \text{и}\qquad \sum_{\alpha}p_{\alpha}=\sum_{\beta}p_{\beta}=1.$$

It is obvious that p_α and p_β are the probabilities of detection of a phonon state $|\alpha\rangle$ in the ground electron state and a phonon state $|\beta\rangle$ in an excited electron state. If phonons are regarded as being in equilibrium, then p_α and p_β are the Boltzmann probabilities. In the case of the elements

$\rho_{10}(\Omega,t)$, $\rho_{01}(\Omega,t)$, $\rho_{00}(t)$ and $\rho_{11}(t)$, we find that the system (19) readily yields the following system of equations:

$$\dot\rho_{10}(\Omega,t)=-i(\Omega-i/2T_1)\rho_{10}(\Omega,t)+\Lambda[I^g(\Omega)\rho_{00}(t)-I^e(\Omega)\rho_{11}(t)],$$
$$\dot\rho_{01}(\Omega,t)=i(\Omega+i/2T_1)\rho_{01}(\Omega,t)+\Lambda[I^g(\Omega)\rho_{00}(t)-I^e(\Omega)\rho_{11}(t)],$$
$$\dot\rho_{00}(t)=-\Lambda\int_{-\infty}^{\infty}\frac{d\Omega}{\pi}[\rho_{10}(\Omega,t)+\rho_{01}(\Omega,t)]+\frac{1}{T_1}\rho_{11}(t),$$
$$\dot\rho_{11}(t)=\Lambda\int_{-\infty}^{\infty}\frac{d\Omega}{\pi}[\rho_{10}(\Omega,t)+\rho_{01}(\Omega,t)]-\frac{1}{T_1}\rho_{11}(t),\tag{22}$$

where

$$I^g(\Omega)=\sum_{\alpha\beta}p_\alpha\langle\alpha|\beta\rangle^2\delta(\Omega-\omega_{\beta\alpha}),$$
$$I^e(\Omega)=\sum_{\alpha\beta}p_\beta\langle\alpha|\beta\rangle^2\delta(\Omega-\omega_{\beta\alpha}).\tag{23}$$

The quantities $I^g(0)$ and $I^e(0)$ are functions of the laser frequency ω_b. They describe real absorption and fluorescence bands of an impurity center.

The system of equations (22) is derived assuming that phonons, i.e., vibrations of atoms around their equilibrium positions, are the only lf excitations of the medium. In the case of amorphous bodies there are not only phonons but also lf excitations corresponding to tunnel transitions of atoms or groups of atoms with a change in the equilibrium position.[8] Therefore, real lf excitations of amorphous materials may be more complex than in crystals. However, if $\langle\alpha|\beta\rangle$ is understood to represent overlap integrals not of the oscillator functions, but of the function describing real lf excitations of the amorphous medium, then the system (22) can be applied also to amorphous media.

The functions $I^g(0)$ and $I^e(0)$ had been calculated on many previous occasions using the framework of a theory of optical band profiles both of crystals[5,6,9-11] and of amorphous media,[12-14] and the interaction with these lf excitations was considered without recourse to perturbation theory. The system of equations (22) allows us to identify how real absorption and fluorescence bands affect the dynamics of elements of the density matrix. This is the required system of equations. In contrast to the Bloch equations, the system (22) is infinite-dimensional. Nevertheless, this system can be easily solved rigorously as a result of the Laplace transformations. In contrast to the Bloch equations, the system (22) gives the correct result and this is true, for example, of the profiles of dips in the populations of atomic levels.

4. DIPS IN LEVEL POPULATIONS

As the simplest example of a practical application of the new system of equations (22) we consider the population dip that appears under steady-state excitation conditions. It follows from Eq. (22) that the total population does not change with time, because $\dot\rho_{00}+\dot\rho_{11}=0$. Under steady-state conditions we have $\dot\rho_{10}=\dot\rho_{01}=\dot\rho_{00}=\dot\rho_{11}=0$ and, therefore, Eq. (22) yields the following equations for the difference $w(\infty)=\rho_{00}(\infty)-\rho_{11}(\infty)$:

$$w\left\{1+2\Lambda^2T_1\int_{-\infty}^{\infty}\frac{d\Omega}{\pi}\frac{1/2T_1}{\Omega^2+(1/2T_1)^2}[I^g(\Omega)+I^e(\Omega)]\right\}$$
$$=1-2\Lambda^2T_1\int_{-\infty}^{\infty}\frac{d\Omega}{\pi}\frac{1/2T_1}{\Omega^2+(1/2T_1)^2}[I^g(\Omega)-I^e(\Omega)].\tag{24}$$

