Narrowing of the exciton lines using WAHUHA method of solid state NMR spectroscopy

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Abstract. A method for allocating of two thermodynamic reservoirs which are not related to each other in high density exciton gas in semiconductors using the Schwinger representation for the projection operators of the effective spin (pseudospin) of the excitons is proposed. It is shown that the method of narrowing the NMR resonance lines in solids under the influence of a sequence of four electromagnetic pulses of the WAHUHA type can be applied for the line narrowing of the recombination emission and absorption of light by excitons in optical spectroscopy. We found out that, in contrast to the averaging to zero of the magnetic dipole-dipole interaction between nuclei, the exciton-exciton interaction is averaged only partially. This analysis for the excitons can be extended to other quasiparticles of boson type, i.e. biexcitons, polaritons and magnons, in solids.

1. Introduction

Methods for the high-resolution NMR in solids, leading back to the pioneering work of Waugh, Huber and Haeberlen [1] (method WAHUHA), allow us to detect and investigate the NMR spectra, in spite of the large broadening of resonance lines (exceeding the spectral bandwidth of recording systems), caused by magnetic dipole-dipole interactions between nuclei [1-5]. The width of the optical resonance lines corresponding to the electron and exciton transitions (in the visible region) or to the electron-vibrational transitions (in the infrared region) are due to the interaction of electrons, holes and excitons with phonons and with each other. In particular, at high levels of optical excitation of semiconductor crystals, followed by the generation of the excitons of high density, the main mechanism of broadening of the lines for recombination emission and absorption of light by excitons at low temperatures is the mechanism of the pair interaction between excitons during their intra-band scattering on each other.

At low temperatures, with increasing of the concentration \( n_{\text{ex}} \) of Wannier-Mott excitons in semiconductors, when the average distance between them is comparable to the exciton radius \( a_{\text{ex}} (n_{\text{ex}} a_{\text{ex}}^3 \leq 1) \) depending on the parameters of the crystal, the exciton system evolves by one of the following ways: the formation of excitonic molecules (biexcitons) [6, 7], the formation of electron-hole drops and electron-hole liquid (condensation in coordinate space) [8-10], Bose-Einstein condensation of excitons and biexcitons (condensation in quasi-momentum space) [11-16], Bose condensation of excitons in a strong electromagnetic field [16]. In all these cases, the exciton-exciton interaction is dominant and makes a major contribution to the widths of the lines of recombination radiation. Except the case for the \( \delta \)-shaped peak emission due to the exciton Bose condensate and
associated with the behavior patterns of macro-doped exciton mode, the exciton-exciton interactions lead to a broadening of the exciton lines of recombination emission and absorption of light.

In this paper we discuss the possibility for narrowing of the exciton lines of absorption of light, whose widths are due to the intra-band exciton-exciton collisions, under the influence of a sequence of four terasound pulses, similar to a WAHUHA sequence of four electromagnetic pulses used in multipulse solid state NMR spectroscopy. To this end, the Hamiltonian of exciton-exciton interaction, written in the occupation number representation, is transformed into a convenient form to perform coherent averaging using average Hamiltonian theory. The transformed Hamiltonian of exciton-exciton interactions are reminiscent (up to a factor 3) of the form for the secular part of the spin-spin interactions operator in the theory of NMR. It is shown that due to no exact match in the form of the operator of exciton-exciton interactions with the secular part of spin-spin interactions, application of the WAHUHA method leads to a partial coherent averaging of the exciton-exciton interactions, in contrast to the complete averaging (up to zero) of the magnetic dipole-dipole interactions in a spin system.

2. Hamiltonian of the exciton system in Schwinger representation

Let’s consider a crystal containing high density excitons, taking into account only one (the lowest) of the exciton band. It is assumed that the exciton ground state is non-degenerate in the orbital and spin quantum numbers. The interaction between excitons is caused by the elastic exciton-exciton scattering within a non-degenerate exciton band. In this case, the width of optical absorption line related to the quantum transitions from the ground state of the crystal in a non-degenerate exciton band will be determined by the processes of intra-band exciton-exciton collisions. Hamiltonian of the exciton system in the occupation number representation is given by [15]

\[
\mathcal{H} = \sum_k [E_{ex}(k) - \mu] A_k^+ A_k + \frac{1}{2V} \sum_{k,k',q} V_{k'q} A_{k'q}^+ A_k^+ A_{k-k'q} A_{k-k'q},
\]

where \(A_k^+\) and \(A_k\) are the exciton operators of creation and annihilation, \(E_{ex}(k)\) is the energy of exciton formation with wave vector \(k\) and quadratic dispersion law, \(V_{k'q}\) is the Fourier transform of the energy of interaction between two excitons, \(\mu\) is the chemical potential of the system, and \(V\) is the volume of the crystal.