Here the integrals with respect to Ω represent convolutions of the optical band frequencies with a Lorentzian function of natural half-width $1/T_1$. The integration increases the half-width of each Lorentzian peak in an optical band by an amount $1/T_1$. If we allow for this factor, we can then represent Eq. (24) in the form

$$w(\infty)=\frac{1-2\Lambda^2T_1[I^g(0)-I^e(0)]}{1+2\Lambda^2T_1[I^g(0)+I^e(0)]}.\tag{25}$$

At low intensities we can simplify the treatment by including only the term linear in Λ^2 in Eq. (25). We obtain then for the ground-state population dip

$$1-\rho_{00}(\infty)=2\Lambda^2T_1I^g(0).\tag{26}$$

Since the absorption band $I^g(0)$ consists of a narrow zero-phonon line and an associated phonon wing, it follows that the dip contains all these elements, in agreement with the experimental results.[15,16] Equation (26) is the well known result from linear spectroscopy.

We shall now show that in the special case when an optical band consists only of a zero-phonon line with the Lorentzian profile, Eq. (25) gives the same results as the Bloch equations. It is shown in Refs. 5, 9, and 10 that the zero-phonon lines in the absorption and fluorescence spectra are resonant and broaden equally at all temperatures. We therefore have

$$I^g(0)=I^e(0)=e^{-f(T)}\frac{T_2^{-1}}{\Delta^2(T)+T_2^{-2}},\tag{27}$$

where

$$\Delta(T)=\omega_b-\omega_{10}-\delta(T),\tag{28}$$
$$1/T_2=\gamma(T)/2+1/2T_1.\tag{29}$$

Here, $\gamma(T)$ and $\delta(t)$ are the half-width and the shift of the zero-phonon line and are due to an electron–phonon interaction quadratic in **R**. The part of the interaction of Eq. (2), which is linear in R, determines primarily the magnitude of the Debye–Waller factor $\exp[-f(T)]$ and does not contribute to the broadening and shift of the zero-phonon line. Specific expressions for $\gamma(T)$ and $\delta(T)$ can be found in Refs. 5, 6, 9, and 10. Substituting Eq. (27) into Eq. (25), we obtain

$$w=\frac{\Delta^2+(1/T_2)^2}{\Delta^2+(1/T_2)^2\{1+4\Lambda^2\exp[-f(T)]T_1T_2\}}.\tag{30}$$

This is the familiar result from saturation spectroscopy. It follows from the optical Bloch equations.[1,17]

5. REDUCTION TO THE OPTICAL BLOCH EQUATIONS

We have seen in the preceding section that when a phonon wing is ignored in an optical band, Eq. (25) simplifies and becomes Eq. (30), which is the solution of the Bloch equations. We shall first demonstrate that if in the system of equations (22) the profile of an optical band is described by a Lorentzian, the actual system (22) reduces to the system of the optical Bloch equations.

Integrating the first term in the system (22) subject to the initial condition $\rho_{10}(\Omega,0)=0$, we find that

$$\rho_{10}(\Omega,t)=\Lambda\int_0^t d\tau\exp\left[-i\left(\Omega-\frac{i}{2T_1}\right)(t-\tau)\right]$$

$$\times[I^g(\Omega)\rho_{00}(\tau)-I^e(\Omega)\rho_{11}(\tau)]. \qquad (31)$$

Integrating Eq. (31) with respect to the frequency Ω and then assuming that the optical bands have the Lorentzian profiles, we obtain

$$I^g(\Omega)=\frac{\gamma(T)/2}{(\Omega-\Delta)^2+[\gamma(T)/2]^2}=I^e(\Omega). \qquad (32)$$

Bearing in mind that

$$\int_{-\infty}^{\infty}\frac{d\Omega}{\pi}\frac{\gamma(T)/2}{(\Omega-\Delta)^2+[\gamma(T)/2]^2}\exp\left[-i\left(\Omega-\frac{i}{2T_1}\right)(t-\tau)\right]$$

$$=\exp\left[-i\left(\Delta-\frac{i}{T_2}\right)(t-\tau)\right], \qquad (33)$$

where T_2 is defined by Eq. (29), we find that instead of Eq. (31), we now have the expression

$$\rho_{10}(t)=\int_{-\infty}^{\infty}\frac{d\Omega}{\pi}\rho_{10}(\Omega,t)$$

$$=\Lambda\int_0^t d\tau\exp\left[-i\left(\Delta-\frac{i}{T_2}\right)(t-\tau)\right][\rho_{00}(\tau)-\rho_{11}(\tau)]. \qquad (34)$$

Differentiating this equation with respect to time, we obtain a differential equation for $\rho_{10}(t)$:

$$\dot\rho_{10}(t)=-i(\Delta-i/T_2)\rho_{10}(t)+\Lambda[\rho_{00}(t)-\rho_{11}(t)]. \qquad (35)$$

The equation for $\rho_{01}(t)$ is obtained from Eq. (35) by the complex conjugation operation:

$$\dot\rho_{01}(t)=i(\Delta+i/T_2)\rho_{01}(t)+\Lambda[\rho_{00}(t)-\rho_{11}(t)]. \qquad (36)$$

Adding the last two equations from the system (22) to Eqs. (35) and (36) and introducing the Bloch-vector components

$$u=-i(\rho_{10}-\rho_{01}),\quad v=\rho_{10}+\rho_{01},\quad w=\rho_{00}-\rho_{11},$$

we readily obtain (from the four equations describing ρ_{10}, ρ_{01}, ρ_{00}, and ρ_{11}) the following three Bloch equations

$$\begin{aligned}\dot u&=-u/T_2-\Delta v,\\ \dot v&=-v/T_2+\Delta u+2\Lambda w,\\ \dot w&=-2\Lambda v+(1-w)/T_1.\end{aligned} \qquad (37)$$

The dephasing time T_2 is related to the half-width $\gamma(T)$ of the zero-phonon line by Eq. (29). An expression for $\gamma(T)$ which does not utilize the smallness of the quadratic electron–phonon interaction was obtained by the present author some twenty years ago.[18] Frequent attempts had been made subsequently to calculate by a microscopic approach the dephasing time T_2 directly from the optical Bloch equations.[2,3,19,20] These calculations resulted in breakdown of the relationship described by Eq. (29). An analysis of this discrepancy, carried out previously by two groups of authors,[21,22] showed that the discrepancy appeared because the methods used to calculate T_2 were less accurate than the method for calculation of $\gamma(T)$. This conclusion was confirmed in Ref. 22 by a comparison of various theoretical expressions for $\gamma(T)$ and $2/T_2$ with the experimental results. It was found that damping of the photon echo signal is described less satisfactorily by the expressions for T_2 deduced specially for this purpose than by the expression for $\gamma(T)$ obtained about twenty years ago using nonlinear spectroscopy.[18] The dynamic approach to dephasing developed here avoids all the above problems and contradictions, establishes the relationship (29), and—which is particularly important—it provides a recommended procedure for microscopic calculations of $\gamma(T)$ and, consequently, of the time T_2.

6. CONCLUSIONS

The main purpose of the present paper was to derive for the density matrix a system of equations which would allow for real and not idealized optical bands of impurity centers. This was the system of equations (22). We could see that this system is in fact more general than the optical Bloch equations, because it gives the correct results in those cases when the Bloch equations are inconsistent. At the same time, the system (22) is not too complex and allows us to consider from the practical point of view the various effects in nonlinear optics and spectroscopy. This was demonstrated in the present case by the spectroscopy of dips, whereas in Ref. 23 this was done using the example of a two-pulse photon echo. It must be stressed particularly that the use of the dynamic (nonstochastic!) approach made it possible to refute explicitly all the approximations made in the derivation of the system (22) and particularly to relate the spectral functions $I^g(\Omega)$ and $I^e(\Omega)$ in the system of equations (22) to expressions which have been calculated long ago and successfully using the framework of linear spectroscopy of impurity centers. This makes it possible to resolve a number of previously published contradictions in the theoretical expressions for the dephasing time T_2 and of the half-width $\gamma(T)$ of a zero-Bloch line.

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