The form of Hamiltonian (1) differs from the Hamiltonian which describes the Zeeman interaction of nuclear spins with a constant magnetic field, and the secular part of the operator of magnetic dipole-dipole interactions between nuclear spins [3]

\[
\mathcal{H}_{spin} = \mathcal{H}_Z + \mathcal{H}^0_d, \tag{2}
\]

\[
\mathcal{H}_Z = \gamma \mathcal{H}_0 \sum_j I_{Zj}, \tag{3}
\]

\[
\mathcal{H}^0_d = \gamma^2 \hbar \sum_j \left( \sum_{i,j} r_{ij}^{-3} P_2(\cos \theta_{ij}) (I_i I_j - 3I_{Zi}I_{Zj}) \right), \tag{4}
\]

where \(\gamma\) is the gyromagnetic ratio of studied nuclei, \(I_{Zj}\) and \(I_{Zj}\) are operators of the projections of nuclear spin on Z-axis (the direction of the static magnetic field \(H_0\)), \(\theta_{ij}\) is the angle between this direction and the direction of a vector between spins \(i\) and \(j\), and \(P_2(x) = (1/2)(3x^2 - 1)\) is the Legendre polynomial.

For the implementation of narrowing of NMR lines in solids under the influence of a sequence of WAHUHA electromagnetic pulses, it is well known that it is essential to depict the main contribution to the width of the NMR lines by the secular part \(\mathcal{H}^0_d\) of the operator of magnetic dipole-dipole interactions at high magnetic fields, which commutes with the operator \(\mathcal{H}_Z\)

\[
[\mathcal{H}_Z, \mathcal{H}^0_d] = 0. \tag{5}
\]
This leads to a separation of two non-related to each other thermodynamic reservoirs: Zeeman, due to the interaction with a constant magnetic field $H_0$, and dipole-dipole, due to the secular part of dipole-dipole Hamiltonian $\mathcal{H}_d^0$ [3]. In this case, the energy of each system separately is an integral of motion and one might obtain a situation when the temperatures of each reservoir will be different.

A comparison of Hamiltonians $\mathcal{H}$ and $\mathcal{H}_{\text{spin}}$, given by equations (1) and (2), has not determined if the exciton system can be divided into two independent thermodynamic reservoirs similar to the case of interacting nuclear spins in a strong magnetic field. However, the analogy between $\mathcal{H}$ and $\mathcal{H}_{\text{spin}}$, and, accordingly, the possibility of separation of two independent thermodynamic reservoirs in the exciton system can be brought out, if the Schwinger representation for angular momentum is used in Eq. (1) [17].

We introduce now the effective spin operator $I_{k,k'}$, the projection of which on the directions $X, Y, Z$ can be presented in the form

$$I_{k,k'}^X = \frac{1}{2} \left( A_{k,k'}^+ A_{k,k'}^- + A_{k,k'}^-, A_{k,k'}^+ \right),$$
$$I_{k,k'}^Y = \frac{1}{2} \left( A_{k,k'}^+ A_{k,k'}^- - A_{k,k'}^-, A_{k,k'}^+ \right),$$
$$I_{k,k'}^Z = \frac{1}{2} \left( A_{k,k'}^+ A_{k,k'}^- - A_{k,k'}^-, A_{k,k'}^+ \right).$$

(6)

After some transformations using Eqs. (6), the Hamiltonian (1) can then be presented as follows:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{ex}} Z,$$

(7)

where

$$\mathcal{H}_0 = \sum_{k^1} \left[ E_{\text{ex}}(k^1) - \mu \right] S_{k^1,k^2,q}^Z - \sum_{k^2} \left[ E_{\text{ex}}(k^2) - \mu \right] S_{k^2,q,k^1}^Z + \frac{1}{2} \sum_{k} \left[ E_{\text{ex}}(k) - \mu \right],$$

(8)

$$\mathcal{H}_{\text{ex}} Z = \frac{1}{2V} \sum_{k,k',q} V_q \left( S_{k,k',q}^Z - S_{k',q,k}^Z - S_{k,q,k'}^Z + S_{k',q,k}^Z \right).$$

(9)

It was taking into account when deriving the Hamiltonian $\mathcal{H}_0$ from (8) that the operators $A_{k^1,q}^+ A_{k^2,q}^- \text{ and } A_{k^2,q'}^+ A_{k^1,q'}^-$ which realize the two-boson representation of the pseudospin $z$-component for $S_{k^1,q,k^2,q'}$ operator, i.e.

$$S_{k^1,q,k^2,q'}^Z = \frac{1}{2} \left( A_{k^1,q}^+ A_{k^2,q}^- A_{k^2,q'}^- A_{k^1,q'}^+ \right),$$

(10)

satisfy the condition

$$A_{k^1,q}^+ A_{k^2,q}^- + A_{k^2,q'}^+ A_{k^1,q'}^- = 1.$$  

(11)

The Hamiltonian $\mathcal{H}_{\text{ex}}$ from (9) was obtained neglecting the rare processes of pair collisions during which two excitons, having before collision impulses $k_1$ and $k_2$ (in $\hbar$ units), get after collision the impulses $k'_1 = k_2$ and $k'_2 = k_1$, respectively. Taking into account these processes, this leads that the averaged energy (on the exciton occupation numbers) of interaction between excitons decreases by the value of

$$\delta E = \frac{1}{2} n_{\text{ex}} \sum_q V_q.$$

Comparing equations (8) and (9) with equations (3) and (4), respectively, we can see that there is a deep analogy between the problem of elastic intra-band exciton-exciton collisions in semiconductors
and the problem of the magnetic dipole-dipole interactions between nuclear spins in a strong magnetic field. In a system of excitons of high density, as well as in the case of interacting nuclear spins in a strong magnetic field, there are two unrelated with each other thermodynamic reservoirs, similar to Zeeman and dipole-dipole reservoirs in the case of nuclear spins systems. However, there is a significant difference between exciton-exciton and dipole-dipole reservoirs consisting in the absence of factor 3 in the operator $S_{k,k+q}^Z S_{k,k+q}^Z$ found in (9), and in the presence of such a factor in the operator $I_{Z_i} I_{Z_j}$ (see equation (4)). As it will be shown in the next section, this leads to the fact that, in contrast to spin systems for which the magnetic dipole-dipole interactions are averaged to zero under the influence of a sequence of four WAHUHA electromagnetic pulses, the impact of a sequence of four WAHUHA terasound pulses leads only to a partial averaging of the exciton-exciton interactions in the case of exciton systems.

3. Coherent averaging of the exciton-exciton interactions

In contrast to the system of interacting nuclear spins for which the dipole-dipole reservoir can be identified only in the presence of a strong magnetic field, the “exciton-exciton” reservoir with the corresponding Hamiltonian $\mathcal{H}_{ex}$ always exists due to the fact that the energy of exciton-exciton interaction is much smaller than the eigenvalues of the operator $\mathcal{H}_0$, which is an analog of the Hamiltonian for the interactions of nuclei with magnetic field. Due to a quasi-discrete energy spectrum of excitons and a finite reduced Brillouin zone, the projection operators of the total effective spins $S^Z_f = \sum_k \sum_q S^Z_{k,k+q}$ and $S^Z_Z = \sum_k \sum_q S^Z_{k+q,k}$ have though a large, but finite number of eigenvalues. Therefore, the formalism developed for systems with a finite number of degrees of freedom can be applied to them.

Let’s consider now the impact of a sequence of four WAHUHA 90-degree terasound pulses on the system of effective spins periodically repeated with a period $t_c > T_2$ ($T_2$ is the transverse relaxation time of excitons). For pure direct-band semiconductors $T_2 \sim 10^{-9}-10^{-7}$ s [8] and, therefore, in order to perform such experiments as WAHUHA in the case of high-density excitons in direct-band semiconductor, when defining processes are intra-band scattering of excitons on excitons, the terasound impulses are needed. In the case of indirect excitons, for which the value of $T_2$ is three orders of magnitude higher, one can also use a sequence of hypersonic pulses.

In accordance with the criterion of applicability of the method of coherent averaging [3, 4], we assume that the energy of the exciton-exciton interaction is a small perturbation in comparison with the energy of interaction of coherent terasound with excitons. The interaction Hamiltonian of terasound with excitons can be presented in the form

$$\mathcal{H}_I = \sqrt{N_{q\sigma}} \sum_k \{ g_{\sigma}(q) S^Z_{k,k+q} \exp(-i\omega_{q\sigma}t) + H.c. \}, \quad (13)$$

where $S^X_{k,k+q} = S^X_{k,k+q} + iS^Y_{k,k+q}$, $g_{\sigma}(q)$ is the imaginary exciton-phonon coupling constant, and $N_{q\sigma}$ is number of terasound phonons with frequency $\omega_{q\sigma}$, wave vector $q$ and polarization $\sigma$. The equation (13) corresponds to the interaction of excitons with monochromatic terasound wave of high amplitude (macro-completed mode) when the corpuscular structure of terasound field is neglected ($\langle b_{q\sigma} \rangle = \langle b_{q\sigma}^+ \rangle \approx \sqrt{N_{q\sigma}}$).

Evolution operator of the system (propagator) at the time moment corresponding to the end of the cycle ($t = 6t_c$) is given by

$$U_{int}(t_c) = \exp\left(-\frac{i}{\hbar} \mathcal{H}_{ex}^Z \right) P_x \exp\left(-\frac{i}{\hbar} \mathcal{H}_{ex}^Z \right) P_y \exp\left(-\frac{i}{\hbar} \mathcal{H}_{ex}^Z \right) P_x \exp\left(-\frac{i}{\hbar} \mathcal{H}_{ex}^Z \right) P_y \exp\left(-\frac{i}{\hbar} \mathcal{H}_{ex}^Z \right) P_x \exp\left(-\frac{i}{\hbar} \mathcal{H}_{ex}^Z \right), \quad (14)$$

which, taken into account the result of action of the operators
\[ P_{\pm} = \exp \left( \mp i \frac{\pi}{2} \sum_{k,k'} S_{k,k'}^\xi \right) \]  \( \xi = X, Y \) (15)

on \( \exp \left( -\frac{i}{\hbar} H_{\text{ex}}^Z \tau \right) \), takes the form

\[ U_{\text{int}} (t) = \exp \left( -\frac{i}{\hbar} H_{\text{ex}}^X \tau \right) \exp \left( -\frac{i}{\hbar} H_{\text{ex}}^Y \tau \right) \exp \left( -2 \frac{i}{\hbar} H_{\text{ex}}^X \tau \right) \exp \left( -\frac{i}{\hbar} H_{\text{ex}}^Y \tau \right) \exp \left( -\frac{i}{\hbar} H_{\text{ex}}^X \tau \right), \]  (16)

where \( H_{\text{ex}}^X \) and \( H_{\text{ex}}^Y \) are obtained from \( H_{\text{ex}}^Z \) by replacing \( Z \) by \( X \) and \( Y \), respectively. Here, \( \tau \) is the time during which the system develops under the influence of the effective "exciton-exciton" Hamiltonian (free development), and after then the first terasound impulse is applied to it.

After using the Magnus expansion to the operator \( U_{\text{int}}(t_c) \) in (16) (see, for example, [4]), the following expression for the average Hamiltonian is derived in zero approximation

\[ \overline{H_{\text{ex}}^{Z(0)}} = \frac{1}{3V} \sum_{k, k', q} V_{q} S_{k, k', q} S_{k, k', q}, \]  (17)

Equation (17) shows that, in contrast to the spin systems with magnetic dipole-dipole interaction, the exciton-exciton interaction is not averaged to zero. A scalar part of the interaction diminished by one and half times remains. This is due to the different forms for the effective Hamiltonian \( H_{\text{ex}}^Z \) and the truncated Hamiltonian of the magnetic dipole-dipole interactions.

4. Discussion and conclusions

In this paper we show that, by introducing the projection operators of the effective spin (pseudospin), the Hamiltonian of intra-band exciton-exciton scattering can be reduced to the form which is almost similar to the secular part of the operator of magnetic dipole-dipole interactions in spin systems. In this pseudospin formalism two independent thermodynamic reservoirs can be separated in the exciton system, by analogy with the Zeeman and dipole-dipole reservoirs in spin systems, with energies as integrals of motion. In contrast to the magnetic dipole-dipole reservoir, which can be separated only in the presence of a strong static magnetic field, the "exciton-exciton" reservoir exists even in the absence of interaction with any external constant fields.

For all elementary excitations in solids obeying Bose-Einstein statistics, the paired processes of elastic collisions, in which the quasi-particles remain within the same energy band, can be described by similar Hamiltonians (in the form of second term in (1)). Our analysis for excitons can then be extended to other elementary excitations of bosonic type (biexcitons, polaritons and magnons). In each of these cases it is possible to introduce a pseudospin, the selection of two non-connected with each other thermodynamic reservoirs, and, in the framework of coherent averaging techniques, one can use multi-pulse methods of NMR spectroscopy of solids for narrowing of the corresponding spectral lines of emission or absorption. A similar analysis can be also done in regard to the processes of inelastic scattering of quasi-particles with a turn to other branches of the elementary excitations spectrum.

According to the averaging Krylov-Bogolyubov-Mitropolsky method, it was shown in the article [18] that the expression for the average Hamiltonian, based on the Magnus expansion, is non-secular in higher orders of the perturbation theory. Authors of the article [19] have developed a method of canonical transformations which allows to study the dynamics of spin systems in a variety of multi-pulse experiments, and the thermodynamic effects in multi-pulse NMR spectroscopy of solids have been studied based on this method. These generalizations of the average Hamiltonian method should also be taken into account when the effects of multi-pulse sequences on excitons and other quasi-particles of bosonic type are considered. In this framework of the average Hamiltonian method, we have shown only that the multi-pulse techniques developed in the solid state NMR spectroscopy can be applied, in particular, to the optical spectroscopy of excitons.

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